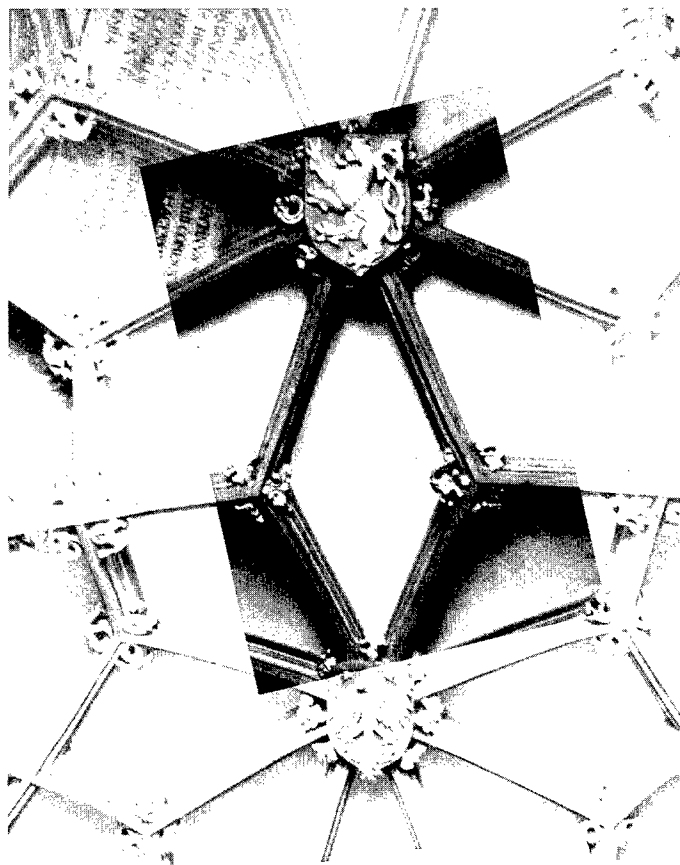9th International Conference

INTERGRANULAR AND INTERPHASE BOUNDARIES IN MATERIALS

Prague, Czech Republic, 6-9 July 1998

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WETTING OF GRAIN BOUNDARIES IN METALS AND CERAMICS

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The wetting of grain boundaries has traditionally been associated with phenomenon of metal embrittlement but high resolution transmission electron microscopy has revealed that wetting of grain boundaries is more general, can occur over a variety of microstructural length scales and exhibits a rich-variety of manifestations. For instance, wetting in silicon nitride ceramics prepared by liquid phase sintering is manifest as the existence of a nanometer wide silica-rich film along the grain boundaries, apparently irrespective of the crystallographic misorientation across the boundaries. In contrast, experiments on bicrystals of Fe-Si reveal that penetration of zinc down grain boundaries depends critically on the grain boundary crystallography. In other materials, such as ZnO-based varistors the grain boundaries are wet at high temperatures but the liquid retracts to the multiple grain junctions on cooling to leave a distinct grain boundary segregation layer.

In seeking to understand the underlying physical reasons for such wetting and dewetting of grain boundaries, a number of related approaches have been taken and will be described. One, is to treat the wetting and dewetting of grain boundaries as a phase transition. This can be couched in both conventional, macroscopic quantities, for instance in terms of wetting angles and surface energies, as well as in microscopic terms. Another approach is to consider the balance of forces across grain boundaries, including both short and long-range forces, such as vander Waals forces. From these sorts of theoretical considerations as well as from carefully defined experiments, there is increasing evidence that there is a thermodynamics of grain boundary wetting just as there is for free-surface wetting, albeit more complex. This provides a rationale for both controlled experiments in grain boundary wetting as well as for exploiting it for creating materials with complex microstructures.

MOLECULAR-DYNAMICS SIMULATION OF GRAIN-BOUNDARY MIGRATION*

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A molecular-dynamics method for the simulation of the intrinsic migration behavior of individual, flat grain boundaries is introduced and validated. A constant driving force for grain-boundary migration is generated by imposing an anisotropic elastic strain on a bicrystal such that the elastic-energy densities in its two halves are different. For the model case of a large-planar-unit-cell, high-angle (001) twist boundary in Cu we show that an elastic strain of ~1% - 4% is sufficient to drive the continuous, viscous movement of the boundary at temperatures well below the melting point. The driving forces thus generated (at the high end of the experimentally accessible range) enable a quantitative evaluation of the migration process during the time frame of 10^{-9}s typically accessible by molecular-dynamics simulation. For this model high-angle grain boundary we demonstrate that[1] (a) the drift velocity is, indeed, proportional to the applied driving force thus enabling us to determine the boundary mobility, (b) the activation energy for grain-boundary migration is distinctly lower than that for grain-boundary self-diffusion or even self-diffusion in the melt and (c) in agreement with earlier simulations the migration mechanism involves the collective reshuffling during local disordering ("melting") of small groups of atoms and subsequent resolidification onto the other crystal.

1. B. Schoenfelder, D. Wolf, S. R. Phillpot and M. Furtkamp, Interface Science **5**, 245-262 (1997).

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Application of surface ab initio methods to electronic structure and atomic configuration of interfaces in metallic materials

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The theoretical methods currently used to study electronic properties of surfaces, both in metals and semiconductors, may be divided into two groups: (i) standard band-structure techniques using slabs or supercells and (ii) Green's function (GF) techniques capable to treat a true semi-infinite solid. The methods in the first group are mostly ab initio and avoid often any shape approximation of atomic potentials. On the other hand, they introduce artificial boundary conditions (periodicity) to the problem. The latter limitation is removed by the methods of the second group, which are mostly empirical, based on the tight-binding (TB) models. They have a great appeal due to their simplicity and applicability to various surface-related phenomena, but there is no guarantee that the parameters of the TB model fitted to the equilibrium bulk state will be transferable to lower-symmetry configurations.

However, in the last decade first-principles techniques based on the GF approach have also been developed. These are, for example, the layer-KKR method, scattering theoretical method (STM), and surface Green's function method based on the TB linear muffin-tin orbitals method (LMTO). These methods account properly for the semi-infinite geometry of the surfaces and the LMTO-based approach retains the simplicity of the empirical TB schemes together with the accuracy and reliability comparable with the layer-KKR or STM method.

All these approaches were very successful in explaining a variety of surface phenomena but, till now, they have not been applied to internal interfaces very frequently. The purpose of this contribution is to review various surface ab initio electronic structure methods and to assess their applicability to studies of internal interfaces. Illustrative examples will be presented, in particular the results obtained by using TB-LMTO surface Green's function method.

HIGH RESOLUTION STUDY OF A NON PERIODIC GRAIN BOUNDARY IN GOLD.

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Thin films of gold in <110> orientation are produced by physical vapor deposition onto a [100] germanium single crystal substrate. Due to the symmetry of the system, two orientation variants form which are related by a 90° rotation, resulting in a "mazed bicrystal" structure with many grain boundaries of fixed misorientation but variable inclination. Amongst these, it is common to observe planar facets in which the grain boundary plane is parallel to {110} of one crystal and to {100} of the other crystal. Such facets have been observed by high resolution electron microscopy. One of these facets is shown in figure 1. As the atomic planes on each side of the boundary plane have irrational spacings, the boundary is not periodic and the CSL concept cannot be used. However, some equivalent groups of atoms can still be found along the boundary. They can be considered as the structural units of the boundary. Their distribution as well as their degree of similarity has been quantitatively established. Their spatial sequence gives rise to special effects in the calculated diffractograms of the boundary. A model of the boundary has been calculated using a Finnis-Sinclair type potential fitted to the lattice parameter, elastic constants and cohesive energy of gold. The total energy of the system has been minimized using a static relaxation method. A sequence of structural units which is strictly equivalent to the experimental sequence has been found. The results will be discussed with respect to the standard theories of grain boundaries and to that of the quasicrystals.
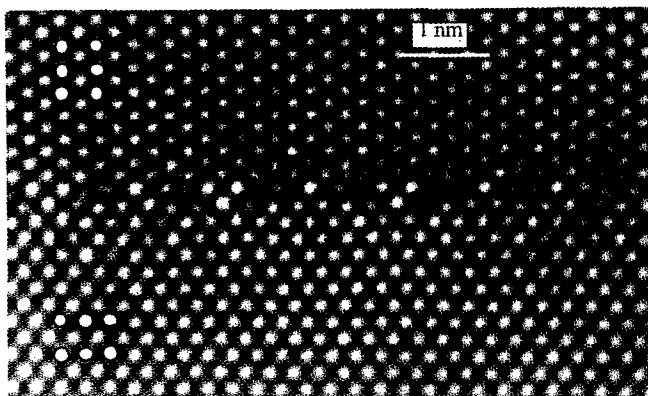
Figure 1 : High resolution image of a non periodic gold grain boundary. The boundary plane is parallel to {110} of the upper crystal and to {100} of the lower one.

DEFECT STRUCTURES AT INCOHERENT TWIN INTERFACES

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An understanding of interfacial defects is important to developing a full description of grain boundary behavior. In this presentation we analyze the interfacial dislocations at $\Sigma=3\,[01\bar{1}]$ incoherent twin (ICT) boundaries in FCC metals. Although the perfect boundary structures for the $\Sigma=3$ system are now well understood on the basis of experimental observations and atomistic modeling, there is still much to learn about the interactions and properties of interfacial dislocations at such interfaces. Two types of interfacial dislocations are anticipated and observed for $\Sigma=3\,[01\bar{1}]$ interfaces: namely, dislocations with Burgers vector $a/6<\bar{2}\,11>$ and $a/3<111>$. Such defects can arise at the interface as a means of accommodating deviations from perfect coincidence and/or through a lattice dislocation dissociation reaction. We will discuss two examples for which a detailed understanding of the such defects aids in understanding grain boundary structure and behavior.

First, we consider the case of $a/3<111>$ dislocations lying on an incoherent $(2\bar{1}\bar{1})$ twin boundary in aluminum. Because the Burgers vector of such a dislocation lies in the boundary plane, it is possible for the dislocation to move by glide. This concept is confirmed by experimental observations as well as by atomistic calculations showing only a small energetic barrier to translation of the dislocation. The dislocation itself is calculated and observed to exist in a dissociated state consisting of two components separating the boundary into regions of opposite rigid body translation. In addition to gliding, these dislocations play a role in coherent twin formation by a non-conservative climb process. Second, we discuss interfacial dislocations at an incoherent twin boundary in copper. It is now well established that the copper ICT boundary consists of a narrow, dissociated region of 9R stacked material. The width of the 9R layer is sensitive to strain as shown by atomistic calculations and *in situ* HRTEM observations. Additionally, errors in the 9R stacking sequence, which can be related to the presence of secondary grain boundary dislocations, are common. These dislocations, of Burgers vector type $a/6<\bar{2}11>$, may be of either pure-edge (90°) or mixed (30°) character. By accounting for both the orientation and sense of the dislocation's Burgers vector it is possible to explain the fault period.

Acknowledgements:

IN SITU HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF INTERFACES IN PHASE TRANSFORMATIONS

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Understanding the details of atomic motion at interphase boundaries is critical to understanding the mechanisms and kinetics of phase transformations in solids. This presentation discusses the results from a combination of *in situ* high-resolution transmission electron microscope (HRTEM) techniques that were used to understand interface dynamics and mechanisms of phase transformations at the atomic level. *In situ* hot-stage HRTEM was used to obtain real-time images of interface motion, with a time resolution of 1/30th of a second, during a variety of phase transformations. In addition to revealing the atomic structure of these interfaces, the images reveal features such as the nucleation rate and velocities of kinks which propagate along ledges during the diffusional growth of precipitates in Al-Ag and Al-Cu alloys, the role of interstitial hydrogen during growth of hydrides in Ti-H alloy, and the presence of compression waves ahead of advancing martensite interfaces in Co-Ni alloy. We have recently used energy-filtering transmission electron microscopy (EFTEM) to form compositional maps with subnanometer spatial resolution during *in situ* HRTEM experiments on Al-Ag and Ti-H alloys. An example of an EFTEM image taken at 290°C is shown in the figure below. This technique enables one to determine the chemical changes which occur at interfaces during transformation. With the video capabilities of current computers, it is possible to produce real-time image simulations of dynamic processes in the HRTEM for direct comparison with experimental images. The simulations are valuable because they reveal atomistic processes on time scales that are accessible by experiment. Initial examples of such simulations will be shown for motion of ledges in the Al-Ag system. The *in situ* HRTEM and EFTEM results are interpreted in terms of current models of interphase boundary structure and motion in solids.
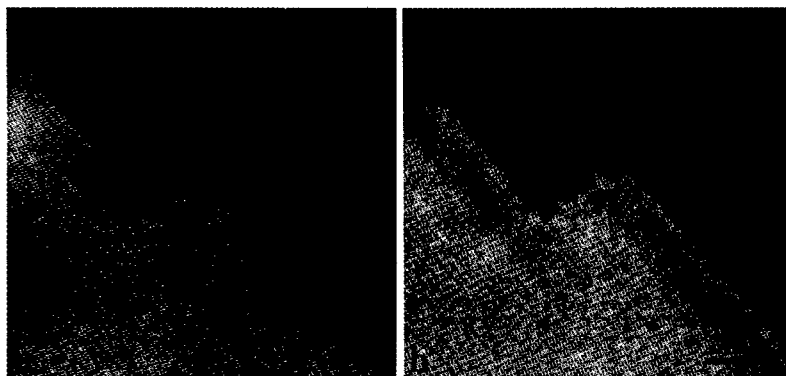
Figure - (a) Unfiltered and (b) zero-loss HRTEM images of a ledge (arrow) migrating across the face of a γ' precipitate plate in an α matrix during *in situ* heating of an Al-Ag alloy at 390°C. Note the improved contrast and clarity in the zero-loss image.

THE EFFECT OF THERMOMECHANICAL PROCESSING ON INTERFACIAL CRYSTALLOGRAPHY IN METALS

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The structure of the intergranular population in metallic materials can be manipulated by appropriate thermomechanical processing. This premise forms the basis for 'grain boundary engineering' where a material is processed so as to approach an optimised population of boundaries, usually in terms of its resistance to intergranular degradation during service. As yet, the relationship between processing routes and mechanisms for the evolution of boundary population crystallography is unclear. This paper will examine evidence for the effect that combinations of cold work and annealing have on the grain boundary crystallography, drawing strongly on recent experimental data from copper and nickel, particularly with regard to the boundary plane populations and twinning interactions.

Thermomechanical processing relevant to grain boundary engineering, and involving cold work and/or annealing, can be categorised are as follows:
- Annealing alone
- Small strains plus annealing
- Cold work plus annealing
- Cold work plus annealing iterations

The requirement when optimising the crystallography of grain boundary populations is to maximise the ratio of 'special' grain boundary area to 'random' grain boundary area. Hence, a small grain size is usually desirable. Annealing alone, which promotes grain growth (i.e. mobile boundaries) therefore does not produce an optimised grain boundary population. The present work has shown, however, that annealing at low temperatures produces a 'fine tuning' effect at boundaries which allows individual boundaries to approach an optimised structure. The fine tuning of boundaries has been found to be greatly enhanced by small prestrains. Cold work plus annealing results in recrystallisation, which does not produce an optimised boundary population, again because mobile boundaries are generated. However, repeated cycles of cold work plus annealing produces modified boundary statistics, mainly due to repeated twinning. This is demonstrated by recent investigations on copper.

GRAIN BOUNDARIES IN SUPERPLASTIC CERAMICS

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Superplasticity in fine-grained ceramics has been examined in a past decade. The superplastic flow in ceramic materials has been discussed mainly from the analysis of flow stress-strain rate relationship as in metallic materials. This is the, so-called, phenomenological approach to identify the accommodation process associated with grain boundary sliding. Actually, a lot of knowledge has been obtained through this type of approach, and hence the phenomenological analysis will also be a major stream for superplasticity research. However, some recent data on superplasticity in ceramics cannot be understood from this type of macroscopic analysis only, and require more microscopic information such as grain boundary structure, atomic bonding state in grain boudaries etc. For instance, superplastic flow in tetragonal zirconia polycrystal(TZP) is seriously affected by the presence of grain boundary glass phase. High-temperature flow stress is reduced by the glass doping into TZP and the flow stress level is dependent on the type and amount of the glass phase doped. It is noted that the flow stress reduction due to glass doping does not usually result in the enhanced tensile ductility. The elongation to failure is very much enhanced by pure SiO_2 doping but is deteriorated by a small addition of dopant cation in SiO_2 glass. Such a small dopant effect on tensile elongation is likely to be caused by the segregation of cation in and/or near grain boundaries. High-temperature stress-strain behavior in high-purity, polycrystalline Al_2O_3 is very sensitive to a small dopant cation. This is also caused by grain boundary segregation of cation. The change of superplastic flow in these ceramics may be explained in terms of the change in atomic bonding state due to the segregation.

GRAIN BOUNDARY DIFFUSION IN INTERMETALLIC COMPOUNDS

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The mechanical properties and thus the applicability of intermetallic compounds as advanced high temperature materials largely depend on their microstructure which is closely related to the atomic mobility in grain- and interphase boundaries. Boundary diffusion behaviour in intermetallics, however, is a widely unknown field due to its complexity as compared with metals. In compounds grain boundary properties will depend on the lattice structure of the adjacent bulk crystals, the ordering energy and the chemical composition with respect to stoichiometry. Due to the existing broad spectrum of these parameters among different compounds new interesting features and basic information on boundary properties can be expected from systematic experimental and computational investigations in this class of materials.

Prominent compounds in this context exist in the systems Ni-Al and Ti-Al, namely: Ni_3Al and NiAl with $L1_2$- and $B2$-structure, respectively, and Ti_3Al and TiAl with $D0_{19}$- and $L1_0$-structure, respectively. All four compounds reveal a broader composition range in their structural existence with varying point defect population on their sublattices.

Having measured bulk self-diffusion of ^{63}Ni and ^{44}Ti in the corresponding compounds, grain boundary diffusion of these tracers was investigated in dependence on temperature and composition, so far in Ni_3Al, α_2-Ti_3Al and γ-TiAl. The results will be presented and discussed in relation to available computer simulation studies of the grain boundary structures and grain boundary related point defect information in the different compounds.

RADIATION INDUCED GRAIN BOUNDARY SEGREGATION

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Radiation induced grain boundary segregation has been a recognised phenomenon for many years. The early work of Johnson and Lam [1] showed that for Zn-Ag alloys surface segregation could be induced by charged particle irradiation. Further work at Argonne labs by Okamoto and Wiedersich [2] indicated that GB segregation could be promoted in a variety of systems, including steels. Johnson and Lam [1] produced an elegant rate theory or Inverse Kirkendall theory (IK) based model to explain the effect, and this model has been developed in recent years by various workers like Perks and Murphy [3], Simonen [4] and Grandjean [5].

Another theory based on the concept of impurity-point defect complex migration to GB sinks during non-equilibrium processing such as irradiation has been developed by the Loughborough group [6]. This more simplistic model uses fewer parameters than the IK model and allows more successfully for microstructural effects. The model can be used to show that the dominant complex causing GB segregation during neutron irradiation is that based on the self-interstitial: vacancies play a relatively minor role. Grain size and dislocation density also have a large role to play in controlling the process.

The complex model will be used to illustrate examples of successful application of radiation-induced GB segregation theory to modern nuclear industrial situations. The examples are drawn from ferrous material experiences. The case of phosphorus in pressure vessel steels is shown to be particularly dependent on the interstitial (C and N) content of the steel. In core components made from stainless steel Cr is an important element from the irradiation-assisted stress corrosion cracking viewpoint and its segregation behaviour is very much controlled by minor elements such as phosphorus and hafnium.

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INTERFACIAL MICROCHEMISTRY AND EFFECTS
ON ENVIRONMENTAL DEGRADATION

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Grain boundary composition controls intergranular (IG) corrosion, stress corrosion cracking (SCC) and hydrogen-induced cracking (HIC) of many metallic alloys. Solute segregation and precipitation by equilibrium and nonequilibrium processes can degrade or enhance performance of many materials in corrosive environments. Interfacial microchemistry effects on environmental degradation will be summarized along with highlights demonstrating the use of various techniques to characterize and quantify these effects. Examples from recent research at the author's laboratory will be described and discussed including impurity segregation in iron and nickel-base alloys promoting IG corrosion, SCC and HIC; precipitation of chromium carbides and depletion of chromium in sensitized stainless alloys causing IG corrosion and SCC; radiation-induced and quench-induced nonequilibrium segregation influencing IGSCC in austenitic stainless alloys; and segregation-precipitation in aluminum alloys resulting in IG corrosion and SCC. Complete assessment of material microstructure and microchemistry is necessary to make accurate correlations to environmental degradation. For materials with similar microstructural characteristics, threshold grain boundary compositions can be identified which promote IG failure. However, the influence of specific solutes is quite different among the various degradation mechanisms and threshold compositions are a function of environmental (e.g., electrochemical potential) and mechanical (e.g., strain rate) test conditions.

The primary methods that are used to characterize grain boundary composition and structure at high resolution are analytical transmission electron microscopy (ATEM) and scanning Auger microscopy (SAM). These techniques are employed in combination with lower resolution techniques to properly characterize the bulk material microstructure. Unique tools are also available to evaluate the effects of interfacial microchemistry and microstructure on environmental degradation including crosssection ATEM measurements of SCC crack tips, in-situ SAM investigation of corrosion reactions and nanometer-scale examination of surface deformation, dynamic corrosion events and crack initiation using atomic force microscopy. Such approaches can supply direct insights into parameters controlling environmental degradation and help develop a comprehensive understanding of crack initiation and growth mechanisms.

Modelling nonequilibrium grain boundary segregations

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Non equilibrium interfacial segregations have their origin in the non conservation of point defects at interfaces; under appropriate circumstances, point defect fluxes to or from interfaces can be triggered which, because of inverse Kirkendall effect, induce an alteration of the composition field in the vicinity of the interface. While this effect has long been modelled in a reliable manner in the special case of dilute ideal solid solutions, describing concentrated alloys raises interesting problems, the solution of which is not fully established. We discuss the available models and present recent advances, based both on kinetic mean field approximations (vacancy and interstitial drag) and on Monte Carlo simulations (vacancy drag).

oral presentations

Grain Boundary Wetting During Anomalous Grain Growth in a Superalloy

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Many studies have been performed on the classical mechanism of grain boundary wetting [1, 2]. By classical is meant that a liquid phase wets a grain boundary intersecting the free surface of the solid phase of the same material. Much less is known about wetting in the solid state, i.e., the wetting of a grain boundary, in a polycrystalline material, by a grain of the same phase. In the present context, grain boundary wetting implies that the front of a large recrystallised grain totally isolates a specific grain from the polycrystalline matrix. This occurs by the diffusion-controlled motion of the front of the large grain, as it spreads out along the whole boundary of the small grain.

In fact, a similar situation has been observed in commercial aluminium by Bowles and Boas [5] but no quantitative study of this phenomenon was performed. In what follows, the grain boundary energies of several wet grains and of one large embedding grain are qualitatively estimated in a superalloy by measuring the local misorientations. This leads to a distinction between several possible situations, depending on the nature of the grain boundaries that are found in the final wet microstructure. A simple thermodynamic model is proposed [4] to explain this phenomenon of wetting in the solid state, particularly in the case where the misorientations are not those associated with low energy boundaries.

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TRIPLE JUNCTION STRUCTURE AND PROPERTIES

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Triple junctions, where three grain boundaries meet, are an essential feature of polycrystalline microstructure. In any material whose properties are determined by its grain boundaries, there are also triple junctions which may make separate contributions to the material properties and behavior. In this paper we describe a number of theoretical and experimental findings about triple junction structure and properties.

In systems that exhibit even quite modestly anisotropic grain boundary energy, the morphology of triple junctions is controlled in large part by symmetry: grain boundaries adopt symmetrical configurations adjacent to the triple junctions in a very large fraction of all cases in gold, for example. We consider the energy balance that leads to such configurations and show that they are generated not so much by energy minimization, as by the removal of the driving force for grain boundary migration leading to metastable configurations.

Incompatibilities among the translation states of grain boundaries abutting a triple junction generate dislocation contents at the junction, and we show that these are a function of the position of the junction in addition to the details of the structures of the individual boundaries. This leads to periodically varying triple-junction energy and pinning of the junctions in a Peierls-like mechanism. Several alternate means of relaxing the misfit strain are also demonstrated. The importance of triple junction "core energy" is examined in a study of high-symmetry junctions in diamond.

Examples of the impact of triple junctions upon material properties include findings that (i) they are the most potent sources of glide dislocations allowing the yield of polycrystalline thin films and (ii) that they exhibit segregation that varies from junction to junction, and may exceed that at the adjacent grain boundaries by an order of magnitude.

In the light of our observations, we discuss the various means of categorizing triple junctions that have been proposed.

ATOMISTIC SIMULATIONS OF GRAIN BOUNDARY TRIJUNCTIONS

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Abstract

The role of grain boundary junctions in grain growth process has received little attention. The excess free energy of the common line of intersection of the three crystalline interfaces, the trijunction lines, must be a factor in the evolution of junction morphology and grain switching rearrangements that are part of the grain growth process; under certain conditions it is conceivable that this energy could arrest grain growth. We report results of an atomistic molecular dynamics simulations of a periodic three-dimensional Lennard-Jones system consisting of three FCC grains rotated 30 degrees about a common <001> axis. This configuration yields six trijunctions, also along <001>, and their associated symmetric tilt grain boundaries. An aluminum specimen with such grains was manufactured and studied using high-resolution electron microscopy by Dahmen and co-workers. They found highly symmetric trijunctions that were later classified by Cahn and Kalonji as alternating among two symmetry classes. Our simulations of such a system address the following basic questions: (i) which classes of trijunctions occur, (ii) what is the atomic structure in the vicinity of the trijunctions, (iii) what are their energies, and (iv) how does the structure and energy of our system vary as a function of grain size.

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TRIPLE JUNCTION MOBILITIES: AN ATOMISTIC STUDY

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In traditional models of grain growth, the triple junctions (i.e., where three grain boundaries meet) are assumed to influence grain boundary migration only through their maintenance of fixed grain boundary angles (which is necessary for normal grain growth). These triple junctions were assumed to have no dynamics of their own, but simply follow the motion of the grain boundaries that meet there. We have performed a series of molecular dynamics studies to determine if and how grain boundaries affect curvature driven boundary migration and to determine the intrinsic mobilities of these triple junctions. The simulation geometry consists of a straight, symmetrical tilt grain boundary intersecting an otherwise U-shaped half-loop grain boundary at its apex, as shown in the figure below. First, several simulations were performed to determined the equilibrium (stationary) grain boundary dihedral angle for several different triple junctions by systematically varying the misorientation across the initially vertical, tilt boundary. Subsequently, molecular dynamics simulations were performed on each of these triple junctions at a fixed temperature. After an initial transient, the junction migrates with a self-similar shape and with a steady-state mobility. The dynamic junction angle was found to be indistinguishable from those predicted from the equilibrium (stationary) triple junction simulations. Comparison of the grain boundary migration rates with those previously determined migration rates with the U-shaped half-loop geometry show that for small equilibrium junction angles, the overall junction migration rate is determined by the intrinsic triple junction mobility. As the junction angle increases, the overall junction migration rate is increasingly governed by the intrinsic mobilites of the curved boundaries. The present data allows us to determine grain boundary triple junction mobilities as a function of grain misorientation (dihedral angles) and temperature. The mechanisms that control grain boundary triple junction mobilities will also be discussed.
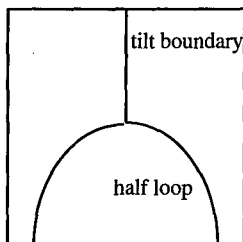
AB INITIO CALCULATIONS OF SiC-METAL INTERFACES

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It is of great importance to study ceramic-metal interfaces for practical applications of ceramics. Currently, it is possible to apply *ab initio* calculations based on the density-functional theory to such complex systems by virtue of the development of the first-principles molecular dynamics method [1]. In this paper, we report our recent *ab initio* calculations of SiC-metal interfaces. This is the first *ab initio* calculations of "reactive" ceramic-metal interfaces between covalent solids and metals in contrast to previous *ab initio* calculations of "non-reactive" interfaces between ionic solids and metals. We examine stable configurations, energies and electronic properties such as Schottky-barrier height (SBH), which is very important in the electronic applications of SiC.

We deal with the β-SiC(001)/Al (1x1) interface, for which the C-Al and Si-Al interactions can be clarified by dealing with both Si-terminated and C-terminated interfaces. The supercell contains a slab of 9 SiC(001) layers with 5 Al(001) layers stacked on both surfaces. We use the BKL conjugate-gradient technique [2], which can prevent charge sloshing instability [3], and optimized pseudopotentials [4].

We have found that both the Si-terminated and C-terminated interfaces have quite different features, such as atomic configurations, bonding nature, adhesive energy and SBH [5]. The C-Al interaction has both ionic and covalent characters, while the Si-Al interaction has a more metallic character. The adhesive energy of the C-terminated interface is much larger than the Si-terminated one, although both energies are much larger than those of non-reactive interfaces such as the MgO(001)/Al interface. This confirms the hypothesis that reactive interfaces should have greater adhesive energies than non-reactive ones. The significant dependence of the SBH on the interfacial structure is contrary to previous models for the SBH. However, the present result can be reasonably explained by the large interfacial dipole at the C-terminated interface, and is consistent with recent experiments and *ab initio* calculations of metal-semiconductor interfaces. We have also examined similar interfaces of the SiC(001)-Ti interfaces in order to clarify the effects of species of metals and d-orbitals.

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ATOMISTIC STUDIES OF CRACK PROPAGATION ALONG HIGH ANGLE GRAIN BOUNDARIES IN NIAL

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We present atomistic simulations of the crack tip configuration near the high angle grain boundary in NiAl. The cracks are stabilized near a Griffith condition involving the cohesive energy of the grain boundary. Three different configurations of the grain boundary were studied corresponding to different local compositions. It was found that in ordered NiAl, cracks along symmetrical tilt boundaries show a more brittle behavior for Al-rich boundaries than for Ni-rich boundaries. The role of Al content in the boundary energetics is therefore particularly important. For the present investigation we chose structures corresponding to the lowest possible energy for stoichiometric, Ni-rich, and Al-rich high angle symmetrical tilt boundaries. The results show that the Ni-rich boundaries are actually as strong as the bulk. The stoichiometric boundaries are only marginally weaker than the bulk. The Al-rich boundary studied are weaker than the bulk.

For a stoichiometric boundary, the crack does not advance in a brittle manner, but rather it remains in a similar configuration up to stress intensities that are significantly higher than the Griffith critical value.

The results suggest that the grain boundaries in this compound are not intrinsically brittle.
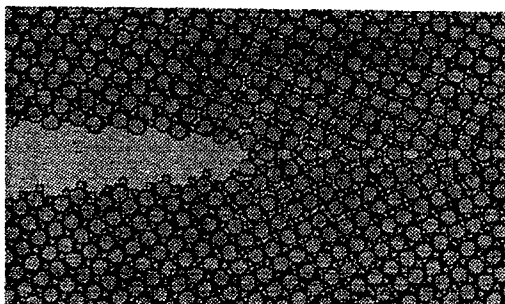
ATOMIC-SCALE STUDIES OF CERAMIC/METAL INTERFACES: STRUCTURE, CHEMISTRY, AND BONDING**

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Experimental research on ceramic/metal interfaces that utilizes transmission electron, high-resolution electron, Z-contrast, and atom-probe field-ion microscopies, and electron energy-loss spectroscopy (EELS) in conjunction with *ab initio* atomistic modeling and molecular dynamics (MD) simulations, is presented. Extensive use is made of atom-probe microscopy (APM) and EELS to address questions concerning the chemistry of the terminating plane and segregation of different solute species to ceramic/metal interfaces. Detailed experimental results are presented for the {222}MgO/Cu [1], {222}CdO/Ag [2], {222}MgO/Cu(Ag) [3], and {222} CdO/Ag(Au) heterophase interfaces. All the ceramic/metal interfaces were created with internal oxidation of high-purity binary or ternary metallic alloys, thereby producing atomically clean heterophase interfaces. Solute-atom segregation was induced at the {222} ceramic/metal interfaces by annealing specimens containing a ternary addition at 500°C. The Gibbsian interfacial excess is determined directly by APM. Results concerning *ab initio* atomistic modeling of the {222}MgO/Cu coherent interface (zero-misfit approximation), using local density functional theory within the plane-wave pseudopotential framework, are presented for two polar (111) and two nonpolar (100) MgO/Cu interfaces and are compared with our experimental observations [4]. MD simulations of the dislocation structure of the {222}MgO/Cu are compared with STEM observations [5]. EELS is used to measure directly the electronic states of the interface. O K and Cu $L_{2,3}$ edges show the formation of metal-induced gaps states (MIGS) within the band gap of MgO, at the interface [6]. Both theory and experiment find the MIGS to be strongly localized at the interface, resulting in a very small interface core-level shift.

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SPECIAL [100] TILT GRAIN BOUNDARIES IN IRON:
A SEGREGATION STUDY

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With respect to structure/property relationships, the grain boundaries can be divided into special and general. Until now, however all special grain boundaries have not been determined yet. A systematic experimental study of solute segregation in numerous bicrystals of an Fe-3.5at.%Si alloy enabled us to find all special [100] symmetrical as well as asymmetrical tilt grain boundaries. The values of the segregation enthalpy vs. misorientation angle for symmetrical grain boundaries, and the deviation angle from the corresponding symmetrical orientation for asymmetrical interfaces were investigated. They can be compared to the grain boundary plane classification [1], reciprocal density of coincidence site Σ and effective interplanar spacing d_{eff}. From the obtained correlation we conclude that the special [100] grain boundaries are:

   a) {012}, {013} and {015} symmetrical tilt grain boundaries, and

   b) (001)/(013) and all (011)/(0kl) asymmetrical ones.

All the other (001)/(0kl) asymmetrical interfaces exhibit minima on the plot of grain boundary segregation enthalpy vs. deviation angle for constant misorientation angle of the two adjacent grains. However, they possess the values on a medium level between those of general and special boundaries. From this point of view, they could be considered as a kind of vicinal interfaces [2].

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QUANTITATIVE STUDY OF THE BI-SEGREGATION TO CU GRAIN BOUNDARIES

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The embrittlement of Cu owing to small additions of Bi and its segregation to grain boundaries (GB) is an early and often investigated phenomenon [1]. The mechanical properties of the material strongly depend on the Bi GB coverage. According to classical segregation theories one expects a strong influence of the GB energy on the GB segregation. To gain a better understanding of these phenomena we investigated the Bi-segregation at different Cu tilt GBs ($s\Sigma3$, $as\Sigma3$, $\Sigma5$, $\Sigma11$, $\Sigma17$, $s\Sigma51$ and $as\Sigma51$ (s: symmetric, as:asymmetric)) which were grown by the Bridgman technique. All specimens were doped with various Bi bulk concentrations and annealed at various temperatures. We studied the segregation by energy dispersive X-ray spectroscopy (EDS) in a dedicated scanning transmission electron microscope using an 'effective scanwidth method' [2]. With this method the Bi GB coverage can be measured independently of specimen thickness and experimental conditions. The GB geometry was checked by high resolution TEM. For comparison with theory the GB energies were calculated by molecular statics simulations with semi empirical many body potentials of Finnis Sinclair type [3].

We found strong quantitative differences of Bi coverage along facetted GBs depending on the GB inclination (FIG. 1) and detected an attractive force between the segregated Bi atoms. From the experimental segregation data the Gibbs segregation free energy ΔG was determined. In the present study we worked out the first experimental prove of a monotonic connection between Gibbs segregation free energy ΔG and GB energy for Cu(Bi) (see FIG. 2). It is shown that namely the high-energy GBs play a crucial role in the embrittlement of Cu by Bi.

FIG. 1: Facetted $\Sigma51$-[110] tilt GB in Cu 60 wt.ppm Bi, T=700°C; Facets $s\Sigma51$: 1.8 ± 0.5 Bi atoms/nm^2 GB area, Facets $as\Sigma51$: no detectable Bi segregation (mdl: 0.5 Bi atoms/nm^2 GB area)
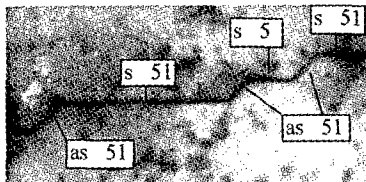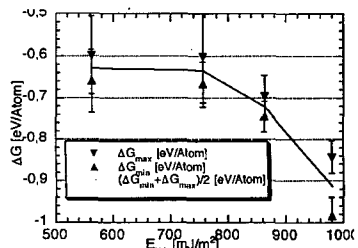

FIG. 2: Monotonic connection between experimentally determined Gibbs segregation free energy ΔG and calculated GB energies E_{KG} for various GB geometries.

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HIGH RESOLUTION ELECTRON MICROSCOPY OF Pd-ZnO INTERFACES

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For many applications like chip packaging and laser cladding the properties of metal-ceramic interfaces are of great interest. The macroscopic properties of the materials depend on the microstructure and chemistry of the interfaces. Little is known about the details of metal-ceramic bonding so a good description is needed. Here, Pd-ZnO interfaces are studied because of the relatively high stacking-fault energy of Pd compared to Ag and the lattice constant being between that of Ag and Cu, both observed on combination with ZnO before [2]. Internal oxidation of a Pd-Zn alloys is used here and is a simple method to obtain many ZnO precipitates inside a Pd matrix for observation by HRTEM.

Palladium was alloyed with 1.6 and 3.2 at % zinc by diffusion of zinc vapor into a 100 μm thick Pd sheet at 1273K for four days in an evacuated quartz tube. After the diffusion treatment the alloy is internally oxidized for 17h at 1073K in air. Microscopy is performed using a Jeol 4000 EX/II electron microscope with 0.165 nm point resolution. The average size of the plate-like precipitates is around 1 μm with a thickness of about 100 nm. The majority have a truncated trigonal shape, with large {0001} basal plane facets parallel to {1$\overline{1}$1} planes in Pd and the [11$\overline{2}$0] direction in ZnO parallel to the [110] direction in Pd.

When observing the ZnO precipitates two striking features show up: (i) on tilted interfaces the tilt is relieved by steps in the ZnO instead of the metal (opposite to Ag-ZnO interfaces) and (ii) the occurrence of sphalerite ('fcc') ZnO surrounded by wurtzite ('hcp') ZnO.

The stepped oxide interfaces can be explained by looking at the shear moduli of the materials, 53 GPa for Pd and 46 GPa for ZnO (wurtzite). This is a rather even distribution compared to the majority of metal-oxide systems where the oxide can be regarded rigid compared to the metal. When we compare Pd-ZnO with the Ag-ZnO system no stand-off dislocations are formed to relieve the small tilt of the interface. This can be explained by the high stacking fault energy of palladium (180 mJ/m^2) compared to that of silver (17 mJ/m^2) [3].

Zinc-oxide exist in a hexagonal (wurtzite) form but it also exists in a metastable cubic (sphalerite) form. Most plate-like precipitates have the hexagonal wurtzite structure. However, for some (small) precipitates it is more favorable to consist of a tetrahedron of four wurtzite ZnO platelets and a nucleus that consists of the cubic sphalerite ZnO. These configurations were also found in internally oxidized Ag-Zn. It is believed that in some cases ZnO nucleates in the sphalerite form and after a certain size the growth is continued as wurtzite ZnO.

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TRANSMISSION ELECTRON MICROSCOPY STUDIES OF THE STRESS ACCOMMODATION IN NICKEL GRAIN BOUNDARIES

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The accommodation of the stresses linked to lattice dislocations which have entered a GB giving rise to extrinsic GB dislocations (EGBDs) are studied in nickel bicrystals. This work has a double originality :

- The investigated GBs progressively depart from singularity : starting with singular Σ 3 {111} GBs, going on with vicinal near Σ 11 {311} GBs and finally considering general Σ 11 {332} GBs. All these GBs belong to Ni bicrystals similarly elaborated, thus containing identical and very small amounts of solute elements.

- The processes are studied using a large range of Transmission Electron Microscopy (TEM) techniques : conventional TEM, weak beam technique, "in situ" TEM and High Resolution TEM (HRTEM). In particular, the weak beam technique, until now rarely used for GBD analyses, presents a good resolution and allows the observation of general GBs. It appears as an appropriate complementary technique to HREM which only applies to particular GBs.

The results show that, in singular and vicinal GBs, complex reactions occur between EGBDs and the GB intrinsic networks, not predicted by any model. They yield the parallelism of all the dislocations, then and only then, the incorporation model may operate. The processes seem to differ in general GBs. According to the weak beam observations, they could be explained by the core delocalization model but this is not so straightforward. Indeed, a dichotomy appears between the observations in weak beam and those in HREM.

The results raise up an open question concerning the "general" GB structure and behavior. Solving this question is a futur requirement in order to progress in the understanding of the role of GBs in the high temperature deformation of polycrystals.

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ANALYSIS OF THE INTERFACIAL RELATIONSHIPS IN GaN/(0001)Al$_2$O$_3$ LAYERS

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For optoelectronic application in the green to UV range, GaN based layers are used. They are grown mainly on sapphire which exhibits a large misfit (16%) on the (0001) surface. Moreover , the atomic stacking and the crystallographic systems are different for the substrate and the epilayer. Experimentally, a large variety of crystallographic defects is observed in such layers. They include the threading dislocations which can be attributed more or less to the large misfit and growth mode which is now accepted to give rise to mosaic layers (1, 2). Moreover, inversion domains (3), prismatic stacking faults (4), and nanopipes (5) are also generated from these interfaces.

Although a lot of results are available on the defects created inside the epitaxial layers, no extensive study of the role played by the interfaces has yet been carried out. It is therefore of interest to study the growth mechanisms which underly the heteroepitaxy. As sapphire and GaN are very different, the interface is crucial in determining the types of defects which are generated inside the GaN layers.

In this work, we have used the topological theory (6) in order to determine the types of crystallographic defects which can be generated at the (0001) sapphire / GaN interface. It is found that like in the case of 6H-SiC/AlN-GaN (7) two parameters are important :
1) the stacking of the two materials,
2) the steps at the Al$_2$O$_3$ surface.

Among other interesting results obtained, it is found that inversion domains can form in GaN layers grown on top of a non stepped (0001) sapphire surface.

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NANOSIZED MATRIX AND GRAIN BOUNDARY LEAD INCLUSIONS IN ALUMINUM.

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Aluminum-lead alloys containing dense distributions of nanosized lead inclusions have been made by rapid solidification and ion implantation. Embedded inclusions grow in parallel-cube alignment with the aluminum matrix, they have cuboctahedral shape determined from a minimization of the total interface energy, and atomically smooth {111} and {100} facets. The smallest inclusions, less than about 20 nm in size, adopt a series of magic sizes determined by periodic minima in the residual strain energy. For even smaller inclusions the energy of the cuboctahedral edges becomes significant leading to changes in the aspect ratio of the inclusions. Inclusions located in grain boundaries in general adopt a single crystal morphology where one part is faceted and grows in parallel-cube alignment with the matrix grain while the other part has a shape approximating a spherical cap. In special cases such as twin boundaries and {111} twist boundaries the inclusions are bicrystalline where each part is aligned with the respective grain and separated by a boundary similar to that of the matrix.

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GROWTH INDUCED GRAIN BOUNDARY PLANE OSCILLATIONS IN YBa₂Cu₃O₇ THIN FILM BICRYSTALS

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$YBa_2Cu_3O_7$ (YBCO) grain boundaries originated from thin film deposition on $SrTiO_3$ (STO) bicrystals are used as Josephson junctions in SQUIDS for electronic applications. One of the most promising processes to obtain such devices appears to be Laser Ablation. On the basis of TEM analyses, previous reports showed that the grain boundary in the YBCO film did not always follow the substrate grain boundary faithfully, but rather undulated about the average boundary plane. In this paper we aim at giving a clear evidence that this undulation takes its origin in the growth mechanisms of the YBCO film on top of the STO bicrystal.

The morphology and crystallography of a $\Sigma 13$ YBCO bicrystal film grown epitaxially by Laser Ablation on a melt-grown oriented $\Sigma 13$ STO bicrystal have been characterised by either transmission or scanning electron microscopy, atomic force microscopy, or microanalysis. An average misorientation of 24° around the <100> tilt axis was found for both STO and YBCO bicrystals. Undulations about the grain boundary plane were found to display a wavelength similar to that of the film roughness, detected by complementary high resolution SEM and AFM imaging and attributed to growth islands. A detailed quantitative Fourier analysis of HREM images demonstrated that the complex undulating boundary structures correspond to zones with different moiré contrasts. Comparison between the experimental moiré interfringe distances and orientation, and what could be expected from a perfect <100> epitaxy showed that each undulation is the result of an overlap between the two parts of the YBCO bicrystal. Nevertheless, local distorsions of the moiré fringes spacing and orientation can only be fully interpreted if one takes into account the orthorhombicity variation observed by FFT close to the grain boundary as well as different cristallographic YBCO variants resulting from the growth of YBCO [001] on top of STO [001].

Based on this analysis a realistic geometric model is proposed for the grain boundary structure. It clearly shows that the grain boundary displays a certain curvature in the thickness of the YBCO layer which cannot be described simply by low indices cristallographic planes or facets; this is thought to strongly affect the superconducting properties such as the phase shift of the order parameter or the critical current density.

DEFECT MECHANISM OF MARTENSITE FORMATION: MODELLING AND EXPERIMENTAL OBSERVATIONS

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Our current understanding of martensitic transformation is based on the crystallographic theory due to Wechsler, Lieberman and Read. The predictions agree well with experimental observations, however these only relate to the final plates. The present work is directed towards developing a more comprehensive model of the transformation which gives deeper insight into the mechanisms operating during the microstructural evolution of the plates from an initially misfitting embryo to the final plate.

A model of the process of martensitic phase transformation, consistent with the phenomenological theory, is presented in which plate growth occurs through the motion of interfacial defects along the interface. A crystallographic framework for describing disconnections (defects with dislocation and step character) is used. The topological properties of these defects (Burgers vectors and step heights) and the diffusive fluxes associated with their motion and interaction are determined quantitatively. It is shown how orthogonal arrays of these defects can simultaneously accommodate misfit and effect diffusionless transformation.

These ideas are applied to the case of a NiTi shape-memory alloy, and the conclusions are compared with our experimental observations obtained using transmission electron microscopy.

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MAGNETICALLY FORCED GRAIN BOUNDARY MOTION IN BI-BICRYSTALS

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Results of investigations of grain boundary migration under a magnetic driving force in bicrystals of high purity (99.999%) bismuth will be presented. For the first time a defined planar grain boundary in a specially grown bicrystals was moved by means of a magnetic driving force. To prove that boundary motion is caused exlusively by the magnetic driving force, the experiment was carried out in two different ways. By changing the position of the bicrystal with regard to the applied magnetic field the direction of the driving force was inverted, and, as expected, boundary motion in two opposite directions was observed.

The mobility of $90°<112>$ symmetrical and asymmetrical boundaries was measured and dependence of grain boundary mobility on temperature was investigated. It was found that the migration parameters (activation enthalpy H and mobility preexponential factor) for the symmetrical boundary (H = 0.57 eV) drastically differ from the migration parameters for the asymmetrical one (H $\cong$ 3.6 eV) and the symmetrical boundary has a higher mobility than the asymmetrical one in the whole investigated temperature range up to the melting point of Bi.

The mobility parameters for the asymmetrical boundary were found to be distinctly different in opposite directions, such that the boundary is less mobile, if the c-axis in the growing grain is perpendicular to the direction of the motion and moves faster, if the trigonal c-axis in the growing grain is parallel to the direction of motion. This result provides evidence that Bi posseses an anisotropy of grain growth perpendicular and parallel to the trigonal axis.

The measurements of the boundary migration in different magnetic fields revealed that even in the region of comparatively small driving forces the boundary velocity changes linearly with driving force.

THE INFLUENCE OF GRAIN BOUNDARY STRUCTURE
ON DIFFUSIONAL CREEP

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A Cu-2wt%Ni-alloy has been deformed in tension in the diffusional creep regime (Nabarro-Herring creep). A periodic grid consisting of alumina was deposited on the surface of the creep specimen prior to creep. The measurement of the grid displacements caused by creep makes it possible to separate the deformation caused by grain boundary sliding from the deformation caused by deposition of material at (or removal of material from) grain boundaries provided that the orientation of the grain boundary plane is known.

It was found that material was deposited at grain boundaries in tension which unambiguously show that the deformation mode is diffusional creep. In the general case deposition of material at (or removal of material from) grain boundaries is found to be coupled with grain boundary sliding and grain boundary migration.

The misorientation across the grain boundaries, and thereby the character of the boundaries, was measured with the use of electron back-scattering patterns. The deformation behavior of the individual boundaries was correlated with the boundary character.

Twin boundaries with a deviation of less than approx. 1.0° from the exact coincident site lattice (CSL) orientation did not participate in the deformation process. Some Σ9 boundaries close to the exact CSL orientation were also found to be inactive. It is expected theoretically that some grain boundary dislocations in transverse boundaries may glide in the negative direction in order that deposition at the boundary by climb of the dislocations can yield a larger positive contribution to the deformation. Likewise it is expected that negative climb may occur at longitudinal boundaries in order that glide can yield a larger positive contribution to the deformation. Both these phenomena have been observed experimentally.

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ROLE OF THE INTERFACE OXIDE/METAL IN THE
HIGH TEMPERATURE CORROSION RESISTANCE OF ALLOYS

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High temperature alloys must be protected in application by growth of dense adherent oxide scales. The adherence of protective scales strongly depends on the microstructure and composition of the oxide/metal interface. Studies are reported and discussed on Auger analyses of the region beneath Cr_2O_3, Al_2O_3 or NiO layers on their metal substrate. Small concentrations of S, C and P were detected in areas which had been connected to the oxide layer, most probably due to segregation in defects, such as misfit dislocations, microvoids, grain boundaries, etc. For high oxygen pressures at the interface (Ni-NiO) P also can be enriched at the inner layer as phosphate. Sulfur starts to segregate to the free-metal surface as soon as the scale and metal separate, stabilizing voids and accelerating their growth to cavities or favoring the detachment of scale in the case of growth stresses. In this surface segregation S displaces C and P from the metal surface. Doping of the alloys with reactive elements such as Y, La, Ce, Ti, Zr Hf ... generally improves the adherence of scales, by favoring the nucleation, scavenging the sulfur, and affecting the growth mechanism of the oxides. These elements are active already in small concentrations, forming small precipitates in the interface and in oxide grain boundaries.

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O 19

INTERFACE DIFFUSION CONTROLLED
REACTIONS IN MULTILAYERS

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We consider the reaction $\alpha+\beta \rightarrow \omega$ where ω is either a solid solution or a stoichiometric compound. We consider this reaction inside multilayers to occcur at a planar interface, and at a temperature low enough such as volume diffusion is frozen and surface diffusion is controlling. We compute both the reaction front velocity and its morphology. It is shown that depending on the conditions of the experiment, two classes of solutions are possible: a single propagating front sweeping the multilayer, or a fingering solution propagating along the interfaces.

DIFFUSION PROCESS AT THE MOVING REACTION FRONT OF DISCONTINUOUS PRECIPITATES IN Ni-4 at.% Sn ALLOY

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The diffusion process at a moving interface is the rate-controlling factor in many solid state phase transformations like discontinuous precipitation (DP). During this reaction a supersaturated parent phase α_o decomposes into alternating lamellae of a new solute-rich β phase and solute-depleted initial α phase. Quantitative studies of this reaction are mainly focused on providing a chemical solute diffusivity ($s\delta D_b$) value which is the triple product of the grain boundary chemical diffusion coefficient (D_b), the grain boundary thickness (δ) and the segregation factor (s).

In the present paper the technique of analytical electron microscopy (AEM) has been used to determine the solute concentration profile left behind the moving reaction front of the DP reaction in a Ni-4 at.% Sn alloy at various ageing temperatures. These profiles have been converted into $s\delta D_b$ values using Cahn's diffusion equation and the data of the growth rate of the discontinuous precipitates obtained from independent measurements, but relevant for the same individual cell for which the solute distribution had already been obtained. This allowed, for the first time, to treat the DP reaction as a local phenomenon occurring in the single cell.

Such a procedure provides the diffusivity data which are very similar to the diffusivities given in the literature for stationary grain boundaries. Simultaneously, the obtained $s\delta D_b$ values are approximately one order of magnitude higher than those calculated by Frebel, Predel and Klisa (*Z. Metallkunde 65 (1974) 311 and 469*), applying a simplified version of Cahn's equation and the values of the α lamellae thickness and the growth rate of the reaction front averaged for the whole population of the cells. Such a result is especially attributed to the higher values of the growth rate obtained in the present study by using a special multistage ageing treatment.

O 21

REVERSAL FROM DEPLETION TO ENRICHMENT OF SOLUTE ELEMENTS IN
RADIATION INDUCED SEGREGATION AT GRAIN BOUNDARIES

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Radiation-induced segregation (RIS) in solids leads to enrichment or depletion of solute elements at point defect sinks depending on the coupling of the respective solute atoms to point defect migration. The resulting compositional change at grain boundaries may alter their structural and physical properties and may also result in a loss of mechanical strength and ductility. RIS at point defect sinks in steel was investigated by energy dispersive X-ray spectrometry in a transmission electron microscope with high brightness (field emission) electron source. The irradiations were carried out with 3.6 MeV Ni^{++} ions at 600°C in a Nb-stablilized steel of type 1.4981. At low irradiation doses RIS is observed to proceed in the same way as commonly reported. At high doses the segregation behaviour was found to be completely inverted at the grain boundaries, i.e. all solute elements, which commonly are radiation-enriched, were now depleted and vice versa. Further on the formation of radiation-induced precipitates and their evolution with increasing dose was investigated in the matrix and at grain boundaries. The observed effect of inverted RIS is discussed in conjunction with the chemical composition of the grain boundary precipitates. The phenomenon of inverse RIS at grain boundaries was observed for the first time in the present study. It could possibly be of practical relevance as a method for solving the problems arising from radiation-assisted sensitization and stress corosion cracking.

LOCAL SEGREGATION AT THE GRAIN JUNCTION ELASTIC SINGULARITY AND ITS EFFECT ON RADIATION EMBRITTLEMENT

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Grain boundaries and junctions in plastically deformed polycrystals are turned into intensive sources of the reactive stress field as neighboring grains, being differently oriented relative to the deforming stress, are subjected to different plastic strains. The internal stress considered has been analytically evaluated within the scope of two-dimensional semi-continual model and shown to have a strong singularity at the triple junction line. The hydrostatic component of the stress generated by grain junctions interacts with point defects, attracting the latter to the junction vicinities and thus allowing intensive local segregation on the near-junction areas of grain boundaries.

The re-distribution of interstitial impurities in deformed iron polycrystal has been considered at moderate temperature and shown to form near grain junctions the areas of elevated concentration (more than twice as high as the average one) being of the order of 1 μm. With the assumption of sharp local decohesion within respective regions of grain boudaries, the impurity effect on radiation embrittlement is discussed in case when the mean impurity concentration is moderate, most part of boundaries is free of segregation and the fracture surface observed is mostly transgranular. It is concluded that under the circumstances the impurity effect is to facilitate the **nucleation** of a brittle crack at the **local** interfacial region of elevated segregation, while further development of the crack occurs in the transgranular manner. The model suggested is in a satisfactory agreement with the data on radiation embrittlement of pressure vessel steels.

EFFECT OF INTERACTION BETWEEN DEFECTS AND SOLUTES   ON GRAIN
BOUNDARY SEGREGATION AND   ITS MIGRATION

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Grain boundary migration is caused generally due to volume
diffusion via vacancy for the recrystallization and grain
growth during annealing at elevated temperature. On the
other hand, the grain boundary migration often occurs at
relatively lower temperatures under irradiation environments
such as light water and first breeder reactor. Furthermore,
such radiation-induced grain boundary migration gives rise
to solute segregation simultaneously at grain boundary.
In order to investigate the radiation-induced grain boundary
migration mechanism based on the interaction between solutes
and point defects,a 316 stainless steel and Ni-(1-5)at%Si
model alloys were electron-irradiated using a high voltage
electron-microscope. Boundary migration was often observed
in stainless steels and the model alloys during irradiation.
The boundary migration rate changed during irradiation and
three migration stages were observed:first one is the
migration occurred at the early stage of irradiation, and
with further irradiation the migration rate slowed down
(second stage), and then moved again with high rate (third
stage). The incubation period before starting of first stage
was also observed. This incubation period depended on
irradiation temperatures and solute concentration. From
temperature dependence of boundary migration rates at first
stage and incubation periods, activation energy for boundary
migration was estimated. The activation energies for each
alloy were very low compared to migration energy for
vacancy. It is suggested from these results that the grain
boundary migration under irradiation is caused by
preferential flow of undersized solute via mixed dumbbell
mechanism toward grain boundary and the rearrangement of the
solute. In the consequence the undersized solutes segregate
at the grain boundary. Furthermore the boundary migration
rate became higher and incubation period shorter with
increasing undersized solute. This fact suggests that net
flow of the solute combined with interstitials is increased
with increasing the concentration.

POST-IRRADIATION ANNEALING AND INTERGRANULAR
SEGREGATION AND DESEGREGATION OF SULFUR AND PHOSPHORUS

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It is recognized that the formation of interstitial and vacancy defects promotes Cu rich precipitation and intergranular P segregation, giving rise to embrittlement, in neutron-irradiated ferritic alloys. In order to gain better understanding of dynamic interaction between defect and impurity fluxes, the effect of post-irradiation annealing (PIA: at 573-958 K for 0.1-1000 h) on the intergranular S and P segregation and microhardness has been examined in Cu-doped, P-doped and Cu-P-doped ferritic alloys all containing residual S. In a Cu-doped alloy, PIA (688 K-873 K) produced a greater S segregation rate than thermal annealing. As shown in Fig. 1, intergranular P enrichment was achieved during an early stage of PIA at lower temperatures in P containing alloys while P desegregation and S segregation proceeded at higher PIA temperatures. Although a P-doped alloy showed stronger irradiation effects on the P segregation than a Cu-P-doped alloy, both had similar effects of PIA except at 573 K. There was a tendency for the microhardness to increase with increasing amount of segregated P in the P containing alloys. The segregation kinetics of S and P were analyzed by applying a modified McLean theory and the P desegregation process was examined based on a Gaussian relaxation model. The activation energies for the S and P segregation during the PIA were estimated to be 34 Kcal/mole and 7 Kcal/mole, respectively, in the Cu-doped and P containing alloys. The P desegregation observed during higher temperature PIA was found to be controlled by the vacancy exchange mechanism.
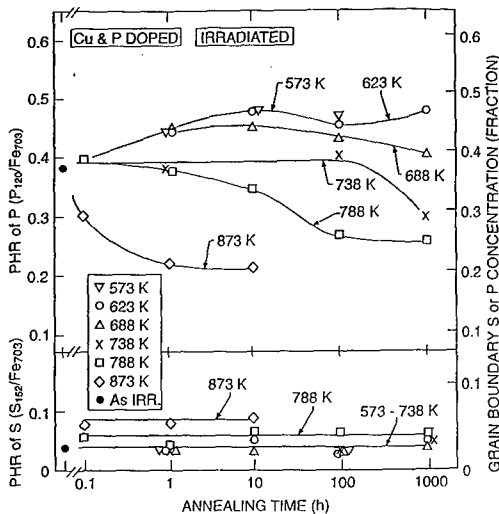
Figure 1. Variations of segregated P and S in Cu-P-doped alloy during post-irradiation annealing. The closed points indicate the data of irradiated alloy.

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VACANCY-INDUCED STRUCTURAL TRANSFORMATION OF SI GRAIN BOUNDARIES

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Incorporation of impurities is the most obvious way to modify the structure of grain boundaries, and hence the properties of materials. Here we explore the possibility of inducing structural transformations in *intrinsic* grain boundaries via the preferential segregation of native point defects such as vacancies and interstitials with or without external stress. We find that novel structural transformations with unusual properties can indeed be induced, which opens up another dimension in the pursuit of materials engineering. Ultimately, the *combined* incorporation of native point defects and impurities may lead to even more novel grain boundary structures. The motivation for the present study was provided by Scanning Transmission Electron Microscope (STEM) observations on a tilt grain boundary in Si. Atomic resolution images of the grain boundary core revealed that the 300 keV electron beam affects a localized region of the grain boundary core. In this presentation, we report extensive calculations for the particular boundary imaged by the STEM. We find that the affected region in the electron micrograph corresponds to columns where the formation energy of vacancies and vacancy complexes are very low. Further investigations reveal the possibility of a cooperative phenomenon, where chains of divacancies in some of these columns induce a structural transformation of the grain boundary. In the transformed boundary all atoms regain their fourfold coordination, while leaving "pipes" along which the average local atomic density is reduced by ~ 10%. Upon examination of the transformed core, we find that a pure edge dislocation of the original core has dissociated symmetrically into two mixed dislocations with the same total Burgers vector as that of the edge dislocation. The activation energy for the structural transformation is very small, only ~ 20 meV per atom participating in the transformation, and can be made negative under compressive stress, implying the possibility of a spontaneous transformation. Furthermore, within the low-density pipes of mixed dislocations there are long Si-Si bonds, which are ideal sites for the segregation of dopants in the form of substitutional dimers.

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ELECTRICAL CONNECTIVITY AND MICROSTRUCTURE IN $YBa_2Cu_3O_{7-\delta}$ FILMS FABRICATED ON ROLLING-ASSISTED BI-AXIALLY TEXTURE SUBSTRATES

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The "weak-link" electromagnetic properties of grain boundaries in the high-T_c superconductors drives the need to bi-axially texture these materials for wire and tape (i.e., high current) applications. The team at Oak Ridge National Laboratory has developed a method to produce bi-axially textured superconductor on a flexible metal substrate that has the potential for industrial scale-up to the km length wires needed for magnet and other high current technologies. Their "Rolling-Assisted Biaxially-Textured (RABiTS^{TM})" substrates for superconducting "wires" consist of a strongly cube-textured Ni tape produced by rolling and recrystallization. CeO_2 and yttria stabilized ZrO_2 (YSZ) buffer layers are grown epitaxially on the Ni metal. $YBa_2Cu_3O_{7-\delta}$ films deposited on the YSZ top layer inherit the bi-axial texture of the Ni metal tape. Critical current densities at 77K and 0T as high as 3 $MAcm^{-2}$ have been achieved recently. Magneto-optic of flux penetration into the $YBa_2Cu_3O_{7-\delta}$ films provides a visualization of the degree to which the supercurrent still is splayed into percolative paths by defects in the film. Films with J_c values less than 1$MAcm^{-2}$ show clear evidence of granular connectivity and a dependence of the J_c value on the extent of granularity. (The newer, higher J_c film studies are in progress.) This presentation will describe results of our on-going studies of the microstructure of the buffer and $YBa_2Cu_3O_{7-\delta}$ layers and their relationship to the electromagnetic granularity and the J_c value of the film. SEM and TEM studies show that dense, uniform layers of high-J_c YBCO can be deposited on the highly columnar and porous appearing YSZ layer that results from e-beam evaporation of the buffer layers. Magnetron sputtered YSZ has a considerably less columnar morphology and a denser microstructure, but the YBCO grown on top of it appears to be less uniformly dense, has a lower J_c, and shows increased granularity. These types of microstructure-property relationship studies of RABiTS tapes will be presented. This work is supported NSF MRSEC on Nanostructured Materials at the University of Wisconsin & Oak Ridge National Laboratory.

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PROPAGATION BEHAVIOUR OF INTERGRANULAR STRESS CORROSION CRACKING OF CU-9AT%AL BICRYSTALS SHAPED TO THE DOUBLE CANTILEVER BEAM SPECIMEN

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Intergranular brittle fracture is a predominant mode of Stress Corrosion Cracking (intergranular SCC) in most alloys. Bicrystal studies have found that susceptibilities of the intergranular SCC, which is usually defined to be the inverse of time to fractures, are closely associated with the grain boundary(GB) energy and structures [1]. In the present study, the intrinsic crack initiation and propagating behaviour of GB are examined, and the effect of GB structures on these behaviour are discussed, employing the bicrystals shaped to the Tapered Double Cantilever Beam (TDCB) under a constant anodic potential. The TDCB specimen enables us to measure a crack growth rate from a load relaxation curve without a direct observation of crack length.

Two bicrystals with symmetrical [100]-tilt boundaries were produced by the Bridgman method. Rotation angles around tilt axis of these bicrystals are 30° and 40° ($\Sigma 5$) respectively. GBs were located perpendicular to loading axes so that cracks propagate along the GBs. Constant opening displacements were applied under the constant anodic potential where the highest susceptibility was obtained by potentiostatic tests in an ammoniacal solution.

It was observed that crack was nucleated at the GB in all the specimens tested and continued to propagate along the GB until the cessation of the propagation. The applied load decreased with increasing testing time from the beginning of the crack growth and was finally saturated into a constant value. From the load relaxation curve, the relationship between da/dt and g-value was calculated for each specimen, where a is crack length and g-value is energy release rate. The da/dt-g curves could be divided into at least two stages. The crack propagated at a constant velocities irrespective of the g-value during almost the whole crack growth(Stage II). When the g-value was significantly reduced due to the load relaxation, the da/dt began to decrease rapidly with decreasing g-value until the crack growth was stopped (Stage I). The obtained threshold g-values for the SCC were certainly different between the two bicrystals. It is probable that the different threshold values were attributed to the GB structures.

1)M.Yamashita, T.Mimaki, S.Hashimoto and S.Miura:Phil.Mag.A, 63, (1991) 695.

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ANISOTROPY AND OXYGEN ACTIVITY DEPENDENCY OF THE LIQUID OR SOLID METAL-OXIDE FREE INTERFACIAL ENERGY: CASE STUDY ON MgO - Cu

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With the present study of the equilibrium shape of liquid or solid metal inclusions in oxides or oxide inclusions in solid metals a novel approach for the study of anisotropy and oxygen partial pressure dependency of metal-oxide free specific interfacial energies is presented. In the case of solid-liquid or incoherent or nearly incoherent solid-solid interfaces the precipitate equilibrium shape is determined by the anisotropy of the free interfacial energy and can be explored following the Wulff's theorem.

Liquid copper inclusions in MgO

After internal reduction of mixed (Mg,Cu)O oxides at various oxygen chemical potentials above the copper melting point, followed by a equilibration heat treatment, the equilibrium shape of liquid copper inclusions in MgO is determined by a TEM study.

Liquid copper inclusions within magnesia adopt cubo-octahedral shape. The relative importance of the two types of facets depends on the oxygen chemical potential. At low oxygen activities truncated cube shape is adopted with $\{001\}_{MgO}$ main and small $\{111\}_{MgO}$ facets, at high oxygen activities $\{111\}_{MgO}$ increase in size.

MgO precipitates in solid copper

MgO precipitates in Cu obtained by internal oxidation of (Cu,Mg) alloys and equilibrated at oxygen activities covering the whole coexistence range of copper and MgO change their equilibrium shape from a perfect octahedron over a truncated cube and to less defined faceted shape. The variation of precipitate equilibrium shape is interpreted in terms of the variation of interfacial energy with the oxygen chemical potential. Thermodynamic models as the Gibbs' adsorption isotherm or atomistic models on electronic structure of the interface and the type of interfacial bonding are used to explain the evolution.

At high oxygen activities, when the copper(I)oxide activity becomes almost one, copper has a high tendency to form metal-oxygen bonds across the interface and is therefore preferentially found in contact with polar $\{111\}_{MgO}$ planes terminated by oxygen, where it suffers important charge transfer while adopting a formal valence state of Cu^{1+} in a Cu_2O-like structure. The interface in this configuration possesses an excess in oxygen compared to stoichiometric MgO which, in the Gibbs' language, can be considered as the excess of adsorpt oxygen in the interface. At intermediate oxygen activities, charge transfer between copper and oxygen becomes very weak, promoting then mixed, neutral $\{001\}_{MgO}$ planes in contact with copper planes as low energy configuration. At very low oxygen activities, when the magnesium activity becomes close to one, a strong tendency to form metal bonds exists. As a consequence, low energy configurations are expected to show interfaces between polar $\{111\}_{MgO}$ planes terminated by a magnesium layer and copper.

NANOSCALE AND DYNAMIC INTERFACE RESEARCH
IN THE SOLID JUNCTION PROJECT FOR THE 21st CENTURY

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Reviewed and presented are the research activities of the Tanaka Solid Junction Project related to nanoscale interface science. The Tanaka Solid Junction Project is a national project running from Oct. 1993 to Sept. 1998 and controlled by Japan's Science and Technology Agency. The project aims to isolate the factors controlling heterogeneous interface formation during joining and the thin film deposition process, with the ultimate aim of elucidating the basic principles that make interfaces designable. Key factors that affect interface formation processes and their properties are not only atomistic behavior at the interface, but also stress/strain and the lattice defect distribution around the interface, and even the electrical structure at the interface.

To obtain answers to these questions, we are making efforts to accelerate the following areas of research.

(1) Direct observation and control of interface formation---ceramic/metal

(2) Nanoparticle bonding and control by an electron beam---metal/metal, ceramic/metal

(3) Nanoscopic and electronic structure of metal/Si interfaces---semiconductor/metal

(4) Residual stress/strain in heterogeneous interfaces---ceramic/metal, semiconductor

(5) Theory and simulations to make interfaces designable

In the presentation, recent results related mainly to (2)(3)(4) above will be introduced .

poster presentations

EQUILIBRIUM ATOMIC STRUCTURE OF THE Σ=5 (210)[001] TILT GRAIN
BOUNDARY IN FCC CRYSTALS

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By using computer simulation, we investigate the atomic configurations of the
Σ=5 (210)[001] tilt grain boundary in fcc crystals that minimise the internal energy of
the bicrystal. Two cohesion models have been used the first of which is a n-body
potential adapted to copper whereas the second is the Lennard-Jones potential, well
adapted to the case of solids in which dispersion forces are dominant.

Whatever cohesion model is used, energy minimisation shows that two stable
configurations of this boundary exist at T=0 K one of which is non-symmetrical. In the
case of the Lennard-Jones potential these results contradict the suggestion made by
previous work that only the symmetrical configuration is stable.

At T≠0 K, molecular dynamics calculations show that both configurations
transform to a new symmetrical configuration, definitely different from that found to be
stable at T=0 K. The position of the central boundary plane in the low and high
temperature symmetrical boundary structures are different and thermal fluctuations
trigger oscillations of the boundary between them. Thus, our results shed in light a
possible atomic scale migration mechanism for the studied boundary.

Part of these results have already been obtained by previous work. The latter
concluded in favour of an interfacial allotropic phase transition while present work
offers a different interpretation of the temperature dependent behaviour of this
boundary.

ON THE APPLICABILITY OF THE CSL MODEL TO GRAIN BOUNDARIES AND TRIPLE JUNCTIONS IN NON-CUBIC MATERIALS

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There is certainly nothing new in posing the problem that the Coincidence Site Lattice (CSL) theory may not be all-encompassing. Nevertheless, surprisingly large number of researchers have firm trust in the CSL approach, and works appear where its validity in all situations is taken for granted. First, it is necessary to distinguish a 'physical' model from a geometrical approach. The underlying idea in all the models of the grain boundary (GB) structure, which are trying to link physics and crystallography, is that the GB adopts a low-energy structure dictated by some geometrical lattice. While the CSL model is a purely geometrical theory, the widespread misconception is that there is a firm correlation between the reciprocal density of coincident sites Σ and physical properties of grain boundaries. Despite the fact that significance of the Σ value has been questioned many times before, it is still being widely used as the main (and, sometimes, the only) parameter describing the GB structure. The present paper is an attempt to demonstrate that while the CSL model is a very useful geometrical approach, any physical conclusions drawn on the basis of some 'magic' numbers, such as Σ, should be treated with caution.

The following examples are considered in the current paper.

1) HRTEM studies have shown that in monoclinic zirconia, twin boundaries seem to be structurally singular. Unlike the cubic lattice, several distinct types of twin boundaries exist in this material. In the framework of the constrained CSL model, these could be characterized by $\Sigma = 1$, 3 and 71. Thus, in the given case the magnitude of Σ tells nothing about the special structure of grain boundaries. Triple junctions of such boundaries are observed where (*i*) the Σ-product rule is not fulfilled and (*ii*) there is a misorientational mismatch of about 1.6° creating a junction disclination.

2) Depending on the choice of lattice constraints, the {110} twin boundaries in orthorhombic YBCO could be ascribed either $\Sigma=1$ or a large Σ value (e.g. 59). Both variants, however, encounter certain difficulties. In the former case, Burgers vectors of the GB dislocations cannot be predicted. In the latter variant, grain boundary faceting cannot be analyzed correctly.

3) Most data, accumulated so far, indicate that symmetrical tilt ("twin") boundaries along low-index crystal planes posses special structures. General consideration of such boundaries in lattices of low symmetry (tetragonal, orthorhombic, monoclinic and triclinic) shows that, depending on the lattice constants, they can have very large Σ values.

Summarizing, Σ is probably a secondary, not primary parameter describing the GB structure. Therefore, for example, a GB character distribution with respect to Σ might be a classification according to a secondary parameter. Discussions of the upper limit of Σ and allowable deviations from 'specialness' based on this parameter have little physical applicability.

THE VARIETY OF STRUCTURES OF
THE Σ=3 INCOHERENT TWIN BOUNDARY IN β-SiC

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The study of grain boundaries (GB) by high resolution electron microscopy (HREM) is now one of the main tools for understanding materials. Especially, the structure of Σ=3 incoherent twin boundary has long been discussed in many materials (Au[1], Si[2], Ge[3], Diamond[4], SiC[5]) experimentally and theoretically. A rigid body translation of one grain relative to the other is important part of the atomic relaxation of a grain boundary. The presence of a rigid body translation along the common <111> direction was found in some materials[1, 2, 3], whereas no rigid body translation was found under different conditions[2] or in other materials[4]. In fact, these authors found also that the translation state was sensitive to the environment of the boundary. Finally, the inclination of the boundary plane can also be a possible factor in the decrease of the energy. In fact, a minimum of the energy has been found theoretically[6] for a deviation angle of 8 degrees away from the symmetrical position in Cu.

In the present study, several types of Σ=3 {211} incoherent twin boundaries of different length in β-SiC, and its junction with a Σ=3 {111} coherent twin boundary have been investigated by HREM (JEM-3000F) and compared with a theoretical study[5].

Fig. 1 shows several types of Σ=3 and Σ=9 in β-SiC. The theoretical study[5] indicated that Si should reconstruct at the GB. Structure models for different Σ=3{211} GBs matched well with both of HREM images and the theoretical study. The details will be discussed.

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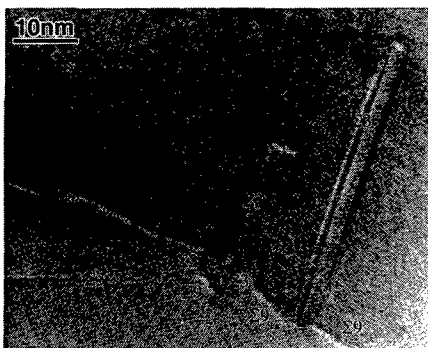

Fig. 1   HREM image of β-SiC

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ON THE EXISTENCE OF PERIODIC INTERFACES
IN THE LAYERED COMPOUND TlBiS$_2$

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TlBiS$_2$ is a layered, narrow-gap semiconducting ternary compound which is also referred to as pseudo-PbS, as Tl and Bi lie on both sides of Pb in the periodic table. Similarly to PbS, it has a NaCl-type structure with a slight elongation along $[111]_R$, which creates a rhombohedral lattice (space group: $R\bar{3}m - D_{3d}^5$). It is also referred to as pseudo-cubic, as it can be described by a nearly cubic multiple cell of lattice parameters a'_R =12.434 Å and α_R =88.64°. [1]

In this NaCl-type structure, one of the f.c.c. sublattices contains both the Tl and Bi atoms mixed in the same plane or occupying distinct planes, creating the superstructure which has already been observed in TlBiSe$_2$ [2]. This superstructure arrangement perpendicular to the $[111]_R$ direction produces the extra spots in this direction and in the middle of the basic ones. Apart from this superstructure spots, another family of extra spots exists in the electron diffraction patterns.

These spots lie approximately along the [114]* directions. Our preliminary interpretation of the electron diffraction patterns in combination with the electron microscopy images is that an interface modulated structure rises, because of the periodic insertion of interfaces parallel to (114) planes and with a shear vector not parallel to (114). Such interfaces are not conservative concerning the stoichiometry, i.e. probably the overall composition is modified by the presence of these interfaces.

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DEFECT STRUCTURE AND PROCESSES IN A 1-D PERIODIC INTERFACE

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The majority of experimental observations and atomistic simulations of interfaces are concerned with two dimensionally periodic structures. However, most interfaces in engineering materials have a more general character, and it is important to study these.

The present work describes computer simulation of a one-dimensionally periodic interface and represents the first step towards more general interfaces.

The particurar interface investigated can be described as a [1-210]/90° tilt boundary in Ti, where the boundary plane is (10-10) in one crystal and (0001) in the other. This configuration exhibits periodicity along the tilt axis but is inconmensurate perpendicular to this. A many-body potential of the Finnis-Sinclair type has been used in the simulation. The minimum energy structure has been determined and the nature of defects and their response to applied stress investigated. In contrast to periodic interfaces, the defects are not localised in some cases.

Non-empirical modelling of interfaces in alloys

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Abstract

In the framework of the coherent potential approximation we show that parameters of the interaction potentials for disordered tungsten-boron and iron-aluminium alloys are strongly depended on the concentration. These calculations were provided within Linear Muffin-Tin Orbitals formalism in the atomic sphere approximation. Calculation data for A2-phase for different concentrations were used to extract the interaction parameter, $V(0)$, for disordered solid solutions and were compared with the parameter treated from the X-Ray scattering data. We obtained the strong concentration dependence of $V(0)$. Such a behaviour of $V(0)$ leads to the fail of the application of the regular solid solution model to the phase relations study in alloys. Parameter $V(\vec{k}_s)$, which is responsible for ordering tendency, also depends on concentration and it is in an accordance with the experimental data. The obtained potentials were used for the interface boundary modelling.

ATOMISTIC STUDY OF Σ=5 (310) TILT GRAIN BOUNDARIES IN NIOBIUM AND MOLYBDENUM COMBINING AB INITIO AND EMPIRICAL METHODS

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Atomistic simulations of grain boundary structures in body-centered cubic transition metals have revealed a significant covalent contribution to interatomic interactions. While this contribution is fully accounted for in ab-initio calculations, in empirical schemes of evaluation of the total energy, that are commonly used in studies of grain boundaries, it is either neglected or taken into account approximately. In this work we investigate the atomic structure of Σ=5 (310)/[001] symmetrical tilt grain boundaries in Nb and Mo and compare ab-initio local-density-functional calculations, using a mixed-basis pseudopotential method, with two different empirical schemes and with available experimental HRTEM observations. The empirical schemes considered are central-force potentials of the Finnis-Sinclair type and bond-order potentials based on a tight-binding model which incorporates the angular character of bonding arising from the d-electrons. In both these cases the evaluation of the total energy and its derivatives is carried out in the real space and scales linearly with the system size. The comparison of calculations performed using different descriptions of atomic interactions assesses the adequacy of the empirical schemes, reveals the relative significance of different contributions to the total energy in the study of grain-boundary structures and may guide further improvements of empirical schemes.

MD-SIMULATIONS OF THE ATOMIC STRUCTURE OF A NEAR-Σ25 [2 4 . −1] ALUMINA INTERFACE IN ORDER TO DESIGN ADVANCED MATERIALS

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α-Alumina has a large field of application as substrate material for several electronic devices as well as for structural composite materials. The atomic structure of these interfaces have to be studied in detail in order to design special advanced materials: Special grain boundaries are promising candidates for electronic devices and heterogeneous interfaces are important for FGM-materials or Zirconia-toughened materials.

Symmetrical tilt grain boundaries with low Sigma values were searched by three different methods and the most promising candidate was selected for studies of the atomic structure.

The Molecular Dynamics Simulations were performed by including the long-range Coulomb interaction by using the Morse potential. A special set of parameters was used, which fits well to macroscopic properties of single crystal experiments. This set of parameters allows calculating physical properties of not only the single crystal or the bicrystal, but also of material compounds. Especially the calculation of the KIC value is possible.

The atomic structure of the near-sigma-25 [2 4 . −1] symmetrical tilt boundary in a-axis orientation was chosen for detailed study of the atomic structure. At the grain boundary core stable structural units are found, show atomic arrangements and bonding lengths that are different than those in the single crystal.

These calculations allows to give an outline for producing newly designed interfaces with higher bonding strength.

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ATOMIC LEVEL STUDIES OF DISLOCATION NETWORKS IN NIOBIUM-SAPPHIRE INTERFACES

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Electron microscopic studies of interfaces in the niobium-sapphire system revealed a variety of misfit dislocation networks [1,2] and recent atomistic modeling combined with the high resolution electron microscopy (HREM) suggested a relationship between the core structure of these dislocations and bonding at the interfaces [1]. In this paper we present atomistic modeling of $(0001)_{Al_2O_3} \parallel (111)_{Nb}$ and $(0001)_{Al_2O_3} \parallel (110)_{Nb}$ interfaces combined with simulation of HREM images of the structures found in the atomistic studies. Atomistic calculations are carried out using a very simplified model for the atomic interactions: many-body central force potential for Nb and a pair potential reflecting variable strength of bonding for interaction across the interface. The goal is to reveal the impact of the bonding strength between the two materials upon both the type of networks of misfit dislocations formed in Nb at or near the interfaces and on the core structure of these dislocations. In this context we also investigate the possible standoff of the dislocations away from the interface which is an important characteristics of their overall structure. Simulated HREM images then reveal the possible de-localization of the dislocations both parallel and perpendicular to the interfaces which is a prominent feature of their cores. These simulations will also be directly compared with available experimental observations.

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MD-SIMULATION OF THE ATOMIC STRUCTURE OF SPECIAL TILT GRAIN BOUNDARIES IN ZINC OXIDE

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The electronic properties of Zinc Oxide varistors strongly depend on the atomic structure of grain boundaries. Symmetrical tilt grain boundaries with a low Sigma value were searched by three different methods.

The Molecular Dynamics Simulations were performed by including the long-range Coulomb interaction by using the Buckingham-potential.

The results show stable atomic structural units at the grain boundary core with open rings of atoms with a larger number (10 or 8) of atoms than in the single crystal. The bonding lengths for the most promising candidates have been characterized. The figure on the right side shows the atomic structure of the near Σ29 a-axis grain boundary with an misorientation angle of 101.6°. The bulk bonding length have a deviation of more than 10% compared to the single crystal bonding length.

These structural units found by these simulations are stable even after long time simulations. The excess volume inside the core allows electrons to be trapped in this energetically favorable places and the electronic band gap for varistor applications will be smaller as shown in previous works. It is the goal of further engineering on atomic scale to influence this gap and the barrier height at grain boundaries more precisely for practical applications.

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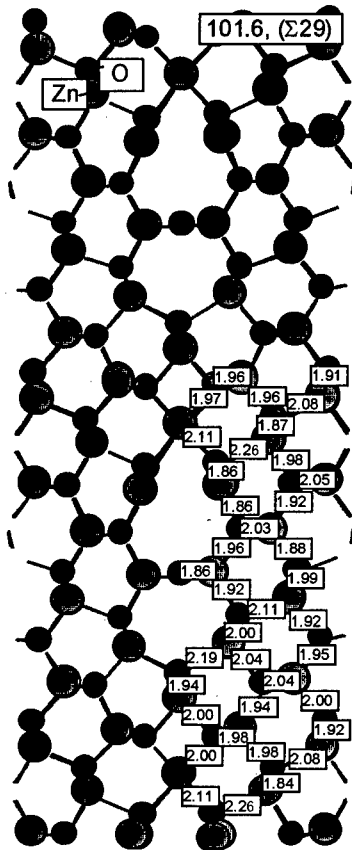
COMPUTER SIMULATION AND HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF THE Σ5 (210) AND (310), [001] TILT AXIS GRAIN BOUNDARIES IN MOLYBDENUM

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We present the results of a parallel study of the atomic structure of the Σ5, (210) θ=53.13° and (310) θ=36.87°, [001] tilt axis grain boundaries in bcc Mo, by computer simulation and High Resolution Electron Microscopy (HREM).

Excess energy values of different boundary configurations are obtained via a quasi-dynamical minimisation scheme while cohesion is described by a new n-body, central-force, phenomenological potential which satisfactorily reproduces static and dynamical properties of the bulk material.

HREM observations and numerical modelling both show the symmetric configuration of the Σ5, (210) θ=53.13° boundary to be of the lowest energy. The calculations show the stable Σ5, (310) q=36.87° configuration to be closely mirror symmetric, though the experimental verification is still incomplete. After few oscillations, the interplanar spacing near the boundaries converges rapidly to its bulk value while producing an overall expansion of the bicrystal. Qualitative agreement is found between calculated and experimentally determined expansion values.

These results contradict the conclusions of recent simulation works emphasising on the need to consider angular cohesion forces for a satisfactory description of grain boundaries structure in bcc transition metals.

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INVESTIGATION OF ASSEMBLIES OF GRAIN BOUNDARY DISLOCATIONS IN NANOSTRUCTURED COPPER BY COMPUTER SIMULATION OF X-RAY DIFFRACTION PATTERNS

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Unique properties of nanostructured materials are due to a long range area of grain boundaries and their specific defect structure. In particular, extrinsic grain boundary dislocations (EGBD's) are present in nanostructured materials processed by severe plastic deformation (SPD) and their density can reach extreme values (1 nm^{-1}) [1]. Low temperature annealing leads to a significant decrease in density of EGBD's and a concurrent radical change in properties of nanostructured materials even if a fine grain size still remains unchanged. It testifies a leading role of EGBD's in this process. However, it is not clear yet which configurations of EGBD's assemblies are possible , how they change during annealing and what assemblies are responsible for unusual properties of nanostructured materials processed by SPD.

To solve the problem comparative analysis of the results of experimental X-ray structural studies (such as shape, integral intensity, broadening, shift of centroids of X-ray peaks) [2] and the data from computer simulation of X-ray diffraction patterns of nanostructured materials was used. The simulation has been carried out on the basis of the kinematic theory of X-rays scattering [3] taking into account various configurations of EGBD's assemblies.

The conclusion about the possible configurations of EGBD's assemblies in nanostructured materials processed by SPD and the evolution of these defects during heating was made.

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ATOMISTIC SIMULATIONS OF Σ5 (310) [001] GRAIN BOUNDARIES IN STOICHIOMETRIC B2 Fe-Al AND DO$_3$ Fe$_3$Al WITH AN ANGULAR FORCE SEMIEMPIRICAL POTENTIAL

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A semiempirical embedded atom method potential including a non central additive term [1] is used to simulate the properties of Σ5 (310) [001] grain boundaries in stoichiometric B2 Fe-Al and DO$_3$ Fe$_3$Al [2]. Excess energy values of different configurations are obtained via a quasidynamical minimisation scheme with different local and bulk compositions. In all cases relaxation effects appear to be very important for the determination of the lowest energy structures.

For stoichiometric B2 FeAl with fixed local composition equal to the bulk composition two configurations very close to the symmetric, S and the pseudo symmetric, PS (half period translations in both [1,-3,0] and [0,0,1] directions) structures are the only stable ones with comparable excess energies (958 and 943 mJ/ m^2). The study of the point defect energies in the grain boundaries compared to the bulk [3] reveals a strong tendency to Al or Fe segregation at or near the grain boundary plane in both structures, leading to various metastable configurations at T=0K with energies lower or close to those of the non segregated structures. The most stable structure (PS-Fe) appears to be the PS one with a purely Fe central pseudo symmetry plane (767 mJ/m^2). Conversely in the case of DO$_3$ Fe$_3$Al the favoured structure is a symmetric one with Al segregation at the boundary plane.

The effect of a small deviation from the stoichiometric bulk composition has been studied for stoichiometric B2 FeAl. On the Fe rich side the relative and absolute stability of the PS-Fe structure increases drastically (309 mJ/m^2) whereas on the Al rich side two Al rich structures (one S and one PS) are favoured (338 and 332 mJ/m^2). Preliminary results of simulations in the reduced grand canonical Monte Carlo ensemble confirmed the tendency to Fe segregation for the PS structure for the stoichiometric B2 FeAl at non zero temperatures.

Finally, molecular dynamics simulations of the PS-Fe most stable OK structure as a function of temperature reveals a solid state structural transition of the grain boundary with increasing temperature at 1600K from the PS-Fe to a S-Fe structure.

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COMPUTER SIMULATION OF TILT GRAIN BOUNDARIES IN ALLOYS WITH L1₂ AND B2 SUPERLATTICES

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Computer simulation of grain boundaries (GB) was carried out in intermetallic compounds Ni_3Al with $L1_2$ superlattice and NiAl with B2 superlattice. In this work studies simmetric tilt grain boundaries $\Sigma=5$ [100](012) and $\Sigma=5$ [100](013) (special boundaries) with an axis of turn [001] and with angles of disorientation $\theta = 53.1°$, $36.9°$. The atomic interactions have been described by Morse empirical central-force potentials constructed with using equilibrium properties of investigated crystals. These potentials were tested at calculations of atomic structure and energy of planar defects such as antiphase boundaries, superlattice intrinsic stacking faults, complex stacking faults and other.

The atomic structure and energy of GB was calculated by a method of construction of γ-surface using three relaxation techniques: rigid two-dementional relaxation in which the atoms at shift one grain relative to another are in sites of corresponding lattices, rigid three-dementional relaxation and full atomic relaxation.

It is shown that $\Sigma=5$ tilt GB in Ni_3Al and NiAl have 4 and 2 unique GB core structures accordingly. Atomic structures and energies of all types of GBs are calculated. Reorganisation of GBs from one state to the other are investigated. It is shown, that a direction of GB slipping in both alloys is [100]. The simulations show the characteristic oscillatory and multilayer relaxations that been observed on an other plane defects (SF, APB) that have been observed previously. Value of the GB free volume are calculated. Comparisons of our results with geometrical model of coincidence site lattice (CSL) was carried out. Structure of GBs in alloys with $L1_2$ superlattice are being described good in model CSL. In alloys with B2 superlattice GBs in model CSL are unstable, the stabilization is achived by additional displacement on some vector along plane of defect.

INTERFACES TRANSFORMATION DURING INDENTATION, SHOCK, SHEAR AND FRICTION OF NANOPARTICLES BY MD-SIMULATION

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The short review of author's results concerning the investigation of inter-atomic interaction in metals and ceramics as well as the computer simulation of contacted nanoparticles interaction is presented [1-6]. The technique was modified for calculation of the adhesive interparticles bonds, adhesive energy and force, friction force, viscosity and hardness of contact, the Fourier-spetrum of mass center vibrations, etc., in couple with structure transformation of interface.

Nonlocal empirical potentials were constructed for bcc and hcp transition metals accounting elastic, thermodynamic and electron-gas properties [1,2]. Also new analitical self-equilibrated Me-Me, Me-X and X-X potentials are presented for diborides, mononitrides and monocarbides by the example of $TiN-TiB_2$ compound.

Processes of nanoindentation, pressing and stretching of α-Fe-roughness with W-surface was computer simulated at atomic level. Atomistic mechanism of contact creating with followed breaking was investigated. Crowdion mechanism of plastic deformation under indentation was confirmed [3].

Mechanism and elementary act of adhesion friction and wear of atomic-sharp W-roughness over Fe-surface were investigated both in constant height and force modes. Force criteria for wear, seizure and fracture of asperity during friction were suggested and atomic-force image of defect surfase was obtained [4,5].

Athermic shear of special $\Sigma=3$ and $\Sigma=9$ tilt boundary was investigated. Atomistic mechanism was studied of shear energy to transform into hypersonic phonon vibrations, named as the effect of "phonon skidding". The epitaxial mechanism accompanied the boundary migration during sliding was observed [6].

The effect of hypersonic vibrations generation under inelastic shock of nanoparticles is predicted, forming the dynamically steady vibration and translation state [7]. Resonance principle of this vibrations to amplify and powder compacting to activate was advanced by the method of a selective ultra/hyper-sonic radiation synchronized with a shock [8].

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ATOMISTIC SIMULATIONS FOR STRUCTURES AND ENERGIES OF TILT GRAIN BOUNDARIES IN α-ALUMINA.

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We have carried out atomistic computer simulations to study the equilibrium configurations and energetics of a series of tilt grain boundaries in α-Al_2O_3. Both symmetric and asymmetric boundaries for different grain misorientations were investigated by static energy minimization. For all simulations supercells with two-dimensional periodicities along the grain-boundary planes and up to several hundred atoms were used. The interatomic interactions were described by an empirical ionic shell model. Results for interface energies and atomic structures for a variety of tilt grain boundaries will be presented and put in comparison with available experimental HRTEM images. The rhombohedral and the prismatic twin grain boundaries have been found to have very low interface energies. Whereas some low-energy interfaces exhibit bulk-like atomic coordinations, others show rather open structures or considerable atomic disorder.

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CALCULATION OF THE ENERGY OF EXTENDED DEFECTS IN ZINC BY THE SEMI-EMPIRICAL TIGHT-BINDING METHOD

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The empirical many-body potentials which are available for simulation of defects in zinc are those proposed by Igarashi, Khantha and Vitek (1991) and by Mikhin and de Diego (1996). They both give a negative energy for the $(11\bar{2}2)$ twin boundary which is not satisfactory. To take into account the effects of the electronic distribution in a better way we have used the semi-empirical tight-binding method.

The method is based on the calculation of the matrix elements of the electronic hamiltonian in the nearest-neighbour tight-binding approximation of Harisson. They are then treated by the Lanczos-Haydock recursion on method. A local calculation of the density matrix is performed by a linear scaling method, as in the method of Li, Nunes and Vanderbilt. The attractive electronic contribution to the energy in thus obtained. The other contribution is the repulsive short range interaction between ions and is treated a two body potential.

The equilibrium atomic configuration at zero temperature is that of minimum energy. The interatomic forces are calculated by numerical gradients, each atom being submitted to very small displacement until the change of energy is less than 10^{-3} meV.

By using this relaxation procedure the parameters are fitted on perfect crystal properties : lattice parameters c and a, elastic properties.

A first calculation with a basis restricted to s and p orbitals gives the stability of the h.c.p. structure with a c/a ratio equal to 1.801 instead of 1.856. The energy of the stacking fault is improved with respect to preceeding calculation. the energy of the $(11\bar{2}2)$ and $(10\bar{1}2)$ twins are obtained and are positive.

An improvement is obtained by including the d orbitals. The h.c.p. structure is the stable one with the exact values of the c/a ratio, and satisfactory values of the energy of the extended defects (stacking fault, and the two twins) are obtained.

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MODIFIED STILLINGER-WEBER POTENTIAL FOR PLANAR DEFECTS MODELING IN III-V NITRIDES: AlN, GaN, InN

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The III-V nitrides exhibit large direct bandgap, a feature wich is very promising for short wavelength optoelectronic devices. Atomic scale simulations of these compounds are greatly needed to interpret high resolution electron microsopy (HREM) observations of interfaces and defects. For efficient computations, we adapt the Stillinger-Weber (SW) potential, initially designed and widely used for modeling in silicon.

The weak point of the classical SW potential is the fact that it is not able to distinguish the zinc-blende and the wurtzite structures. To overcome this limitation, we have added a third neighbor term.

For a given compound, the parameters of the potential are fitted to the experimental bulk properties: lattice parameter, c/a ratio, cohesive energy. Validity tests are performed by comparing the predicted elastic constants to the experimental ones. Then the potential can be used for atomistic simulation of interfaces or other defects.

We give the values of parameters of the potential for the three compounds: AlN, GaN and InN. Our predicted elastic constants are in the range of available experimental values.

We have used our GaN parametrization to determine the atomic structure of the $\{1\bar{2}10\}$ planar defect by energy minimization. The result corresponds to the ideal $1/2<1\bar{1}01>\{1\bar{2}10\}$ stacking fault model.

Our modified SW potential allows fast atomic scale calculations, to predict static and dynamic properties of large defects with a satisfactory accuracy.

RELATIVE STABILITY OF TWO STRUCTURES OF THE Σ = 11 <011> TILT GRAIN BOUNDARY IN SILICON AND GERMANIUM BY THE TIGHT BINDING METHOD

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The $\Sigma = 11$ <011> tilt grain boundary may exhibit two possible atomic structures usually named A and B. High resolution electron microscopy studies have shown different behaviour for silicon and germanium. At low temperature the B structure has been observed in germanium and the A one in silicon. Several empirical potentials such as those proposed by Keating, by Baraff Kane and Schlüter, and by Stillinger and Weber give the A structure as the stable one in silicon, in agreement with the experiments. Less numerous empirical potentials are known for germanium, but recently, Widler and Teichler use the Weber's bond charge model and show the stability at zero temperature of A structure in silicon and B one in germanium. We have adapted the semi-empirical tight-binding method to the study of grain boundaries, to have a way to combine empirical features and quantum results with a reasonable computing times. We use the tight-binding parameters proposed by Mercer and Chou for silicon and germanium. The repulsive part of the energy has a simple analytic form and the electronic part is calculated by the recursion method. The matrix elements are calculated in the tight binding approximation of Harrison and the calculations are performed with a linear scaling method adapted from Li, Nunes and Vanderbilt. The atomic structure is relaxed by comparing the energy of each atom after a small displacement until the minimum energy is obtained. The results obtained show that the stable structure is A for silicon and B for germanium. They are compared with those obtained with other potentials, in the following table giving the energy in mJm^{-2}.

Material	Silicon			Germanium		
Structure	A	B	E_B-E_A	A	B	E_B-E_A
Keating	803,4	844,6	41,2	656,2	691,0	34,8
Stillinger-Weber	622,6	644,5	21,9	553,2	572,6	19,4
Baraff	328,2	328,2	0,1	242,8	242,1	- 0,7
Wilder-Teichler	467	478	11	373	366	- 7
Mercer-Chou	518,2	569,7	51,5	461,7	448,5	-13,2
Experiment			> 0			< 0

The question which arise is : which is the origin of the difference in potential and behaviour of silicon and germanium which are so close in many other respects ?

AB INITIO STUDY OF ELECTRONIC AND GEOMETRIC STRUCTURES OF METAL/CERAMIC HETEROPHASE BOUNDARIES.

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The adhesion geometries of coherent cube-on-cube interfaces between spinel ($MgAl_2O_4$) and the two metals Al and Ag were determined by ab-initio band-structure calculations in the local density approximation (LDA). For $Al/MgAl_2O_4$, for which experimental data are available, the calculated optimum interface geometry is in excellent agreement with HRTEM measurements (distance d_{int}: 1.90 Å calc., 1.92±0.04 Å exp.).

The work of adhesion W_{ad} is calculated for three different high-symmetry translation states between an Al-O terminated (001) surface of the spinel and the (001) surface of each of the metals. The binding energy curves display a distinct optimum for the adhesion of aluminum atoms on top of the spinel oxygen ions at a W_{ad} value of 2.4 J/m². For silver several adsorption sites are isoenergetic at 1.1 J/m² and the intersections of the $W_{ad}(d_{int})$ curves indicate a low-energy dissociation path.

A further analysis of the electronic structure in the $Al/MgAl_2O_4$ system reveals the charge redistribution in the metal towards the oxygen ions as the main contribution to bonding. On the contrary, polarization of the metal film is the major effect observed on the adhesion of Ag to the spinel substrate.

AB INITIO STUDY OF GRAIN BOUNDARIES IN SiC AND Si

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It is of great importance to study the atomic and electronic structure of grain boundaries in SiC and Si. Grain boundaries in SiC dominate various properties of SiC ceramics and grain boundaries in Si dominate the properties of polycrystalline Si used for solar cells or thin film transistors. Currently, it is possible to perform *ab initio* calculations of such complex systems by using the first-principles molecular dynamics method based on the density-functional theory [1]. Also it is possible to obtain a lot of information on the atomic and electronic structure of grain boundaries by using recent techniques of high-resolution transmission electron microscopy (HRTEM). In this paper, we report our recent *ab initio* calculations of coincidence tilt boundaries in SiC and Si. Results are compared with our previous tight-binding (TB) calculations [2], and with our recent HRTEM observations in SiC [3].

We deal with several $<011>$ tilt boundaries in SiC and Si. In the case of SiC, polar and non-polar interfaces are constructed by inverting the polarity of grains. We use the conjugate-gradient technique for electronic minimization [1] and optimized pseudopotentials [4].

For the boundaries in Si, fourfold configurations constructed by structural units such as odd-membered or six-membered rings are stable within small bond distortions, although distorted bonds have reduced bond charges. No electronic states exist inside the band gap, although states with large probabilities at the interface regions are observed near the band edges. These features are similar to previous TB results.

For the polar and non-polar interfaces of the boundaries in SiC, fourfold configurations are also stable, although the C-C and Si-Si wrong bonds are introduced. The C-C and Si-Si wrong bonds have bond lengths and bond charges rather similar to those in bulk diamond and Si. The wrong bonds induce localized states at the band edges. The present results are in good agreement with the HRTEM observations, which reveal the presence of structural units and wrong bonds at the interfaces. Relaxed configurations have been compared with the HRTEM images in detail.

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USING CHEMICAL BONDING TO DETERMINE INTERFACE BEHAVIORS IN RARE-EARTH DOPED SILICON NITRIDE

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Through microstructure designing the mechanical properties can be tailored in the covalent bonded Si_3N_4 ceramics. That is because in Si_3N_4 the intergranular regions are ubiquitously dwelled with amorphous oxide/oxynitride phases, which dictate the grain growth and morphology as well as the physical properties of the grain boundary. It has been found that the grain morphology changes systematically with rare-earth ions of different sizes in the amorphous phases, the same is true for the thickness of amorphous films covering every grain boundaries. It is very important to know how different rare-earth ions affect the interface properties, thus to lead to different microstructures.

EELS is a useful tool to reveal local structural and chemical nature. For silicon nitride, oxynitride and oxide, the chemical bonding is reflected in the near-edge structures of their silicon L edges in a systematic way. This relation is empirically extended to characterize the chemical bonding of the interface regions in a model system, provided by M. Hoffmann, of Si_3N_4 with minor (15 wt.%) or dominant (~95 wt.%) amounts of rare-earth (La or Yb) base oxynitride glasses. Differences between the interfaces and their matrices in EELS signals are sorted out to reveal the bonding nature of the interfaces. This process can also lead to measure other physical and chemical properties from ~1 nm thick interface regions. A dedicated STEM was used for this work; it can provide an energy resolution better than 0.7 eV and an EELS spatial resolution better than 1 nm. Chemical and bonding profiles also can be obtained with this instrument.

The silicon atoms in the La (or Yb) and Al segregated grain boundary films have bonding nature significantly more covalent as compared with silica due to the presence of nitrogen in the films, similar to the undoped Si_3N_4 samples. However, the interfaces between Si_3N_4 and the rare-earth-based glasses are more covalent than the grain boundary films. This is opposite to the undoped samples where the grain boundary films are more covalent than the interfaces between Si_3N_4 and SiO_2 glass pockets. This different trends signify that the rare-earth atoms take an active role in interface bonding.

Grain boundary film composition changes with the ion size as well as the grain surface structure. La segregation to the films is ~9 times higher than Yb. It is also observed that La are trapped inside the grains between successive cycles of growth growth while Yb can not be trapped; this is consistent with the higher La segregation level to the grain boundary. It might be the primary reason that La is more effective in poisoning the grain growth at the basal plane to achieve much higher specific ratio than Yb-doping.

(Keywords: EELS, Si_3N_4, grain boundary, bonding)

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TEM INVESTIGATION OF METAL-OXIDE INTERFACES
IN THE Ni-20Cr SYSTEM

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This study deals with the oxidation behaviour of thin Ni-20Cr strips, between 500 and 900°C. The purpose is to get a better understanding of the oxidation process and of its influence on adhesion and mechanical behaviour of nickel based alloys. Thin strips of 200µm were under consideration in order to enhance the oxide scale effect on the deformation.

Analytical TEM investigations were performed on cross-sectional specimens oxidised at various times and temperatures in order to specify:
- the nature and morphology of the oxide layers,
- the metal-oxide interface structure (orientation relationship) and adhesion,
- the structural and chemical evolutions in the alloy beneath the oxidised surface (defects, chromium depletion).
According to the oxidation conditions (temperature, time), the growth of oxide scales is described, in relation with oxidation kinetics. The structure of the resulting metal-oxide interfaces is characterized as well as outer and inner oxidation areas.
From two hours up to two days oxidation in air environment, an external scale of NiO columnar grains and internal precipitates of Cr_2O_3 are formed at 600°C whereas at 900°C, a continuous layer of Cr_2O_3 is observed adjacent to the alloy, below a two-zoned layer composed of NiO and $NiCr_2O_4$. Special orientation relationships, with respect to the underlying alloy, are evidenced during oxide growth. Chromium depletion in the alloy is related to the oxidation process.

Following these structural observations, the oxidation effect on the creep behaviour of Ni-20Cr strips at different temperatures is discussed, according to the oxidation mechanism evolution. The weakening or strenghtening effect depends on the testing temperature and is linked to the nature of the oxide which acts as a diffusion barrier.

THE CHARACTER OF STEPS ON GAMMA / ALPHA-2 INTERFACES IN TiAl-BASED ALLOYS WITH THE LAMELLAR MICROSTRUCTURE

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Alloys based on the intermetallic compound γ-TiAl have considerable potential for use in aerospace applications because of their low density, high strength and good oxidation resistance. The alloys with the best combinations of properties often have a lamellar microstructure which consists of thin alternating plates of the γ phase and the α_2-Ti$_3$Al phase which gives a closely spaced array of parallel planar interfaces within each lamellar colony. These plates exhibit a well-defined orientation relationship with $\{111\}\gamma$ //(0001)α_2 in the interface and <110>γ //<1120>α_2 and the character of these interfaces plays a crucial role in determining the mechanical properties of the alloys. Transmission electron microscopy (TEM) has been used to show that the interfaces contain arrays of dislocations which accommodate the difference between the lattice parameters of the two phases and steps with defect character whose motion produces the α_2 to γ transformation (e.g. Mahon and Howe 1990; Zhao and Tangri 1991). Analyses of high resolution electron microscopy (HREM) images from such steps have been used to suggest that they correspond to Shockley partial dislocations with Burgers vectors a/6 <112>γ in the plane of the interface (e.g. Singh and Howe 1992). This nomenclature has led to some misleading comparisons being drawn between the behaviour of the steps and that of Shockley partial dislocations in the γ phase.

In our work we have studied lamellar interfaces in TiAl-based alloys containing 48 at.% Ti, 44 at.% Al and 8% of other transition metal additions. These alloys were designed to have little or no misfit between the α_2 and γ phases and are thus convenient for studies of interfacial dislocations because there are no misfit dislocations present. In this paper we will present a HREM study of the character of the steps in which the results of circuit mapping are compared with the Burgers vectors which would be expected on the basis of the topological theory of interfacial defects (Pond 1989). It has been found that the steps with 30° character and Burgers vectors of a/6<112>γ and a/3<112>γ are most common. The flux equation developed by Hirth and Pond (1996) has been used to show that the mass transport required for the motion of these steps is dependant only on the step height, and not on the Burgers vector. The significance of these observations for the α_2 to γ transformation will be discussed.

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DIRECT DETERMINATION OF DOPANT SEGREGATION SITES AT GRAIN BOUNDARIES

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We present a direct determination of the atomic sites for segregation of a dilute solution of impurities by a combined experimental and theoretical approach. Z-contrast imaging is used to directly locate the atomic sites selected by arsenic segregated to a symmetric <001> tilt boundary in silicon with near single atom sensitivity. The images indicate that arsenic not only substitutes for silicon in a few selected sites in this boundary but that it also selects just one of the two roughly identical atomic configurations in this planar defect.

The specific sites chosen have been further examined using first principles calculations, which indicate that isolated As dimers are the preferred segregation configuration. These calculations indicate that paired arsenic atoms can attain their preferred three-fold coordination in the GB core without forcing neighboring Si atoms to become over- or under-coordinated.[*] This is accomplished with segregation energies ranging from 0.32 to 0.52 eV/As atom in good agreement with experimentally determined values that range from 0.4 to 0.65 eV. Thus, our segregation-through-repulsion mechanism of paired impurities provides an explanation for the experimental evidence that n-type dopants will segregate to GBs in Si and Ge.

The synergistic combination of experiment and theory establishes that segregation can occur in defect-free boundaries as the result of cooperative chemical forces. Our observation of the selected segregation sites and concentration, the calculated values for the segregation energies in various GB sites and configurations, and the assumption of thermal equilibrium all are found to provide a remarkably self-consistent, atomic-scale picture of the segregation of As to this silicon GB.

0.2 nm
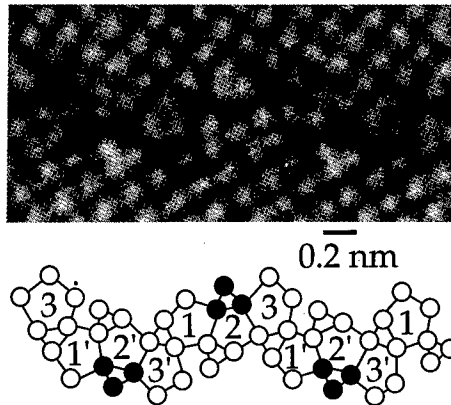
Z-contrast image of a symmetric 23° <001> tilt boundary in silicon doped with arsenic and a schematic of the projected atomic column positions. The columns associated with As, indicated as grey in the schematic, are found to be the brightest features in the boundary.

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THE MECHANISM OF EMBRITTLEMENT OF COPPER BY BISMUTH

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The embrittlement of copper by the presence of trace amounts of bismuth was first reported more than a century ago. It has since been established that the embrittlement is associated with intergranular segregation of the bismuth, but the microscopic role of impurity segregation on the mechanical response of the grain boundary is still poorly understood. In this paper we present an atomic resolution investigation of the structure of copper grain boundaries with and without bismuth segregation. Z-contrast images directly identify the atomic sites where bismuth segregates in the grain boundary. These experimental observations match the theoretical predictions of Vitek et al.[1] The images combined with a spatially resolved chemical analysis (EELS and EDS) confirms the presence of Bi and reveals the effect of this impurity on the electronic structure at the grain boundary. Density functional theory calculations are used to interpret the electronic structure as revealed by EELS and suggest a natural explanation of the mechanism of the boundary embrittlement.
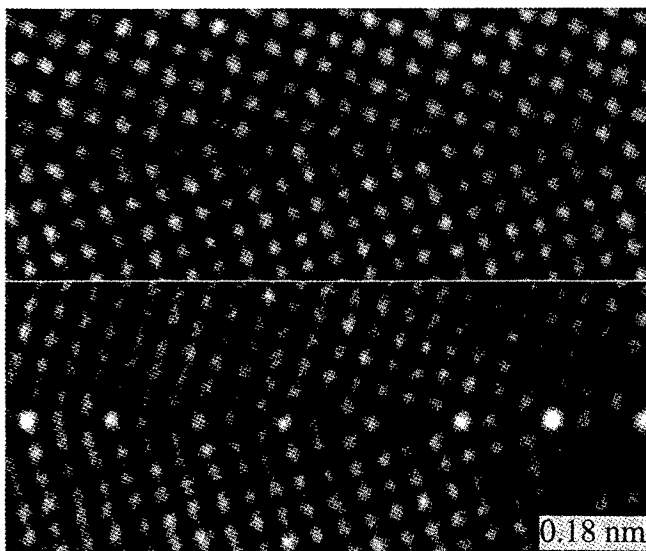
Z-contrast images of symmetric 37° <001> Cu tilt grain boundaries. Top image is from a pure Cu boundary. The bottom image is from a Bi-doped boundary. The Bi segregation sites are the bright features in the boundary.

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IMPURITY INDUCED STRUCTURAL TRANSFORMATION OF AN MGO GRAIN BOUNDARY

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Small concentrations of impurities that segregate to the grain boundaries of a polycrystal can have a profound effect on the properties of the material. Perhaps the best example is the catastrophic brittle intergranular failure of metals that follows the diffusion of certain elements to the more open structures present at the boundary core. In nearly all of these cases, the impurties segregate without significantly affecting the atomic configurations at the boundary . Much of the theoretical work on impurity segregation in grain boundaries is in fact based on such an assumption. There is also a possibility that segregated impurities can induce a structural transformation of the grain boundary core. However, direct experimental determination of the resulting atomic arrangements has not yet been possible.In all previous experimental work, direct determination of the atomic arrangements in the grain boundary core was not possible. In this presentation, we report direct imaging of the atomic positions in a grain boundary in MgO using Z-contrast imaging. The images clearly indicate impurities are segregated to particular atomic columns. The chemical identity of the impurity was determined by high spatial-resolution electron energy loss spectroscopy to be calcium. Combining first principles total-energy calculations of different grain boundry structures with an earlier determination of the structure of pure MgO grain boundaries, we conclude that Ca segregation induces a structural transformation of the boundary core.
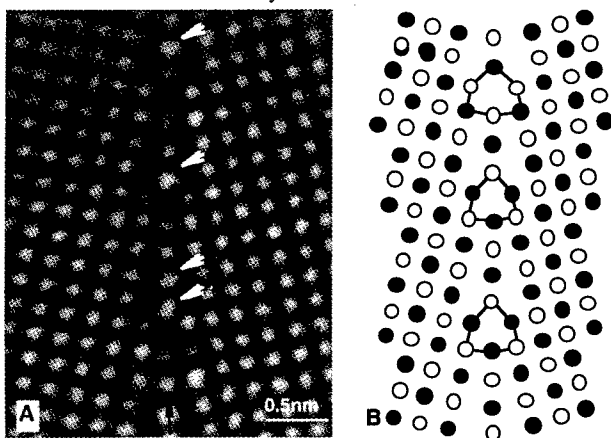
Z-contrast image (A) and derived model (B) of a Ca-doped 24.5° <001> MgO tilt boundary.

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THE ATOMIC STRUCTURE OF TILT GRAIN BOUNDARIES IN
GaN LAYERS GROWN ON (0001) SAPPHIRE : A CASE STUDY,
THE Σ31 (11 $\bar{4}$ $\bar{7}$ 0) SYMMETRIC GRAIN BOUNDARY

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Due to the lack of substrates, GaN layers for optoelectronic application in the green to
UV range, are grown by MBE or MOVPE on sapphire at 800 and 1100°C respectively
on top of a lower temperature buffer layer grown at temperatures close to 600°C (1).
Although the GaN layers exhibit a mosaic structure with rotation angles up to 4-5° in
the worst cases, the buffer layers can exhibit higher angle grain boundaries (2-3).

In this work, a systematic analysis of the coincidence rotation around the [0001] axis
has been carried out (Σ7,Σ13, Σ19, Σ31, Σ37, Σ43, Σ49). The structural units for these
seven Σ's have been constructed for GaN or AlN. A detailed experimental analysis was
carried out in the Σ31 boundary found inside an AlN buffer layer grown on sapphire at
800°C by molecular beam epitaxy.

Geometrical models of this boundary were constructed and found to exhibit 4, 5, 6, 7
and 8 atom rings.

The geometrical models were relaxed using a modified Stillinger-Weber potential (4).
Next, the relaxed models were used for image simulation using the multislice
programme of the electron microscopy software (5) and the results were compared to
the experimental micrographs.

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GRAIN BOUNDARY STRUCTURE IN BaTiO$_3$ WITH A SMALL EXCESS OF Ti-SITE DOPANT

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The grain boundary structure was examined in BaTiO$_3$ doped with Ti-site dopants mainly by high resolution electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). It was found that the grain boundaries of Ti-site excess BaTiO$_3$ were mostly facetted with {210} type habits. The difference in chemical bonding state between grain interiors and grain boundaries was detected with EELS spectra. From a comparison of EELS spectra with the calculated one obtained from molecular orbital method (DV-Xα method), the facetted boundaries are likely to have an extra Ti-O bond having a rutile-like structure. HRTEM image cleared the existence of an ordered structure along the habits. The ordered structure of the facetted boundaries revealed by HRTEM image can reasonably be explained by the presence of an extra TiO$_2$ bond.

It is known that the abnormal grain growth takes place when a small amount of Ti-site dopants is added to BaTiO$_3$. The abnormal grain growth results from the strong suppression of normal grain growth, which is well-interpreted from kinetic analysis of the abnormal grain growth behavior in BaTiO$_3$ with a small excess TiO$_2$. The inhibition of normal grain growth observed in Ti-site excess BaTiO$_3$ may be caused by the formation of the habits.

MICROSTRUCTURAL INVESTIGATIONS OF INTERFACES IN PVD TiN COATED TOOL STEELS

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During the last few years there has been an increasing interest in Titanium-nitride (TiN) films deposited by physical vapour deposition methods [1], due to its successful use in a variety of thin film applications. TiN films with compositions in the phase region ε-Ti_2N + TiN were deposited on tools steel substrates with different hardness and surface roughness by a BAI 640R unit, using a triode ion plating (e-gun) with high plasma density. The coated substrates were submitted to a rolling contact fatigue test technique (modified pin-on-ring test) to obtain some clarification of the mechanism of interfacial failure. The advantage of this technique over scratch and indentation tests is that the critical load is a sensitive measure of the bonding conditions at the coating-substrate interface and it remains insensitive to the testing conditions [2].

Tests were run using PVD coated rings finished by polishing or grinding to produce different surface roughness. It is evident that the state of the substrate surface before coating has a strong influence on the bonding strength of hard coatings [3].

TiN coatings with a thickness value between 5 and 6 μm reproduces the original substrate surface and exhibit a columnar microstructure with dense grain boundaries. From the experimental results it is clear that under the present testing conditions, fatigue failure of the coating-substrate composites is initiated at the interface region, and the interfacial failure stress is closely associated with the coating-substrate bonding conditions. Indeed, such factors as smooth substrate surface and polishing before coating, which are known to substantially improve the coating-substrate bonding strength [4], also improve the interfacial failure stress. Based on microstructural investigations (SEM, TEM), two mechanisms of crack propagation under pure rolling conditions were found, depending on the substrate hardness. For the softer substrates the cracks propagate mainly perpendicular to the surface, while for the harder substrate the cracks are generally originated at the interface and grow in the coating parallel to the surface. When subcracks are formed and grow perpendicular to the interface, a small piece of material is released, resulting in the so-called spalling failure.

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MODIFICATION OF Ag/ Mn_3O_4 INTERFACES BY DISSOLUTION OF Sb OR Zn IN Ag STUDIED WITH HRTEM

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The structure and chemistry of heterophase interfaces often govern the performance of composite mterials. Solute segregation to the hetero-interfaces is known to affect the adhesion at the interfaces[1]. However, in contrast to segregation at grain boundaries only very few studies have addressed segregation at metal/ceramic interfaces[2]. In the present study a segregating element, Sb, is dissolved in an Ag matrix containing a highly dispersed ceramic phase in the form of Mn_3O_4 precipitates with sizes of 10-20 nm. The influence of this dissolution on the precipitate morphology and structure is studied using HRTEM.

The Mn_3O_4 precipitates in pure Ag are obtained by internal oxidation of Ag-3at.%Mn in air at 900 ^{0}C. This system is well characterized[3] and the precipitates have octahedral shape since they are bounded by 8 {111} planes (close packed oxygen planes) of the tetragonal spinel lattice of Mn_3O_4. These {111} planes all tend to be parallel to the {111}'s of Ag. However, due to the tetragonal distortion of Mn_3O_4 this parallellism can only be achieved for one pair of {111} facets. At another pair of facets a tilt of 7.6^0 occurs between the (111)'s of Mn_3O_4 and Ag which is accounted by ledges in the Ag.The dissolution of a few at.% of Sb in the Ag matrix is achieved by annealing the Ag/ Mn_3O_4 sample in an evacuated quartz tube also separately containing a tiny amount of Sb, resulting in a relative homogeneous distribution of Sb in the Ag. HRTEM observations showed 2 major effects of the Sb dissolution on the precipitates: (i) a change from a precipitate sharply facetted by solely {111} to a globular shape with sometimes also short {110} and (001) facets and (ii) a partly reduction of Mn_3O_4 in MnO for a part of the precipitates.

The lower interfacial strain energy for Mn_3O_4/Ag with respect to MnO/Ag is probably responsible for the tendency to keep the outer core of the precipitate Mn_3O_4. The reduction of Mn_3O_4 in MnO can be understood since annealing in Sb vapor will result in equilibrating the sample with respect to the dissociation pressure of Sb-oxide and this pressure is significantly lower than the original oxygen partial pressure used for internal oxidation. To test this explanation, a pure Ag/Mn_3O_4 sample was annealed in Zn instead of Sb vapor. The dissociation pressure of ZnO is in-between these pressures for MnO and Mn_3O_4 and therefore full reduction of Mn_3O_4 in MnO is expected. This expectation was indeed confirmed: only MnO precipitates with {100} truncated octahedral shapes were observed in the Zn treated sample.

On Ag surfaces Sb appeared, from several elements tested, to be the most efficient to induce layer-by layer growth[4]. This efficiency requires Sb to be a strongly segregating element and to significantly reduce the energy of steps (Schwoebel barrier) at the surface[4]. Analogous to these observations for free surfaces, Sb is also expected to segregate to the Ag/oxide interface and to reduce the energy of steps/ledges (unavoidable due to the tetragonality of Mn_3O_4 with respect to the cubic matrix) at the interface. The lower the step energy the more globular the equilibrium shape of the precipitates become[5].

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STRUCTURE OF A [101] TILT GRAIN BOUNDARY IN A MOLYBDENUM BICRYSTAL

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A molybdenum bicrystal containing a [101] tilt boundary has been observed by weak beam dark field and high resolution electron microscopy. Several diffraction conditions confirm the presence of a set of parallel dislocation lines with a spacing 19Å as shown in figure 1a. The same spacing has been found in the HREM images as shown in figure 1b. The total misorientation has been measured using the Kikuchi line technique (1). It does not correspond to a pure tilt configuration. The measured tilt component ($\theta = 54.4°$) is intermediate between the two major coincidences $\Sigma = 41c$, $\theta = 55.88°$ and $\Sigma = 11$, $\theta = 50.48°$. The Brandon criterion (2) indicates that both coincidences can be used to describe the boundary. The Burgers vectors of the observed dislocations can be indexed in terms of the DSC lattices of both coincidences and the application of the Frank formula gives a reasonable agreement between calculated and measured dislocation spacings.

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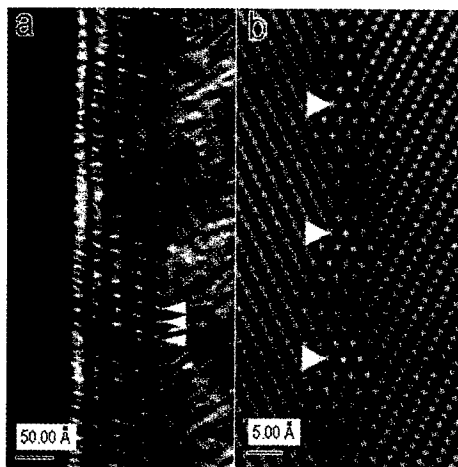
Fig 1 a) weak beam image **g=020**
b) filtered HREM image , atomic positions are white. (400kV)

TWIST ANGLE DEPENDENCE OF JOSEPHSON EFFECT
MEASURED IN THE [001] TWIST BOUNDARY OF
$Bi_2Sr_2CaCu_2O_X$ SUPERCONDUCTOR BICRYSTALS

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Josephson junctions having both the direct (S/S) and indirect thin silver layer (S/Ag/S) structures were fabricated by solid state joining of the (001) surface of two flaky $Bi_2Sr_2CaCu_2O_X$ single crystals. A small area junction of 100~200 μm in diameter was fabricated by Ar^+ ion selective etching of one of the two thin single crystal superconducting $Bi_2Sr_2CaCu_2O_X$ flakes. A 2~100 nm thick silver layer was deposited on the (001) planes by a sputtering method just prior to the joining of the surfaces to produce S/Ag/S junctions. It is clear that the critical current I_c of the S/Ag/S junction was the function temperature with $I_c=I_{OH}(1-T/T_c)^2$ for $T \geqq 0.6Tc$, and $I_c=I_{OL}(-G/T^{1/2})$ for $T \leqq 0.5T_c$. In the S/S junction, the high I_c values were obtained when the [001] twist angle θ was 23°, 28°, 37°. Our results indicated that the Josephson effect is strongly influenced by both the temperature T and the [001] twist angle θ in the S/S and S/Ag/S junctions.

GRAIN BOUNDARY OBSERVATION OF Al-DOPED SINTERED β-SiC BY BOTH HRTEM AND STEM

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Combination of HRTEM and STEM has been known as a powerful tool for material investigations, so that it has been employed to investigate grain boundaries in recent years. Both high-resolution transmission electron microscope (HRTEM: Topcon 002B with point resolution of 1.8 Å) and scanning transmission electron microscope (AEM: VG-STEM 601 UX) were carried out to observe the structure and chemistry of grain boundaries of Al-doped sintered β-SiC. Two specimens, as sintered and deformed Al-doped sintered β-SiC were provided. It was shown by HRTEM images that there are secondary phases at grain boundaries of both specimens and revealed by energy dispersive x-ray spectroscopy (EDS) that Al and O segregated at grain boundaries. Additionally, it was discovered that the chemistry of grain boundaries were different form of aluminium oxides from the as-sintered specimen to the deformed specimen.

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Atomic Structure and Chemical Bonding State of Sapphire Bicrystals

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Sapphire bicrystals which have <0001> tilt boundaries were fabricated by joining at high temperature. These bicrystals include small angle boundary, $\Sigma 3$ boundary, $\Sigma 7$ boundary and high angle boundaries. The grain boundaries were investigated by high resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS). In order to determine the location of atoms at the boundaries, computer simulations were performed to compare the experimental HREM images. EELS was used to evaluate the chemical bonding state at the grain boundaries, and its fine structure was quantitatively interpreted by calculating the theoretical EELS for realistic grain boundary models obtained from HREM image simulation.

A first principles molecular orbital (MO) calculation using DV-Xα cluster method was used for the theoretical calculation. The dependence on the bond overlap population (BOP) was calculated by the DV-Xα method for a cluster model (for example, $(Al_2O_{10})^{14-}$ for $\Sigma 7$ grain boundary) as a function of O-O atomic bond length across the grain boundaries. In the case of $\Sigma 7$ grain boundary, BOP is maximized at a O-O bond length of approximately 0.13nm. This agrees well with the atomic model obtained from HREM image comparison.

Furthermore, grain boundary energy was measured by thermal grooving technique for all of grain boundaries, and compare their atomic structure and chemical bonding state to prospect the relationship between the grain boundary characteristic and the physical properties, grain boundary energy, mechanical strength and so on, in alumina.

$(1\bar{2}10)$

$(2\bar{1}\bar{1}0)$

2 nm
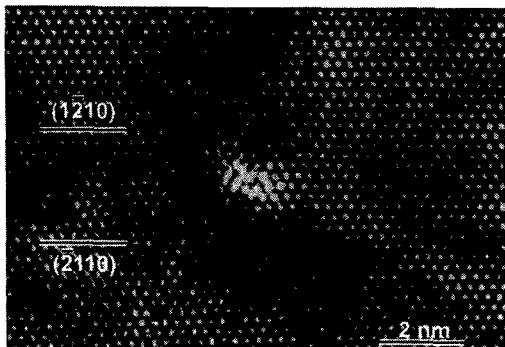
HREM micrograph of <0001> $\Sigma 3$ tilt grain boundary in the sapphire bicrystal fabricated by high temperaure joining technique.

DISSOCIATION OF MISFIT DISLOCATIONS AT γ/α₂ INTERFACES IN A TI₆₀AL₄₀ ALLOY.

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The heterointerfaces of a lamellar $Ti_{60}Al_{40}$ compound have been investigated by high resolution electron microscopy. The microstructure of this alloy consists of alternate TiAl (γ) and Ti_3Al (α₂) plates. To date, two kinds of dislocations have been observed, most of them accommodating the length misfit, with $1/6<112>_\gamma$ Burgers vectors parallel to interfacial facets (1-5) and others with a $1/3<111>_\gamma$ Burgers vector perpendicular to the facets (6). Sometimes, quite different dislocations can be observed with a split core and skew Burgers vectors relative to facets. Due to the difference in elastic constants, the equilibrium position of these latter dislocations can be out of the heterointerface, a geometry already observed for the Nb/Al_2O_3 interface (7). In this latter case, all dislocations are identical and have an edge component parallel to the interface. The present investigation reports on a case of dislocations with skew Burgers vectors relative to the $\{111\}_\gamma//\{0001\}_{\alpha2}$ facet orientation, the observation direction being $<110>_\gamma//<11\bar{2}0>_{\alpha2}$. The pseudo-periodic dislocation array compensates both the parametric and angular misfits. The configuration is rather complex because all misfit dislocations are not identical and some of them are dissociated. Two types of Burgers vectors, $1/2<110>_\gamma$ and $1/6<114>_\gamma$, have been determined and three different kinds of configurations are depicted: they consist in a $1/2<110>_\gamma$ dislocation lying in TiAl phase close to the hetero-interface, associated or not with a $1/6<112>_\gamma$ dislocation ledge (DL) lying in the boundary. The height of the DL is either $2\ d_{\{111\}\gamma}$ or $4\ d_{\{111\}\gamma}$.

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STM IMAGING OF MISFIT DISLOCATIONS

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STM observations of free surfaces in metal or semiconductor lattice mismatched systems have revealed sometimes strain relaxations due to crystalline defects, see e. g. [1-5]. For some particular systems related to epilayers with constant thicknesses h equal to a few atomic monolayers, the deformation of the free surface can be registered at atomic-scale. However, the interpretation of these images are not straightforward, one difficulty being the complexity of the three dimensional strain fields associated with these crystalline defects, see e. g. [5-9].

In the present work, some solutions are given for the elastic displacement field u of the free surface of a bimaterial assuming linear elasticity and periodic limiting boundary conditions. Applications to theoretical STM images are illustrated for InAs/(111)GaAs with epilayer thicknesses equal to 3 and 5 monolayers (length misfit = 8%). Examples illustrate STM images of edge MD networks: (i) a parallel set of MDs, (ii) a honeycomb network with undissociated triple nodes, (iii) a hexagonal network for which each other node is split, which gives rise to triangular shapes of interfacial faults limited by Shockley partials, (iv) a triangular network. Some of the computed images are compared to recent experimental evidences published in the literature for the InAs/GaAs heteroepitaxy [7-9].

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ASYMETRIC INCOMMENSURATE GRAIN BOUNDARIES. A JOINED ELECTRON MICROSCOPIC AND NUMERICAL ATOMIC STUDY IN NICKEL.

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Incommensurate grain boundaries are difficult to study because they are not periodic [1]. We have obtained high resolution electron microscopy observations (HREM) of an *a priori* incommensurate asymmetric (331)/(111) tilt grain boundary in nickel. In order to understand its atomic structure, we have simultaneously performed numerical atomistic simulations of the same grain boundary using a tight-binding N-body potential adapted to nickel [2] together with a (quenched) molecular dynamics structure optimisation algorithm. We have built and relaxed several atomic models which are approximants to the ideal (331)/(111) and which reproduce the structural units observed in HREM. We present the results of these atomistic simulations versus the microscopic observations.

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SHOCKLEY PARTIALS AND GRAIN BOUNDARIES IN β-SiC. A JOINED ELECTRON MICROSCOPIC AND NUMERICAL ATOMIC STUDY

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During sintering of β-SiC with B and C additives, grain growth results in the formation of faulted β-SiC and α-SiC. The structures of the observed grain boundaries depend on the growth mechanism which is itself related to the polytype [1]. We are dealing with defects in the β-phase.

Defects are identified and their structure characterized by HRTEM performed at 300kV (Scherzer resolution = 1.7 Å). We have developed atomistic calculations (molecular dynamics) with the angular N-body Tersoff potential adapted to SiC [2] in order to compare with our HRTEM observations.

The β-grains contain many boundaries consisting of a pile up of a few 1/6<112> dislocations. The boundaries are observed in a {110} plane. Depending on the number of involved dislocations, the projection of the resultant Burgers vector is equal to 1/12<112>, 1/6<112> or zero. We propose a reconstruction for a 30° Shockley partial which is very similar to the core of the 30° Shockley partial in silicon [3]. In the case of small {112}Σ=3 boundaries, there is no rigid body translation between the grains and thus the Bourret and Bacmann model cannot apply [4]. We propose a model derived from Pond et al. [5].

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ON THE USE OF ELECTRON MICROSCOPE IMAGES TO DETECT AND CHARACTERIZE MICROTWINS IN FCC MATERIALS WHEN THE NET DISPLACEMENT ACROSS THE MICROTWIN IS ZERO

by

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In this paper, the authors discuss the problem of detecting microtwins in FCC materials when the net displacement across the microtwin is zero. The manner in which the problem arises can be seen by first recalling that a twin in FCC materials can be generated by successive displacements of (111) planes by $a/3[111]$ which converts the stacking sequence from ABC to CBA. If these displacements are limited to a relatively small number then a microtwin is formed, as shown in the figure below. Since each displacement, $a/3[111]$, corresponds to an intrinsic stacking fault, the microtwin can also be thought of as a succession of adjacent intrinsic faults. The diffraction contrast image can therefore be calculated in two ways, one based on a microtwin model and the other by employing a stacking fault model. It should be noted that the theoretical results to be presented in this paper have been verified by the authors by showing that both ways of calculating diffraction contrast images give the same contrast.

It is next of interest to consider the displacement of the lower matrix in the figure below with respect to the upper matrix which will, in general, be $(ma)/3[111]$ where $m = 1, 2, 3 \ldots$. These displacements, therefore, are in effect either 0, $a/3[111]$ or $2a/3[111]$. The latter two cases have been considered in a previous paper by the authors [1] and will not be discussed here. The case of zero effective displacement will arise when the displacement is $m = 3n$ and $n = 1, 2, 3 \ldots$. If one looks at image contrast from a stacking fault model point of view, the displacement vector of the fault configuration in these cases is $\mathbf{R} = 0$. As a result one would expect that there would be no contrast in diffraction contrast images since the contrast depends on the value of $(\mathbf{g} \cdot \mathbf{R})$. Theoretical calculations carried out by the authors verify that this is in fact so in the strong beam images normally used to detect and characterize stacking faults or microtwins. In this paper, the authors present a method based on the use weak beam images which permits these microtwins to be detected and the number of successive displacements, $a/3[111]$, to be determined.

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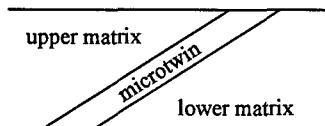
NEAR COINCIDENCE RHOMBOHEDRAL TWIN IN ALUMINA

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The rhombohedral twin orientation in alumina has been obtained by diffusion bonding and studied by transmission electron microscopy. It corresponds to a $\Sigma 7$ near coincidence orientation with a grain boundary (GB) plane parallel to $(01\bar{1}2)$.

The grain boundary contains two arrays of dislocations with the same line direction and alternatively distributed Burgers vectors (cf figure). These vectors are translation vectors of the DSC lattice (b_3 and b_2+b_1) where b_1, b_2, b_3 are the basis vectors of the DSC. b_1 is the shear vector of the twin orientation and b_2, b_3 are irrational vectors out of the GB plane. The associated step vectors are large, up to 1.75nm. The dislocations account for the deviation (0.9°) from the near coincidence orientation, measured by standard Kikuchi analysis.

Starting from symmetry considerations on the various dichromatic complexes of the perfect twin, all possible unrelaxed atomic configurations are constructed. Oxygen terminated GB structures as well as those passing through non occupied aluminium sites are selected on the basis of optimal compacity at the interface. Corresponding simulated images are compared with experimental high resolution images (cf inset).
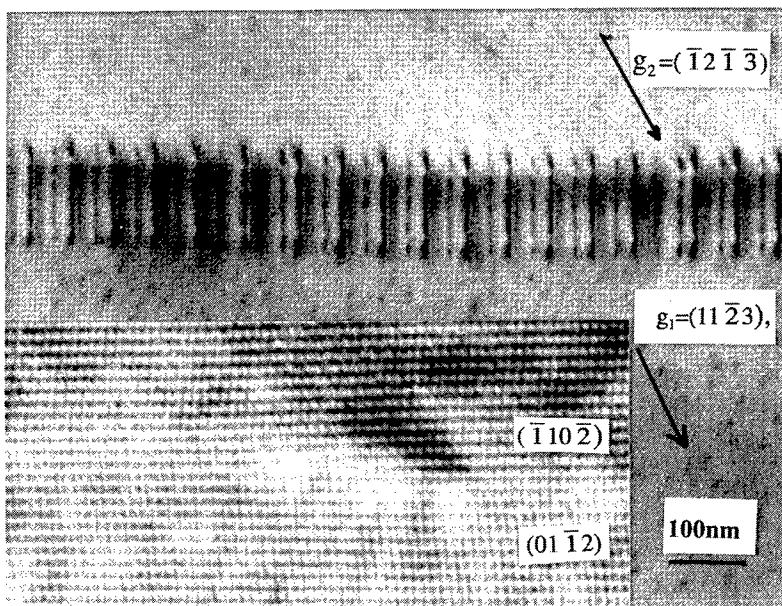
Figure : Two arrays of dislocations in a near coincidence rhombohedral twin in alumina (bright field image with a common $g=(11\bar{2}3)_1,(\bar{1}2\bar{1}\bar{3})_2$). Dislocation cores are always associated to a step height (on the inset $b=1/21\,[\bar{7}\ 12\ \bar{5}\ 2]$, $h=1,75$nm).

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ATOMIC STRUCTURE OF GRAINBOUNDARIES IN α-SiC

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A phase transformation occurs uring the sintering of β-SiC powder with B and C additives,. It results in transformation twins made up of α phase (hexagonal or rhomboedral polytypes). The twins grains share a $[11\overline{2}0]$ axis. The diedral angle between {0001} planes is equal to $2\alpha = 41.4°$, 64 °, 64.5° or 65.5°. The atomic structure of the twin boundary depends on the diedral angle [1]. This work deals with the high angle twins.

Grain boundaries were imaged either at 300kV or 400kV (Scherzer resolution = 1.7 Å). Symetric grain-boudaries were imaged along the $[11\overline{2}0]$ axis in twins characterized by a 64 and a 65.5° diedral angle.

In both twins, the boundaries consist of a sequence of two zones of distinct structures. The first kind of zones are formed from C structurals units. These C units are slightly distorted compared to perfect crystals. The second kind of zones consists of structural units whose characteristics depend on the diedral angle. These zones correspond to the dislocations identified in the grain-boundaries and whose resultant Burgers vector is equal to 1/6<112>. Such an array of dislocations was previously observed in a similar high angle twin boundary [2]. The structural units are compared to the structure of the 30° Shockley partial in silicon [3] and to the structure of 30° Shockley partial in β-SiC [1] [4].

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YTTRIUM-SEGREGATED GRAIN BOUNDARIES IN α-Al$_2$O$_3$: AN EELS STUDY

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Segregated grain boundaries have a different chemistry and structure than the bulk of the grains. Yttrium segregated general grain boundaries in polycrystalline α-alumina were investigated by electron energy loss spectrometry (EELS) using a dedicated scanning transmission electron microscope equipped with a field-emission gun (FEG-STEM). Energy loss near edge structure (ELNES) spectra of Al-L and O-K edges from the segregated grain boundaries and from the adjacent bulk alumina were experimentally obtained. Spatial difference method was applied to enhance the grain boundary features. Reference spectra from different Y$_2$O$_3$-Al$_2$O$_3$ binary compounds, i.e. Y$_3$Al$_5$O$_{12}$, YAlO$_3$, and Y$_4$Al$_2$O$_9$, as well as Y$_2$O$_3$ were experimentally measured and theoretically calculated by the ab-initio self-consistent OLCAO method. A comparison between these reference spectra and spatial difference spectra from the grain boundaries was used to study the local chemical and structural environment of the atoms at the segregated grain boundaries.

DETERMINATION OF GRAIN BOUNDARY ATOMIC STRUCTURE USING QUANTITATIVE HIGH RESOLUTION ELECTRON MICROSCOPY*

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Understanding the behavior of grain boundaries and their influence on material performance will require a knowledge of their atomic structure. For example, slip transmission across a grain boundary will depend on the misorientation of the crystals on either side of the boundary, the boundary plane, and any rigid body displacements that are present due to their effects on the DSC lattice and the reaction of Burgers vectors. Another example is segregation of minor impurities which will be sensitive to the arrangements of atoms at a grain boundary due to the size effect.

We have fabricated model grain boundaries for study by diffusion bonding precisely oriented single crystals. The materials studied include FCC metals (Al, Cu) and BCC metals (Nb, Ta). High resolution electron microscopy has been used to characterize the atomic structure of the grain boundaries. Comparison to atomic models of grain boundary structure has been made through high resolution image simulation. The comparisons have been performed on a quantitative basis. The quantification has required careful preparation of the experimental data. The imaging parameters of the microscope have either been determined experimentally or determined through an optimization procedure matching the measured contrast in perfect crystal regions of the specimen with simulated images. Grain boundary structure is then matched by using an optimization routine which holds the imaging parameters fixed and varies the positions of the atoms in the atomic model used to produce the simulated image. Errors in the positions of the atoms in the atomic model have been assessed through a rigorous statistical analysis.

The positions of atoms residing in the grain boundary (with error bars) can be used to evaluate differing schemes of atomistic simulations. For example, in the case of Al, calculations based on the Embedded Atom Method and the Local Density Approximation give slightly different predictions of grain boundary structure. Qualitatively the boundaries appear the same, but the atoms reside at slightly different positions, with differences that can exceed 0.1 Å. These differences can be resolved by the techniques of quantitative matching and simulation optimizations discussed above.

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AUGER ELECTRON SPECTROSCOPY ON GRAIN BOUNDARIES OF COLD WORKED AISI-304L AND 304 STAINLESS STEELS

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Auger Electron Spectroscopy (AES) has been performed on grain boundaries of two austenitic stainless steels of type AISI-304L and AISI-304. The aim of this work was to study grain boundary microchemistry by AES after simulating irradiation effects on microstructure and microchemistry, creating defects in microstructure by cold work and promoting segregation by subsequent heat treatments. With that purpose materials were cold worked to 10 and 30%, and afterwards, they were heat treated with three different heat treatments (500 °C, 100 and 1000 hours and 400 °C, 1000 hours) at a temperature low enough to avoid the loss of the effects produced by cold work. Cold worked materials were compared to non cold worked with the same heat treatments. In total nine different conditions were studied.

Microstructure in the as-received condition of the AISI-304L consisted of delta-ferrite phase in an austenitic matrix with no intergranular nor transgranular precipitates, while the AISI-304 showed a completely austenitic matrix with intergranular chromium carbides.

Auger results from AISI-304L showed that Phosphorus was present at grain boundaries in all materials conditions. Sometimes, it was accompanied by Molybdenum and by Chromium enrichment. Those analyses were attributed to ferrite/austenite interfaces while those where Phosphorus was found alone were thought to belong to austenite/austenite interfaces. Cold work was shown to affect Phosphorus segregation except for 400°C, 1000 h. An increase of temperature from 400 to 500°C enhanced Phosphorus segregation to grain boundaries when material was cold worked, while a longer duration of heat treatment was observed to decrease or enhance Phosphorus segregation depending on the degree of cold work.

On the other hand, Auger results from AISI-304 showed that Phosphorus did not appear on grain boundaries for all conditions, and when it appeared it was always in a lesser extent than in AISI-304L. No Molybdenum nor Chromium enrichment were found in this material under the conditions studied. It was observed that cold work enhanced Phosphorus concentration at grain boundaries at 500°C, 1000 h and that a longer duration of the heat treatment only seemed to affect if the material was cold worked.

Finally, a HNO_3/Cr^{6+} corrosion test was performed. The results showed that the weight loss of the AISI-304L was always higher than the weight loss of the AISI-304. This fact is in good agreement with the different distribution of Phosphorus on interfaces which is higher in 304L than in 304.

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THE DISTRIBUTION OF SEGREGATED ELEMENTS TO GRAIN BOUNDARIES MEASURED BY AUGER ELECTRON SPECTROSCOPY

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Auger electron spectroscopy is used extensively to determine the levels of segregation of impurity and solute atoms to grain boundaries in metals and alloys. To undertake a measurement using Auger electron spectroscopy specimens are fractured at low temperature to reveal intergranular fracture surfaces. Measurements are then made at a number of locations on these surfaces to establish a measure of the segregation. In particular consideration is given to the distribution of the measured segregants between the two corresponding fracture surfaces using one half of the fractured specimen. The value for composition obtained is then doubled on the assumption that equal proportions of the segregated species are retained on each half of the overall fracture surface. The present work has examined the nanochemistry of grain boundaries an iron 3% nickel steel following an embrittling step cooling heat treatment from a temperature of 873K. The two corresponding fracture surfaces, following fracture at a temperature of 77K, have been examined in detail. In particular consideration is given to the distribution of the segregated species over individual intergranular fracture surfaces for one grain and between the two matched corresponding surfaces on each half of the fractured specimen. The results are discussed with respect to the observed fracture paths, the statistics of the Auger electron spectroscopy composition measurements and the overall composition and distribution for a given grain boundary with respect to the particular boundary orientation.

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BORON AND CARBON SEGREGATION TO GRAIN BOUNDARY IN B- AND C-DOPED SILICON CARBIDE

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Covalent bonded ceramics SiC and Si_3N_4 have intrinsically high hardness, but their fracture toughness can only be increased with the microstructure designing by inhomogeneous grain growth or by introducing refractory grain boundary phases, both are related to the grain boundary segregation. B and C doped SiC eliminates the otherwise ubiquitously present oxide phases at the intergranular regions, thus offers more flexibility in boundary phase engineering. However, boron has never been detected at grain boundary so far and people generally accepted that the small amount of boron additives were incorporated into the lattice of SiC, most likely to replace Si as p-type dopant. This material is also the one, probably the only one in both Si_3N_4 and SiC families, to have clean grain boundary and without amorphous film to wet the boundary.

The recent development, both instrumental and methodological, in analytical electron microscopy provides better means to analyze small chemical changes from interface regions. Boron segregation to the grain boundary in a B and C doped β-SiC has been detected by spatially-resolved EELS in a dedicated STEM. The material was doped with 0.3 wt.% of boron and 2 wt.% of carbon, and sintered by hot press at 2000 °C for 1 hour. The system has an energy resolution of 0.4 eV and is capable to provide a probe of 0.5 nm in diameter containing sufficient electron current, both maximize the signal-to-background. The parallel detector has been upgraded to have much reduced statistic noise. The detection of boron signal at grain boundary was realized using combined energy difference and spatial difference mode to remove the remaining hindrance from the systematic gain variation. The amount of boron segregation is at ~14 at./nm^2 level.

The near-edge structures in EELS can reflect the bonding nature of the probed element. The detected boron signal from grain boundary in SiC resembles the one in a Si-B-C-N amorphous precursor material where boron is bonded to carbon, indicating a similar bonding picture in this study. Indeed carbon excess at the grain boundary was also detected to be 14±7 at./nm^2. Both B and C excesses are above 1 monolayer. An independent way measures a minimal chemical width of ~0.4 nm at the grain boundary, and more detailed bonding study on silicon and Fresnal contrast method both reveal chemical widths >1 nm. However HREM, in this work as in many others, did not find a distinct amorphous film in this material. The whole chemical picture relates the boron segregation to the over-stoichiometric carbon, and thus underlines the basic structure and properties of grain boundary. Indeed, both boron and carbon segregation were not observed in a liquid-phase sintered SiC where oxide films cover the grain boundaries.

(Keywords: SiC, EELS, grain boundary segregation, bonding)

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CALORIMETRIC INVESTIGATIONS OF GRAIN BOUNDARIES PROCESSES IN MICROCRYSTALLINE NICKEL

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There were carried out calorimetric investigations of the microcrystalline commercially pure nickel (99.98%). The object of investigation had special microstructure with characteristic size of structural elements ~100 nm. This structure was obtained by the special methods of intensive plastic strain (ECAE - technology). (The samples were prepared by Dr. V.I.Kopylov.) The measurements were carried out using the differential scanning calorimeter Perkin-Elmer DSC-7 in continuous heating modes (20° to 400°C) and isothermal annealing modes in the temperature range (200° to 400°C). When investigated in the modes of isothermal annealing at different temperatures it was revealed that the heat flow experimental dependencies W on the time t have very complex, non-monotonous character. At the curves W(t) there are observed some peaks of heat emission the quantity, the intensity and duration of which has essential dependence on the temperature. Calorimetric data analysis used in combination with the structural investigations carried out in parallel and with sample mechanical characteristics measurements allowed to restore the presentation of Ni microstructure evolution during annealing and to explain the heat emission characteristics at various temperatures.

It is shown that in the common case the evolution of Ni microcrystalline defective structure consists of the three processes:
1) defective structure rearrangement within the fragment (grain) volume and in near-boundary areas, terminated by the high-angular non-equilibrium grain boundaries (GB) formation;
2) non-equilibrium grain boundary defective structure rearrangement terminated by formation of the equilibrium boundaries;
3) the GB migration.

The investigations shown that at low temperatures T≤250°C the calorimetric curves have three regions reflecting the running of the said three processes. The heat quantity released on these phases at T=250°C is 15, 70 and 15% correspondingly. At high annealing temperatures T>290°C the first and the second processes follow rather quickly, practically merging (not subdividing), and at the curves W(t) there are observed only two areas. At the same time, the quantity of the energy released in these areas is 30 and 70%, correspondingly. In this work there was evaluated the activation energy of the said processes and there was developed the model explaining the laws observed.

THE COMPLEXES OF PLANE DEFECTS IN ORDERED ALLOYS

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The formation energy of plane defects is important characteristic of sliding process in ordered alloys. It quite possible the situation in deformed patterns when the complexes of plane defects are found more stable than unite defect. The complexes of parallel plane defects have been simulated in this work. The example of such complexes are multilayer defects - the couple of twins separated by one or several interplane distances. The investigation have been carried out at examples of model alloys FeAl (B2), NaTl (B32), $AlCr_2$ (C11b), Fe_3Al (D0$_3$), Ni_2AlNb (L2$_1$), Ni_4Mo (D1a). The interatomic interactions were proposed as pair and central. The crystal was presented as set of infinite subplanes. Each of them is the totality of atoms disposed at unite plane and unite sublattice. The relaxation of defect was executed by displacement of subplanes as whole in direction of forces acting at them.

The highly demonstrative information about plane defect is the distribution of its formation energy among the crystal planes. The relaxation of the defect lead to reduction of the multitude of this distribution and formation of one or several maxima. The interaction of plane defects is more effective at imposition of maxima of these distributions.

The special method allow to visualise both the atomic configuration of defect in arbitrary orientation and the picture of microdeformations which arises at transition of crystal in equilibrium state. By using the method it was revealed for alloys on the base of BCC lattice that there are two types of atomic configurations near the stacking faults. In the first case the lattice different from original one arises near the defect. In the second case take place the tendency to restoration of the strucrure of the ideal crystal such manner, that original shift distribute evenly among all planes of crystal block.

The profiles of the energy surfaces have been constructed for more important sliding systems. It have shown that number of different minima is determined by number of atoms in primitive cell.

ORIENTATION DEPENDANCE OF THE STRUCTURE IN ROLLED AND ANNEALED TUNGSTEN SINGLE CRYSTALS

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The study of the structure that formed in tungsten single crystals with orientations (001)[110], (001)[100] and (110)[$\bar{1}$10] during rolling deformation and subsequent high temperature annealing was carried out.

A strong orientation dependence of the structure has been revealed. The structure of the (001)[110] crystals was characterised by a homogeneous distribution of the dislocations with the dislocation density of 10^{10} cm^{-2} at the reduction of 90%. The annealing of these crystals after the deformation resulted in polygonization. The samples remained single-crystal structure with initial crystal orientation and only subboundaries of different types were observed. In the crystals with orientations (001)[100] and (110)[$\bar{1}$10] at the reduction of 10-15% cell structure was observed, and on increasing the deformation up to 30% these crystals were destroyed. Recrystallization with forming high angle grain boundaries took place in these crystals during high temperature annealing. A detailed analysis of the crystals structure permitted to explain the absence of recrystalization in the crystals with a definite ((001)[110])orientation.

The experimental results on the structure evolution during rolling and annealing in tungsten single crystals as well as results concerned boundary and subboundary structure are discussed in this work.

Study of Interfaces in Silver-based Composites

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Abstract

Carbon is insoluble in silver up to very high temperatures, its solubility does not exceed 0.02 at% and a problem of wettability of carbon fibers by silver arises. This wettability is extraordinary small and does not allow to fabricate the composite material. Thus the interface bonding in silver-carbon composites is extremely weak. Increasing interfacial strength for Ag-C is generally carried out in two ways: forcing a fiber reaction with the matrix, and making the matrix dissolve the carbon fiber. We study by HR SEM technique the morphology of the silver-carbon interfaces for composites produced by the wetting of carbon precursor phase by the melt of the host material. The analysis of the silver-carbon interface shows the existence of the bonding region about 50 nm.

REFERENCE STRUCTURES FOR HIGH ANGLE GRAIN BOUNDARIES IN WIDMANSTÄTTEN TITANIUM MICROSTRUCTURES

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Whilst the coincident site lattice (CSL) model has been used very successfully to model the reference structures exhibited by vicinal high angle grain boundaries (HAGBs) in materials with cubic crystal structures, there is very little experimental evidence to support the constrained CSL (CCSL) model for HAGBs in non-cubic materials (e.g. Bollmann 1982, Chen and King 1988). Moreover, it has been shown recently that there are fundamental weaknesses in the CCSL approach (MacLaren and Aindow, 1997a) and there is some evidence to suggest that reference structures may instead be related to periodicity in, or near to, the boundary plane (Grimmer et al 1990; Lay, Ayed and Nouet 1992). In a recent study of a HAGB in α-Ti (MacLaren and Aindow, 1997b), it was shown that by using the topological theory of interfacial defects (Pond, 1989), the O-lattice algorithm (Bollmann, 1982) can be applied to reference structures other than CSLs or CCSLs and here again a two-dimensional reference structure was found.

In the present work we have performed detailed TEM investigations of the structure and defect content of HAGBs in pure Ti heat treated in the beta phase field and then cooled to give many Widmanstätten alpha laths in each prior beta grain. The majority of the HAGBs are thus formed between adjacent alpha laths which exhibit different variants of the Burgers orientation relationship with respect to the parent beta grain. The equivalence of certain variants means that there are only six crystallographically distinct relative orientations which are adopted between laths in a prior beat grain and indeed axis/angle pairs measured experimentally are all subtle variations on these. In this paper we will present an analysis of the reference structure adopted by one example of each of the two most common types of HAGB in this material. It will be shown that for the most common orientation there is no viable CCSL and a two-dimensional reference structure is adopted. For the other example where the common axis is [0001], however, the orientation lies close to that for a true CSL and in this case it is not possible to distinguish between a two- and a three-dimensional reference structure experimentally. The significance of these observations for the apparent discrepancy between the reference structures adopted in cubic and hexagonal crystals will be discussed.

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WETTING AND NON-WETTING BEHAVIOUR OF SILICON CARBIDE GRAIN BOUNDARIES

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Extensive electron microscope investigations in the literature have shown that silicon carbide (SiC) grain boundaries are free from intergranular films. On the basis of equilibrium film thickness calculations[1], it has been proposed that the attractive forces between SiC grains are very large because SiC has a very high refractive index and as a result of which intergranular films cannot exist at equilibrium at SiC grain boundaries.

Our transmission electron microscope studies on silicon carbide-silicon nitride particulate composites have shown clear evidence for the existence of film-free grain boundaries and SiC grain boundaries containing intergranular films. The reasons for this difference in behaviour from that predicted by Clarke's model are discussed.

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INTERACTION BETWEEN PLANAR DEFECTS AND THREADING DISLOCATIONS IN GAAS ON SI THIN FILMS.

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Heteroepitaxial layers of GaAs and related compounds on Si substrates may provide all kinds of optoelectronic devices required for Si-based optoelectronics. However, a necessary prerequisite is the minimazation or elimination of crystal defects' densities[1,2]. This task requires an extended insight into crystal defects and develop new schemes to reduce their density.

In this paper we will report on the interrelation between planar defects and threading dislocations in GaAs-on-Si heterostructures. GaAs films grown by Molecular Beam epitaxy on vicinal Si (100) substrates with tilting angles of $0°$ - $9°$ toward [011] have been investgated by Transmission Electron Microscopy. A threading dislocation density in the mid 10^8 cm^{-2} range appears in 2 μm as-grown films on moderate angle values ($1.5°$ - $6°$). The dislocation density is minimized significantly for tilting angles bellow $1°$. However planar defects start appearing with increasing density as the angle reduces below $1.5°$. The appearance of antiphase domain boundaries and microtwins is characteristic for $1°$ and $0.5°$ tilting angle. These observations indicate that planar defects are absorbing efficiently, during growth, the initially created threading dislocations.

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STRUCTURAL EVOLUTION WITH TEMPERATURE
OF MBE Au/Ni MULTILAYERS.

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Despite the large misfit between Au and Ni (15%), it has been shown that Ni can grow coherently on (001)Au by MBE [1]. An intermixing occurs during growth, which reduces partially the stress and permits Ni to grow coherently up to 5 monolayers on (001)Au (fig.1).
The stability with temperature of these multilayers has been investigated by HREM which shows an anisotropic chemical decomposition upon annealing (fig.2). This has been confirmed by in-situ X-Rays experiments [2]. For comparison, $Au_{1-x}Ni_x$ epitaxial alloys on (001)Au were studied. The influence of temperature, local composition and strain has been studied.
The very early stages of the decomposition of Au/Ni multilayers has been investigated by in-situ HREM experiments.
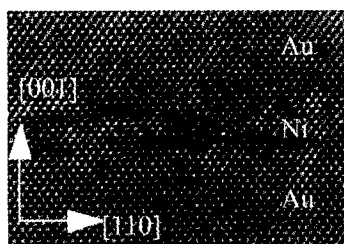
fig.1 : Part of Au/Ni multilayer before heat treament: Ni grows coherently on (001)Au. (Jeol 4000EX)
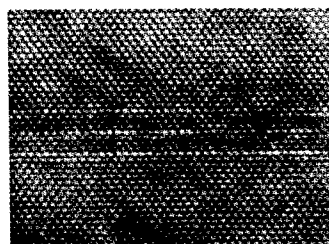
fig.2 : Part of Au/Ni multilayer after heat treament: the decomposition is clearly visible.(Jeol 4000EX)

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VARIATION OF CHEMICAL BONDING AT MgO - Cu INTERFACES WITH INTERFACIAL STRUCTURE AND INTERFACIAL CHEMISTRY

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Different MgO-Cu interfaces are obtained by internal oxidation of (Cu,Mg) alloys, where MgO precipitates are formed within copper, and by internal reduction of (Mg,Cu)O mixed oxides, where copper inclusions form within the magnesia host matrix. The orientation relationships between matrix and precipitate phase and the interfacial planes are determined by conventional TEM. The atomistic structure of the interfaces is analysed by HREM. The chemical bonding across the interfaces is studied by transmission electron energy loss spectroscopy with high spatial resolution.

The combined analysis shows that structure and chemical bonding at the MgO-Cu interface vary with the reaction conditions:

For the polar $\{111\}_{MgO}//\{111\}_{Cu}$ interfaces (MgO and Cu in topotactical or pseudo-twin orientation) equilibrated at 900°C and $a_{O2}=10^{-8}$, it is shown that the terminating lattice plane in magnesia is occupied by oxygen atoms. HREM contrasts and plane distances at the interface are consistent with a Mg-O-Cu bonding with a interplanar distance close to that of bulk MgO. While the interfaces are flat over large distances, steps occur occasionally. The constant double height of these steps (-Mg-O-) allows to preserve all along the interface the metal-oxygen bond. By EELS an important charge transfer is identified across the interface, yielding Cu-L features characteristic of copper in the Cu^{1+} state and in a Cu_2O like environment. Features of the O-K edge are also modified; edge enlargement and the presence of a low energy shoulder confirm bonding of oxygen to Cu^{1+}. The M-L edge at the interface is not modified compared to bulk MgO. A semiquantitative analysis of the different bond contributions in terms of experimental cross section ratios in the spatial difference mode indicates approximately one monolayer of Cu_2O at the interface.

At mixed $\{001\}_{MgO}//\{001\}_{Cu}$ interfaces (MgO and Cu in topotactical orientation) formed at 900°C and $a_{O2}=10^{-8}$, a less important charge transfer at the interface is observed compared to the $\{111\}$ type interface. MgO-Cu interfaces formed at the same temperature and lower oxygen activities reveal changes in the charge transfer compared to those equilibrated at high oxygen activities.

MICROSTRUCTURE OF Al/α-Al2O3 INTERFACE FABRICATED BY SURFACE ACTIVATED BONDING AT ROOM TEMPERATURE

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Surface activated bonding (SAB) has been developed as a non-heat-treating method of joining dissimilar materials by Suga et al.[1]. and widening its applicability. The joining mechanism, however, has not been studied in detail due to its complex phenomenon of 1) "surface activation" process, 2) initial interface formation and 3) macroscopical adhesion. In this study, Al and α-Al2O3 were chosen since they form a strong interface as reported [2] and the "surface activation" process and the initial stage of interface formation of SAB studied by observating the interfacial microstructures using transmission electron microscopy.

Ar sputtering as "surface activation" caused γ-Al2O3-like structure on the α-Al2O3. On the other hand, small protrusions of a hight of 5-10nm existed on the pre-joining surface of Al. The initial interface formation takes place between the top of the small protrusions of Al and γ-Al2O3-like surface of α-Al2O3. The top region of Al small protrusions deformed under a loading pressure, many micro-twins being introduced (Fig.1). It is considred that this disordered region with microtwins in the Al region at the interface formed due to the applied and residual stresses at the interface which should work as a driving force for micro-twin formation and that Al atoms re-arranged only near the interface with a preferencial orientation with the Al2O3 surface.
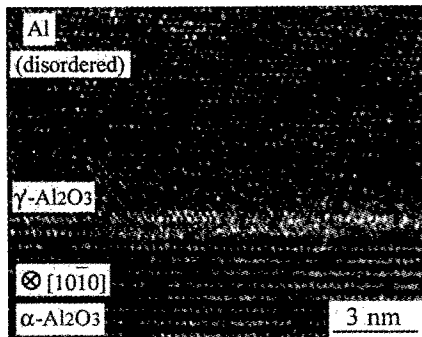
Fig.1 Microstructure of Al/α-Al2O3 interface

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BALL MILLING DRIVEN FORMATION OF INTERFACES IN POWDERS OF
SUPER α_2-TI$_3$AL ALLOY

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We investigated the interfaces produced during deformation of powder particles of the super α_2-Ti$_3$Al alloy undergoing ball milling treatment as a function of the duration of the process, by using Conventional and High Resolution Electron Microscopy (CTEM, HREM).

The as received particles consist mainly of two different ordered phases, the ordered DO$_{19}$ structure of Ti$_3$Al intermetallic compound and the B$_2$ ordered structure of Ti$_2$AlNb. The grains of the powder particles form planar homophase and heterophase interfaces. During the processing, particle sizes decrease until an equilibrium is reached between fracturing, welding and refracturing. The α_2-Ti$_3$Al ordered phase undergoes an order-disorder phase transformation, whereas the Ti$_2$AlNb phase still remains ordered. Later in the process, nanocrystalline Ti$_2$AlNb is observed to coexist with nearly amorphous α-Ti$_3$Al. At this stage, the optimum mechanical intermixing between the various components of the alloy is achieved.

By further ball milling a new phase is progressively formed and quite remarkably each particle of this new phase forms a single crystal. Its structure belongs to the rhombohedral crystal system that can be also described either by an hexagonal or a distorted f.c.c. unit cell. The small spherical particles of the new phase deform by twinning: we observe the formation of (100) twins of the rhombohedral crystal structure and equivalently either (-111) twins of the distorted cubic lattice or the (10-11) of the hexagonal lattice.

NANOSCOPIC ANALYSIS OF A Ag-Cu-Ti/SAPPHIRE INTERFACE

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In this experiment we studied detailed structure of the brazed interfaces between sapphire and Ag-Cu-Ti alloy by transmission electron microscopy and energy dispersion spectroscopy. Active brazing is one of the most important methods used to join ceramics to metals or to other ceramics. Clarification of the interface structure and formation process is essential not only for industrial applications but also for fundamental studies on metal-ceramic wetting at interfaces. Our research has been focused on the nanostructure of the interface, identification of the reaction phases, the orientation relationship between sapphire and reaction phases, and the formation kinetics of reaction phases.

The system under investigation is a joint made of sapphire/Ag-Cu-Ti alloy, a metal filler widely used in industry. The sapphire substrates were polished parallel to a variety of low-indexed planes, and stacked with a filler metal sheet, the nominal composition of which was 66.7Ag-27.4Cu-4.9Ti (in mass percent). They were brazed by annealing at 900°C for 300 sec in a vacuum of 5×10^{-5} Pa. The resultant joints were cross-sectioned, mechanically thinned, and finished for TEM observation by a focused ion beam technique to minimize the preferential sputtering perpendicular to the incident electron beam.

The typical reaction products were Ti_3Cu_3O and TiO, in the form of polycrystalline layers of 1-3 microns and 10-50 nm in thickness, respectively. The stacking sequence of these layers and bulk materials was Ag-Cu eutectoid / Ti_3Cu_3O / TiO / sapphire, which is in good agreement with that reported in literature. In some cases it was revealed that discrete TiO grains of 10-50nm size formed at the Ti_3Cu_3O/sapphire interface, which is otherwise atomically flat. Combined with the fact that Ti_3Cu_3O grains appeared to be recrystallized (large grains and flat boundaries), the formation process could be that the Ti_3Cu_3O/sapphire interface formed first, followed by TiO precipitation as a result of the reaction between sapphire and Ti_3Cu_3O.

Occasionally, copper-aluminum-oxide (titanium free!) was discovered adjacent to sapphire. Cu-Al-O can be rombohedral and the orientation relationship was

$$[11\bar{2}0]Cu\text{-}Al\text{-}O//[10\bar{1}0]Al_2O_3 \text{ and } (10\bar{1}0)Cu\text{-}Al\text{-}O//(11\bar{2}0)Al_2O_3$$

Lattice mismatch between the (0003) planes of these phases is negligible, which may be the reason for the presence of this thermodynamically unpredictable phase.

INHOMOGENEOUS ELECTRONIC PROPERTIES AT Au/CaF$_2$/n-Si(111) INTERFACES STUDIED BY BALLISTIC ELECTRON EMISSION MICROSCOPY

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We have performed ballistic electron emission microscopy (BEEM) measurements on the Au/CaF$_2$/n-Si(111) system in which calcium fluoride (CaF$_2$) (about 2 monolayers (ML)) was introduced between Au and Si(111) substrate. It was found that the electronic potential barrier was modified on the nanometer scale by using the CaF$_2$ intralayer formed at 700°C. A BEEM image clearly shows the coexistence of two types of terrace for each of which the BEEM I-V spectrum has a different shape. A typical threshold voltage of the BEEM current for one type is about 0.75 V. In contrast, the second type shows a threshold voltage of about 3.5 V, which is much higher than the value of the first type. We confirm that the coexistence of the two types of terrace in the BEEM image is attributed to the different degrees of CaF$_2$ coverage between them. At the second type of terrace, a Au/2 ML CaF$_2$/1 ML CaF/Si(111) interface exists, although the first type has a Au/1 ML CaF/Si(111) interface without a CaF$_2$ intralayer.

Si/Si INTERFACE BONDED AT ROOM TEMPERTURE BY Ar BEAM SURFACE ACTIVATION

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Wafer direct bonding by the surface activation method utilizes Ar beam sputter etching in a vacuum. This treatment enables the bonding at room temperature. In addition, for the bonding of very flat specimens such as Si wafers, external bonding load is not necessary[1]. These are the advantages as a low damage bonding method. We have thought that the role of Ar beam etching is removing surface contaminant. At the same time, incident Ar atoms cause various effect at surface region. In this work we investigate the structure of Si/Si interface prepared by the method and the effects of Ar beam etching.

The bonding procedure is the same with previous report[1,2]. The acceleration voltage of the Ar beam is varied from 0.6 to 1.8 kV. Measured strength in the tensile test shows no dependence on the Ar beam energy and fracture from the silicon bulk is observed. By TEM, many contours which represents local strain are observed near the interface (figure 1). The strain is expected to result from surface roughness before bonding. In the high resolution image, an intermediate layer is observed. The thickness increased when Ar beam energy increase (figure 2). This layer recrystallized after annealing (figure 3). These means that the layer contains high density defects which seems to be generated by Ar beam irradiation. These defects often affects the various property of the interface. Therefore, the condition of the Ar beam etching is determined carefully considering the application. 1)Takagi, et al., Proc. iib'96, (1996), 169. 2)Takagi, et al., Appl. Phys. Lett., 68(1996), 2222
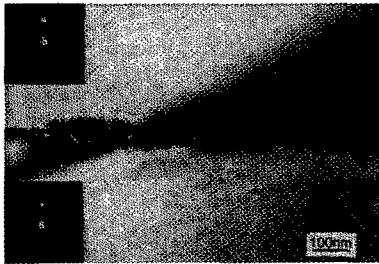
Figure.1 TEM image of Si/Si interface
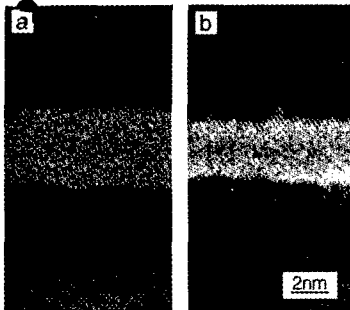
Figure.2 High resolution image of Si/Si interface bonded by a) 1.2kV and b) 0.6kV Ar beam etching
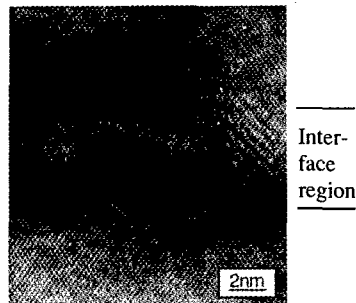
Inter-
face
region

Figure.3 High resolution image of Si/Si interface after annealing at 700 °C 2 hours

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IMPLEMENTATION OF BOLLMANN'S METHOD IN THE STUDY OF EPITAXY STRAINS Zr/ZrO₂ DURING THE ANIONIC OXIDATION OF ZIRCONIUM.

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In the course of the anionic oxidation process of a metal, the transformation of a part of metal into oxide generates strains induced by the change of crystal structure.
To evaluate the influence of these strains on the kinetics of zirconium oxidation, a theoretical model has been developped [1].

This model needs, among other, to know the epitaxy strain associated to the contact of each zirconia crystal with the metal [2] [3]. In order to evaluate this contribution, Bollmann's method has been used [4].

Mainly used in the study of two superposed materials with adjoining crystalline structures and few disorientated lattices, this method allows to evaluate, among several given orientations of two crystals, the particular one that corresponds to an optimal adequation of both lattices. It relies on the calculation of an optimal transformation matrix A^{tr}, which links a vector of the first lattice to another more neighbour of the second lattice.

Applied to the study of the zirconia formed on a zirconium sample, several problems must be solve :
        - the metal (hexagonal) and the oxide (monoclinic or tetrahedral)) have very different crystalline structures, what imposes several selection criteria to determine the optimal orientations,
        - X-rays diffraction analyses have showed the presence of many textural components in each zirconia phase of the oxide layer[5].

We present in this paper, the required procedures adopted for the selection of A^{tr} matrix in the case of Zr/ZrO₂ phase boundaries. Some selection criteria of ideal orientation proposed by Bollmann will be compared to the volumic fractions of orientations experimentally obtained. From the current model that has been developed in our lab, the kinetics behaviours can be calculated for different zircone orientations and compared to experimental values. So, this approach gives now a previsional tool for the selection of the interfacial textures and the kinetics data.

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CERAMIC-METAL INTERFACES IN CAPACITOR-DISCHARGE JOINED OXIDE AND NON-OXIDE CERAMICS

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A capacitor-discharge joining technique has been used to fabricate alumina-metal-alumina, zirconia-metal-zirconia, silicon carbide-metal-silicon carbide and silicon nitride-metal-silicon nitride joints using thin foils of aluminium, titanium or amorphous alloys as interlayers. The technique involves passing a high energy pulse through a conductive interlayers, so converting the interlayer into a liquid-vapour "plasma" which wets and bonds the pieces of ceramic being joined.

In order to understand the bonding mechanism, the interfacial microstructures of the bonds were examined in great detail using an optical microscope, a scanning electron microscope, conventional as well as high resolution transmission electron microscopes and a dedicated scanning transmission electron microscope. The bond strengths of the joints were assessed by shear testing.

The results obtained from the microstructural investigations coupled with the shear test measurements revealed that the highest bond strengths were obtained when there was a distinct reaction layer between the ceramic substrate grains and the interlayer. In this presentation, the relationship between microstructure and joint strength will be demonstrated.

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THE ATOMIC STRUCTURE OF THE PURE EDGE THREADING
DISLOCATIONS IN GaN/Al$_2$O$_3$ LAYERS

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Highly efficient devices are nowadays made in GaN layers grown on Al$_2$O$_3$. They are blue light emitting diodes (LED's) and green to UV laser diodes. Due to the very large misfit (16%) with the substrate, the active layers contain high densities of defects ($10^9 - 10^{10}$ cm^2). The main part of these defects are threading dislocations from mosaic growth in which slightly rotated islands are limited by sub-grain boundaries of a threading dislocations (1, 2). The high efficiency of the fabricated devices implies that these defects exhibit a strikingly low electrical activity.

In this work, we have analysed the core structure of the dislocation forming the low angle boundaries using HREM, anisotropic elasticity calculations and image simulations. Mainly two configurations of the core made of 8/6 and 5/7 atom rings, have been observed.

The results agree with the recent theoretical investigations which showed a reconstructed 8/6 core for the threading dislocations (3). However, the observation of the 5/7 atom ring (4) appears to imply that the Ga-Ga or N-N bonds present inside its core do not play a crucial role on the electrical activity of the devices.

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DISCLINATIONS AT GRAIN BOUNDARY TRIPLE JUNCTIONS:
BETWEEN BOLLMAN DISCLINATIONS AND VOLTERRA DISCLINATIONS

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In grain boundary triple junctions, the crystallographic constraints for defects are less restrictive than in single crystals. Therefore, there are defects present in triple junctions which cannot exist in single crystals such as the Bollmann disclination which is defined by the crystal misorientations and the Volterra disclination being defined by a rotational displacement field. The two disclination types have some properties in common: they are „rotational" defects, they obey a continuity rule, and the dislocation balance (Burgers vector conservation) is not fulfilled at the disclination line.

It is shown, however, that there is a major difference between the two defects: the Bollmann disclination has no stress field whereas the Volterra disclination has a very strong stress field. Therefore, the existence of Bollmann disclinations and their properties do not depend on the size or shape of the three joining crystals but only on their misorientations. In contrast the Volterra dislocation: the strong stress field requires a short screening length for the sake of the associated strain energy. A short screening length can be provided by other defects such as a free surface or other disclinations which cancel the long range stresses. In polycrystals, the screening length corresponds to the distance between neighboring grain boundary junctions. Therefore, the properties of Volterra disclinations depend on the grain size.

A brief overview of Bollmann and Volterra disclinations is given covering a case example of a Bollmann disclination in a hexagonal lattice, Bollmann disclinations in nickel, and the statistics of Bollmann disclinations in random and fiber textured fcc polycrystals. Examples for materials with Volterra disclinations include pentagonally twinned fcc particles, silicon-germanium epitaxial films, materials which undergo deformation twinning, and nanocrystalline materials.

INVESTIGATION OF THE ATOMIC STRUCTURE OF THE a + c THREADING DISLOCATION GENERATED AT THE GaN/Al$_2$O$_3$ INTERFACE

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GaN layers for optoelectronic applications are epitaxially grown on sapphire, which exhibit a misfit of 16%. This results in the formation of layers containing high densities of defects ($10^9 - 10^{10}$ cm^2). These are mainly : **a**, **a** + **c** and **c** threading dislocations which originate at the interface and propagate through the active GaN layers (1, 2). The layers result in a mosaic structure of subgrains limited by these dislocations. The obtained layers are used to fabricate efficient optoelectronic devices such as LED's and laser diodes (3). This implies that these defects do not have a high electrical activity.
In this work, we present the first results obtained on the atomic structure of the **a** + **c** dislocation which has a mixed character. The occurrence of such dislocations means that some islands of the GaN mosaic layers have their **c** axis slightly tilted.
The techniques used are HREM and extensive image simulation using the electron microscopy software (4). The models are generated by anisotropic elasticity calculations, each of them consists in a box of thickness t in the middle of which the dislocation is located. Each box is cut into supercells of .25 nm thickness and the image simulation is carried out using the multislice routine, in this way the modification of the atomic positions with depth can be taken into account. The Eshelby effect is taken into account in the calculation of the atomic positions close to the surface The calculated images are compared to the experimental micrographs.

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INTERFACES IN EPITAXIAL HETEROSTRUCTURES OF YBa$_2$Cu$_3$O$_7$/BaTbO$_3$

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The structure and defects of the interfaces in heterostructures of YBa$_2$Cu$_3$O$_7$/BaTbO$_3$ are investigated by high-resolution transmission electron microscopy. Two types of interfaces, type I and type II, are found. At interface type I a Cu-O chain plane of YBa$_2$Cu$_3$O$_7$ connect a TbO$_2$ plane of BaTbO$_3$ (fig.1a). In this interfaces misfit dislocations lie in [110] and [$\bar{1}$10] directions and therefore the misfit localization is not visible along the [100] and [010] viewing directions. The misfit strain is mainly restricted within a narrow interface layer. At interface type II, BaO planes is the terminating plane of the BaTbO$_3$ layer facing the Cu-O plane of YBa$_2$Cu$_3$O$_7$ (fig.1b). For this interface, misfit is well localized at misfit dislocations with their lines parallel to [100] and [010] directions and the nearby lattices are strongly strained and distorted. In the films including the BaTbO$_3$ layer prepared at about 780°C the interfaces between YBa$_2$Cu$_3$O$_7$ and BaTbO$_3$ show type I only. Interface type II appears in the films containing the BaTbO$_3$ layer deposited at about 500 °C. The different dislocation configurations for the two type interfaces are discussed in the light of O-lattice theory and structure models of the interfaces are suggested on the basis of image simulation.

(a)   (b)
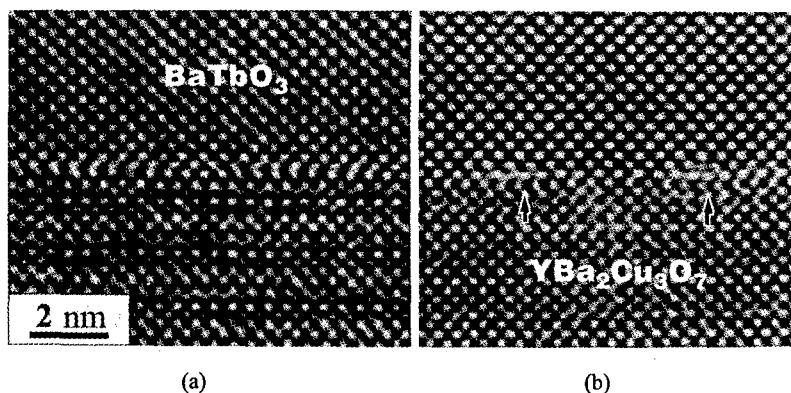
Fig. 1. (a) [100] lattice image of interface type I. No misfit localization is visible in this viewing direction. (b) [100] lattice image of interface type II. Misfit dislocations are indicated by arrows.

MAXIMUM ENTROPY LINEAR IMAGE RESTORATION FOR Al2O3 GRAIN BOUNDARY AND NiSi2/Si INTERFACE

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High resolution transmission electron microscopy has been extensively applied to study the interfacial structure for many years, see e. g. [1-5]. However, due to the dynamical scattering of the incident electron with the atomic potential of atoms and the aberration effect of contrast transfer function of a objective lens, the recorded HRTEM image losses the 1:1 relationship with the true structure and the resolution is limited to slightly better than 0.2 nm. A series of under-focused images have to be recorded and compared with the simulated images to qualitatively determine the possible structure.

In our research, we used the maximum entropy method (MEM) [6-7] to de-convolute the contrast transfer function from a series of under-focused HRTEM image to extract the information of the unaberrated specimen exit wave in the case of the weak phase object. A Lagrangian function containing negative entropy and constraints of constant flux of electrons as well as a Kai square function was minimized using conjugate-gradient technique to obtained the solution of the optimum exit wave.

For compound materials, many of possible structural models of interface can' be deduced from the (contrainted)-CSL theory. It was found that MEM is very useful to quantitatively distinguish many possible interfacial structures in the compound interfaces. We have applied MEM for quantitatively determining the Al2O3 grain boundaries and NiSi2/Si atomic faceting interfaces. The detail analyses and results of the interfacial structure deduced using MEM from a series of HRTEM image will be presented in the conference.

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QUANTITATIVE ANALYSIS OF CoSi$_2$/SiC INTERFACES

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The ultimate purpose of this study is to understand the structure of the interface between the eutectic CoSi$_2$-CoSi and SiC(6H). Sandwisches of SiC/CoSi$_2$-CoSi/SiChave been prepared using the eutectic in powder. A subsequent heating permits to obtain two interfaces whose structure has been investigated by High Resolution Electron Microscopy (HREM) and Imaging Filtering (IF). HREM technique permits to measure the local distortions in the vicinity of the interfaces and IF (GIF on a Jeol 3010) permits to obtain chemical mapping by a selection of the electrons suffering a specific energy loss.

Conventional TEM shows that no simple cristallographic orientations exist between CoSi$_2$ or CoSi and SiC. No extra phase has been detected at the interface. Quantitative HREM has been performed that shows that the distorsion in CoSi$_2$ or CoSi parallel to the interface is less than the detection limit i.e. $\pm$ 0.005nm in our measure conditions (fig.1a,b). In SiC only the last interplanar distance at the interface is affected.

Co chemical mapping has been performed using the L23 peak. At the interface CoSi$_2$/SiC, Co profile exhibits a variation over 3 atomic planes i.e. 1. nm which in fact corresponds to the resolution of the method in this mode. Thus, the main result is that there is no long distance diffusion of Co in SiC.These results show clearly that no intermixing occurs at the interface which seems to be abrupt from the chemical point of view (on less than 3 atomic planes). (fig.2a,b)
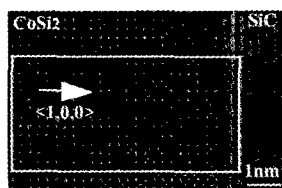
fig 1a: HREM image (jeol4000EX)

fig 2a:Co map (Jeol3010+GIF)

fig 1b : distortion profile from (1a)

fig 2a:Co profile from (2a) (Jeol3010+GIF)

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STRUCTURE-PROPERTY RELATIONS IN DIRECTIONALLY SOLIDIFIED OXIDE EUTECTICS

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When properly grown, directionally solidified eutectics exhibit aligned lamellar or fibrous microstructures which contain large numbers of crystallographically identical heterophase interfaces amenable to analysis by electron microscopy or for measurement of mechanical properties. Over the last decade we have investigated a large number of lamellar directionally solidified oxide eutectics (CaO-ZrO2,MnO-ZrO2,NiO-ZrO2,etc.),both for their interfacial structure (using TEM, AEM, CBED, and EELS) and for properties as reflected in crack propagation or phase transformations. The paper will cover the characterization of these interfaces and the connection between all length scales of interface microstructure and its influence on residual stresses and crack propagation behavior in directionally solidified eutectics.

NON-EQUILIBRIUM GRAIN BOUNDARIES IN ULTRAFINE GRAINED MATERIALS PROCESSED BY SEVERE PLASTIC DEFOMATION

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The recent investigations have shown that severe plastic deformation leads to formation of ultrafine grained structure in different metals, intermetallics and semiconductors [1]. Many of the processed materials have extraordinary properties due to their unusual structure associated with both a small grain size, less than 100 nm, and non-equilibrium structure of grain boundaries having long range stress fields.

The given work presents the results of TEM, HREM, XRD and Raman studies aimed to reveal features of the grain boundary defect structure in order to develop a structural model of nanocrystals processed by severe plastic deformation. Special attention is focused on investigation of elastic distortions of crystal lattice at grain boundaries testifying the presence of high density of grain boundary dislocations and disclinations. It is shown that recovery of ultrafine grained structure starts from the migration of non-equilibrium grain boundaries and preceeds the grain growth. Moreover, a distinction in a mean grain size of as-prepared samples determined by TEM, XRD and Raman scattering is noticed. The obtained results are discussed on the basis of the proposed structural model of a nanostructured state. According to this model severe plastic deformation results in the formation of a specific grain boundary defect structure associated with high level of internal elastic strains and distortions of crystal lattice. An important role of the grain boundary defect structure in displaying of high strength and superplastic properties is illustrated by mechanical behaviour of a number of ultrafine grained materials.

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STRUCTURAL CHARACTERISTICS OF TWIN BOUNDARIES IN DEFORMED
POLYCRYSTALLINE ZIRCONIUM

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Deformation twins in thin foils of deformed polycrystalline Zr are observed along the [1-210] viewing direction, by High Resolution Electron Microscopy (HREM). The twinning mode has elements $K_1 = (10\text{-}12)$ and $\eta_1 = [10\text{-}1\text{-}1]$. The resolution of the observation separates the atomic columns revealing the image of the structure of the interface. The interface consists of steps separating planar and defected segments. The planar areas correspond to the K_1 twin plane while the step height of the defected areas varies and has dislocation character. The shorter step corresponds to the so-called $b_{2/2}$ twinning dislocation.

Models of the relaxed structures of both, the perfect twin and the $b_{2/2}$ twinning dislocation, are constructed using many-body potential calculations based on two different potentials. The resulting atomic positions are used for image simulations using the EMS software package. The simulated images are compared with the experimental ones. The results show that one of the potentials used leads to a satisfactory relaxed structure for the perfect twin boundary as well as for the boundary containing a $b_{2/2}$ dislocation.

THE SURFACE CHEMICAL REACTIONS AND SELFORGANIZATION PROCESSES DURING SINTERING OF HIGH DISPERSION METAL PARTICLES

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The powder metals have more complicated structure than compact ones, because the surface energy of particles composes the great part of the whole system energy and the ratio of summary area of the boundaries to the volume in the ultradispersion powders may be by 10^4 - 10^5 times greater than for usual polycrystal metals.

The active role of different types of surfaces and boundaries formed during the process of consolidation of ultra-(<200nm) and fine (1-20μ) dispersion metal powders (Ni,Cu), obtained by different metallurgical methods, was investigated by Auger (AES), XPS, TEM and computer simulation methods. In original state the particle surfaces were covered by oxide films, which thickness and morphology were defined by particle size and production method. The influence of atmosphere enviroment (hydrogen, helium) was investigated. The following phenomena were observed during the consolidation process: (1) destruction of oxide films and additional oxidation during powder pressing; (2) growth of the particle oxidation degree with the pressure elevation; (3) disappearance of oxide-metal boundaries and formation of interparticle boundaries, that realized by phase transitions, boundary faceting and boundary dissociation during sintering; (4) shift of the reduction and dissociation temperatures to the lower values during sintering; (5) coincidence of the temperature of the reduction (or dissociation) of the oxide films with active shrinkage of powder during consolidation.

The influence of surface morphology and energy, the thickness of oxide film and size of original particles on the processes of agglomeration and formation of intra- and interparticle boundaries was investigated. It was shown, that processes of the interparticle boundary formation are realized by chemical reactions and phase transformations such as crystal-amorphous-crystal state [1]. It was found that the rigid -body like translation and rotation of the parts or the whole of individual particle are the dominant mechanism of deformation. The atomic model and theoretical estimation of influence of surface chemical reactions on degree of powder shrinkage for Ni powders with different particles sizes were made.

The processes of structure selforganization are typical for investigated nonequilibrium system of powder particles [2,3]. They become apparent in fractal behaviour of interparticle boundaries during their interaction, in the formation of faceted boundaries with characteristic orientation relationships, such as low index plane orientation and parallelity of dense packed directions of neigbour particles; in removal of boundary mismatch by shift processes like twinning and boundary dissociation and formation of special intraparticle structures etc.

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Interblock Boundaries with Variable Crystallogeometrical Parameters in Thin-Films Selenium Crystals

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The special feature of real structure rhombiform crystals of hexagonal selenium, growing in amorphous films at the temperature of crystallization *180-160 °C*, is the lattice elastic ratational bending around the axis *«C»* conciding with short rhombus diagonal in the direction, and the interblock twist boundaries with disorientation vector ω parallel the lattice rotation axis, |ω| changes along the boundary /1/.

Electron microscope investigations carried out with the aid of the bend-contour technique /1/, have made it possible to detect the interblock twist boundaries, along of which both modulus and the dsorientation vector sign changes. The sign variation of the disorientation vector ω is revealed according to the change to the alternation order of contours pairs *hkl'* and $\overline{hkl}$ into the neighbouring blocks and observed both for the dangling twist boundaries and for the boundaries emerging at the crystal growth front. Interblock twist boundaries with variable crystallogeometrical parameters includng modulus and disorientatn vector sign are low-angle boundaries and part of the boundary with |ω|=0 can reach *0,7 microns*.

The formation model of interblock twist boundary with the modulus variable along the boundary and disorientation vector sign ω is the developing of formation model of twist boundary with being variable along the border |ω| /2/.It is based on the superposition of two relaxation types of elastic lattice bending including discretic relaxation leading to the boundary formation, and continuous uniform relaxation, forming crystallogeometrical boundary parameters finally.

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SHAPE CHANGES OF NANOSIZED LIQUID PB INCLUSIONS IN AL AT ELEVATED TEMPERATURES

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We present TEM results from an experimental study of the morphological changes of liquid Pb and (Pb,Bi) inclusions embedded in an Al matrix. Such inclusions are insoluble up to the bulk melting point of aluminium.

We use rapidly solidified samples which gives inclusion sizes in the range from 20 to 250 nm. The experiments consist of heating cycles of the liquid inclusions from their melting point around 600 K up to around 800 K and back to their solidification. The solid Pb and (Pb,Bi) inclusions are topotactically aligned with the Al matrix, with an incoherent boundary. The shape is a cuboctahedron with hexagonal 111 facets and square 100 facets. We have found a hysteresis in the morphology of the liquid inclusions. Immidiately after melting the 100 planes bulge outwards and become rounded whereas the 111 planes stay flat until the temperature reaches 750-800 K, where the inclusions become rapidly spherical. During subsequent cooling the inclusions retain their spherical shape until solidification. Since atomic and vacancy mobility in the aluminium matrix is high at all temperatures above the melting point, we suggest that diffusion cannot be rate controlling. The experiment was made with pure Pb and Bi added as an impurity to test the possibility that the presence of impurities in the interfaces was rate controlling, and found that this is not the case.

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SUBATOMIC-SCALE FIELD ION MICROSCOPY AND ANALYTICAL MODEL OF GRAIN BOUNDARIES

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The first atomic-level observations of grain boundaries (GBs) by the method of field-ion microscopy (FIM) made a valuable contribution to the progress in understanding atomic structure of the intergranular boundaries. But the definition of the fine-scale atomic structure of the GB core is below the routine resolution of a FIM. In this work the method of indirect magnification is used in FIM investigations of the atomic structure of GBs. The method offers a further degree of FIM resolution. The calibration of individual atom displacements against the known deformation field of the single lattice dislocation showed that the method allowed to detect a subatomic local displacement in the vicinity of line and planar defects of order of 0.01 nm. A computer simulation of symmetrical GBs was also produced. The technique used in the computer experiments was the pair-wise version of the molecular dynamics method.

The data provided by the subatomic-level FIM combined with real-space computer simulation showed that in addition to the rigid-body translations of lattices at symmetric grain boundaries observed in tungsten crystals, there also exist zonal displacements of atomic planes. In the present paper the applicability of analytical model of high-angle GBs [1,2] to description of the relaxation due to rigid-body translations of lattices of the adjacent grains and zonal plane displacements was investigated. Analyzing the atomic morphology of symmetric boundaries in different translation states showed no changes of geometry of atomic layers in GB cores. It is established that the atomic configuration of the cores of symmetric grain boundaries can be adequately described by using a limited numbers of parameters, which characterize the translation state of boundary-core planes. These allows for a rigorous analytical analysis of symmetrical GBs in a commensurate case. It was shown that taking into account of the rigid plane translations allowed to obtain analytically the same atomic configurations as in case of detailed molecular dynamics solution. Subatomic displacements at an incommensurate GBs are determined by the FIM methods and analyzed in terms of the reciprocal-space analytical model.

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ATOMIC STRUCTURE AND MICROTOPOGRAPHY OF INTERFACES BETWEEN CRYSTALLINE AND AMORPHOUS PHASES IN TUNGSTEN

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The morphology of interface between crystalline and amorphous phases in tungsten is investigated at the atomic level. The experiments were performed in a field ion microscope (FIM) with the samples cooled to 21 K. Amorphization of microcrystals was fulfilled directly in the microscope by ultrafast quenching from the liquid phase produced by high voltage pulses of a nanosecond duration. Analysis of the morphology of the interfaces on a series of FIM images obtained in the process of field evaporation to a depth of order of 10^2 nm showed that the boundaries at the microscopic level are rough. Microprotrusions 1-5 nm high and 2-15 nm wide were observed. In a number of samples atomically smooth planar sections surrounded, as a rule, by microscopically rough regions were noticed on the interfaces. The area of the atomically rough regions falls within comparatively wide limits: $10-10^2$ nm^2.

The exceedingly small width of the interface is noteworthy. The regularity in the arrangement of the atoms in the crystalline phase remains right up to the interface: the configuration of the concentric atomic steps at FIM images corresponds to the computer images of ideal single crystals. The displacements of atoms were determined according to the local deformation at the boundary of the concentric atomic steps on close-packed atomic faces by means of indirect magnification. Inelastic displacements up to 5×10^{-2} nm in magnitude were observed only near the cores of the interface. A quantitative determination of the interfacial width was made by employing the change occurring in the thickness of the imaged surface layer on amorphization. The average density of the imaged atoms in the crystalline state is 2.2 times higher than that in the amorphous state. A practically jumplike change in imaged atom surface density was observed on section of width 0.3-0.4 nm. Therefore the width of the interface between crystalline and amorphous phases can be taken as equal to one lattice parameter.

In the cases when crystallographic planes with low Miller indices intersected the interface at an angle close to 90°, microregions where atoms formed close-packed planar groups- paraplanes- were observed in the near-interface layer of the amorphous phase. Similar paraplanes have been observed before in three-dimensional regions of metallic glasses [1]. Field evaporation of the samples bared structural nonuniformities of the interface. It was revealed an alternation of the non-mated sections and regions of orientational matching of the close-packed crystallographic planes and paraplanes in the amorphous phase.

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GRAIN BOUNDARIES - OBSTACLES TO PLASTIC DEFORMATION

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The influence of grain boundaries (GBs) on plastic deformation i.e. the interaction of slip dislocations with the GBs and their possible transmission through the interface was studied. Three types of Fe-4at%Si bicrystals with different mutual orientation of Burgers vectors and slip planes in the two grains with respect to the GB corresponding to the easy, more difficult and difficult slip transfer were investigated using white beam synchrotron radiation topography *in situ* and *post mortem*. It was found that the GB forms a strong barrier in all cases, the slip transfer cannot be fully explained by the geometric criterion.

Additional energy is necessary to create the GB dislocation which compensate the difference in Burgers vectors of slip dislocations in the two grains. However, the slip bands stopped at the GB even in the geometrically most favourable case, where the Burgers vectors and slip planes in both grains are parallel. Easy slip transfer has been observed only exceptionally. Several explanations of this effect were proposed, namely:
- the GB dislocations which compensate the deviation from the exact coincidence
- image forces
- the local structure of the GB e.g. steps
- segregation of impurities or precipitates

The dissociation of dislocation has no significant effect in this material.

Comparing various internal stresses the repulsive image forces seem to be the most important reason for the impediment to the easy slip transmission in symmetrical $\Sigma 3$ {112} bicrystals.

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COMPARISON OF TENSION AND COMPRESSION DEFORMATION OF Fe-Si
BICRYSTALS - RTG TOPOGRAPHY OBSERVATION

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Bicrystals of Fe-4at%Si alloy were deformed by tension and by compression. The slip pattern was observed using white beam synchrotron radiation topography *in situ* and *post mortem*. Interaction of slip bands with grain boundaries (GBs) was studied and the effect of the slip geometry in both bicrystal grains with respect to the GB was evaluated. It was found that the GBs form strong barriers to the slip transmission. The slip transfer through the GB cannot be fully explain by the geometric criterion and it is more affected by the stresses due to the slip bands in the first-deformed grains and by the local structure of the GB.

Differences between the samples deformed by tension and by compression were observed. Unlike tensile experiments, in compression the slip bands are narrower and well separated. Fans and groups of slip bands appear only rarely. Slip transfer through the GB was observed more frequently. These effects can be explained by the properties of the two types of deformation. A variety of effects related to the slip transfer observed *in situ* and *post mortem* can be explained by different regimes of deformation.

A model of slip transfer through the GB is proposed.

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CHARACTERISATION OF (340)/(010) ASYMMETRICAL GRAIN BOUNDARY

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As an example of asymmetrical grain boundaries with the [001] rotation axis in the bcc lattice, the (340)/(010) boundary will be discussed. Four low energy atomic structures of this boundary were found by computer simulation. They are composed of capped trigonal prisms and distorted tetrahedra. The latter are in the unrelaxed form building units of the perfect bcc crystal. Two types of polyhedra are differently combined on the period of grain boundary structure. Local characteristics such as atomic volume, energy and pressure will be analysed and their correlation, that may be important for segregation phenomena, will be investigated. In addition to the expected correlation between decreasing atomic volume and increasing local hydrostatic pressure, there is a relatively large number of atom sites which do not obey a simple linear relationship between atomic volume and pressure.

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INTERFACE DISLOCATIONS IN TiAl

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TiAl in the form of polysynthetically twinned crystals with lamellar structure is often considered as a new light-weight high-temperature material for structural applications. In order to shed light on the role of interfaces in plastic deformation of this material, the observed dislocation structure of the interfaces between 120° rotation domains will be discussed. Due to small tetragonality of the γ phase with an almost cubic $L1_0$ structure, the mismatch of the $\{111\}$ planes across the interface is compensated by hexagonal or trigonal dislocation networks. Assuming different Burgers vectors of misfit dislocations, several types of observed dislocation networks will be analysed and the most justified interpretation will be selected. It is believed that the misfit dislocations can affect significantly the transfer of plastic deformation to the neighbouring rotation domain and thus influence the macroscopic mechanical properties of ordered TiAl alloys with lamellar structure.

DIFFUSION ON POLYSYNTHETICALLY–TWINNED INTERFACES IN TiAl

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The utility of polysynthetically-twinned (PST) TiAl, which contains a high density of parallel, atomically flat interfaces within a set of identical crystallographic orientations, as a potential model system for a detailed investigation of interface diffusion is explored. Macroscopic PST crystals were grown in an optical float zone furnace. Thin films were cut from oriented crystals and polished with <110> and <112> directions normal to the film. After sputter cleaning, Ag was deposited on one side of the TiAl thin films. Auger spectra were obtained from these films over a wide range of sputter/anneal conditions. The Al and Ti concentrations were analyzed as well as the important impurity elements, S, Ar, C, N and O. Ag diffusion on the interfaces was confirmed. Using the present data and existing knowledge of the microstructure and crystallography of PST TiAl, the potential of this material for providing a detailed understanding of the atomistic mechanisms of interface diffusion is analyzed.

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ANISOTROPY OF GRAIN BOUNDARY DISLOCATION STRUCTURE

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Various properties of metals and alloys are significantly influenced by grain boundaries (GB). Studies of e.g. grain boundary diffusion, migration and sliding have shown that the GB microstructure plays a decisive role. Low Σ coincidence boundaries are an important group of high angle GBs. In a polycrystal their frequency may attain up to 30% [1]. Exact coincidence is observed rarely, generally there is some deviation from it. According to the secondary grain boundary dislocation (GBD) model [2] this deviation is accommodated by GBDs. For mixed deviations (tilt and twist) the network of GBDs is complex and inherently anisotropic [3]. This anisotropy must be considered e.g. in studies of diffusion along the GB [4,5].

In this contribution the anisotropy of the dislocation structure will be treated for two cases of low Σ symmetrical boundaries. As shown in [3] the following decomposition of general deviation from coincidence orientation is physically meaningful: a rotation on the GB normal (twist component) and the remaining part which is a tilt on an axis lying in the boundary plane.

In the first structure one of the basic *dsc* vectors lies in the boundary plane (or nearly in the boundary plane) and can form a hexagonal network with two other basic *dsc* vectors inclined to the boundary plane. This network is responsible for the whole twist component and for a small part of the tilt component. The fourth *dsc* vector is perpendicular (or nearly perpendicular) to the boundary plane and cannot react with the other three. An independent array of edge dislocations parallel to the tilt deviation axis accommodates the main part of the additional tilt. In the second structure one of the *dsc* vectors is perpendicular (or nearly perpendicular) to the boundary plane and can form a hexagonal network with other two *dsc* vectors inclined to the boundary plane. The fourth *dsc* vector lies in the boundary plane (or nearly in the boundary plane) and cannot react with the other three. The hexagonal network accommodates both the twist and tilt component. For large twist to tilt ratios an independent array of parallel screw dislocation with the fourth Burgers vector is necessary to eliminate shear stresses. An example of the first case is e.g. $\Sigma 5$ (310) [001] 36.87°. The second structure is found in e.g. $\Sigma 3$ (1 $\bar{1}$ 2)[110] 70.5°.

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GRAIN BOUNDARY FACETING TRANSITION AND ABNORMAL GRAIN GROWTH IN NICKEL

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When polycrystalline Ni is heat-treated in a carburizing atmosphere, the grain boundaries show faceting transition. Above $0.7Tm$, where Tm is the melting temperature, the grain boundaries observed under a transmission electron microscope are smoothly curved. Below $0.7Tm$, the grain boundaries become faceted. It appears that the grain boundary faceting is actually induced by oxygen, and carbon reacts with oxygen to reduce such an effect. Similarly, in alumina, the addition of a small amount of silica induces grain boundary faceting. The theoretical models for the faceting of grain boundaries of arbitrary orientation and for the effect of additives are examined.

RÔLE OF ZIRCONIUM ON THE MICROTWINNING FORMATION
IN QUENCHED Sm2Co17 MAGNETIC ALLOYS

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Excellent magnetic properties of Sm_2Co_{17} materials alloyed with Fe,Cu and Zr result from their cellular microstructure : $Sm_2(Co,Fe)_{17}$ *(later: 2:17)* rhomboedral matrix limited by $Sm(Co,Cu)_5$ *(1:5)* cell boundaries, both cut by $(Sm,Zr)Co_3$ *(1:3)* platelets, parallel to the basal plans of the previous phases. This microstructure is formed by heat treatment in the range of 500-900°C, on initially homogenized and quenched material. Our previous work let us coclude that this initial state corresponds to the disordered 1:7 phase. However, no direct observation of this phase could be done : in all cases (quench rate and temperature), some atomic order is created during the quenching, so at room temperature, a more-or-less ordered 2:17 phase is observed. This phase is microtwinned, with the twins thickness mainly of 6 atomic plans, and the twin plans parallel to the (0001) of 2:17 phase. Nevertheless, if the electron diffraction patterns (E.D.P.) of quenched structures are similar to those of 2:17 phase, some new diffraction pics appear.

The purpose of this work was to determine the origins of : (i) additional diffraction pick in the E.D.P., and (ii) microtwinning, with the emphasis put on its regularity.

A series of E.D.P. was simulated (with the EMS programme) and compared to experimental patterns, to identify the reasons of formation of additionnal pics. The 2:17 hexagonal phase does not correspond to the observed E.D.P., no more than the 2:17 rhomboedric phase, even if its regular microtwinning is simulated. On the contrary, a good accordance between simulated and experimental E.D.P. was obtained with the hypothesis of Zr segregation on the twin plans. This hypothesis is founded on the fact the at high temperature, the dissolution of Zr-rich 1:3 platelets changes the matrix chemical composition to exceed the Zr solubility limit at lower temperature. In the quenching conditions, the atoms mobility seems to be sufficient to allow the Zr segregation on few atomic plans, but not sufficient to approach the equilibrium by a Zr-rich phase (1:3) precipitation. The observation of regular microtwinning on 6 atomic plans is in good accordance with a model, for the twin plan saturation in Zr corresponding to its concentration in the 1:3 phase.

An indirect experimental evidence of this hypothesis was obtained by observation of a sample in which the Zr - rich platelets were only partially dissolved : in this case, the twins thickness is clearly inversely proportionnal to the Zr content in the matrix.

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MICROSTRUCTURE AND GRAIN BOUNDARY MISORIENTATIONS IN HEAVILY DEFORMED COPPER

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An ultrafine-grained (UFG) microstructure with a high fraction of large-angle boundaries is generated in copper by severe plastic deformation using equi-channel angular extrusion (ECAE). This microstructure is relatively stable during storage at room temperature. To display the peculiarities in the microstructural evolution during mechanical processing in UFG and conventional coarse-grained (CG) copper, the UFG samples were cold-rolled and naturally aged at ambient temperature. Microstructures, macrotextures and local orientations were investigated in the as-rolled conditions and after storage. The change in strain path from ECAE to rolling deformation resulted in break of ultra-fine grains by dislocation boundaries and in a decrease of the fraction of large-angle boundaries. Strong rolling textures were generated in these samples. Large recrystallized grains growing at the expense of the deformed microstructure were recognized in the aged conditions. Local orientations measured by the EBSP technique proved their that most of these grains were cube-oriented grains. Their growth during storage at ambient storage transforms the microstructure into a partially recrystallized state. These phenomena are interpreted in terms of both, enhanced nucleation tendency and large driving force for recrystallization, composed of grain boundary energy and dislocation energy in the rolled UFG sample.

A NOVEL APPROACH TO GRAIN BOUNDARY WETTING IN METALS: "SELF- INDENTATION" KINETIC MECHANISM

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The critical question in understanding GBW in solid-liquid metal systems is where the matter from the groove cavity comes to. Classical GB grooving by Mullins which involves capillary force induced diffusion with subsequent deposition on the outer surface explains neither the GBW profile (absence of the ridges at the surface, nearly flat and parallel walls conjugated by convex-down arch near the tip) nor linear GBW kinetics often observed above T_W, the transition temperature from partial to complete wetting (CGBW). Moreover, when available at large magnification, the micrographs show that the dihedral angle at the root, Θ_R is by no means zero but has well appreciable value, 100 ± 30 deg., even within the CGBW field.

This shows that transition to CGBW signalized by $\Theta_{AP}(T) \to 0$, with Θ_{AP} being the apparent dihedral angle found from the slope of the flat wall, is not related directly to the wetting GB phase transition at $T = T_W$, but rather to a change in the *groove kinetic regime.*

To account for these observations, a novel kinetic mechanism of CGBW is proposed. It involves extension of GB groove drained by self- diffusion flux I_{GB} of *"solid"* atoms *into the GB.* The driving force for this flux stems from the imbalance in the GB and interphase surface tensions γ_{GB} and γ_{SL} acting at the groove root.

The key physical idea in considering the imbalance is as follows. Near $T = T_W$ the equilibrium dihedral angle θ_0 is expected to be very small imposing thus the barrier for the access of liquid phase to the groove tip. In order to ensure an intimate contact between the liquid and solid at the tip of advancing groove, the "dynamical" angle $\Theta_D \approx \pi/2 >> \Theta_0$ should be established and maintained here.

This means that mechanical equilibrium at the root does not exist and that the linear force $F_\gamma = \gamma_{GB} - 2\gamma_{SL} \cos(\Theta_D/2) = \gamma_{GB}[1 - \cos(\Theta_D/2) / \cos(\Theta_0/2]$ points into the solids. Its hydrostatic component causes the self-diffusion flux I_{GB} into GB considered to be a perfect sink allowing grains to move apart normally to the GB plane ("swelling"). This mechanism is called "Self - Indentation" since, in analogy with zero-creep experiments, it can be equivalently described as the contraction of the GB slab caused by plastic deformation— diffusional creep — under the action of the compressive stress $\sigma_\gamma = F_\gamma / \delta_{GB}$, where $\delta_{GB} =$ the GB thickness.

With this model, the problem of the groove shape and kinetics reduces essentially to that for GB grooving under an arbitrary GB flux (L. M. Klinger, E. E. Glickman, V. E. Fradkov, W. W. Mullins and C. L. Bauer, J. Appl. Phys. 78(6), 3833 (1995)). The only difference is that the flux I_{GB} should be coupled now with the liquid diffusion flux $I_L(K)$ of the "solid" atoms dissolved in liquid in equilibrium with the local curvature K of the groove walls.

It is shown that the model captures the major observed features of CGBW, namely, the groove width and concave profile, the tip velocity independent on time, and the "swelling" effect. It predicts that when Θ_0 (T) increasing with reduction of temperature reaches Θ_D at some $T = T_{WI}$, the driving force F_γ for the mass transfer into GB disappears, GBW mechanism changes thus to the classical Mullins grooving, and discontinuity in the $\Theta_{AP}(T)$ dependence should occur near this wetting transition temperature.

Finally, several critical experiments required for direct verification of the self- indentation mechanism of CGBW are proposed..

TIE LINES OF THE GRAIN BOUNDARY WETTING PHASE TRANSITION IN THE Zn-RICH PART OF THE Zn–Sn PHASE DIAGRAM

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The temperature dependence of the contact angle θ at the intersection of grain boundaries in Zn bicrystals with the solid Zn/liquid Zn–Sn interphase boundaries have been studied. For this purpose, two Zn bicrystals were grown with $<10\overline{1}0>\{1000\}$ tilt boundaries having misorientation angles $\phi=16°$ (small angle grain boundary) and $\phi=60°$. These boundaries possess different energies. The temperatures T_w of the grain boundary wetting phase transition for these two boundaries were determined and the corresponding tie lines in the two-phase (Sn)+L field of the Zn–Sn phase diagram were constructed. Above T_w the contact angle $\theta=0$ and a layer of the liquid phase substitutes the grain boundary. The temperature of the wetting transition $T_{w1} = 382\pm1°C$ for the boundary with the high energy ($\phi=60°$) is lower than $T_{w2} = 386.5\pm1°C$ for the boundary with the low energy ($\phi=16°$). Above the temperature interval where all the grain boundaries become wetted, the solid phase may exist only as isolated single crystalline "islands" in the "sea" of melted phase.
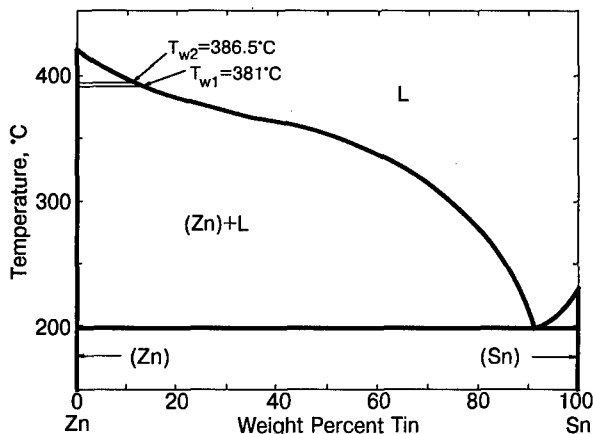
The Zn–Sn bulk phase diagram (thick solid lines) along with the tie lines of the GB wetting transition (thin solid lines).

LIQUID GROOVING OF GRAIN BOUNDARIES
IN METALS AND CERAMICS

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Grain boundary (GB) grooves appear at the emergence of GB at the surface of crystalline materials. In the case of metal surfaces under vacuum the mechanism of their formation is well described by Mullins. In spite of its importance the case of the solid/liquid is as yet studied insufficiently and the mechanism of liquid grooves formation is as yet not correctly understood.

We will examine systematically recent results on thermodynamics and kinetics of liquid grooving in metals and oxides, the influence of different factors (temperature, nature of solid and liquid, stresses, chemical interaction, etc.), the possible evolution of separated liquid grooves to liquid- channel grain boundary structures.

We shall discuss some new models of liquid grooving with emphasis on the cases of ultra fast liquid penetration.

We shall discuss also the most important applications of the phenomenon (superplasticity, high ion conductivity, etc.).

STRUCTURE OF TRIPLE LINE
IN REACTIVE Ag-Cu-Ti/SiC WETTING SYSTEM

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It is important to understand interface formation mechanism since interfaces affect materials properties. Our group has been focused attention on a reactive wetting triple line where interface is formed through chemical reactions and reported the existence of preceding reaction layer and its structural change as a function of wetting time in Ag-Cu-Ti/Si$_3$N$_4$ system[1]. To confirm the phenomena at the front of the triple line in other reactive system, we studied the triple line in Ag-Cu-Ti/SiC reactive system.

A reactive brazing alloy with the composition of 67.7mass%Ag-27.4mass%Cu-4.9mass%Ti was melted and spread on a SiC substrate under a vacuum of 10^{-3} Pa. After the wetting experiment, wetting triple lines were roughly observed using a scanning ion microscope (SIM). Then the specimens were cut to a suitable size and the triple lines were observed in detail using a transmission electron microscope (TEM). An energy-dispersive X-ray spectroscopy (EDX) analyzer equipped with the TEM was sometimes used to characterize reaction products. Reactive wetting experiments were also performed using a scanning electron microscope (SEM) equipped with a hot stage. *In situ* observations of the triple line behaviors were carried out using this apparatus.

Reaction product was observed in front of the wetting triple line. It was formed by the first chemical reaction which occurred at the wetting interface. By cross-sectional observation using TEM, it was clarified that a single-layered structure with a thickness of about 30 nm was formed. However, it has been reported that a multilayered structure consisting of a few reaction products was formed at the interface in Ti/SiC system[2]. The reaction time between liquid metal and the SiC substrate was very short near the triple line. Thus it is considered that there was not enough time to form a multilayer near the triple line. No layer thinner than 30 nm could be found. This indicates that there is a critical thickness of reaction product, as has been reported for the solid/solid interface[3]. Discussion will be done concerning on the atomistic scale wetting behavior in TEM which has been reported by Iwamoto and Tanaka[4].

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ANISOTROPY OF LIQUID METAL (Fe, Cr) -ALUMINA FREE INTERFACIAL ENERGY

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Nanosize iron or chromium metal inclusions within an alumina host matrix are obtained by internal reduction of single or polycrystalline solid solutions of alumina with chromia or hematite. Above the metal melting point, liquid metal inclusions are obtained. Upon long time annealing the liquid metal inclusions adopt their equilibrium shape in the host crystal. Rapid quenching allows to freeze this equilibrium shape and to study it on cross sectional thin foils by transmission electron microscopy. Following the Wulff's theorem of free crystals the three dimensional shape of the inclusions is interpreted in terms of the anisotropy of the liquid metal-alumina free specific interfacial energy.

Metal precipitates are formed at two different temperatures and at oxygen activities of 10^{-20}. Under these conditions, in the liquid iron-alumina system basal (0001), prismatic $\{11\bar{2}0\}$ and $\{11\bar{2}3\}$ alumina planes constitute the low energy interfaces. In the liquid chromium-alumina system in addition to these planes other low energy interfaces are detected.

THE LOCAL STRESS TENSOR OF INTERFACES AND ITS EFFECTS ON SEGREGATION*

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Using Monte Carlo (MC) simulations of the atomic structures of interfaces, we systematically study the relationships between local strain and solute-atom segregation at internal interfaces.   Specifically, grain boundaries or heterophase boundaries in crystalline materials exhibit an interesting asymmetry: they are constrained in the plane of the interface to match the bulk lattice constants of the phase on either side, but expansion is freely allowed perpendicular to an interface.   This implies that the interfacial free energy is never minimized with respect to interfacial area in a real system: any reduction in the energy of an interface through changing its area is more than offset by the elastic energy increase in the bulk phases.   Through computer simulations, however, the energetics of strain both parallel to and perpendicular to an interface can be separated, and the local stress tensor at every atomic site can be calculated.   In many systems, segregation at an interface can be explained by differences in atomic radii, i.e., atomic-size misfit-effect; solute atoms preferentially occupy interfacial sites of lower or higher hydrostatic pressure because those solute atoms are either larger or smaller, respectively, than the solvent atom.   Many interfacial sites, however, experience nonhydrostatic stresses that can be of opposing sign on different axes. In this case the calculation of a size effect is not straightforward. For example, consider the case of an interfacial site in tension in the plane of an interface and in compression out of the plane. A calculation based on size-effect or local hydrostatic-stress might suggest that this is not a preferred site for a larger solute atom. Because the interface, however, is free to relax perpendicular to the plane of the interface, the out-of-plane compression may not be a factor in the dynamics of a real system. We investigate the interrelationships of the effects of atomic structure, local strain and solute segregation in a series of crystallographically distinct grain boundaries in f.c.c. alloys. Embedded atom method (EAM) type potentials are employed for modeling atomic interactions, and Monte Carlo (MC), molecular dynamics (MD) and energy minimization techniques are utilized for calculating atomic positions and solute segregation.   We correlate solute-segregation behavior with each of the components of the local stress tensor with and without a segregant, and attempt to draw general conclusions about segregation at interfaces.

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SEGREGATION AND WETTING IN A TILT GRAIN BOUNDARY : A MONTE-CARLO SIMULATION

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Using Monte-Carlo simulations coupling atomic displacements and change in chemical identity (grand canonical ensemble), we have studied the segregation isotherm for the different sites of the $\Sigma = 5$ (310) [001] tilt grain boundary in Cu-Ag system. First of all we detail the influence of the segregation on the crystallographic structure of the grain boundary. Then, taking into account a previous study related to the analysis of the driving forces of intergranular segregation in the dilute limits [1], we emphasise the influence of interactions between segregating atoms in the grain boundary. In particular, even though the Cu-Ag system is characterised by a strong tendency to phase separation in the bulk, an order-disorder transition restricted to the grain boundary plane can be obtained at very low bulk concentration. Moreover we study the behaviour of the grain boundary when the bulk concentration approaches the bulk solubility limit (remaining in all cases in the domain of the solid solution), both in the Cu-rich and the Ag-rich part of the phase diagram. We then compare the grain boundary behaviour to the surface one, for which a complete wetting of the Cu(Ag) solid solution by the Ag rich phase was observed [2].

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MONTE CARLO SIMULATION OF SOLUTE-ATOM SEGREGATION AT GRAIN BOUNDARIES IN SINGLE-PHASE BINARY FCC ALLOYS*

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Monte Carlo (MC) techniques (Metropolis algorithm and overlapping distributions MC [1]) have been used extensively to explore systematically the eight-dimensional grain boundary (GB) phase space for both twist and tilt boundaries in dilute single-phase binary f.c.c. alloys; the atomic interactions are described by EAM potentials [2-6]. We use lattice statics calculations initially to determine the lowest energy GB structures and then MC simulation to calculate the distribution of solute atoms and the Gibbsian interfacial excess at elevated temperatures for each GB structure studied. Accurate segregation free energies for individual sites in GBs are calculated with the overlapping distributions MC technique and segregation entropies are determined and found to be a linear function of the segregation internal energies for the same GB sites. The effects of both the five macroscopic and three microscopic degrees of freedom (DOFs) are studied and it is demonstrated that the Gibbsian interfacial excess is a complicated function of both macroscopic and microscopic DOFs [7]. Also a GB's atomic structure determines the partitioning of segregating solute atoms between the cores of dislocations and in the elastic stress fields of GB dislocations [7,8]. We also demonstrate that none of the geometric criteria suggested in the literature is capable of predicting the propensity for GB segregation, much less the magnitude [7]. Experimental segregation results have been obtained on selected binary alloys employing combined transmission electron and atom-probe microscopies, which demonstrate the importance of the macroscopic DOFs in determining the value of the Gibbsian interfacial excess for a specific GB [9].

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INTERGRANULAR SEGREGATION, INTERGRANULAR ORDERING AND
ORDERED PHASE PRECIPITATION: A MONTE-CARLO SIMULATION.

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An empirical many-body potential has been used to model an Al-Mg alloy up to
25 % Mg. The bulk phase diagram has been roughly estimated in this range at T=300K,
via Monte-Carlo simulations in the transmutational ensemble. It exibits a solid solution
up to 18,5 % Mg and switches to a DO_{22} ordered phase by means of a first order phase
transition.

The core structures of the $\Sigma=5$ (310) [001] grain boundary (GB) have been
computed in pure Al. The well known C structure[i] is the most stable at T=0K, and has
been used as the initial structure for simulations in the alloys. These simulations have
been performed in a concentration range extending from the infinitely dilute limit to the
end of the solid solution domain.

The calculation of segregation energies of Mg impurity and local pressures on
each GB atomic site shows that the sites under tension are favorable to Mg segregation.
Since $r_{Mg} \approx 1.12 r_{Al}$, size effect seems to be the dominant factor for segregation in the
dilute limit. At higher bulk concentration (C_{bulk}), the Mg concentration at site i in the
GB appears to be strongly dependent on the occupancy of the neighbouring sites.
Monte-Carlo simulations are required to optimize site occupancies while relaxing
atomic positions and GB volume. Using this algorithm, we obtained the following
results.

At low C_{bulk} ($C_{bulk} \approx 0.5$ %), a 2D ordered structure is observed in the interface
plane. The average concentration in this plane (C_0) is 25 %.

At intermediate C_{bulk} (=6.3 %), an other 2D ordered structure exists (C_0=50 %).
A depleated zone of four (310) planes is present on each side of the boundary. It is more
likely to stem from local compresions induced by the saturated boundary plane than
from « local chemical ordering ».

At C_{bulk} closer to the bulk transition (C_{bulk}=17.3 %), a 3D ordered phase of the
D1a type appears at the GB. Its maximum extension is 15 (310) planes. This phase is
not stable in the bulk at this temperature. Its structure shows an amazing matching with
the grain boundary geometry.

Preliminary results show that the DO22 phase precipitates without preference at
the interface D1a-bulk and in the bulk.

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INFLUENCE OF ATOMIC STRUCTURE
ON GRAIN BOUNDARY SEGREGATION
IN Cu(Ag) AND Ni(Au) SYSTEM

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The purpose of this study is to compare the segregation of Ag and Au impurities at different grain boundaries of copper and nickel (respectively): $\Sigma 11(113)$ and $\Sigma 11(332)$.

The relaxation at $T = 0$ K of geometrical structures have been achieved by using a quenched molecular dynamical procedure. The particles interact via a N-body potential derived from the Second Moment Approximation of Tight Binding Scheme [1].

The ultimate aim of this work is to forecast the driving force for the intergranular segregation in these systems. The analysis of the segregations factors shows clearly that the driving force for intergranular segregation of Ag and Au in Cu and Ni respectively is the size effect.

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THE PROPERTIES OF THE RESIDUAL IMPURITY SEGREGATIONS FORMED NEAR THE GRAIN BOUNDARY CORE IN METAL POLYCRYSTALS

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The temperature dependence of the composition of the residual impurity segregations formed near the grain boundary core (segregations-2) was studied for Cr, Pd, Ta, W and Pt using a new method [1], which combines the nuclear gamma resonance spectroscopy (NGRS) and the preferable intercrystalline diffusion. In these metals the segregations-2 constitute complexes comprising vacancies and interstitial impurities. These complexes and single point defects form a stationary region with a high concentration of point defects (SRHCPD) near the grain boundary (GB) core. The thermal dissociation of the complexes leads to the appearance of free vacancies in the SRHCPD. The concentration of these free vacancies is 10 orders of magnitude higher than the equilibrium concentration. The vacancies in the SRHCPD provide the diffusion pumping of the substitutional ^{57}Co atomic probes from the GB core to the adjacent regions of the lattice at a temperature of $0.18T_m$, where T_m is the melting point. Single interstitial impurities migrate to the sink (the GB core) and determine a linear dependence of the isomer shift and the width of the component-2 of the NGR spectrum on the concentration.

The dissociation of the SRHCPD at high temperatures leads to the appearance of an expanding region with a high concentration of point defects (ERHCPD). The expansion of the region with a high concentration of point defects is responsible for a sharp decrease in the activation enthalpy of the ^{57}Co pumping from the GB core to the lattice regions adjacent to the GB. The "vacancy–interstitial impurity" complexes disintegrate completely in the ERHCPD.

The activation enthalpies of the thermal dissociation of the vacancy–interstitial impurity complexes in the SRHCPD, binding of single interstitials in the SRHCPD, the SRHCPD disintegration, binding of the vacancy-interstitial impurity complexes, and pumping of the ^{57}Co atomic probes from the GB core to the adjacent lattice regions in tantalum, tungsten, platinum and palladium were determined.

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THE PROPERTIES OF THE RESIDUAL IMPURITY SEGREGATIONS FORMED IN THE GRAIN BOUNDARY CORE IN METAL POLYCRYSTALS

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The temperature dependence of the composition of the segregations-1 formed in the grain boundary (GB) core was studied for Cr, Pd, Ta, W, Pt and Au using a new method [1], which combines the nuclear gamma resonance spectroscopy (NGRS) and the preferable intercrystalline diffusion. The "vacancy–impurity" complexes, which constitute the segregation-1 in the GB core of tungsten, platinum and palladium, do not dissociate until the segregation-1 itself disintegrates. The concentration of these complexes in the GB core is several times as high as the corresponding concentration outside the core. The energy of the interaction between the complexes and the GB core is several-fold higher than in the stationary region with a high concentration of point defects (SRHCPD). The SRHCPD dissociation temperature coincides with the disintegration temperature of the segregation-1 in the GB core.he relaxation of the GB core structure in polycrystalline tungsten was detected at a temperature of about $0.35T_m$, when the composition of the lattice regions outside the GB core no longer differs from the volume composition and these regions acquire their "own" physical properties. Here T_m is the melting point. The isomer shifts of the spectral components-1, which are due to the atomic-probe-occupied state in the GB core, continue to change with increasing temperature. This reflects the relaxation of the GB core structure in tungsten, which was distorted by the segregated "vacancy–interstitial impurity" complexes.

SEGREGATION IN ADVANCED STEELS

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Many researchers have investigated grain boundary and surface segregation in steels by Auger electron spectroscopy (AES) with an emphasis on grain boundary embrittlement. For advanced steels, e.g. ultra-low carbon steels, segregation mechanisms are also of interest which are associated with the texture development. Ultra-low carbon steels are increasingly being used in automotive applications because of their excellent formability which is texture dependent. While embrittlement may be an issue in these steels as well, it is in general difficult to reveal the grain boundary in situ by intergranular fracture. Thus, scanning AES is employed to obtain information on grain boundary segregation by mapping the surface segregation kinetics in polycrystalline material. This approach had first been applied for an Fe-3%Ni alloy embrittled by Sb segregation. Both surface and grain boundary segregation were studied thereby confirming the relationship between preferential surface segregation of Sb from grain boundary areas with its grain boundary segregation levels.

Surface segregation kinetics studies were then performed in a number of commercial ultra-low carbon steels microalloyed with Nb and Ti where the Ti levels range from 0.04 to 0.08 at%. Despite these microalloying elements are added to scavenge interstitially soluted C and N, AES investigations at 873 K reveal in both steels substantial C surface segregation. In addition, S segregation is observed in competition with C. The scanning results indicate preferential S segregation from grain boundaries whereas C segregation originates from the bulk. The amount of S segregation depends strongly on the Ti content and decreases as microalloying with Ti increases. This can be attributed to the fact that Ti forms sulfides thereby reducing the amount of S in solution which is available for segregation The segregation kinetics is described based on diffusion models taking into account the repulsive interaction of S and C as well as the role of Ti. Conclusions on the grain boundary segregation are proposed. Further investigations are initiated to characterize the effect of texture and thermomechanical processing steps on the segregation behaviour.

SEGREGATION AT INTERPHASE BOUNDARIES
IN OXIDE-DISPERSION STRENGTHENED FERRITIC STEELS

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Distribution of impurity and alloying elements at and in the vicinity of matrix - dispersoid interphase boundaries in a powder metallurgy Fe-Cr ferritic steel strengthened by disperse TiO_2 particles is studied by Auger electron spectroscopy as a function of annealing time. Strong multilayer Cr segregation is observed in sub-interface layers of the ferritic matrix; the width of the enriched zone is estimated to be 2 - 4 nm. At some boundaries, the Cr segregation is accompanied by a rather weak S and C segregation in a monolayer regime.

The Cr segregation causes pronounced transformations in the chemical composition of the dispersoids. Two different types of the TiO_2 particles depending on Cr behaviour are found to form in the steel in the course of annealing. In the first case, Cr enriches mainly in nearest subsurface layers of the TiO_2 dispersoids. In the second case, the Cr atoms penetrate into the dispersoid to its full depth and form complex three-dimensional $(Cr,Ti)_xO_y$ - compounds.

The observed multilayer segregation is found to be induced by long-range elastic stresses around the dispersoids in as-extruded steel and it proceeds as a stress relaxation process with annealing time. To study segregation kinetics the Cr behaviour is simulated as one-dimensional diffusion in the field of long-range elastic stresses. Analytical equations describing solute - interface long-range elastic interaction are derived to calculate the solute concentration as a function of time and distance. As follows from the results of these calculations, the segregation process quickly reaches a steady state in a close vicinity of the dispersoids. This results in a quick and intensive enrichment of a few subsurface layers accompanied with a rather slow and moderate depletion of distant regions around dispersoids.

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DEPENDENCE OF SEGREGATION OF BORON ON NATURE OF GRAIN BOUNDARIES IN A NICKEL BASE SUPERALLOY

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The properties and behaviour of grain boundaries (GBs) are strongly affected by local chemistry and atomic structure and the nature of GBs plays a significant role in many metallurgical processes, such as grain growth, creep, interfacial cavitation and stress corrosion. In .many Ni superalloys intergranular liquation has been observed in heat-affected-zones (HAZ) during welding resulting in microfissuring. This liquation has been attributed to the segregation of B to the GBs during pre-weld heat treatments which lowers the melting point of GB material. Therefore, during welding the segregated GBs in the HAZ can liquate resulting in the development of microfissures due to welding stresses. The focus of this investigation was on the determination of the nature of GBs, in terms of the coincident site lattice (CSL) classification of GB geometry and its correlation with the segregation of B on GBs and their tendency to liquate when heated to welding temperatures.

The thermal cycles actually experienced by the HAZ during welding were simulated with a Gleeble 1500 thermo-mechanical simulation system on Inconel 718 containing boron. The intergranular liquation in the simulated samples was characterized by SEM. It was observed that well-developed liquation occurred at some of the GBs, while others remained unwetted, although they experienced exactly the same thermal cycle. It was also found that at some GBs melting occurred only at certain segments that were intersected by twin boundaries. This implies that the different parts of a twin-intersected boundary may respond to the thermal cycle in different ways, which may depend on the local structure of the GB.

In order to correlate the intergranular liquation behaviour and the nature of GBs, orientation imaging microscopy (OIM), based on the analysis of electron back-scatter diffraction patterns, was performed on the Gleeble simulated samples. The nature of GBs in the region of interest was characterized by low angle boundaries ($<15°$), CSL boundaries ($\Sigma 3$ to $\Sigma 49$) and random boundaries. A close correlation between the nature of GBs and their tendency to liquate was observed. Liquation was observed to occur with high frequency on random boundaries while on CSL interfaces it depended upon the value of Σ. As the value of sigma reduced so did the frequency of GB liquation. No intergranular liquation was observed on twin boundaries ($\Sigma 3$) and on low angle boundaries.

The secondary ion mass spectroscopy revealed that random boundaries were invariably segregated with B and the intensity of B segregation reduced as the value of Σ for CSL interfaces reduced. Since B reduces the melting point of nickel alloys, its segregation on random boundaries caused them to liquate and develop microfissures.

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ROLE OF VANADIUM ON PHOSPHORUS GRAIN BOUNDARY SEGREGATION IN LOW ALLOY STEELS

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The role of vanadium on phosphorus grain boundary segregation in three low alloy Cr-V-C-P steels (Table 1) was investigated. The steels were heat treated according to the schedule: austenitization 1323 K/0.5h, quenching in 10% KOH solution, tempering at 923 K/2 h, water cooling, aging at 853 K for 0.1, 0.5, 1, 5, 10, 100, and 1000 h, and water cooling. Auger electron spectroscopy was used to determine the phosphorus grain

Table 1. Chemical compositions of investigated steels (in wt.%).

Steel	Cr	V	C	P	Mn	S	Si
1	0.89	-	0.115	0.045	0.333	0.0039	0.234
2	0.88	0.258	0.136	0.047	0.337	0.0035	0.238
3	0.88	0.507	0.134	0.040	0.332	0.0039	0.228

boundary concentrations. In all three investigated steels the phosphorus grain boundary concentrations approached the maximum level already after aging for 1 h (Figure 1). In contrast to the previous results [1] on Fe-V-P and Fe-V-P-C model alloys in these steels the phosphorus grain boundary concentration increases with the bulk vanadium content.
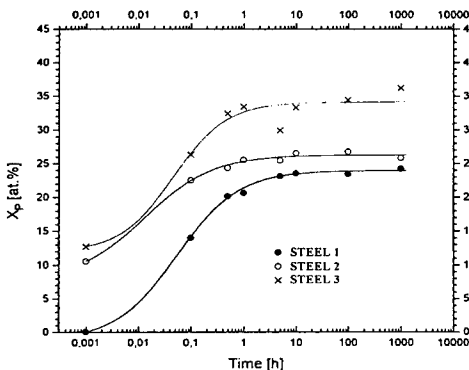
Reference

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Figure 1.
Levels of phosphorus grain boundary concentration at 853 K as a function of aging time for investigated steels.

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COMPETITION BETWEEN SEGREGATION OF SULFUR AND hBN PRECIPITATION

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We have studied the competition between sulfur segregation and hexagonal boron nitride precipitation (hBN) onto the surface of an austenitic stainless steel by Auger spectrometry, SEM and TEM.

The hBN film is obtained by superficial precipitation of boron and nitrogen in supersaturation in the the steel during an annealing between 700 and 800EC. The c axis of the crystallites of boron nitride are normal to the surface of the metal whatever the orientation of the metallic substrate grains. Therefore the BN film is thicker if the surface of the grain of stainless steel is (111) or near (111) due to an epitaxial relation (0001) ∥ hBN (111).

The competition between segregation and precipitation is studied by in-situ AES at different temperatures in the range 600°C- 800°C. If the temperature of annealing allows the sulfur to segregate before the nucleation of BN, the film is not observed. On the other hand, if the nitride appears first, the sulfur can segregate at the interface stainless steel - boron nitride and then limits the growths of the film. In such a case both BN and steel peaks are detectable on the AES spectra (See Fig 1-b)
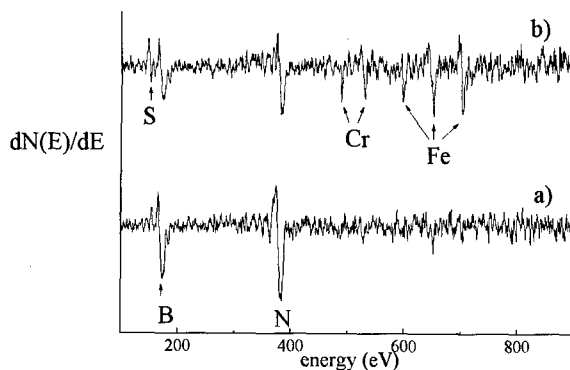
Figure 1: AES spectra of boron nitride film on stainless steel

MECHANISMS AND EFFECTS OF BORON GRAIN BOUNDARY SEGREGATION IN (B2) FeAl ALLOYS

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Ordered FeAl alloys with a B2 structure exhibit good properties at intermediate temperatures and an excellent resistance to corrosion. Nevertheless, like many other intermetallics, these alloys present an intergranular brittleness at room temperature. For a decade, it has been known that doping by few dozens ppm of boron prevents the intergranular failure of FeAl and even provide some ductility in Fe-rich alloys. Boron effect is imputed to its segregation to grain boundaries.

First of all, the effect of boron on the mechanical properties of FeAl was investigated in alloys containing between 40 and 50 at% Al. The solubility limit at 500°C in Fe-40Al was estimated between 400 and 800 ppm B. Above this limit, Fe_2B precipitates are observed but they are not deleterious to the mechanical properties.

In order to understand how boron improves the properties of FeAl alloys, the mechanism governing its segregation was studied. Thanks to Auger electron spectrometry, the characteristics of boron segregation were determinated. In all FeAl alloys studied, containing between 40 and 50 at% Al, boron segregation is observed. In any cases, its level is low (less than 15%) but efficient to change the fracture mode from intergranular to mixed (transgranular and intergranular).

Some of its characteristics can be explained by an equilibrium segregation : the increase of the intergranular content of boron with its nominal concentration, the existence of a level of segregation stable with time, ... Several models (including McLean and Fowler) were compared to describe it.

Nevertheless, the kinetics of boron segregation at 400°C cannot be explained by an equilibrium segregation. Indeed, the maximum level is attained too rapidly to be governed by boron diffusion. Hence, an assumption of a non-equilibrium segregation was made, implying the dragging of boron atoms to grain boundaries by migrating vacancies. As a matter of fact, FeAl alloys can retain high concentrations of vacancies after quenching from high temperature. These vacancies eliminate efficiently during a long annealing at low temprature (typically 400°C). To verify the hypothesis of a non-equilibrium segregation, the interaction between boron atoms and vacancies eliminating at 400°C was studied. By isothermal dilatometric experiments and the comparaison of the kinetics of vacancies elimination between boron-free and boron-doped alloys, it was observed that in presence of boron, the elimination of vacancies is clearly accelerated. This experiment confirms existence of an interaction between boron atoms and vacancies : they form complexes migrating to grain boundaries more rapidly than free vacancies and leading to a non-equilibrium segregation of boron.

Boron segregation results of two mechanisms : a non-equilibrium one providing a rapid kinetics of segregation and an equilibrium one permitting the stability of segregation with time. As a consequence, no « segregation heat treatment » is necessary for boron to improve the properties of FeAl alloys.

INTERFACE AND GRAIN BOUNDARY SEGREGATION OF IMPURITIES IN A 3CR12 STAINLESS STEEL

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The 3CR12 stainless steel is a special low alloy stainless steel developed in South Africa and the interface and grain boundary segregation characteristics of this alloy are therefore not available in literature. On the other hand are these segregation results typical of stainless steels and the complex segregation behaviour found in these samples may serve as a model for similar steels. Three samples of varying P content were prepared and the surface segregation studied in UHV by Auger electron spectrosc opy as a function of time and temperature in the temperature range 400°C - 700°C. Not only did the doped phosporus segregate to the surface, but a complex site competition with two other segregating species, S and Sn, was observed. The alloy thus forms a quaternary segregating system and approximate values of the segregating parameters (segregation energy ΔG_i and interaction parameter Ω_{ij}) as well as the diffusion coefficient D_i have been obtained.

The grain boundary segregation in the same alloy has also been studied in the same temperature range. A fracture stage was used to expose the segregated grain boundaries in the UHV system and surface composition maps were obtained in approximately 1 hour. The time and temperature settings were taken from the interesting regions found in the surface segregation studies.

The relation between the surface and grain boundary segregation will be discussed. Particular attention will be given to the values of the segregation parameters ΔG and Ω as found for the surface and the bulk, as well as the numerical procedures required to extract these parameters from the complex data sets.

ORDERED MONOLAYER OVERSTRUCTURES FORMED ON Cu SURFACES THROUGH SEGREGATION

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Recent studies in this lab concentrated on the segregation of metal dopants in dilute copper alloys. Typical dopants included tin, antimony and silver with concentrations in the order of 0.1 at% - 0.2 at%. The kinetics and equilibrium segregation of these dopants for the (111), (110) and (100) copper orientations were investigated in the temperature range 400°C to 600°C by Auger electron spectroscopy. It was found that all three dopants segregate strongly in copper, enabling the deter mination of the diffusion parameters D_0 and E and the segregation energy ΔG.

By comparing the results of the various dopants in the copper orientations, it was found that the equilibrium surface coverage of tin and antimony stayed constant over the whole temperature range. This is in contrast to silver where a decrease in concentration with increase in temperature was observed. This change in equilibrium surface coverage corresponds to a dramatic change in the segregation kinetics as well. At the same time a difference in the structure of the ordered monolayer overstructure is al so observed for the different dopants and copper orientations. These differences will be discussed in terms of the interaction Ω between the dopants and the surface structure.

THE EFFECT OF NITROGEN ON THE SEGREGATION KINETICS OF MOLYBDENUM IN A Fe-3.5%Mo-N(100) SINGLE CRYSTAL STUDIED BY A CONSTANT TEMPERATURE HEATING METHOD

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The study of the kinetics of segregating species in binary alloys has proven an effective and easy way to obtain the segregation parameters from the surface coverage *vs* time curves at the various temperatures. In this way the pre-exponential factor D_0 and the activation energy E of the diffusion coefficient and the segregation energy ΔG could be determined for Sn in the Cu matrix [1]. These studies have now been extended to include ternary alloys in an attempt to also characterise the se gregation kinetics in more complex alloys that are favoured in practical applications.

A Fe-3.5%Mo-N(100) single crystal has been chosen for this investigation. It has been found by Auger electron spectroscopy studies in UHV that molybdenum does not segregate to the surface of an iron crystal unless nitrogen is present on the surface. Due to the attractive interaction between molybdenum and nitrogen, a surface compound of these elements grows epitaxially on the (100) surface [2]. The source of this nitrogen can either be nitrogen impurities in the Fe matrix that cosegregate to the surface or nitrogen atoms from the ambient. The segregation kinetic behaviour of this surface compound formation was studied in the range 500°C to 650°C. At temperatures below 500°C the formation of the surface compound is too slow to be studied without contamination of the residual gases. At temperatures higher than 650°C desorption of N takes place, leading to the desegregation of Mo and the degeneration of the surface compound. It will be shown that the diffusion paramet ers of molybdenum and nitrogen as well as the interaction coefficient between the two species could be obtained by a Darken fit of the data.

[1] EC Viljoen, J du Plessis, HC Swart and GN van Wyk, Surf. Sci. 342 (1995) 1
[2] B Eltester and C Uebing, Surf. Sci. 347 (1996) 39

SURFACE SEGREGATION ON Fe-25%Cr-2%Ni-0.1%Sb SINGLE CRYSTALS

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Abstract

Surface segregation is investigated on Fe-25%Cr-2%Ni-0.1%Sb single crystals by means of Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). The impurities sulfur and nitrogen act as additional segregating species in the system under investigation. Segregation phenomena are studied on the (100) oriented surface at temperatures up to 750° C.

At temperatures up to 500°C, cosegregation of nitrogen and chromium causes the formation of the two-dimensional surface compound CrN. A further increase of temperature causes surface segregation of antimony and cosegregation of nickel. The replacement of chromium and nitrogen by antimony and nickel is fully reversible: Annealing of a surface that is covered with nickel and antimony at about 500°C leads to substitution by chromium and nitrogen.

For temperatures higher than 650°C or long annealing times, sulfur segregation takes place. Heating to temperatures higher than 700°C results in segregation of large amounts of sulfur accompanied by chromium and nitrogen.

For the Cr-N saturated surface, the Sb-Ni saturated surface and the sulfur covered surface well ordered LEED patterns are observed. On the basis of these patterns, we propose structure models.

HIGH TEMPERATURE OXIDATION OF Ag-COATED Ni TAPES

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We have shown that Ni oxidation of Ag-coated Ni polycrytalline tapes which undergo thermal treatments performed in air leads to diffusion of Ni through the Ag coating.

Results will be presented here showing the effect of very thin CaO layers, deposited by sputtering directly onto a Ni textured tape prior to the Ag coating, on the decrease of the kinetics of oxidation at high temperatures of Ag-coated Ni substrates (and of the resultant diffusion of Ni into Ag). The kinetics of oxidation has been followed by TGA. The microstructural characterization includes EPMA (electron probe microanalysis) and TEM (transmission electron microscopy) studies on cross-sections of the composite specimens.

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FIRST-PRINCIPLES STUDY OF ORDERING AND PRECIPITATION IN LIGHT-WEIGHT ALUMINUM ALLOYS

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We demonstrate a first-principles theoretical approach for studying the ordering and precipitation in aluminum alloys. The method involves mapping atomically-relaxed first-principles total energies onto an effective Hamiltonian. The effective Hamiltonian is composed of two contributions: coherency strain and chemical energy terms, the latter contribution containing both interfacial energy and the thermodynamic driving force. Thus, this approach represents a first-principles method which contains all of the terms in classical theories of homogeneous second-phase precipiation. By combining this Hamiltonian (which is comprised of both real- and reciprocal-space terms) with a mixed basis Monte Carlo algorithm, we are able to study the thermodynamic and structural properties of Al-rich alloys, both at high and low temperatures such as: (i) Fluctuations (or short-range order) in disordered solid solutions, which often form the precursors of precipitation behavior, (ii) Coherent metastable ordered phases, (iii) Coherent metastable phase boundaries, and (iv) Precipitate shape, structure, and ordering.

The method has been applied to three Al-rich alloy systems which make for an interesting comparison, due to the different relative contributions of strain and chemical energies: Al-Mg, Al-Cu, and Al-Ni. We find that the coherency strain is crucial towards understanding the precipitate shape and structure, and further that *anharmonic* elastic effects are very important in these large size-mismatched systems. Specifically, the anharmonicity of the elastic response of the solute atoms leads to anomolously soft coherency strain for certain preferred orientations and thus leads to the observed precipitate shape [e.g., (001)-planar in Al-Cu and Al-Ni and more spherical in Al-Mg].

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Pb inclusions in the Al-Si eutectic system

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Rapid solidification of binary monotectic alloys produces a fine dispersion of small particles embedded in a matrix. For an appropriate ratio of the respective melting point and an extremely low mutual solubility of the two constituants, the melting and solidification behaviour can be monitored in-situ by TEM. In this process the particules can reach easily their equilibrium shape and therefore their structure and morphology can be directly associated to their position with respect to the matrix.

Aluminium -lead binary system has produced, over the last few years, a large amount of experimental results but the natural extension of this approach to the isomorph system Si-Pb has been limited by the technical difficulties in quenching silicon. As an alternative to obtain a fine scale precipitation of lead in silicon, the eutectic Al-Si alloy, containing a small amount of Pb, has been been rapidly quenched producing, within the same sample, particles of pure lead in the aluminium phase, in the silicon phase, at the interface Al-Si and finally, at the twins present in the silicon phase.
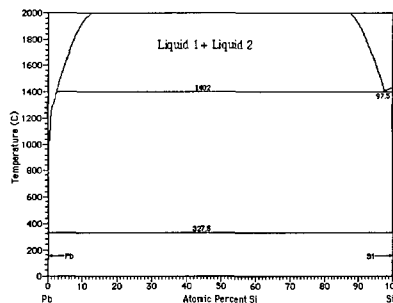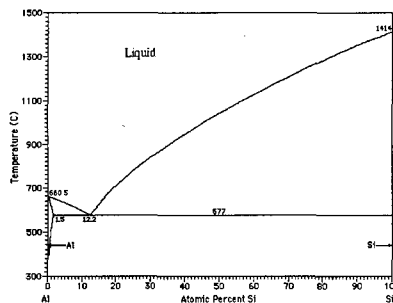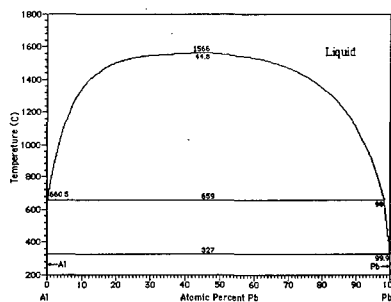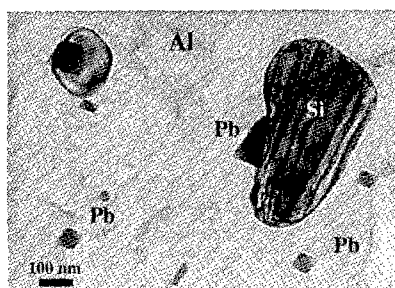
TEM micrograph of Pb inclusion in the eutectic Al-Si alloy. Note the difference in morphology between inclusions in the bulk of aluminium grains and at the Al-Si interface.

THE EFFECT OF GRAIN BOUNDARY STRUCTURE FORMATION
ON β - PRECIPITATION IN AGED **Al-Mg** ALLOYS

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After long-term natural aging of concentrated Al-Mg alloys the following sequence of the decomposition stages of the supersaturated solid solution was found: $\alpha_{solid\ solution} \rightarrow$ modulated structure $\rightarrow$ ordered G.P. zones. The decomposition inside grains is accompanied by grain boundary precipitation. The precipitates are metastable β' or stable β phases. After two or more years of natural aging, the grain boundary precipitates form a continuous film.

Aluminum - magnesium alloys are usually used in an as-quenched state. However, during their utilization their plasticity and stress corrosion resistance sharply decrease. It was made conclusion that this properties are sensitive to film - like grain boundary precipitates β' and β phases. Special thermomechanical treatments were worked out to produce different grain boundary structures and study the influence on the grain boundary precipitation, mechanical properties and stress - corrosion resistance.

It was found that slow heating of deformed alloys from the room temperature to the quenching ones favors the formation of various grain boundary structures, from polygonized to completely recrystallized ones. It was possible to obtain special boundaries with misorientation angles close to 21 or 37°.

The effect of the boundary migration rate during recrystallization on the boundary structure was studied, too. To obtain different recrystallization conditions, various regimes of deformation and recrystallization anneals were used. Different types of grain boundary structure were found: low - angle, faceted, planar random types of boundaries.

The results obtained show that special boundaries or low - defect faceted boundaries that can be produced using thermomechanical treatments remain free of precipitates during subsequent aging. This allow to conserved the ductility and stress - corrosion resistance after long - term aging such that one can find in as - quenched alloys.

SILVER INTERCALATION IN MISFIT COMPOUNDS

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Misfit layer compounds are built of alternate double layers of MS (M= Pb, Sn, Bi, Sb, Ln) and one or two layers of a transition metal dichalcogenides TS_2. The MS and TS_2 subsystems have a different geometry in the a-b plane, the stacking direction being **c**. Utilizing the electrochemical titration technique the comparison of thermodynamic properties of systems Ag-(*) was performed, where (*) - TiS_2 , $PbS_{0.59}TiS_2$ or $PbS_{1.18}TiS_2$, respectively. The partial Gibbs energy of the system as function of silver content at temperature 473 K is shown in Fig.1 for $PbS_{0.59}(TiS_2)$. The presence of two single phase regions was found as for Ag_xTiS_2 system.
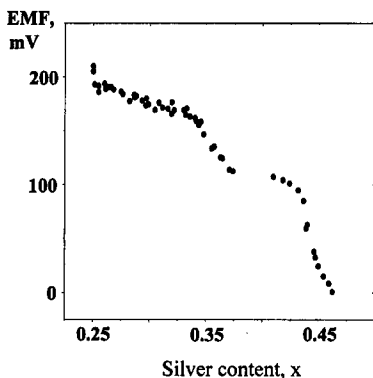
Fig.1 The Gibbs energy as function of intercalated silver for Ag- $PbS_{0.59}TiS_2$ system.

The amount of silver atoms which may be intercalated into $PbS_{0.59}TiS_2$ is very close to this value for Ag_xTiS_2. This fact shows that the main role at silver intercalation belongs to the electron transfer from Ag atom to conduction band of the host lattice. Silver intercalation into $PbS_{1.18}TiS_2$ leads to its decomposition onto PbS and $Ag_x PbS_{0.59}(TiS_2)$. From this fact we conclude that silver occupies the empty gap between TiS_2 layers and may not be placed between PbS and TiS_2 layers. The analysis of thermodynamic functions (entropy and enthalpy) is performed and the fragment of the phase diagram in temperature range 420 - 570 K is built.

BONDING AND STABILITY OF Cu/α-Al$_2$O$_3$ INTERFACES

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Metal/ceramic interfaces play a crucial role in materials science and for various industrial purposes. In technical applications these interfaces are often exposed to high temperatures and different atmospheres. This often results in a change of the mechanical stability via the morphology and electronic structure of the interfaces. We present a comprehensive analytical electron microcopy (AEM) and fracture mechanics study of this connection on a metal/ceramic-interface model system: Cu/α-Al$_2$O$_3$.

The specimens were produced by UHV diffusion bonding of bulk Cu to α-Al$_2$O$_3$ single crystals. Two different Cu materials were used, either pure Cu (noted: Cu) or Cu containing 83±12 ppm oxygen (noted: Cu(O)). After bonding the interfaces were annealed in an oxygen partial pressure at 1000°C between 20 and 120 h. Four point bending tests showed an increased fracture energy ((5±2)x) for the Cu(O)/α-Al$_2$O$_3$-interfaces compared to the Cu/α-Al$_2$O$_3$-interfaces. The annealing treatment had no measurable influence on the fracture energy of both interfaces.

TEM-investigations showed that the Cu/α-Al$_2$O$_3$-interfaces were flat. We used spatially resolved electron energy loss spectroscopy (SREELS) to determine the electronic structure at the interfaces. Both Cu/α-Al$_2$O$_3$-interfaces from oxygen free Cu contained regions referring to metallic Cu^0 and other regions referring to Cu^{1+} at the interface. Conversely TEM studies at the oxygen containing Cu(O)/α-Al$_2$O$_3$-interfaces revealed that ~ 15 % of the not annealed interface was covered with an interfacial layer (20 - 50 nm thick) of either CuAlO$_2$ or Cu$_2$O. SREELS revealed metallic Cu^0 in the other regions of the interface. The annealed Cu(O)/α-Al$_2$O$_3$-interfaces showed a closed interface reaction phase of CuAlO$_2$ (20 - 80 nm thick, FIG. 1).

The increased mechanical strength of both Cu(O)/α-Al$_2$O$_3$-interfaces compared to the Cu/α-Al$_2$O$_3$-interfaces is explained by the introduced interface roughness [1]. The closed CuAlO$_2$-layer at the annealed Cu(O)/α-Al$_2$O$_3$-interfaces reduces elastic strain due to its intermediate thermal expansion coefficient (compared to Cu and α-Al$_2$O$_3$).

FIG. 1: TEM dark field micrograph of a 120 h at 1000°C annealed Cu(O)/α-Al$_2$O$_3$-interface containing a closed CuAlO$_2$-layer.

1.   Evans, A.G., Rühle, M., Dalgleish, B.J. & Charalambides, P.G. *Mat. Sc. Eng.A* **126,** 53-64 (1990).

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THE ROLE OF AUSTENITE BOUNDARIES IN THE PROCESS OF AUSTENITE TO FERRITE TRANSFORMATION

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Two different ways of the ferrite grain formation were experimentally observed by the high temperature optical microscopy. Thermal decoration in vacuum and DIC were used to monitor the microstructure transformation. Two kinds of the ferrite grains can be distinguished which has different delay time, grains shape, and growth speed. Records of the austenite to ferrite transformation in low carbon steel are demonstrated.

SIMS and scanning Auger microprobe were used to study the carbon redistribution above Ar_3 and on the different stages of the austenite to ferrite transformation. Transformation was studied in isothermal conditions with the deformation applied during transformation (dynamic case) or without deformation (static case).

High resolution of the method allowed monitoring the carbon redistribution in scale of austenite grain.

Attraction of the carbon by the grain boundaries is typical for the initial stage of the transformation, but amount of carbon, which is attracted by the different parts of boundaries, is quite different.

The role of austenite boundaries in the process of austenite to ferrite transformation is discussed.

PHYSICAL MECHANISMS OF NON-EQUILIBRIUM PHASE TRANSITIONS IN AMORPHOUS SOLIDS

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The problem of the interphase boundary stability is of great importance. We investigated the strongly non-equilibrium phase changes in non-crystalline materials - rapid laser driven recrystallization (EC) and solid state amorphization (SSA). A new approach to the theoretical description of these phenomena is suggested [1,2].

It is shown that EC and SSA phenomena may be based on a common physical mechanism of the decay of a special state formed on the interphase boundary. According to suggested approach the non-equilibrium phase changes go through an intermediate excited states which are characterised by absence of any type of the medium or long range order. Excited states are described as high-energy vibrations of disordered network localised at a scale $L \sim 1$ nm corresponding to the medium range order scale L_c and having a lifetime $\tau \sim 10^{-9}$-10^{-10} s. Localised phonon modes lead to a stronger coupling with the electrons and consequently work as an extra source of excitation of the electronic subsystem and as an origin of the anomalous diffusion regime, which results in an enhancement of the concentrational diffusivity D_N. The localised phonon states store the energy on the interphase boundary and control the heat transfer process through the phase boundary, that leads to the renormalization of the thermal diffusivity D_T. Hence the excited states become the necessary condition for the appearance of the self-sustaining wave of the interphase boundary movement in amorphous materials.

The simple models of EC and SSA are suggested and analysed. The predicted threshold characteristics of EC and SSA are found to be consistent with the existing experimental data. The structure on the spatial scales 10^{-7}, 10^{-6}, 10^{-5} cm of the solids undergo fast phase transitions is discussed.

For the experimental parameters, corresponding to semiconductors undergoing SSA by high pressure phase retension, the solution in the form of a self-sustaining wave with velocity V is obtained. The stability region of such a decision is analysed in detail. The possible physical scenario of SSA are discussed in connection with the amorphous semiconductors obtained via high pressure phase.

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[2]. S.V.Demishev, T.V.Ischenko, F.V.Pirogov, Phys. Solid State 37, 331, (1995).

MECHANISM OF DISCONTINUOUS COARSENING
IN A Zn-4 AT.% Ag ALLOY

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We have recently reported the occurrence of discontinuous coarsening (DC) in a Zn-4 at.% Ag alloy for the first time. In this study, a detailed kinetics analysis has indicated that DC in this alloy is a boundary diffusion controlled secondary reaction that replaces the primary precipitation (*i.e.*, discontinuous precipitation) products with an identical but coarser aggregate during prolonged isothermal aging at the same (DCI) or another temperature (DCII) than that for the primary reaction. In the present study, we will report the mechanism of DCI/DCII with specific reference to the probable initiation sites and sequence, growth morphology and direction, *etc.*

A typical DC colony comprises a lamellar two phase aggregate maintaining a statistically constant distance of separation during isothermal growth at a given temperature (Fig. 1). Such constancy of interlamellar spacing is maintained by both branching and renucleation mechanisms. The DC colonies may grow either on one side only or on both side of the nucleation site. In this regard, probable sites for initiation of DC among various internal interfaces available have been identified. Finally, it has been demonstrated that DCI and DCII follow identical transformation mechanism despite marginal difference in the product morphology and available chemical driving force for the reaction.
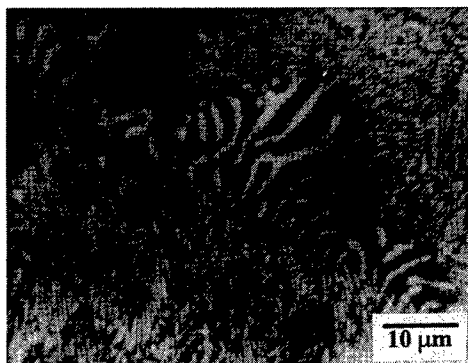
Fig. 1: Isothermal growth of a DCI colony. T = 433 K, t = 50 h.

METASTABLE AND EQUILIBRIUM DECOMPOSITION OF THE β-PHASE IN Cu-In SYSTEM

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According to the Cu-In equilibrium diagram, the high temperature β-phase undergoes eutectoid transformation into α and δ on cooling below 847 K. In an earlier investigation, the present authors have concluded that β (on quenching and aging) decomposes through a moving boundary transformation controlled by interphase boundary diffusion. The present study, however, indicates that a duplex microstructure is present in the prior β region ahead of the eutectoid reaction front (RF) (Fig. 1). Close microstructural resemblance between the eutectoid colony (in relief) and prior β matrix across the RF in Fig. 1 suggests that a moving boundary discontinuous coarsening of previously transformed β may be operative in the present alloy. However, a detailed microstructural investigation through optical, scanning and transmission electron microscopy indicates that the prior β region undergoes a time dependent pre-precipitation through a static boundary mode. The latter precedes/accompanies the moving boundary eutectoid transformation initiated at the prior β grain boundaries. Furthermore, X-ray diffraction analysis substantiates that β is present in the microstructure when such pre-precipitation products appear in the prior β regions. Thus, it is concluded that eutectoid transformation in the Cu-In system is preceded/accompanied by a continuous mode of metastable decomposition of β.
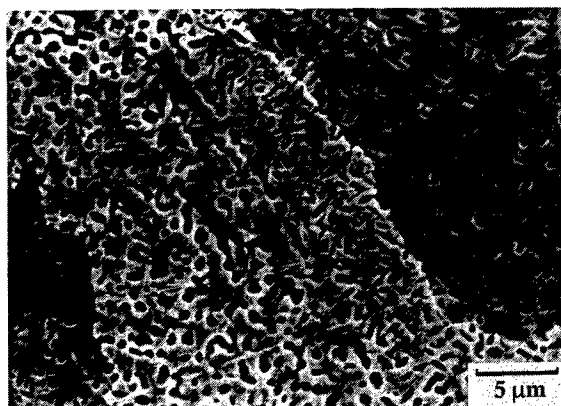
Fig. 1: Growth of eutectoid transformation in a Cu-In alloy after 2 h at 750 K.

Effects of light impurities on the electronic structure of the $\Sigma 11(11\bar{3})/[110]$ grain boundary in Ni

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The first-principles discrete variational method (DVM) within the framework of the density-functional theory (DFT) using the local-density approximation (LDA) is employed to study the effect of light impurities (B, C, N, O, H, P and S) on the electronic structure of the $\Sigma 11(11\bar{3})/[110]$ grain boundary (GB) in Ni. We perform the electronic structure calculations by utilizing the polyhedral atomic-cluster model. The calculated results show that neither B nor C strongly influence the bonding between host metals in the GB region; the interaction between host metals is only slightly decreased by B and C. In addition, both B and C form a strong bonding state with their neighbouring host metals. Our study also indicates that S and P strongly decrease the cohesion between host metal atoms in the GB region, and that the bonding tendency between S or P and the host metal atoms across the GB plane is very weak. The calculations of environment-sensitive embedding energies (ESEs) show that preferential segregation of impurities towards the GB may be expected. We conclude that the influence of impurities segregating on the GBs is closely associated with their effects on: (i) the decrease of the bonding between host atoms due to the presence of impurities; (ii) the bonding between the impurity atom and the host metals; and (iii) the site-competition ability of impurity atoms.

ANALYTICAL CALCULATION OF THE SEGREGATION PROFILE AROUND A GRAIN BOUNDARY IN BINARY ALLOYS

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Using a mean-field formalism an analytical method of calculating the segregation profile around a grain boundary in a binary alloy is presented. The method is general and applies to any pair or Finnis-Sinclair type many-body interaction potential and any range of interaction. For demonstration the concentration profiles for various special potentials are derived. The increased concentration of one atomic species as a function of distance from the boundary is found to decay rapidly after the first few planes and asymptotically reaches the proper value in the bulk. In a particular case theoretical results are compared to Monte Carlo simulations using a Finnis-Sinclair type potential for a $\Sigma 5$ twist boundary in Cu_3Au.

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HIGH RESOLUTION ELECTRON MICROSCOPY OF HYDROGEN–SEGREGATED MgO/Pd INTERFACE

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Modern super high-resolution microscope enables us to observe even atomic potential, or change in electron density distribution. Each elemental column of the silicon-carbon pair in the α–SiC viewed from <11-20> direction, for example, is distinguishable by the difference in image contrast which is due to difference in electron scattering power of carbon and silicon. In the present study such excellent ability of modern electron microscope is employed to analyze the atomic structure change of a metal/ceramic interface caused by minor impurity segregation.

Growing a MgO crystal slowly in a dilute Al–Mg alloy well-defined ceramic/metal interface which was suitable for precise high resolution electron microscopic investigation was obtained. Hydrogen was then injected into the specimen by electrolytic method. Heating the specimen at 800 K the injected hydrogen was evacuated from the specimen leaving segregated ones in the interface. Amount of the segregated hydrogen in the interface was estimated to be monoatomic layer.

MgO/Pd interface was parallel to a (111) plane of the both materials. Atomic structure was very well defined. No mismatch dislocation was recognized in spite of lattice mismatch presented. An absence of the mismatch dislocation can be one of major cause of weakness of the metal/ceramic interface against repeated heat cycle or applied external forces.

Segregated interface gave apparently characteristic image contrast, appearing brighter than the non-segregated original interface. Interplanar distance at the interface in the direction perpendicular to the interface was increased by 20% at the interface even though no change was detectable in the matrix. Calculated images were compared with the picture image to evaluate the mainly affected condition on the occurred change and concluded that both the contrast change in the image and the change (increment) in planer spacing were attributable to the reconstruction of atomic bonding due to invasion by the impurity hydrogen.

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ATOMISTIC SIMULATION OF GRAIN-BOUNDARY MIGRATION OF TILT-GRAIN BOUNDARIES

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Molecular-dynamics simulations are used to investigate continuous migration of tilt-grain boundaries. It is shown that the application of an appropriate external strain to a bicrystal of Cu results in a continuous migration of flat tilt-grain boundaries. The propagation of tilt boundaries of low index tilt axes, namely [001] and [110], is determined as a function of both the external driving force and the temperature. The temperature dependence of the grain-boundary mobility as well as the details of the atomic-level migration mechanism of these grain-boundaries are investigated. It is shown that for some tilt-grain boundaries sliding and migration are coupled.

ATOMISTIC SIMULATION AND MECHANISMS OF GRAIN BOUNDARY MIGRATION: A TWO-DIMENSIONAL STUDY

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We present the results of molecular dynamics simulation of constant curvature, intrinsic grain boundary migration, using the U-shaped half-loop bicrystal geometry employed in the experiments performed by Shvindlerman, et al. We first examine the dependence of the steady-state migration rate on the driving force, viz. the curvature of the grain boundary, by varying the half-loop width at constant temperature and misorientation ($\theta=30°$, a general grain boundary). Examination of the half-loop shrinkage rates show that for sufficiently large half-loop widths, the grain boundary velocity is linearly proportional to the boundary curvature, in agreement with absolute reaction rate theory. Next, we fix the half-loop width and misorientation and extract the intrinsic (reduced) mobilities of the grain boundary at varying temperatures. Analysis of the data demonstrates that intrinsic grain boundary mobility M is an Arrhenius function of the temperature T, with an activation energy Q close to half the bond strength of the simulated system, i.e. $M=M_o\exp(-Q/kT)$. For the low Σ (=7) grain boundary and grain boundaries close to $\Sigma 7$ (near-special grain boundaries), Arrhenius plots of mobility vs. inverse temperature extrapolate to a single temperature (i.e., a temperature exists where the mobilities of these grain boundaries are identical). This temperature is approximately equal to the melting point of the system simulated. This implies that the activation energy of grain boundary migration Q is not independent of the pre-exponential factor M_o and any change in each is compensated by the other (i.e., the so-called compensation effect).

Examination of the grain boundary structure during migration shows the generation of vacancies at the grain boundary and grain boundary pull-off from these vacancies. This is attributed to the liberation of the grain boundary excess volume into the simulation cell, as the grain boundary area is reduced during curvature driven migration. Finally, examination of the atomistic mechanisms of grain boundary migration show that while well-defined atomic hops across the boundary do occur with high frequency, it is the sudden, correlated motion of much larger groups of atoms that dominate the curvature driven grain boundary migration process. Furthermore, the number of atoms involved in the correlated shuffles is characteristic of each type of grain boundary and controls the migration rate of the particular grain boundary.

NUMERICAL ESTIMATION OF MOVING PHASE BOUNDARY Ste NUMBER

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Numerical computation of a coupled heat and mass transfer problem in porous media is described. A moving phase boundary is solved using finite differences and implicit Crank Nicholson schemes. The method works over a fairly wide range of Ste numbers with a variable step. A Fortran programme was written and implemented on a DEC VAX.

The calculation algorithm includes:
1) assumption of an initial time step and temperature distribution for starting material
2) solving for liquid and solid regimes by the Crank Nicholson method with the assumed time step, and obtaining new temperature and concentration profiles
3) estimating the thermal balance at the phase interface and recalculation of time step
4) applying the refined time step again to get iterated profiles and solving for the interfacial balance
5) repeating the above cycle till convergence in time step is reached
6) advancing one spatial step into the medium (freezing progresses)
7) repeating above cycle till convergence achieved
8) continuing till boundary is attained.

The method is applicable to an unknown interfacial temperature and variable thermal properties. Analytical methods of calculations with interfacial position obtained from a transcendental equation are also described.

MAXIMUM-ANGLE LOW-MOBILE GRAIN BOUNDARIES IN METALS AND ALLOYS

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The experimental data published earlier in literature on the growth of grain into monooriented matrix are considered in this work.

In such experiments samples are usually used in form of the single crystal plates. First the plate is deformed uniformly in order to not to disturb the initial orientation of single crystal. Then the plate is deformed locally, either by pressing the indentor, which have the irregularly shape of the tip and is made and is of more hard material, into the plate at several places, or by cutting the edge of the plate by cutters. Finally the sample is annealed. After such a treatment in the regions of great local deformations the small gains are risen with different orientations. Near them the large grains are risen which sizes are hundred times as large as those of the small grains. The large grains border on the small ones by the narrow sides. The orientations of the original single crystal and the large grains are commonly determined by X-ray methods. Further the axes directions and the minimum misorientation angles between the original single crystal and the large grains are evaluated. Finally, these experimental distribution of misorientations are compared to the standard distribution of random misorientations.

Since the seventies there have been only few investigations of such a type, most of which were mainly carried out on the single crystals of alloy Fe+3%Si, Al and Ti [1]. The experimental results of those works indicate that the grains, which deviate from the original single crystal by maximum angles relative to the minimum misorientation axes, are mach less probably grown to large sizes than the grains deviated by high angle. The number of the large grains with maximum misoriented angles is much less than that would follow from the misorientation of isotropic polycrystal (with no crystallography texture). This suggest that the maximum-angle grain boundaries are less mobile then high angle ones.

Therefore it seems more reasonable to divide all the grain boundaries into the three, rather than two groups, which is in common in modern literature. In cubic lattice metals and alloys beside the low-angle low-mobile (less than 10-15⁰) and the high-angle high-mobile (from 10-15⁰ to 40-45⁰) grain boundaries there exists the third group of maximum-angle (from 40-45⁰ to 63⁰) low-mobile ones. The maximum angle grain boundaries differ from low-angle ones in that the mobility of the former can be increased with the temperature, but that of the latter cannot. On the basis of such systematic the method is developed by us of predicting the crystallographic texture generated during the primary and the secondary recrystallization in b.c.c. and f.c.c. metals and alloys, in particular, in the Fe+3%Si alloy.

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Moving interfaces in shape memory alloy bicrystals

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Interaction of grain boundaries (GB) with point defects and dislocations have been long time investigated for their importance in metal plasticity. Not much attention was paid to the interaction of mobile planar defects with GB. It takes place in shape memory alloys (SMA) deforming by mobile interfaces due to thermoelastic martensitic transformation (MT). SMAs are artificial functional materials developed solely for their unique stress-strain-temperature response. While a SMA single crystals may exhibit up to 25 % recoverable strain, large elastic anisotropy, GBs and random oriented grains in polycrystals allow just 4 % of the recoverable strain in the same alloy.

We investigated the interaction of moving β_1 / β'_1, β_1 / γ'_1 phase interfaces with oriented grain boundaries in Cu-Al-Ni SMA bicrystals. Phase transitions were induced by applied external compressive stress and/or by thermal change. Stress-strain-temperature behaviour was followed and specimen surface was observed by in-situ optical microscopy and recorded on video. The thermomechanical responses of bicrystals and component grains were compared and discussed from point of view of geometrical characteristics of the MT and bicrystal geometry. A video record of the GB – mobile interface interactions will be presented.

GRAIN BOUNDARY MIGRATION IN FE-3%SI

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Grain boundary (GB) migration was studied on Fe-3%Si bicrystals, using both the reversed-capillary technique and the method of constant driving force. The reduced mobility of the completely dragged motion was determined using the reversed-capillary geometry with samples of technically pure material. On high purity Fe-3.5%Si bicrystals with [001] tilt boundaries with different angles the reduced mobility of the free moving boundary was determined in the temperature range from 944° C to 1104° C, using in most cases the constant driving force technique. In-situ observation of the fastest migrating boundary confirmed the results obtained by conventional methods. For the free motion the activation enthalpy and the pre-exponential factor of the reduced mobility were determined for the different types of tilt boundaries studied. Activation enthalpy and logarithm of the pre-exponential factor are linearly related, i. e. comply with the compensation effect. The obtained results were in good accordance with literature data of grain boundary mobility in Fe-3%Si bicrystals. With respect to the present and the literature data a compensation temperature of 1113° C ± 50° was found, slightly below the eutectic temperature of 1200° C of the system Fe-Si. For the reversed-capillary technique experimentally observed shapes of the moving GB were compared to theoretically predicted shapes. It was found that a better fit is obtained when taking into account the drag effect by impurities. It was shown that owing to this drag effect for the reversed-capillary technique, contrary to the constant driving force technique, a steady state motion, strictly speaking, is not possible, and the shape of the boundary is not conserved in the course of migration. Thus displacement-independent geometry factors used for calculation of the mobility can only be approximations in the case of a free motion.

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COOPERATIVE EFFECTS OF INTERFACES MOTION IN COARSENING CELLULAR STRUCTURES

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There are many physical systems consisting of homogeneous domains separated by interfaces, so called cellular structures: ordered domains in alloys, magnetic domains, grains in polycrystal, gas bubbles in soap froth etc. We have here a simple physical situation when the system volume V being the sum of volumes of all cells, the volume
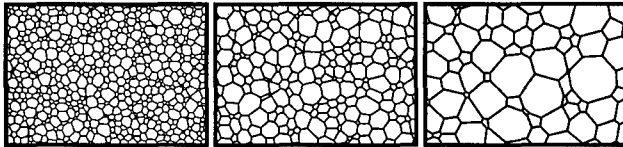
specific energy and the interface specific energy E are constant. The internal energy of the system $\mathcal{E}$ is completely defined by the interface area Σ. For any two neighbouring cells the volume decrease of the smaller one (down to complete disappearance) and the simultaneous volume increase of the greater one diminish Σ. This permanent topological possibility to decrease $\mathcal{E} = E\Sigma$ makes the system intrinsically unstable. Large cells "eat up" small ones and the mean cell size increases during this process, named "coarsening". A remarkable property of this statistical dynamic system is the occurrence of a stable steady-state regime of evolution when all macroscopic system variables (e.g. mean cell size) obey simple time scaling laws and the cell size distribution function has a universal scaling form. There is a great number of publications devoted to the question of "refinements" of individual cell dynamics to get a good agreement of the cell size distribution function with experimental data. Surprisingly small attention has been paid to cooperative behaviour of cells in the structure, although the existence of interesting self-organisation effects is almost evident here. Indeed, if we have a good look at the experimental figure we can see a strong size correlation of adjacent cells. Near a small cell the probability to find another small cell is grater then a large one, and vice versa, near a large cell the probability to find another large cell is grater then a small one. In other words we observe space-correlated fluctuations of the cell interface density $\rho(x,t)$. In this paper* the phenomenon are consistently analysed at micro-, meso- and macroscopic levels. At the microscopic level the structure is described by a probability distribution function in a phase space of cell coordinates and of cell sizes. A microscopic (kinetic) equation for the function is written and a development to a mesoscopic (hydrodynamics) equation of a cellular medium is realised. It has the form of a diffusion-reaction equation with a negative "diffusion" coefficient and with $\rho(x,t)$ playing the role of concentration. Its analysis reveals the effect of macroscopic patterning in the cell medium being the result of competition between two stochastic processes: interfaces disappearance (annihilation) and interfaces "uphill diffusion" (collective motion in the direction of $\nabla\rho(x,t)$).

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EXPERIMENTAL DETERMINATION OF NICKEL GRAIN BOUNDARY MOBILITY DURING RECRYSTALLIZATION

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It is now well established that the mobility of a grain boundary is orientation dependent, but in the case of primary recrystallization experimental studies it is very difficult to take orientation into account because this parameter cannot be unambiguously defined except at a very small scale and during a very short time. On the other hand many theoritical models were proposed to estimate the drag effect due to impurities, but there is a lack of experimental results concerning this point. In this paper we show that the grain boundary velocity during recrystallization of nickel can be well fitted by the Cahn, Lücke and Stüwe theory for impurity drag.

The application of in-situ heating scanning electron microscope to the study of the recrystallization of cold worked nickel reveals the process of grain boundary migration. The velocity of grain boundary during recrystallization is plotted against the driving force for grain boundary migration deduced from calorimetric mesasurements (Figure 1).This plot have the characteristic sigmoidal shape and shows an low rate of grain boundary velocity at low deformation ratio. It is shown that grain boundary velocity has not a linear relationship with its driving force that could be well explained by the Cahn, Lücke and Stüwe theory for impurity drag effect. It was previously shown that sulfur segregates both at grain boundary and surface during recrystallization of nickel, that proves a strong interaction between sulfur and grain boundary. The mean values of the mobility and of the interaction energy between moving general grain boundary of nickel and sulfur are deduced from the experimental results at the temperature of 455°C. This study shows that it is possible to use the Cahn and Lücke and Stüwe impurity drag model to measure mean mobility value during recrystallization, but because of the assumptions of the model the value of interaction energy calculated by this way is not realistic.
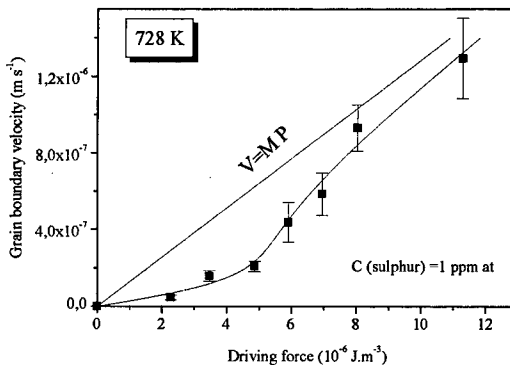
Figure 1: Dependence of grain boundary velocity versus driving force during recrystallization of nickel

GRAIN STRUCTURE EVOLUTION IN 1-D RODS AND 2-D STRIPS POLYCRYSTALLINE ALUMINIUM.

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The grain structure and grain boundary structure evolution in 1-D (bamboo) and 2-D (columnar) structure in polycrystalline aluminium were studied.

We investigated 1-D aluminium rods and 2-D aluminium strips because the study of these polycrystals permits to obtain the crystallographic data of each grain and provides a more straightforward identification of the mechanisms of grain growth, unlike in the 3-D polycrystalline aluminium, where we obtain only averaged data.

It was shown [1], that the 2-D polycrystals were composed of two region types. In the first type regions there are preferential orientation. These regions were called the colonies. The boundaries between the grains were of low angle type. The grains in the second type regions are surrounded by high angle boundaries. In the structure of the 1-D aluminium rods the colonies with low angle boundaries were absent.

We observed the change of mean grain area separately in the colonies and in the whole aluminium strips. It was shown, that the law of mean grain area growth in the colonies is similar to that in the whole strips, although the mean grain area value in the colonies was lower, than the one in the strip.

The influence of strip's thickness on the grain structure evolution in the 2-D structure was studied. We discovered, that the perfect columnar structure was formed in the thin strips: the grain boundaries were normal to the surface of the samples. The influence of surface is reduced in the thick strips and grain boundaries occupied positions with low energy. Such a tendency is also observed in the thick 1-D bamboo structure (rods).

The experimental results on grain growth, character of grain boundary's distribution and preferential grain orientations in the aluminium polycrystals in relation with the initial conditions and annealing time are presented in this work.

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FFECT OF TRIPLE JUNCTION
ON GRAIN BOUNDARY MIGRATION

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Triple junctions together with grain boundaries are the most important structural defects of a polycrystal. In spite of it the influences on grain boundary migration has hardly been studied at all. It is usually assumed that triple junctions don't drag boundary migration and their role is reduced to preserving the thermodynamically equilibrium angles where boundaries meet. However, the movement of triple junction, induced by boundary migration, might involve additional dissipation of energy, in other words, a triple junction might have finite mobility. Firstly the idea that the triple junction may have the finite own mobility was put forward in 1987. The central problem with the experimental investigation of triple junction mobilityis the steady-state motion of a system of boundaries and their triple junction is only possible in a narrow class of geometric configurations. One of a such of grain boundary configurations where the steady-state motion is possible and the ist main features are considered in the current presentation.

The special technique of in-sity observation and recording of the triple junction motion and the results of the experiments on the tricrystals of Zn are reported.

The kinetics of grain boundary system is quantitatively discussed in terms of a triple junction mobility.

The transition from junction kinetics to grain boundary kinetics was observed.

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THE FUNCTION OF TRIPLE JUNCTION DURING GRAIN GROWTH

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The main defects of the microstructure are grain boundaries and triple junctions. They are responsible for grain structure evolution during the grain growth. The kinetic properties of individual grain boundaries are well known in metals. The first experimental data on kinetic properties of triple junctions were obtained in this year only: the transition from triple junction kinetics to grain boundary kinetics was observed, where the drag influence of the triple junction on grain boundary migration was absent [1].

As has been shown in our experiment, there are 3 types of the individual triple junctions:
1. Immobile triple junction.
2. The motion of triple junction is possible. There is no transition from junction kinetics to grain boundary kinetics. The temperature interval of the motion is $(0.95 \div 1)T_m$. The velocity of triple junction motion is low.
3. The motion of triple junction is possible. There is the transition from junction kinetics to grain boundary kinetics. The temperature interval of the motion $(0.8 \div 1)T_m$. The triple junction motion velocity is relatively large.

Polycrystal is not a mechanical mixture of triple junctions and grain boundaries. We observed, that triple junction of the third type can take the lead in the motion of the first or second one. We investigated the question: which type of triple junction can initiate motion of the others. We have come to conclusion that the initiator is the triple junction where the grain boundaries have different crystallographic parameters and different kinetic properties. It is possible to make conclusion about stability of microstructure and texture of materials.

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Motion of the grain boundary system with the triple junction
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IN SITU ELECTRON MICROSCOPY OF GE BRANCHES GROWTH

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The crystallization of Al:Ge amorphous thin films revealed a unique branching morphology that was reported elsewhere[1]. The crystallized area consists of compact Al crystal in which a branched crystalline Ge is formed. Both, the Al crystal and the tips of the Ge branches grow at constant velocity at a given temperature. The dynamic of the crystallization was studied by in-situ Conventional Transmission Electron Microscopy (CTEM) and by in-situ High Resolution Electron Microscopy (HREM) using heating holders and CCD video camera. The velocity of the coupled interfaces is slow enough (few A/sec) enabling to analyze the evolution of small perturbations and the splitting of the branches. We shall report and video demonstrate the dynamics of the Ge branches growth. The analysis of CTEM video records indicates that the interfaces propagate nonontinuously i.e. different parts at the branch tip growth independently at velocities that change with time. Several factors were found to influence the growth velocity, in particular, it was found that the velocity is high at the splitting moment. The analysis of the HREM video records demonstrates that the growth of the Ge crystal occurs on atomic steps at the interface.

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CONTROL OF THE GRAIN BOUNDARY MISORIENTATION DISTRIBUTION FUNCTION THROUGH THERMOMECHANICAL PROCESSING*

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Many important physical and mechanical properties of materials are known to be tightly coupled to the material microstructural features such as chemistry, grain size and shape distributions, textures, and the presence of secondary phases. Intercrystalline defects, e.g., grain boundaries and triple lines, have recently been observed to have a significant influence on corrosion resistance, stress corrosion cracking, and creep, as well as total elongation to failure. Scientific teams at several laboratories have demonstrated that it is possible to exert control over the types of grain boundaries and triple lines in a microstructure and thus begin to engineer properties.

To date, efforts to engineer grain boundaries have primarily concentrated on changing the misorientation distribution function (MDF) through thermomechanical processing so as to increase the fraction of grain boundaries in the microstructure which exhibit orientations characterized by the coincident site lattice (CSL) model. In the CSL model, the grain boundary is characterized by the misorientation of the grains on either side and the plane of the boundary is neglected. Recent investigations demonstrated significant improvement in a number of properties with the increase in fractions of special boundaries compared with random boundaries. The observed improvements in properties appear to result from an alteration to the grain boundary network such that the existence of a high fraction of special grain boundaries interrupts the connectivity of the random grain boundaries.

Fundamentally, grain boundary engineering involves thermomechanical processing: strain and recrystallization. During the recrystallization step, the intent is for special boundaries to replace random boundaries in the boundary network. When the appropriate conditions are obtained, grain boundary engineering appears to produce materials where the grain size gets refined on processing, the fraction of special boundaries increases, and the deviations from exact sigma misorientations decrease. Despite these changes to the microstructure, there is no significant increase in the observed texture, in fact, the texture strength may actually be reduced. What remains in order to fully realize the potential properties of commercial materials is a lack of fundamental understanding in the literature regarding how materials are processed to optimize the MDF, what properties are likely affected by optimized MDF, and if the processes can be successfully applied in a commercial venue.

This paper describes two approaches to the engineering of grain boundaries in copper which have been undertaken at Lawrence Livermore National Laboratory. The first series of experiments studied the effect of small strains and long annealing times and the second series of experiments probed larger, more practical strains and short annealing times

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THE EFFECT OF ANNEALING TEXTURE
ON ORIENTATION CORRELATIONS IN COPPER

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Grain boundary ensembles and orientation correlataions between nearest neighbours are investigated in weakly and strongly textured states obtained during recrystallization and grain growth in pure copper. A state with a nearly random distribution of orientations is characterized by a high fraction of $\Sigma 3^n$ ($n \geq 1$) boundaries. Strengthening of the cube {001} <100> texture leads to an increase in frequency of low-angle boundaries at the expense of other GBs. In both conditions, the misorientation distribution of the nearest neighbours is influenced by the orientation correlation "matrix/twin". Such a correlation is clearly pronounced in weakly textured material, although all mutual misorientations demonstrated no predominance of $\Sigma 3^n$ boundaries. The influence of the orientation correlation is significantly reduced in the presence of extremely strong texture. The distribution of all mutual misorientations in this case resembles the distribution of the nearest neighbours.

COINCIDENCE BOUDARIES ANDTHE PRODUCTION TECHNOLOGY OF GRAIN ORIETED SILICON STEEL

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Primary recrystallized   Fe-3%Si containing Al were nitrided. They were then intermittently annealed with the heating rate of 15°C/ h in 100%N2 atmosphere. The maximum B8 obtained was about 1.94T when the onset temperature of the secondary recrystallization(Tcr) was around 1075°C regardless of the initial grain sizes or nitrogen contents. The maximum B8 decreased with increasing Tcr from 1075°C to 1100°C or decreasing Tcr form 1075°C. This result suggested that Σ 9 boundaries become most mobile around 1075°C regardless of the initial grain size or nitrogen content .

The same primary specimens were coated with MgO and annealed with the same heating rate in 5% H2-N2 .   The maximum B8 obtained was same as the above annealing condition ,however, the initial grain size and nitrogen content was quite contrary in this annealing. The difference of the optimum grain size and nitrogen content for obtaining the highest B8 in both annealing was explained on the assumption that Σ 9 boundaries become most mobile at 1075°C regardless of the annealing methods.

It is demonstrated that the high temperature hot band annealing for the precipitation of AlN is not prerequisite for the evolution of sharp Goss secondary recrystallization when the onset temperature of secondary recrystallization is controlled around 1075°C.

The possibility of producing HI-B without hot band annealing and nitriding treatment after decarburization annealing starting from low carbon hot rolled sheet hot rolled with low slab reheating temperature was shown .

NORMAL AND ABNORMAL GRAIN GROWTH IN TUNGSTEN POLYCRYSTALS

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The formation of very large grains or a large scatter of the grain size in a material due to the onset of the abnormal grain growth can deteriorate drastically the properties of the material. The grain growth has been studied in high-purity flat W polycrystals at 2000°C in vacuum. The onset of abnormal grain growth proceeds without inhibition of the normal grain growth. After appearing of the large abnormal grains the areas with small "normal" grains exist very long. The polycrystal has a bimodal grain structure, both normal and abnormal grains continue to grow (see figure). The orientations of individual grains were determined with aid of the selected area channelling method in the contact area between the abnormally growing large grains and normal matrix. In samples of a larger thickness the abnormal grain growth begins definetely later. The influence of the formation of new grain boundaries with a high mobility on the onset of abnormal grain growth and similarities with the abnormal grain growth in Al alloys are discussed.
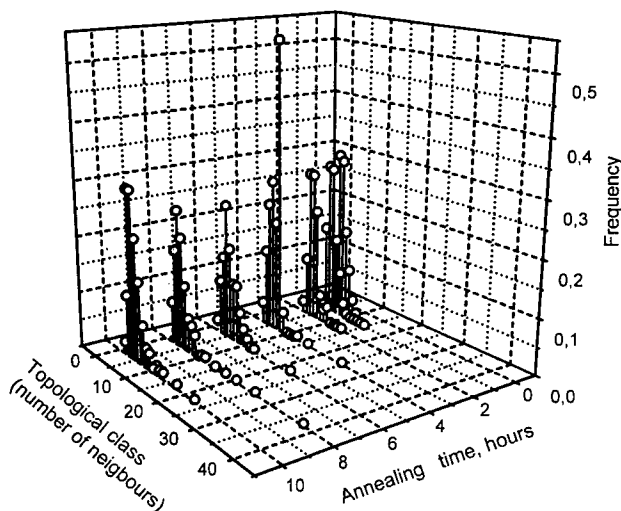
Dependence of the distrubution of grains among topological classes (number of neighbours) on the annealing time

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HYDROSTATIC PRESSURE INFLUENCE ON THE GRAIN BOUNDARY DIFFUSIVE CHARACTERISTICS

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There was carried out the theoretical investigation of hydrostatic pressure influence on the grain-boundary diffusion processes and the high-angle grain boundary migration. There is proposed a new model allowing the description of the boundary free energy changes γ_b, the grain-boundary self-diffusion activation energy Q_b and the boundary diffusivity δD_b under the hydrostatic pressure P. The model is based on the ideas of the high-angular (random) grain boundary islands structure [1].([1] Chuvil'deev V.N. Physica metallov I metallovedenie. V.81, issue 2, 4, 1996. (In Russ.)). The boundary free volume V_b was assumed to be the basic parameter characterizing the boundary structural state. Assuming the existence of proportional dependence between the boundary free volume value change and the hydrostatic pressure value P, there was obtained the equation relating D_b and P. In the work there was also calculated the value of (the so called) grain-boundary diffusion and migration activation volume. It is said that its value depends on the material thermodynamical parameters, the grain boundary free volume and the temperature.

There was carried out the detailed comparison of the model and experiment results.

THEORY OF NON-EQUILIBRIUM
GRAIN-BOUNDARY DIFFUSION

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There was carried out theoretical investigation of the structure, thermodynamical parameters and diffusive characteristics of equilibrium and non-equilibrium high angular grain boundaries. It is explained that the boundary structures may be described using the "island model". At the same time the free volume is the main parameter characterizing distribution of the islands and, correspondingly, the boundary structural state. There is proposed a model allowing to explain the dependence of the free energy and the boundary entropy value on the value of the material free volume and thermodynamical constants. There is proposed a new model of diffusion in the boundary having an island structure. The model is based on the ideas of heterophase fluctuations when there are changed the sizes of the islands having high diffusivity. There were carried out the calculations of the enthalpy, entropy and diffusion activation energy for some pure FCC, BCC and HCP metals.

There is described the structure and the properties of non-equilibrium grain boundaries. There is explained that anomalies in diffusive parameters and thermodynamical characteristics of non-equilibrium boundaries are the result of their free volume increase at the expense of the free volume introduced by lattice dislocations hit into the boundaries and implementing the intragranular deformation of the specimen. There were obtained equations describing the boundary energy and their diffusive parameter changes during their interaction with separate dislocations and with lattice dislocations flow. There was defined the grain-boundary diffusion coefficient dependence on the deformation rate and on the material structure parameters.

In the work there is analyzed the role of the deformation-stimulated diffusion in the processes of the high temperature deformation and superplasticity. There are also discussed the processes of the grain boundary sliding deformation-stimulated migration and the grain growth.

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EFFECT OF SURFACE DIFFUSION ON THE CONTACT FORMATION AND ADHESION OF ATOMICALLY-CLEAN SURFACES OF LEAD, TIN AND Pb-Sn EUTECTIC ALLOY

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Effect of sintering on the contact formation and adhesion of polycrystalline metals in the temperature range of 0.4-0.6 T_m has been investigated. Lead, tin and fine grained (~3μm) Pb-62%Sn alloy as a model materials were chosen in this study. Atomically-clean surfaces were obtained by the method of controllable internal rupture [1]. Grain boundary grooving, smoothing of the surfaces, and formation of the thermal etching figures under annealing at 0.4-0.6 T_m give evidence for pronounced diffusion mass-transfer on the obtained surfaces. Surfaces were contacted and subjected to annealing at zero load. Initial contact of the asperities created a series of contact spots and voids at the interface. The contribution to the contact formation and adhesion from sintering during annealing of the obtained joints up to 10^6s was found to be essential for Pb-Sn alloy only. Restriction of the sintering of pure metals was supposed to be due to fixing a grain boundary at the interface. Its diffusion-controlled grooving at intersection points with the interfacial voids and contact spots leads to suppression of the sintering. It has been shown that the contribution from surface and grain boundary diffusion to the contact formation becomes significant, when not only kinetic but also definite structural and energetic conditions at the interface are met. Such conditions are satisfied for Pb-Sn alloy, exhibiting low phase boundary energy (0.04 J/m^2) and fine-grained (2-3μm) structure. Application of the compression load to the Pb, Sn and Pb-Sn joints during annealing resulted in the temperature and time dependent increase in the adhesion strength due to creep and stress-promoted sintering and at the interface.

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CONSIDERATION OF MECHANISM OF DIFFUSION ALONG NEAR-COINCIDENCE GRAIN BOUNDARIES

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In the present study data of our previous studies of diffusion of Ni [1, 2] and Au [3] along <100> symmetric tilt grain boundaries (GBs) in copper near Σ5 misorientation are tested for bulk-like ("simple" atom-vacancy exchange) mechanism.

In works [1-3] the parameters of the diffusion along Σ5{310} boundary and the cores of the SGBDs were evaluated in the frameworks of CSL/SGBD model [4, 5] explaining a narrow Σ5 minimum observed on the misorientation dependences of GB diffusion parameter ($\equiv$ the triple production). It was found in [2, 3] that the Arrhenius dependences suggested two (low- and high-temperature) ranges divided by an abrupt change of the GB diffusion parameter.

The test suggests that activation parameters of the diffusion along Σ5{310} boundary in the low temperature range are inconsistent with the bulk-like mechanism. While, in the high temperature range activation parameters are within the region where the bulk-like mechanism is possible. This suggests different mechanisms of the diffusion along Σ5{310} boundary in the low- and high-temperature ranges. It is probably due to a some GB transformation. The activation parameters of the diffusion along the cores of the SGBDs and "general GBs" do not contradict the bulk-like mechanism. However, it is not enough to validate this mechanism. Mechanisms of diffusion along GBs near coincidence misorientations are discussed.

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RADIOTRACER DIFFUSION OF NI AND AG IN AG AND NI GRAIN BOUNDARIES AND ORIENTED AG/NI INTERPHASE BOUNDARIES

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Interphase boundary (IB) diffusion along oriented Ag/Ni interfaces was investigated using the radiotracer serial sectioning technique. This system is expected to form "sharp" interphase boundaries because of the very low mutual solid solubility

Specimen preparation was done by careful diffusion welding of Ag and Ni single crystal pairs with (100), (110) and (111) oriented surfaces, from which diffusion samples were cut in two directions perpendicular to the IB. The ratio of the lattice spacings is very close to 6/7, leading to a characteristic superlattice of misfit dislocations.

IB diffusion behavior can be related to the atomistic structure of the interface and to results of computer simulation of vacancy properties [1]. Moreover knowledge of grain boundary (GB) solute diffusion of Ag and Ni in Ni and Ag GBs, respectively, is required for the interpretation of IB diffusion measurements. These experiments were performed with the radiotracer technique under type-B kinetic conditions. While in the present case segregation of Ag in Ni has a negligible effect on IB diffusion, Ni segregation in Ag has to be considered. By comparison of the triple product $P = s \cdot \delta \cdot D_{GB}$ with direct D_{GB} values, resulting from measurements in Harrison´s type-B and –C kinetic regime, the temperature dependence of Ni segregation in Ag was evaluated. The measurements exhibited a fairly large segregation enthalpy of 39.7 kJ/mol and segregation factors of 10^3 to 10^4 in the investigated temperature range.

As an example, ^{110m}Ag diffusion along Ag/Ni cube-on-cube IBs with (110) interphase planes reveals only a small diffusional anisotropy in the directions <110> and <100>, parallel to the misfit dislocations in the IB. Ag Diffusion in this IB is slower than Ag GB self diffusion, but faster than Ag GB solute diffusion in Ni.

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Orientation Dependence of Ge Diffusion in Symmetrical Near $\Sigma = 7$, $\Theta = 38.2°$ [111] Tilt Grain Boundaries of Al

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Grain boundary diffusion of Ge was measured in a series of Al bicrystals with symmetrical near $\Sigma = 7$, $\Theta = 38.2°$ [111] tilt grain boundaries (gbs). The actual orientations of the bicrystals were precisely measured with Kossel technique, the three macroscopic parameters describing the orientation of the grains in the bicrystal were determined. The tilt angles Θ ranged from 34.115° to 41.408°.

Grain boundary diffusion parallel to the tilt axis was measured in the type B kinetic regime in the temperature interval 680 K to 518 K using the radiotracer [71]Ge and our serial sectioning technique. The problem of diffusion stopping oxid layers on the surfaces of the Al bicrystals was avoided by ion-sputter-cleaning and in situ evaporation of the radiotracer.

A characteristic non-monotonic behaviour of the resulting dependence of the measured gb diffusivity $P(\Theta) = s\delta D_{gb}$ (s being the segregation factor of Ge in Al gbs, δ the gb width, D_{gb} the gb diffusion coefficient) on the tilt angle Θ was observed for all five investigated diffusion temperatures. In the immediate vicinity of the ideal $\Sigma = 7$, $\Theta = 38.2°$ [111] gb $P(\Theta) = s\delta D_{gb}$ is minimal, with increasing deviation from the ideal $\Sigma = 7$ gb $P(\Theta) = s\delta D_{gb}$ increases and reveals broad maxima at about $\Theta = 36°$ and $\Theta = 40°$. The orientation dependence of $P(\Theta) = s\delta D_{gb}$ is symmetrical to the ideal $\Sigma = 7$ gb. The opposite dependence is observed for the Arrhenius parameters $P_0(\Theta)$ (preexponential factor) and $Q_{gb}(\Theta)$ (effective activation enthalpy of gb diffusion), which were calculated from the temperature dependence of the measured gb diffusivity. Near the ideal $\Sigma = 7$, $\Theta = 38.2°$ [111] gb P_0 and Q_{gb} are maximal.

The solid solubility of Ge in Al is comparatively large, so the segregation factor s and segregation enthalpy H_s is expected to be small. Therefore, the observed orientation dependencies of $P(\Theta) \doteq s\delta D_{gb}$, $P_0(\Theta)$ and $Q_{gb}(\Theta) = H_s + H_{gb}$ (H_{gb}: activation enthalpy of gb diffusion) reflect the orientation dependence of D_{gb}, D_{gb0} and H_{gb}. The orientation dependence of the gb diffusion will be discussed within the concept of CSL boundaries. No influence of the furthermore determined orientation parameters (twist angle, second tilt angle), describing the grain orientation of the bicrystals, on the gb diffusion, is observed, in contrast to the gb diffusion investigation in Cu near $\Sigma = 5$, $\Theta = 36.9°$ [001] tilt gbs of Budke et al. [1]. This will be discussed with respect to the particular dislocation network inherent in the investigated gbs.

[1] E. Budke, Chr. Herzig, S. Prokofjev and L. S. Shvindlerman, Mat. Sci. Forum **207-209**, 465 (1996).

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THE DIFFUSION PROPERTIES OF THE GRAIN BOUNDARY CORE IN POLYCRYSTALLINE GOLD

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Two methods were used to study the diffusion of ^{57}Co in the grain boundary (GB) core in polycrystalline gold over the temperature interval of $(0.3 \div 0.5)T_{melt}$. The depth profiles were obtained by a traditional method, according to which the diffusion zone ws divided into layers and the "layer concentrations" were measured on a single-channel spectrometer outfitted with a well-type scintillation detector. A new method [1] designed to measure the diffusion coefficient D_{CCR} in the core of the crystallite conjugation regions (CCR) was used to determine D_{CCR}. To this end, the radiation intensity of the sample was measured on an X-ray spectrometer with a planar HPGe detector each time a layer of the diffusion zone was removed. The absolute values of the diffusion coefficient D_{CCR} in the CCR core were determined independently of all the other parameters describing the two-dimensional diffusion flow in a bicrystal.

THE EQUILIBRIUM SITES OCCUPIED IN THE GRAIN BOUNDARY CORE DURING INTERCRYSTALLINE DIFFUSION OF ^{57}Co IN METAL POLYCRYSTALS

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The types of the equilibrium sites occupied by the ^{57}Co atomic probe in the grain boundary core of metal polycrystals were studied by the nuclear gamma resonance spectroscopy and the preferable intercrystalline diffusion method. Two discrete states – one state in the grain boundary core and one state in the regions adjacent to the grain boundaries in the crystallite volume – are occupied in all the matrices (3d-: Cr, Fe, Ni; 4d-: Nb, Mo, Rh, Pd; 5d-: Ta, W, Ir, Pt, Au) examined by the new method [1, 2].

In the matrices (4d-: Nb, Mo, Rh, Pd; 5d-: Ta, W, Ir, Pt, Au), where the ^{57}Co atomic probe represents a small-radius substitutional impurity in the lattice, ^{57}Co occupies interstitial sites in the grain boundary core. In the 3d matrices (Cr, Fe, Ni), where the ^{57}Co atomic probe is not a small-radius impurity, it occupies the sites in the grain boundary core structure. This accounts for the ^{57}Co diffusion mechanisms in the grain boundary core of the matrices studied: the interstitial mechanism in the 4d and 5d matrices, and the vacancy mechanism in the 3d matrices.

GRAIN BOUNDARY DIFFUSION MODELS FOR DIFFUSION IN THIN FILMS UNDER STRESS FIELD IN DIFFERENT KINETIC REGIMES

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The models describing the grain boundary diffusion in thin polycrystalline films for "B" and "C" kinetic regimes under a stress field are proposed.

The stress field influences, on the one hand, the diffusion barrier height and, on the other hand, the diffusion driving force that is connected with the chemical potential gradient.

The different possibilities of stress distribution are discussed.

The cases of constant and instantaneous sources on the surface, which is in contact with diffusant, are discussed.

The conditions of reflecting free surface, infinite sink and rapid surface diffusion on the opposite surface are considered.

The analytical and numerical solutions of these problems are obtained.

Results of the models' calculations are compared with experimental ones.

GRAIN BOUNDARY SELF-DIFFUSION OF ALLOY 800 AND INFLUENCE OF S, P AND C ON GRAIN BOUNDARY DIFFUSION IN ALLOY 800

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Alloy 800 is an austenitic Fe-Ni-Cr steel containing relatively minor amounts of carbon, aluminium and titanium, which are important, however, for its properties. Special grades of Alloy 800 known as 800H, 800HT and 800LC differ in the concentrations of these elements. These industrial specifications have been investigated, and in addition further melts containing phosphorous or sulphur were prepared and studied.

Using a radioactive tracer method the bulk and grain boundary diffusion of ^{59}Fe was determined in these alloys in the temperature range 800 to 1000 °C. For this study the tracer was deposited electrolytically on the samples. After the diffusion annealing thin layers of the specimens were successive abraded and the residual activity was determined. By autoradiographs the use of the approximation of Suzuoka was confirmed; this evaluation method considers the depletion of the tracer on the surface. In Alloy 800H the activation energy of grain boundary diffusion of ^{59}Fe is (209 ± 17)kJ/mol. Dissolved elements especially phosphorous increase the activation energy of the grain boundary diffusion of Fe by their segregation to the grain boundaries.

In addition the influence of the grain boundary diffusion on the growth of creep pores was investigated in the same materials, and the chemical composition of the creep cavities and grain boundaries were analysed by Auger electron spectroscopy (AES). For Alloy 800 + 0.088 wt-%P an enrichment of about 14 at-%P was observed at the grain boundaries. The addition of phosphorous clearly enhances the creep strength of Alloy 800; this can possibly be explained by an additional precipitation of $Cr_{23}C_6$ on the grain boundaries during the creep process.

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GRAIN-BOUNDARY DIFFUSION OF Bi IN Cu BICRYSTALS

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It has been well established that grain-boundary diffusion depends strongly on the character of individual boundaries. For example, it has been reported by many investigators that diffusion is easy on random boundaries but difficult on coincident-site boundaries with low values of Σ. In these studies, however, the diffusivity of a boundary does not show a good correlation with the energy of the boundary. The purpose of this study is to investigate the diffusivity of Bi in various [001] symmetric tilt and twist boundaries of Cu with the intergranular-fracture surfaces of Bi-doped Cu bicrystals and to see the correlation between the diffusivity and the energy of these boundaries. The segregation of Bi on grain boundaries in Cu is well known to result in embrittlement.

Cu bicrystals having various [001] symmetric tilt and twist boundaries were grown by the Bridgman method using two seed crystals. The bicrystals were spark-cut into tensile specimens (5×10×30 mm) with a straight boundary oriented perpendicular to the tensile axis. They were Bi-doped at 1223K for 48h in an Ar atmosphere with a powder pack method. A mixture of Cu (10 parts), Al_2O_3 (10 parts) and Bi (1 part) powders was used for this purpose. Tensile tests were performed at room temperature. After the tests, the intergranularly fractured surfaces were observed by scanning electron microscopy and optical microscopy.

For the [001] symmetric tilt and twist boundaries, a close correlation has been found between the diffusivity of a boundary and the energy of the boundary. The minimum of the boundary diffusivity occurs where the cusps of the boundary energy exist; $\theta=28°$ ($\Sigma=17$), $\theta=37°$ ($\Sigma=5$), $\theta=53°$ ($\Sigma=5$) and $\theta=62°$ ($\Sigma=17$) for the tilt boundaries and $\theta=23°$ ($\Sigma=13A$), $\theta=28°$ ($\Sigma=17A$), $\theta=37°$ ($\Sigma=5$) and $\theta=44°$ ($\Sigma=29A$) for the twist boundaries. The larger the degree of disorder in the atomic arrangement at a boundary, the higher is the boundary diffusivity. The diffusion along the tilt boundaries takes place more easily than along the twist boundaries.

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COMPUTER SIMULATION OF DIFFUSION PROCESSES IN MULTIPHASE DIFFUSION LAYERS

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The aim of this work is to develop a mathematical model of diffusion process in a multiphase system. The paper presents an analysis of the process where a core creates, with diffusing elements, system containing solid solutions or intermediate phases. In this case we obtain, during the diffusion process, multiphase diffusion layers. In the analysis of the process it has been assumed that:

- The flux of the atoms from the atmosphere to the surface is proportional to the difference between their respective activities in the atmosphere and in the alloy
- Concentrations on the phase boundaries are the same as in equilibrium
- Phases that have higher concentrations of an element are created when concentration on the surface exceeds solubility limit
- The kinetics of growth is controlled by diffusion; therefore the position of the moving interphase can be evaluated from the difference of the diffusion fluxes of the element at the phase boundary.

An application running under Microsoft Windows 95™ has been created to simulate this process by numerical methods. The application has a friendly user interface for both data input and a visual presentation of results. The input data are: diffusion coefficients and solubility limits in existing phases, as well as the temperature and the activity of the atmosphere. The results (the distribution of the elements in the diffusion layer, the thickness of layers and the elements' concentrations on the surface) are displayed on the screen.

The paper demonstrates the use of the application to predict the concentration profiles and the layer growth rate during carburizing and nitriding of steel.

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SELF-DIFFUSION IN HIGH-ENERGY GRAIN BOUNDARIES IN FCC METALS[*]

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Molecular-dynamics simulations and an embedded atom potential for palladium were used to study systematically the diffusion behavior in high-energy tilt and twist grain boundaries. A transition from solid-like to liquid-like diffusion is observed at elevated temperatures. In particular, in the high-temperature regime all these high-energy boundaries exhibit very fast diffusion that is characterized by the same, universal atomic mobility and low activation energy (equal to about 30% of the activation energy for perfect crystal self-diffusion). Furthermore, a detailed analysis reveals an isotropic, liquid-like diffusion mechanism, with an activation energy about twice higher than that of the melt. This activation energy can be understood within the framework of two distinct processes: first the thermally activated formation of a liquid-like grain-boundary layer and, second, subsequent bulk-liquid-like atom migration. This liquid-like, high-temperature diffusion behavior is similar to that observed previously in molecular-dynamics simulations of high-energy grain boundaries in silicon[1]. By contrast with this high-temperature mechanism, in the low-temperature regime the grain-boundary region exhibits solid-like diffusion with a much higher activation energy that is governed by the underlying grain boundary structure. These results confirm recent experimental observations of Budke *et al.*[2] which indicate the existence of a temperature induced structural transition in fcc tilt grain boundaries; this transition results in a misorientation-independent, highly disordered diffusion process at high temperatures and a solid-like, misorientation dependent diffusion process at low temperatures.

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SHORT – CIRCUIT DIFFUSION IN NICKEL - ALUMINIUM INTERMETALLICS

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Tracer grain-boundary diffusion (GBD) of Cr-51 and Fe-59 in Ni_3Al modified by iron, chromium and zirconium was studied in the temperature interval from 773 K to 1273 K using the serial sectioning method.

It was found that additions of Fe and Cr up to about 6 at.% do not alter the activation enthalpy Q of chromium GBD, whereas the alloying of Ni_3Al with Zr (up to 1.6 at.%) leads to a significant increase in Q for chromium GBD.

The values of Q for iron GBD in the same materials are smaller than activation enthalpies of Cr GBD and, they slightly increase with increasing concentration of either Fe, Cr or Zr. No difference in Q for Fe GBD in Zr-doped alloys compared to Q for Fe GBD in alloys doped by Fe and Cr was observed. An interpretation of obtained results is proposed, based on the atomic size effect and on the different affinity between Zr and Cr and between Zr and Fe atoms.

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KINETICS AND MECHANISMS OF MASS TRANSFER AT INTERFACES IN BINARY ALLOYS

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Diffusion mass transfer at interfaces such as sintering, coalescence of inclusions (pores), discontinuous precipitation, new phase formation, etc. in binary alloys are accompanied by many phenomena originated from inequality of partial diffusion coefficients: Kirkendall and Frenkel effects, generation and relaxation of "diffusion stresses", segregation effects, which can influence both on the kinetics and leading mechanism of mass transfer.

This paper presents the results of experimental study of pore coalescence kinetics in ensembles, located at interfaces obtained by sintering of two plates of alloy Cu-5at%Sn and, for comparison, two plates of pure Cu. Pore size distribution has been measured on successive stages of annealing at 500 and 800°C. Analysis of pore size evolution carried out by methods of spatial metallurgy shows that the total pore volume per unit area in two-dimensional ensemble stays constant in the course of annealing time. That means that the observed growth of average pore radius is caused by pore coalescence. Two different atomic mechanisms, controlling pore ensemble evolution in pure Cu and in the alloy, have been identified: interfacial self-diffusion in pure Cu with kinetic law $R^4(t)$, and vacancy generation or absorbtion at pore surfaces in the alloy with kinetic law $R^3(t)$. This result shows that formation of solution at the surfaces of dissolving pores (of sub-critical radius) and decomposition of the solution at the surfaces of growing pores (having under-critical radius) are slower than fast interfacial diffusion in alloys.

It has been shown that interfacial mass transfer kinetics in alloys are described by "own" diffusion coefficient:

$$D_{int}^{own} = \frac{D_{int}^A D_{int}^B}{D_{int}^A(1-C) + D_{int}^B C}$$

where D_{int}^A and D_{int}^B are interfacial partial diffusion coefficients, and diffusion segregation of fast diffusion component near vacancy sources has to be taken into account.

THE EFFECT OF SOLUBILITY OF DIFFUSANT ON ITS GRAIN BOUNDARY PENETRATION IN ALUMINIUM BICRYSTALS

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Hitherto experiments on G-B diffusion were carried out in conditionof good solubility of diffusant. So it is interesting if G-B penetration takes place also at low solubility or reactive diffusion. It is very important problem because quite often are applied various composites of elements not forming solid solutions. Also at production of ferrites, cermetals and high temperature superconductors, diffusion is important factor causing cohesion and it is interesting if G-B diffusion plays any role.

The experiments were carried out on [100] bicrystals of aluminium with tilt boundaries and various misorientations. As diffusing atoms were chosen following elements: Au, Co, Ti, Ni, Cr and components of austenitic steel (Fe+Cr+Ni). The covering of aluminium specimens with mentioned elements and revealing the diffusion front proved very difficult. After many unsuccessful trials comparative method was used. One side of each specimen (perpendicular to the common direction) has been covered with one of mentioned elements or austenitic steel and the other with these elements together with copper. Magnetron sputtering in vacuum has been applied. Assumption has been made that if the insoluble elements do not diffuse along grain boundary, they should not change the geometry of diffusion front of copper (shape of G-B diffusion wedge, which could be dictinctly revealed by etching). Two stage diffusion annealing has been applied: first 550 C - 5hr and second 400 C - 192hr. It was impossible to reveal the diffusion front in the specimens covered with one component layer (except of Cu); but from the layers containing copper G-B diffusion occured and various parameters of geometry of diffusion front could be measured. Correlation of G-B penetration has been looked for with various properties of diffusing atoms. The stongest correlation has been stated with the limit of solubility of elements in aluminium. The higher solubility, the stronger influence on G-B diffusion on copper in aluminium grain boundaries. No correlation has been stated between forming intermetalic phase and G-B penetration.

Experiment have been also performed on diffusion of oxygen in G-B of aluminium bicrystal (<100>,45). After electropolishing specimens were annealed 192 hr at 400 C in powdered magnetite. After diffusion the specimen was immersed in HCl solution, which dissolved aluminium matrix and insoluble oxide wedge set up at grain boundary could be observed in scanning microscope. The height of the wedge was 30 μm. The experiment have shown the possibility of G-B diffusion of oxygen atoms The small height of diffusion wedge was probably caused by low diffusivity of oxygen atoms in defects of oxide layer.

SITE PREFERENCE OF ^{57}Co IN Fe$_{72}$Al$_{28}$ AFTER GRAIN BOUNDARY DIFFUSION

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Location of diffused ^{57}Co atoms in single crystal and polycrystalline samples of Fe$_{72}$Al$_{28}$ were investigated by means of Mössbauer spectroscopy. The aim of the present study is to characterize the location that ^{57}Co atoms after grain boundary diffusion in comparison with volume diffusion.

The samples were prepared from a single crystal and from a fine grain poly-. crystal. ^{57}Co was deposited in form of a thin layer on the damage-free sample surfaces. The diffusion anneals were carried out in a vacuum resistance furnace. ^{57}Fe–Mössbauer spectra were taken at room temperature using Na$_4$Fe(CN)$_6$ ·10H$_2$O with iron enriched to about 90% of ^{57}Fe as absorber. Structure of the surfaces of both samples before deposition of ^{57}Co were investigated by Conversion Electron Mössbauer Spectroscopy. On a sample of the original ingot standard transmission ^{57}Fe Mössabuer spectrum was taken for determination of structure of its bulk. Volume diffusion in the single crystal sample was induced by annealing at 1273 K for 20 hours. Annealing of the polycrystalline sample at 903 K for 162 hours was applied to obtain grain boundary diffusion characteristics. Volume diffusion is negligible at this low temperature. Comparison of the spectra taken after the annealing shows some differences between single crystal and polycrystal. Two components were identified in the spectrum of the single crystal. The main component, characterized by sextet with magnetic splitting B_{hf} = 2.3 T and isomer shift δ= 0.18 mm/s, can be ascribed, in accordance. with the standard transmission ^{57}Fe spectrum of the original ingot, to the iron atoms in D0$_3$ superstructure with four Al atoms in nearest neighbourhood (D sites). The second component represents a surface layer containing deposited ^{57}Co atoms. It is represented by a broad sextet with mean B_{hf} = 34.5T. In the spectrum of the polycrystalline sample the components mentioned above were also identified simultaneously with a new dominating component which was described by sextet with B_{hf} = 5.1 T, δ= 0.44 mm/s and quadrupole splitting σ = 1.15 mm/s. The large values of quadrupole splitting and isomer shift of this new component indicate, that the corresponding atoms are placed in an asymmetrical surrounding with lower s-like electron density - on grain interfaces. Additional annealing of the sample causes a decrease in the intensity of the interfacial component, which is in agreement with grain diffusion model.

The above experimental results show that the diffusing atoms occupy at grain boundary interfaces positions different from those in bulk. During the volume diffusion there is strong site preference for the regular iron position in. the Fe$_3$Al superstructure with four Al atoms in the nearest neighbourhood.

SEGREGATION EFFECT ON GRAIN BOUNDARY DIFFUSION IN METALS

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The effect of solute grain boundary (GB) segregation on solute GB diffusion in binary and multicomponent metallic solid solutions will be reviewed with emphasis on recent results.

As the diffusion flux is a product of driving force to kinetic coefficient we recall at-first the main components of the segregation influence on GB diffusion coefficient. Then we will focus on GB diffusion studies carried out in so-called type B kinetic regime by use of different experimental methods, mainly - radiotracers. The results of these studies will be analysed in combination with the results of the type C experiments and with the results of direct studies of GB segregation.

The most important topics of our analysis are as follows:

1) GB segregation of low-soluble solutes will decrease the triple product $P = D_{gb} \cdot \delta \cdot s$ (D_{gb} is the GB diffusion coefficient, δ is GB width, s is enrichment coefficient) and D_{gb};

2) some solutes can decrease P and D_{gb} at very low concentrations;

3) the type of segregation isotherm is important;

4) the competition between segregated solutes is very essential.

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EXTRACTION OF THE SEGREGATION TERM FROM THE TRIPLE PRODUCT
OF GRAIN BOUNDARY DIFFUSION: RECONSIDERATION OF
EXPERIMENTAL DATA.

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It is known that nonlinear segregation effects (saturation of grain boundary (GB), interaction of species in GB, GB inhomogeneity) lead to nonlinear GB penetration plots. In this paper we attempt on the base Fisher-LeClaire approach which was developed for nonlinear segregation in [1] to recalculate previous experimental GB diffusion penetration plots and to extract the segregation term from a triple product of the GB diffusion.

This results of recalculation will be compared with segregation coefficients which were obtained by GB diffusion measurements, namely in type B and type C diffusion kinetics on the one hand [2] and by diffusion of solute B in pure A metal and in the solid solution A-B [3] on the other hand.

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THE KINETICS OF GRAIN BOUNDARY SEGREGATION OF Bi IN POLYCRYSTALLINE Cu

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The grain boundary (**GB**) segregation of Bi in Cu has been investigated in dependence of the annealing time by using polycrystalline Cu containing 25 and 50 at. ppm Bi. The saturated segregation was arrived after 1 h for specimens which were annealed in the two-phase region of the phase diagram (at 500 and 600°C). In the one-phase region the saturation was approached after annealing for 4 h at 850°C. It was found that the kinetics of segregation in the latter case obeys the classical McLean model. However, the McLean model cannot explain the accelerated GB segregation in the two-phase region with the same bulk diffusion coefficient. A simplified model of dislocation diffusion was proposed. In this model it was supposed that the dislocation diffusion is so fast that the Bi atoms, which diffuse from the grains to the dislocations, are immediately transported to the GBs. It means that the bulk diffusion of Bi in Cu is the rate determining process. A linear relationship between the segregation amount (x^Φ) and annealing time (t) was derived:

$$\frac{x^\Phi(t) - x^\Phi(0)}{x^\Phi(\infty) - x^\Phi(0)} = \frac{d\rho D x^S}{2\delta}t$$

where d is the grain size, ρ is the dislocation density, D is the bulk diffusion coefficient, x^S is the bulk concentration and δ is the GB thickness. The figure shows the experimental results in comparison with the calculated lines according to the McLean model and the new model. It can be seen that the model of enhanced dislocation diffusion is valid in the two-phase region, while in the one-phase region the accelerating effect disappears. This can be explained with the precipitation of liquid Bi along the dislocations in the two-phase region.
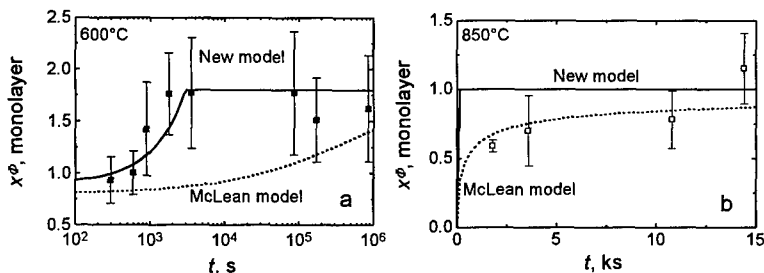
Experimental results and calculated curves according to the McLean model and the new model for Cu–25 at. ppm Bi annealed at 600°C (a) and 850°C (b).

DIRECT ATOMIC OBSERVATION OF REACTIVE WETTING FRONT ON SILICON CARBIDE

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Reactive wetting is the basis for numerous technological processes such as brazing. The chemical reactions that occur during reactive wetting cause a reduction in the free energy of the system and therefore play an important role in the overall dynamics of the wetting process. However, the position of the reaction product with respect to the front of the molten alloy and the formation process of the reaction product are not clear. The reported results allow only indirect conclusions, since the specimens were analyzed after brazing. Thus, direct *in situ* observation of the reactive wetting front is needed.

The interface and reaction between SiC and Ti-containing Ag-Cu eutectic alloy are a suitable model to study using *in situ* high resolution transmission electron microscopy (HRTEM). Among elements in the alloy, only Ti reacts to SiC to produce TiC, while the Ag-Cu eutectic alloy acts as a solvent. The interface between SiC and produced TiC has a coherent character and the atomic array of the interface can be determined.

The experimental procedure is as follows. A 6H-SiC single crystal wafer was cut using a low-speed cutter, mechanically ground and thinned using an Ar^+ beam, in preparation for observations of its atomic structure by HRTEM. An Ag-Cu eutectic foil, which was overlapped by a Ti foil, was carefully placed on the thinned SiC wafer. The samples were mounted on a hot stage holder of a HRTEM and the reaction between SiC and molten Ag-Cu-Ti alloy was observed *in situ* at the nominal temperature of approximately 1063K. During heating, images were recorded using a fiber-optically coupled TV system with a time resolution of 1/60 sec.

Various reaction processes were observed at the reactive wetting front. The reaction began with the dissociation of SiC in contact with the molten alloy. Since the SiC substrate was thin, it was dissociated immediately, which enabled cross sectional observation between SiC and the molten alloy. From the molten alloy, TiC nucleated on several planes of SiC or preformed TiC. In the case of TiC nucleation on SiC, unique orientation relationships between SiC and TiC were observed. These relationships limited the direction of TiC and tended to produce a coincident boundary of TiC. It was also observed that the dissociation of SiC, on which TiC nucleated, caused instability of the TiC structure and changed the orientation. The mechanism of the orientational change was related to the sliding of the {111} plane of TiC.

CELLULAR PRECIPITATION AT DIFFERENT SITES IN COPPER BASED ALLOYS

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The reaction of discontinuous - cellular precipitation which is of diffusional nature, takes place at static or migrating boundaries and advances into grain interiors. The development of this reaction at grain and interphase boundaries which provide diffusivity paths in solids is explained by different mechanisms.

This investigation has been carried out to study the different sites of cellular precipitation in Cu-Sb, Cu-Ag and Cu-In alloys by utilizing optical an scanning electron microscop and X-ray diffraction.

An overview of various sites of discontinuous precipitation like grain boundaries, different interphase boundaries and dislocations in the grain interiors is given. Moreover a change in the development sequence of the first (which gives fine lamellar structure) and the second (which gives coarse lamellar structure) discontinuous reactions is presented.

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TOPOTAXIAL REACTION FRONTS IN COMPLEX OXIDE SYSTEMS STUDIED BY TRANSMISSION ELECTRON MICROSCOPY

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Investigations of solid state reactions in oxides at high temperatures are significant in view of reactions frequently occurring in heterogeneous ceramics and epitaxial thin films of complex oxides. To be able to prevent these reactions whenever necessary and to utilize them whenever possible one has to understand respective reaction mechanisms and kinetics. A series of recent high-resolution cross-sectional electron microscope (HRTEM) studies of reaction fronts in Mg_2XO_4/MgO and MgX_2O_4/MgO model systems (X = Ti, Fe, Al, Cr, In) forming topotaxially at 1000 to 1500 °C showed definite interrelations to occur between the structure of the reaction front, the sign and amount of lattice misfit along this front, the mechanism of the interfacial reaction, and the overall kinetics [1,2]. An atomic-scale model was developed [2] based on the principle of maximum degradation of the free energy (MDR) [3]. Those studies are now being extended.

1. Structure and reaction mechanism at the Mg_2SnO_4/MgO(001) front

The topotaxial reaction $SnO_2 + 2\,MgO(001) \rightarrow Mg_2SnO_4(001)$ is performed at 1200 and 1300°C in air. The Mg_2SnO_4/MgO(001) reaction front having a lattice misfit of positive sign ($f = +2.5$ %) allows one to critically evaluate the conclusions drawn in [1,2]. The results obtained confirm those conclusions for a *gas-solid reaction*, showing that the model is of more general significance for spinel reactions. In particular: (i) the product phase Mg_2SnO_4 consists of tilt domains, which are separated by small angle tilt boundaries, and (ii) there is a network of misfit dislocations at the reaction front with Burgers vectors of type a/2 <011>. The latter are 45° declined to the reaction front thus allowing a *glide* movement of the interfacial dislocations together with the advancing front. However, for a *solid-solid reaction*, only Burgers vectors *parallel* to the front occur for even short reaction times. This surprising observation is discussed in terms of the rigid geometrical conditions at the reaction front in the beginning of the reaction.

2. Structure of $Ba_6Ti_{17}O_{40}$/$BaTiO_3$(001) and $Ba_2TiSi_2O_8$/$BaTiO_3$(001) reaction fronts

Reactions between $BaTiO_3$ and SiO_2 generally occur during sintering processes of $BaTiO_3$ ceramics, if the sintering aid SiO_2 is used. In a model experiment, $BaTiO_3$ (001) single crystal surfaces react with thin SiO_2 films at temperatures between 800 and 1200 °C, entailing the following reactions: $2\,BaTiO_3 + 2\,SiO_2 \rightarrow Ba_2TiSi_2O_8$ *(fresnoite)* + TiO_2 and $6\,BaTiO_3 + 11\,TiO_2 \rightarrow Ba_6Ti_{17}O_{40}$. At 800 °C, the phases $Ba_6Ti_{17}O_{40}$ and $Ba_2TiSi_2O_8$ (fresnoite) form topotaxially, showing definite orientation relationships, which were analyzed by XRD texture analysis. Cross-sectional HRTEM reveals that both $Ba_6Ti_{17}O_{40}$ and $Ba_2TiSi_2O_8$ are growing directly contacting the $BaTiO_3$ substrate. At the $Ba_6Ti_{17}O_{40}$/$BaTiO_3$(001) front, the growth mechanism comprises the restructuring and continuation of the close-packed $BaTiO_3$(111) planes into the close-packed $Ba_6Ti_{17}O_{40}$ (001) planes. The observations are discussed in terms of lattice misfits and interfacial reaction mechanisms occurring at the two reaction fronts.

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THE KINETICS AND DRIVING FORCE OF THE DISCONTINUOUS ORDERING REACTION IN THE Fe-Co SYSTEM

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The discontinuous ordering (DO) reaction occurs in alloys in which the metastable disordered state can be quenched from high temperatures. During annealing of the disordered alloy at such low temperatures at which the atomic mobility in the bulk can be neglected, the atomic ordering occurs only in the regions swept by migrating grain boundaries (GBs). We studied the DO reaction in the Fe-50 at.% Co alloy, which exhibits the A2 (disordered body centred cubic) - B2 (CsCl structure) ordering transformation. The polycrystalline specimens were annealed at 900°C for 24 h to produced a completely disordered structure and than quenched into the ice brine. The kinetics of the DO reaction has been studied in the temperature interval 280 – 400°C. The migration rate of large-angle random GBs, v, obey the Arrhenius relationship

$$v = 2 \times 10^{14} \exp\left(-132 \ \text{kJ mol}^{-1} / RT\right) \ \text{m/s}$$

where R and T are the gas constant and absolute temperature, respectively. For the driving force of the reaction, two possibilites have been considered: purely thermodynamic driving force, caused by the decrease of the free energy of the alloy during ordering, and the coherency strain driving force, caused by the change of the lattice parametr upon ordering. The reversible disordering-ordering heat treatments of the same specimen have demonstrated that the direction of the GB migration for the unidirectional DO morphology remains unchanged, in spite of the fact that during disordering heat treatment the system "forgets" its thermal history. This is a strong argument in favor of the coherency strain model. The simple phenomenological treatment allowed us to establish a relationship between the activation energy of the DO reaction, ΔH_{DO}, and the activation energies for the GB self-diffusion, ΔH_{SD}, and migration, ΔH_M:

$$\Delta H_{DO} = \frac{1}{5} \Delta H_M + \frac{4}{5} \Delta H_{SD}$$

We also performed the analysis of the orientation of individual grains with the help of the automated electron backscattering diffraction technique in a scanning electron microscope, which allowed us to establish a correlation between the DO reaction rate and misorientational degrees of freedom of the GBs. Special GBs with misorientations close to low Σ values (here Σ is the inverse density of coincidence sites) exhibit also a low reaction rate. This supports the idea that the GB self-diffusivity plays a decisive role in determining the kinetics of the DO reaction.

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DISTRIBUTION FUNCTION FOR THE ACTIVATION VOLUME AND ENERGY OF THE DISCONTINUOUS PRECIPITATION REACTION IN THE Cu - 7at. %In ALLOY

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We have investigated the effect of pressure and temperature on the kinetics of the discontinuous precipitation (DP) reaction in the Cu -7 at. % In alloy. For each pressure and temperature the distribution function for the rate of the DP reaction as a function of the grain boundary was determined. Further, the distribution functions for the activation volume and activation energy were determined. The results obtained indicated that the there is no unique migration and diffusion mechanisms valid for all the grain boundaries.

GROWTH OF BCC Fe-Co PRECIPITATE PARTICLES AT BOUNDARIES IN Cu BICRYSTALS

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Bcc Fe-Co and fine coherent fcc Fe-Co particles precipitate on grain boundaries and in a Cu matrix, respectively, by aging a Cu-Fe-Co alloy. We examined the coarsening of bcc Fe-Co particles on various [011] twist boundaries in Cu-Fe-Co alloy bicrystals aged at 723, 748 and 773K (Phil. Mag. Lett., **76**, 69 (1997)). The development of precipitate-free zones during aging also was investigated. It was found that, except for a specific boundary in bicrystals aged at 773K, the particle growth obeyed a relationship of the form $r^n = Kt$ (where r is the mean radius, K is a constant and t is the aging time) with $n=4$. For the special boundary, n lied between 3 and 4. In this study, the growth of boundary bcc Fe-Co particles is examined for various [001] symmetric tilt boundaries in bicrystals aged between 673 and 723K.

Bicrystals, 1mm thick, of a Cu-1.4wt%Fe-0.6wt%Co alloy containing different [001] symmetric tilt boundaries with misorientation angles $\theta = 9 \sim 80°$ were grown by the Bridgman method using two seed crystals. The bicrystals were aged at 673, 698 or 723K for $40 \sim 216$h after a solution treatment at 1253K for 1h. The size of bcc Fe-Co precipitate particles formed on various grain boundaries was examined on a transmission electron microscope after making thin foils. For each boundary and aging condition, about 30 particles were observed with a beam parallel to [001].

The aging time dependence of the average particle radius can be expressed by $r^n = Kt$. The power n is 4 irrespective of misorientation and aging temperature. The value is in agreement with the growth theories of boundary particles. The measured activation energy Q and calculated pre-exponential factor D_0 of grain-boundary diffusivity against misorientation angle curves show several cusps and these curves are similar to the boundary energy against misorientation angle curve. That is, a lower-energy boundary has a lower diffusivity with a larger value of Q and a larger value of D_0.

INFLUENCE OF PHASE TRANSFORMATIONS AND MICROSTRUCTURE ON COERCIVITY OF PERMANENT MAGNETS BASED ON SmCo₅ POWDERS

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The close relation between the three elements of paradigm "Application-Properties-Structure"is clear and important both the material design engineering and the science. In the present work we investigate the phase transformations and magnetic properties of SmCo₅ powders with definite chemical compositions and particle sizes as a function of heat treatment in the interval from20to900°C. Such methods as thermogravimetrical analysis (TGA), X-ray diffraction, optical microscopy and thermomagnetic analysis were used. Sintered materials of the SmCo₅ type have shown the best permanent magnetic properties both as a powder and a compact body formed by procedures of powder metallurgy. These magnetic materials are characterized by high stability of the permanent magnetization during the effect of a demagnetization field and they possess the best ratio of the energy product BH_{max} in the temperature interval of exploitation.

The high reactivity of rare earth metals requires special precautions in each technological stage of the production of permanent magnets based on SmCo₅, because the intergranular phases , such as secondary Sm-Co phases, oxides etc. play a great role in the coercivity mechanism and usually permanent magnets exhibit a complex multiphase microstructure. At the present research the influence of phase transformations, secondary phase distribution along grain boundaries, grain size and domain microstructure on the magnetic properties has been investigated.

According experimental results it was found , that

- up to 240°C the oxidation of SmCo₅ does not occur ;
- the crystal phases such as Sm_2Co_3, Co, CoO, Co_3O_4, $SmCoO_3$, $SmCo_7$, Sm_2Co_{17} were identified and corresponded chemical reactions were established for definite temperature intervals;
- the secondary phases were usually arranged along grain boundaries , they change the coupling behaviour between the hard magnetic grains and considerably influence on the magnetic properties;
- sometimes magnetic domains were observed in the matrix grains and the domain structure is connected with grain size and distribution of the secondary intergarnular phases.

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THEORETICAL INVESTIGATION OF THE THERMAL STABILITY OF NANOSCALE LAYERED SYSTEMS

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Artificially prepared multilayers with specially designed composition depth profiles for particular applications represent frozen systems far from equilibrium. The sharpness of composition profiles in as-deposited layer stacks depends on the deposition technique used, especially on the energy spectrum of impinging particles. Ballistic mixing of atoms can lead to composition smoothening. To improve the desired properties of multilayers, thermal treatment at moderate temperatures is often applied to increase the sharpness of composition profiles in demixing systems. On the other hand, during application of multilayers at elevated temperatures, composition profiles change by interdiffusion. Moreover, multilayers can fail completely by agglomeration of individual layers. In the present work, compositional changes in nanoscale layer stacks during thermal treatment are analysed within the framework of the Cahn-Hilliard continuum theory. The analysis concerns layer stacks consisting of two immiscible components.

The one-dimensional Cahn-Hilliard diffusion equation is known to possess stationary periodic solutions for given periodicity length and mean composition [1]. These solutions characterise the composition profiles which develop as local quasi-equilibrium after short-time annealing. For ultrathin layers, when the thicknesses are comparable with the interface widths, the composition inside a layer depends on its thickness. Furthermore, there is a minimum thickness beyond which layers rapidly dissolve.

The composition evolution, starting from arbitrary initial conditions obtained e. g. from ballistic simulations of the deposition process (computer code TRIDYN), has been calculated numerically. Thickness fluctuations lead to shrinkage and dissolution of the thinner layers and thickening of the neighbouring layers in the course of annealing. However, the resulting one-dimensional coarsening of the layer thicknesses is extremely slow for thicker layers so that other coarsening mechanisms become relevant.

Two-dimensional perturbations and defects in layers stacks, as e. g. lateral thickness variations, can lead to layer agglomeration. The morphological instability of layers has been examined by linear stability analysis and numerical simulations of the composition evolution. The competitive influence of residual stresses and capillary forces on the layer stability are discussed. The resulting instability mechanism of multilayers is compared with other mechanisms proposed in the literature.

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IN SITU HRTEM OBSERVATION OF SOLID-LIQUID INTERFACES

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Melting process of alumina has been studied using in-situ heating experiments in TEM. A newly developed specimen-heating holder was used and dynamical behaviour of a solid-liquid interface has been observed at high resolution which allows the observation of lattice fringes.

Fig. 1 shows the HREM of an example of solid-liquid interfaces in alumina. The solid-liquid interface is very straight and sharp. Fig. 2 shows the motion of the solid-liquid interface and information on the diffusion of molecules at the solid-liquid interface was obtained.

Melting process of aluminium particles has also been studied. The liquid phase nucleated at the surface of the particles and propagated inwards. The morphology and behaviour of the solid-liquid interface was studied.
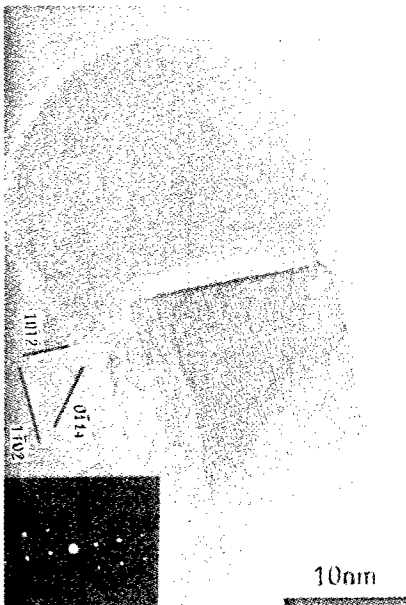
Fig. 1 The HREM image of an example of solid-liquid interfaces in alumina.
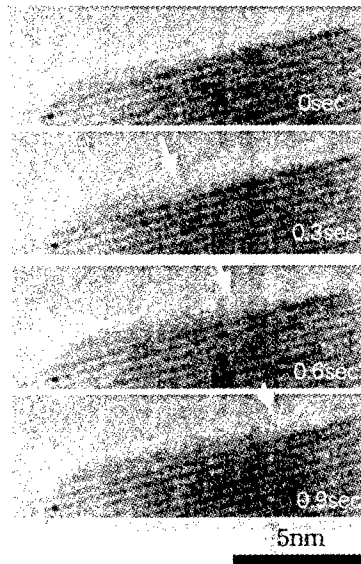
Fig. 2 The HREM images showing the motuion of the solid-liquid interface in alumina. The formation and growth of a monlayer island was observed.

GRAIN BOUNDARIES IN SINTERED CERAMICS PREPARED BY HIGH-STRESSED POWDERS

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A series of reactive ceramic powders, having the weigth ratio of 40% ZrO_2, 40% CeO_2 and 20% Y_2O_3, has been investigated starting both from traditional oxide powders and from precursors obtained after a pyrolytic process according to a previously described procedure [1-2]: in these cases, the starting products were yittrium nitrate hydrated, zirconium acetylacetonate and cerium acetate, using as chelating agents solutions of citric and tartartic acids.

All the starting materials, both precursors and oxides, were then subjected to prolonged cycles of innovative milling treatments, such as Mechanofusion (MF) and Mechanical Alloying (MA): these treatments are common in metallic powder metallurgy, but quite unusual for ceramic powders. Before sintering, all the powders were characterized by DSC and XRD techniques; successively, the powders were pressed, sintered at 1400°C and characterized by XRD and SEM/EDAX techmiques.

The sintered products, obtained from mechanically stressed starting powders, yielded an open porosity higher than these observed after traditional process; large and regularly shaped pores, quite unusual in ceramic materials, appeared in all the sintered products and above all after MF treatrment.

Considerations are then made on the importance of preparation processes on the microstructure and grain boundaries of the sintered materials, which appeared highly rounded after sintering both of the oxide powders and the pyrolytic precursors.

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GRAIN BOUNDARY MODIFICATION DURING LONG-TERM CREEP IN SILICON NITRIDE

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ABSTRACT

Japanese national Project "Research and Development of Ceramic Gas Turbines" involves extensive study of tensile creep behavior of the prospective silicon nitride materials since creep is considered to be a design limitation for the long-term applications at the temperatures above 1250°C. The objective of the current work, which is a part of this Project, is to investigate the changes in the microstructure of the silicon nitride during creep tests lasting up to 10 000 hours with the focus on the grain boundaries containing crystalline and amorphous secondary phases.

The microstructure changes in the commercial silicon nitride SN 88M after creep at the temperatures 1250°C-1400°C in the stress rage of 140 - 430 MPa and lifetime exceeding 10 000 hours were investigated by using X-ray diffraction (XRD), conventional scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy with electron energy loss spectroscopy (STEM/EELS)

SEM/TEM studies revealed intensive cavitation in the amorphous secondary phases at multigrain junctions and two-grain junctions as well as formation of cavities penetrating inside the silicon nitride grains. The comparison of the phase composition of the as-received and creep tested material by XRD revealed intensive changes in the crystalline secondary phase. Rare-earth oxynitrides present at the multigrain junctions in the as-received materials transform during creep into disilicates in the whole bulk. This change was confirmed by STEM/EELS measurements. Possible mechanisms for such transformation include oxidation and the reaction of oxynitride with silica. The former mechanism assumes that silica at grain boundaries is consumed and new silicon nitride is formed whereas the later mechanism involves oxidation of silicon nitride, generation of the additional silica and release of nitrogen. TEM revealed very low amount of the amorphous phase at the grain boundaries and cavity surfaces. EELS confirmed the presence of nitrogen at these interfaces, however, epitaxial growth of silicon nitride grains in the contact with the pockets of the crystalline disilicates was also observed. The new grown layers of silicon nitride are visible due to the layer of rare-earth rich precipitates segregated at the original facets of silicon nitride grains. The orientation of the grain surfaces in these locations is significantly declined from the typical prismatic geometry of the silicon nitride grains. This is considered to be direct evidence of the presence of the solution-precipitation during creep resulting from the reaction of the oxynitride secondary phases with silica.

INSTABILITY OF THE GRAIN BOUNDARY SHAPE DURING HOT STRAINING

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A theoretical model was put forward to describe the development of jaggedness (waviness) of grain boundaries upon hot deformation by analyzing the interaction between the orientation discrepancy defects accumulated at the grain boundaries during deformation. The effect of the deformation conditions on the shape and periodicity of the grain boundary irregularities were analyzed. The model explains the well-known fact of increasing of the irregularity periodicity when the temperature grows.

The results of computer simulation of development of the grain boundary shape irregularities are presented. The simulation demonstrates that an increase in the temperature and a decrease in the deformation rate lead to varying of irregularities shape from a serrated to sinusoidal (wave) one.

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GRAIN BOUNDARY INTERSECTING A FREE SURFACE : STRUCTURAL
EVOLUTION TOWARD EQUILIBRIUM

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By using computer simulation, we study early stages of the evolution toward thermal equilibrium of a $\Sigma=5(210)[001]$ tilt axis grain boundary that intersects an initially flat (210) free surface in copper.

The calculations rely on an adapted, phenomenological n-body potential that satisfactorily reproduces static and dynamical properties of copper.

We report detailed features of elementary diffusion mechanisms that occur at the neighborhood of the grain boundary-surface intersection.

GRAIN BOUNDARY MIGRATION IN Fe- Si ALLOY BICRYSTALS

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ABSTRACT

Migrations of <110> and <001> tilt boundaries in Fe - Si alloy bicrystals have been investigated by Sun and Bauer technique as a function of misorientation angle, driving force, temperature and Si content.   Two distinct regions with different migration behaviour are observed on temperature - dependence of mobility: a drastic change in mobility occurs at a critical temperature.   The critical temperature depends on the driving force and also the grain boundary character.   The activation energy for grain boundary migration is *ca.* 2/3 of that for Fe - atom bulk self - diffusion in the higher temperature region, suggesting that the boundary motion is governed by grain boundary diffusion.   On the other hand, the activation energy increases up to *ca.* 220 kJ/mol in the lower temperature region, being in agreement with that for Si intrinsic - diffusion in α -Fe.   This agreement shows that grain boundary is most likely to move dragging Si atmosphere.   Also, it is of great interest that the mobility for coincidence boundary, particularly $\Sigma 9$ boundary, is higher than that for a random boundary in the lower temperature region, but reverse is the case in the higher temperature region.   In addition, the mobility depends on Si content in the lower temperature region; it increases with decreasing Si content, whereas such dependence is scarcely observed in the higher temperature region. These results obtained here will be discussed from the viewpoint of the interaction between grain boundary and solute atoms.

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INTERFACE STRUCTURE AND THE FRACTURE OF HARD THIN FILMS

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Interface structure and composition are two of the most important factors controlling the performance and reliability of thin films in microelectronic devices. They are particularly important in thin tantalum nitride films where high heat generation, a high structural defect content and high compressive residual stresses can alter properties over long service lives. This concern has motivated the replacement of aluminum oxide substrates with high thermal conductivity aluminum nitride for several applications. However, tests to date lead to contradictory conclusions on reliability. Nanoindentation and nanoscratch tests show that films on polycrystal aluminum nitride exhibit less resistance to fracture than films on single crystal aluminum oxide. These substrates also have different ductilities which have not been accounted for in the fracture energy analysis. However, high resolution TEM suggests that films on aluminum nitride substrates have a more diffuse structure indicative of a greater resistance to fracture. (Figure 1) We have therefore combined continuous nanoscratch testing and high resolution transmission electron microscopy with a novel substrate system that minimizes substrate property differences to determine the fundamental relationship between interface structure and properties in these thin film systems.

The substrate used in this study was created by growing a 50-nm-thick epitaxial layer of aluminum nitride on one-half of a single crystal of aluminum oxide. A thin film of tantalum nitride was then reactively sputtered onto the layered substrate surface to a uniform thickness of 500 nm. Nanoindentation tests showed that the measured elastic moduli of the tantalum nitride film and aluminum nitride and aluminum oxide substrates were essentially equal. These tests also revealed that the use of a thin aluminum nitride layer essentially eliminated differences in ductility between the two substrate materials. As for the fracture results, the nanoscratch and indentation fracture tests showed that the film on both substrate materials failed readily along the film-substrate interface. Most importantly, the fracture energies measured in nanoscratch tests were essentially equal on both substrate materials while indentation fracture tests indicated that the film on aluminum nitride was even more resistant to fracture than the portion of the film on aluminum oxide. In this presentation, these results will be combined with high resolution transmission electron microscopy to show that interface controls properties of hard thin tantalum nitride films on nitride and oxide substrates at the submicron level.

(a)   (b)
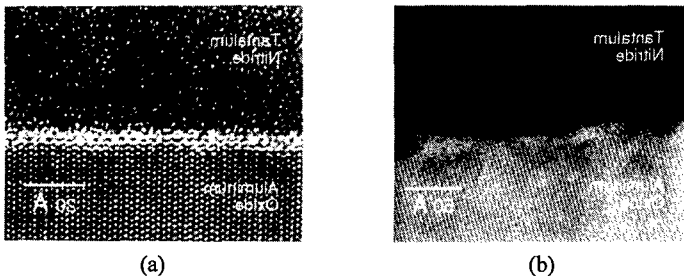
Figure 1. HRTEM suggests that the tantalum nitride film-substrate interface appears more diffuse in (a) aluminum nitride than in (b) aluminum oxide systems.

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INTERPHASE BOUNDARY SLIDING MECHANISM IN FERRITE/AUSTENITE BICRYSTALS

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It is known that a grain boundary sliding(GBS) plays important roles in superplastic deformations, and a number of models based on the GBS have been proposed. Superplasticities, however, were mainly realized by the two-phase alloys, and few report as to behavior of interphase-boundary sliding(IBS) has been reported. In this paper, a model of the IBS mechanism based on our experimental result of γ / α-bicrystal studies is described and discussed.

A creep curve (sliding displacement vs testing time) shows a constant sliding rate v at the initial stage and rapid increase of displacement with increasing time at the next stage under a constant load. The sliding rate v under the initial shear stress τ (=1MPa) was approximately 1.7×10^{-6} m/s and it was $10^2 \sim 10^3$ times higher than those in the (γ / γ) and (α / α)-phases GBSs[1]. The experimental results could be analyzed through the power law of $v \propto \tau^n$, where the · stress exponent n was estimated to be approximately two. It is known that , strain rate sensitivity, m(=1/n) increases to 0.5 in the superplastic deformation of polycrystals. Local plastic deformation in the α-phase(thickness, t$\sim$200 μ m from the interphase boundary) and no plastic deformation in the γ -phase neighboring to the interphase was observed. Subboundary development was observed in the α-phase neighboring to the interphase boundary whereas recrystallization was not observed in both the α- and γ-phase. Furthermore, the activation energy of the sliding was estimated to be 270kJ/mol by temperature change tests, and it can be close to that of bulk self-diffusion of Fe in the α -phase. From these experimental results, a model of the interpahse-boundary sliding is proposed based on the dynamic equilibrium of slips and climb motions of dislocations of the α -phase arrested along the interphase boundary.

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MECHANICAL PROPERTIES OF INTERPHASE BOUNDARIES IN AUSTENITIC-FERRITIC STEEL

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Mechanical behaviour of polycrystalline materials depends in a large extend on internal interfaces, which may react in different ways to the internal stresses that appear during straining. Various kinds of such reactions which lead to the stress relaxation have been already revealed and analysed in single phase polycrystals. Little is known however, about such reactions in the case of interphase boundaries (IBs) and about their influence on mechanical properties of multi-phase materials.

The aim of this work is to investigate possible reactions of IBs in response to the internal stresses in a two-phase austenitic-ferritic steel. The influence of orientation relationship (OR) between phases and the resulting IB structure on macroscopic mechanical properties of the steel has also been studied. This was done by comparing mechanical behaviour of the steel displaying special orientation relationships (ORs) between austenite and ferrite, such as Kurdiumov-Sachs (KS) and Nishiyama-Wassermann (NW) ones, with the steel exhibiting random misorientations between phases. The appropriate thermo-mechanical treatments have been used to produce two series of specimens with different types of ORs.

Different mechanisms of plastic accommodation of stresses resulting from dislocation interaction with IBs were revealed and analysed by means of *in situ* and *ex post* TEM experiments. It was shown that the efficiency of stress relaxation processes depends upon the type of ORs between phases, the crystallography of interfaces and the temperature. To correlate the dislocation processes that occur at IBs with the mechanical behaviour of the steel the hardness measurements and tensile tests were performed at room temperature. It was shown, that the steel with large fraction of special ORs (NW and KS) exhibits lower hardness and yield strength than the steel with randomly disorientate phases. The mechanical tests performed on samples with different grain size revealed, that the hardness increases with the specific surface of interphase boundaries according to the Hall-Petch relationship.

It was concluded that the kind of ORs influences the mechanical behaviour of the two-phase steel. This effect may be explained by different mechanisms of stress relaxation which operate at IBs with different crystallography. It means that, by producing the definite structures of interphase boundaries it is possible to influence the stress relaxation process and by this way to control the mechanical behaviour of two-phase materials.

EFFECT OF NON-EQUILIBRIUM GRAIN BOUNDARY STRUCTURE ON INTERNAL FRICTION IN MICROCRYSTALLINE METALS

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There were carried out experimental investigations of elastic and non-elastic characteristics of microcrystalline copper (99.98%) and nickel (99.98%). The materials studied had special microstructure with characteristic size of the structural elements ~100 nm. This structure was obtained by special methods of intensive plastic strain (ECAE - technology). (The samples were prepared by Dr. V.I.Kopylov.) For measuring of the elastic and non-elastic characteristics there was used of the forced bending modes method for the samples with free ends at the frequency 1-2 kHz. The form of the samples was a plate having the characteristic sizes 2x14x100 mm. In the course of experiments there were defined the elasticity modules E and the internal friction values Q^{-1} in conditions of continuous heating from 293 K to 573 K for Cu and from 293 K to 673 K for Ni and isothermal annealing at the temperature 423 to 488 K for Cu and 513 to 673 K for Ni.

The investigations showed that the elastic modules E and the internal friction Q^{-1} of the microcrystalline materials differ essentially from the corresponding values for the large crystal materials.

Elasticity modules in microcrystalline Cu are 5% lower, and in microcrystalline Ni they are 15% higher than the common values. The internal friction level in microcrystalline Cu are by an order, and in microcrystalline Ni 3 times increases the values characteristic for the annealed materials (~10^{-4} and $5 \cdot 10^{-4}$, correspondingly).

In the process of isothermal annealing of the microcrystalline samples the values E and Q^{-1} are being changed essentially approaching gradually the values characteristic of the annealed material. At the same time the rate and the character of these changes depend on the annealing temperature T; as a rule when T is increasing, the recovery process intensity is increasing. The activation energy of these processes (recovery) in copper is close to the activation energy of the grain-boundary self-diffusion. In nickel the activation energy of the recovery processes is changing during annealing non-monotonously. During the isothermal exposure in copper and nickel there were found new internal friction peaks not observed before. In copper at the level of $5 \cdot 10^{-4}$ when the background values are ~10^{-4} (at T=200⁰C the peak is observed when the exposure is 240 min, at T=215⁰C the peak is when the exposure is 210 min). In nickel the peak is at the level 1.5·10^{-3} when the background level is $8 \cdot 10^{-4}$ (at T=240⁰C the peak is observed after the 90 min exposure; at T=250⁰C it is observed after the 180 min annealing). In this work there was proposed the internal friction model allowing to explain the observed laws.

ROLE OF GRAIN BOUNDARIES
IN STRAIN HARDENING OF
MICROCRYSTALLINE MATERIALS

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There were examined the laws of microcrystalline materials strain hardening. There is shown that the strain hardening is provided by two processes: 1) defects accumulation in grain boundaries; and 2) grain growth. At the initial stage of deformation essential hardening is the result of the rapid increase of internal strain fields, which are created by the misfit orientational dislocations and the products of their delocalization accumulation at the grain boundaries.

There is shown that the nature of the hardening at this deformation stage is defined by the processes of defects diffusive redistribution in the boundaries and depends on the boundary structural state, their free volume and the grain size. After permanent defect density formation at the boundaries the deformation hardening nature is defined by strain-enhanced grain growth. There were obtained equations allowing the calculation of the stress-strain dependence at various temperatures and strain rates.

There is shown the good agreement the theoretical dependence with the stress-strain experimental curves for some of the microcrystalline materials.

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SOLITONS IN THE VICINITY OF A MARTENSITIC PHASE TRANSITION

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Within the framework of two-dimensional Ginsburg-Landau theory weakly nonlinear dynamics of phonon modes in the vicinity of the martensitic phase transition have been investigated. The regarded model is a close approximation for the O_h — D_{4h} cubic-tetragonal martensitic transformation in real crystals. The effective equations describing the interaction of phonon modes in the vicinity of the phase transition point have been derived. Multi-soliton excitations in the vicinity of the martensitic transition have been predicted. These solitons can be interpreted as precursors of the phase transition or as low-amplitude twin patters and remaining traces of low-temperature phase (martensite) against the background of the austenitic phase. The conditions for the existence of particular types of solitons have been found and the solitons stability has been investigated. We suppose that instabilities of solitons are very important as a new mechanism for the anomaly sonic emission in the vicinity of martensitic phase transitions.

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DISLOCATION MECHANISMS DETERMINE MECHANICAL AND FRACTURE PROPERTIES OF GRAIN STRUCTURED MATERIALS

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First finding of this work is the scaling between the deformation stresses of various stages of plasticity and fracture (at atomic, meso- and macroscopic scales) and the close correlation between the fracture surface roughness and deformation properties in alkali halide poly- and single crystals, severe deformed alloys (nanocrystals) and amorphous solids, ceramics under different tests/environments. This universal correlation is fulfilled in the widest temperature, stress and stress rate ranges (up to the shock wave stresses),for crystalline and disodered materials with various volume fraction and state of impurities, different precursor strains and thermal prehistory, etc.

This scaling shows that every point of micro- or macrodeformation curve is closely interconnected with the other points due to the same micromechanisms, but this correlation is governed by the scale length of observation: high differences in the space density of matrix defects and impurity precipitates, in the sizes of grains at various dislocation pathlength scales may infringe the universality of the above scaling law.

The next finding is the proportionality between the sizes of deformation structure units: dislocation spacing in amorphous solids,grains in nano/polycrystalline materials with constant chemical composition, and the reciprocal value of their microhardness (flow stress).

The proportionality between the flow stress and volume fraction of amorphous, nano/coarse grains; between the Young's moduli and threshold stresses of atomic, meso- and macroscopic stages of plastic flow and fracture; scaling of the dependences of total crystal density change and strain versus deformation stress points to the vital role of dislocation cross-slip, climb and the Orowan bowing mechanisms in the strict chain of these stages: dislocation motion and multiplication, their retardation, cell or grain boundary initiation and secondary slip, the increase of dislocation and point defect densities, the transformation of low-angle boundaries into the high-angle ones, polycrystals into nanocrystals and amorphous structures; microcrack nucleation and coagulation through the micropores and microcleavage steps into macrocracks (macrofracture), damage.

Dislocation micromechanisms explain the effect of thermal prehistory and precursor plastic deformation on the structure of fracture surfaces: the crystallographic orientations of slip, the directions of dislocation motion away from the microcrack tips, microcrack growth and coagulation with other microcracks, the role of microcleavage steps and microvoids in the subsequent growth of macrocracks, etc.

The size (mass) distribution of micro- and macrofracture products is governed by the parameters of the precursor plasticity too.

GRAIN BOUNDARIES STRUCTURE AND PROPERTIES OF MICROCRYSTALLINE MATERIAL OBTAINED BY SPECIAL INTENSIVE PLASTIC DEFORMATION METHODS

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There were carried out complex experimental and theoretical investigations of structure and physical-mechanical properties of metallic materials subjected to intensive plastic strain. It is shown that the used special methods of deformation are very effective for obtaining a reglamented structural state and, particularly, for obtaining nano- and microcrystalline structures having the structural element sizes ~100nm. The structures obtained have highly equal axes and homogeneity. They are stable until there are obtained the temperatures $T \sim 0,25\text{-}0,3\ T_m$. The obtained nano- and microcrystalline structures have unique physical and mechanical properties. Their mechanical characteristics are especially demonstrative: in particular, metal strength limits are 2-3 times higher compared to the common values: Al (80/350), Cu (240/480), Ni (400/900), α-Fe (350/1000). (The first number in brackets is a common value σ_B, the second is the value σ_B in metal having microcrystalline structure.) There are also observed anomalies of their thermal and electrical properties: thermal expansion coefficient and temperature coefficient of electric resistance in copper are 2-5% lower than common values. There are observed anomalies of magnetic properties: magnetic permeability increase (for α-Fe in the fields up to 10^3 A/m two times), coercive force increase (for steel Y-10 4 times). There is observed superconductivity characteristics change (for Nb the critical current increase $5 \cdot 10^3$ to $5 \cdot 10^4$ A/cm^2). In this paper there are stated modern theoretical conceptions about the defective structure evolution of nano- and microcrystalline materials during strain and their structural state influence on physical-mechanical properties.

GRAIN BOUNDARY STATE AND MECHANICAL BEHAVIOUR OF NANOCRYSTALLINE INTERMETALLIC COMPOUND NI3AL.

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The structure and mechanical properties of the intermetallic compound Ni_3Al subjected to severe plastic deformation on a Bridgman anvil-type unit and subsequent annealing were investigated.

It was·shown that due severe plastic deformation to the entirely disordered structure with a grain size of 50 nm was formed in the material. The microhardness of samples was 6200 MPa, bending strength was 2800 MPa and a maximum bending was 0.4 mm.

The non-monotonic dependence of mechanical properties (at 293 K) on temperature of annealing was revealed:

In the temperature range 293-420 K long-range ordering parameter S, grain size, internal stresses and microhardness do not change.

In the temperature interval 420-560 K a sharp growth in the long-range ordering parameter S to a value of 0.42 is observed. Towards the end of this stage the crystallite size increases slightly and reaches a value of 150 nm. An increase in temperature to 533K leads to a sharp decrease in ductility to zero and ultimate strength to 1350 MPa.

In the temperature range 620-1150K the value S does not almost change and is equal to 0.6. The TEM investigations show that mean crystallite size grows from 150 nm to 10mkm. At temperatures above 1113 K the value S rises to 0.77 at T=1313K. The striking result of the present investigation is that with rising annealing temperature to 860K an increase in ductility accompanied by an increase in ultimate strength and yield strength is observed. The material in an entirely disordered nanocrystalline state has the maximum strength and ductility.

On the basis of studies of structure, fracture, surface relief and mechanical properties the changes of mechanical properties were analysed.

MECHANICAL CHARACTERIZATION OF SPECIAL, NEAR- AND NON-SPECIAL BOUNDARIES IN ZINC

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Sliding behaviour of symmetric tilt high-angle boundaries with different deviations from coincidence (special) misorientations has been studied during high-temperature deformation of zinc bicrystals. Boundaries with special and near-special misorientations having low crystallographic index planes were investigated. It was shown that there was only a small difference between the rates of grain boundary sliding along the boundaries with special and non-special misorientations. For sliding along the special $\Sigma=9\{1\overline{2}12\}$ boundary, the operation of intragranular basal slip was necessary. At the same time, sliding along twin boundary occured without intragranular slip. For boundaries with special and near-special misorientations a coupling of sliding and migration was observed. As a rule, sliding along boundaries with non-special misorientations was not accompanied by boundary migration. Sometimes, some portions of the boundary migrated but this migration was not coupled with grain boundary sliding. For the special misorientation boundaries, the ratios of migration to sliding had maximum values and were close to the values predicted from the DSC-dislocation concept. At the deviations from special misorientations the decreased ratios of migration to sliding were observed. The greater deviation was from the special misorientation, the lower was the ratio of migration to sliding. The results obtained were in a good agreement with existing classification of interfaces. On the basis of these results a novel method has been developed for revealing special (singular), near-special (vicinal) and non-special (general) grain boundaries.

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LOCAL STRESS IN HIGHLY STRAINED COHERENT InGaAs ISLANDS

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Molecular beam epitaxy of highly strained $In_xGa_{1-x}As(x>0.25)$ on $\{100\}$ oriented GaAs, leads to the 2D-3D transition of the growth mode with formation of coherent islands. Deformations were measured at the atomic scale by image processing of HREM $\{110\}$ projections. The image processing algorithm includes Wiener Fourier filtering with local noise estimation (1) as well as high and low frequency cut off (2). This filtering procedure conserves the information about lattice deformation and improves the signal to noise ratio.

For each experimental lattice point displacement, vectors $\bar{u}_x$ and $\bar{u}_z$ were calculated using the corresponding lattice positions extrapolated from the reference region. The continuous field of $u_x(x,z)$, $u_z(x,z)$ was determined by projecting the displacement values from a discrete lattice by linear interpolation. Experimental deformation maps of $\varepsilon_x(x,z)$ and $\varepsilon_z(x,z)$ were obtained by derivation of the displacements $u_x(x,z)$, $u_z(x,z)$ in x and z directions, respectively perpendicular and parallel to the growth direction of the heterostructure. On the quantitative contour plots with absolute values of deformation, the interval between contour levels is $\Delta\varepsilon=0.002$ which corresponds to a displacement of 1 picometer. The interface can be clearly seen on the $\varepsilon_z(x,z)$ contour plot (fig.1) where a maximum in ε_z is encountered at about 4 nm from the island top. Our results were compared with calculations based on the theory of homogeneous solid under biaxial compression with a sinusoidal undulating surface. The observed relation between ε_x and ε_z, which is quite different from the one predicted from a model corresponding to an island with an homogeneous composition, backs up the hypothesis of indium enrichment within the island and subsequent depletion in the adjacent valleys.
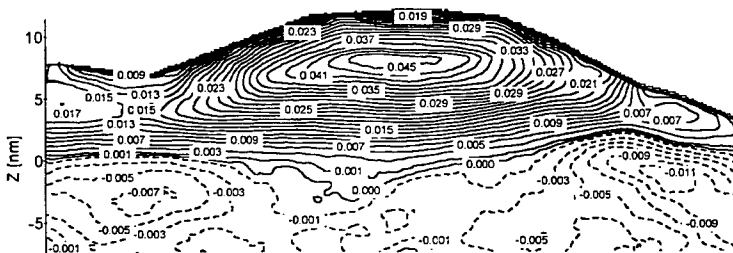
Fig. 1 : $\varepsilon_z(x,z)$ deformation map on a coherent $In_{0.35}Ga_{0.65}As$ island

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GRAIN JUNCTIONS IN DEFORMED POLYCRYSTALS: INDUCED DEFECTS, STRESS SINGULARITY AND EMISSION OF PARTIAL DISCLINATIONS

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Under consideration are three adjoined grains, subjected to different plastic strains as being differently oriented relative to the external deforming stress, and intergranular defects induced with this mismatching. The mesoscopic stress field generated by those defects has been evaluated and shown to be essentially inhomogeneous within grain interiors. The singularity of the stress at the triple junction line is considered to actuate the emission of "broken-off" low-angle boundaries and the conglomeration of point defects.

Geometric analysis of induced interfacial and junction defects in a plastically deformed polycrystal has shown them to constitute a totality of Somigliana dislocations (planar stress sources) stretched on the junction disclination skeleton. A grain boundary bend is considered as a source of partial disclination dipoles which, when moving in crystal, leave after them a misorientation band. Intensity and capacity of such a source are discussed in dependence on the misorientation at the boundary and the bend's geometry. It is concluded that successive emission of partial disclination dipoles with the mechanism considered can eventually form new high-angle boundaries, thus providing the grain fragmentation in plastically deformed polycrystals.

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INTERFACE EFFECT ON DISLOCATION STRUCTURE OF DEFORMED RADIATION-HARDENED LAYERED LiF CRYSTALS

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Interface effect on the evolution of dislocation structure accompanying plastic deformation of LiF model composites under single-slip condition has been experimentally studied. The composites were prepared with X-ray irradiation of layers of LiF single crystals, interfaces between the irradiated ("hard") and unirradiated ("soft") regions being located along the specimen axis. Depending on the orientation of single slip zone relative to the interface, either screw or edge dislocations crossed the interface. Dislocation structure was revealed by selective etching.

It was found that plastic deformation under compression occurs by means of nucleation and development of slip bands in "soft" regions followed by their penetration into "hard" regions. When screw dislocations intersected the interface their density in the irradiated region increased sharply (up to by a factor of three). In edge slip bands, the dislocation etch pit densities were approximately the same in different regions. Under cyclic tension-compression loading, plastic deformation occurred only in "soft" regions practically without penetration of dislocations into "hard" ones. Influence of the irradiation time and of irradiated region size on the yield stress has been studied, too. The obtained results can be explained by a difference in parameters of double cross slip and multiplication for dislocations before and after intersecting the interface.

AB INITIO TENSILE TESTS OF GRAIN BOUNDARIES IN SiC

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It is of great importance to study the structure and properties of grain boundaries in SiC. Currently, it is possible to apply *ab initio* calculations based on the density-functional theory to such complex systems by virtue of the development of the first-principles molecular dynamics method [1]. In this paper, we report our recent novel *ab initio* calculations of the tensile strength, namely "*ab initio* tensile tests" of a grain boundary in SiC.

We deal with the $\{122\}\Sigma = 9$ boundary in SiC. Two kinds of polar and one kind of non-polar interfaces are constructed by inverting the polarity of grains. 64-atom supercells are used. We use the conjugate-gradient technique for electronic mini-mization [1,2] and optimized pseudopotentials [3]. A plane-wave cutoff energy of 60Ry is used. Stable fourfold configurations with no stress contain either C-C or Si-Si wrong bonds for the polar interfaces, and both kinds of wrong bonds for the non-polar interface [4].

In the tensile tests, uniaxial tensile strain is introduced into the above stable con-figurations. First, the cell is stretched in a small increment in the direction normal to the interface, and the atomic positions are changed by uniform scaling according to the change of the cell size. Second, all the atoms are relaxed by the *ab initio* method until all the atomic forces are less than 0.1eV/Å. Third, the total energy and stress tensor are obtained by the *ab initio* method. This cycle is iterated until the interfaces are broken. This procedure corresponds to real tensile tests at T=0K.

We have found that each interface is rather strong because of reconstruction. How-ever, the interfacial C-C and Si-Si wrong bonds have significant effects on the strength and the behavior of fracture. For the non-polar interface, the back bonds of the C-C wrong bonds are broken first because of the short bond length and large strength of the C-C bonds. It can be concluded that the *ab initio* tensile tests are promising tools to investigate the mechanical properties of interfaces such as the intrinsic strength of interfaces and the behavior of interfacial fracture at the atomic and electronic scales.

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Temperature Dependence of Mechanical Behavior of Copper Bicrystals with Dispersed B$_2$O$_3$ Particles

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ABSTRACT

The high temperature mechanical behavior of orientation controlled Cu bicrystals with dispersed B$_2$O$_3$ particles, which behave liquid-like at the temperature over 700K, was studied. Most of the bicrystals having high-angle boundaries fractured intergranularly, though all of the bicrystals with low-angle boundaries fractured trans-granularly. The ductility tended to decrease with increasing temperature and misorientation angle, and with decreasing strain rate. These results were explained by the occurrence of grain-boundary sliding and grain-boundary migration in relation with the state change of B$_2$O$_3$ from solid to liquid with increasing temperature.
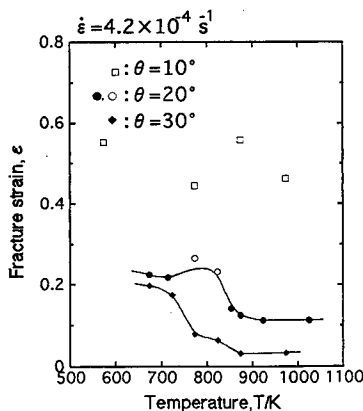
Fig. 1 Temperature dependence of fracture strain. Open and solid symbols indicate transgranular and intergranular fracture, respectively.

CORRESPONDENCE BETWEEN INTERCLUSTER BOUNDARIES IN AMORPHOUS ALLOYS RIBBONS AND THEIR LOW TEMPERATURE STRENGTH AND TOUGHNESS.

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In a number of typical "metal-metalloid" amorphous alloys (AMA) the ductile shear failure is observed down to 0.5 K and it is preceded by the localized plastic shear. The physical reason of retaining the ductility of AMA at such a low temperatures is explained in frames of the polycluster model [1] of amorphous solids by retaining of the dislocation-like defects mobility along intercluster boundaries. State and structure of these boundaries control an ability of AMA to plastic deformation and predetermine their failure mode and the yield stress (the ductile shear failure stress σ_f).

Characteristics of local plasticity and failure were studied experimentally for some AMA. A variation of a clusterous structure was carried out by different ways: changing of alloys chemical composition, thermal treatment of the melt before quenching, changing of the strain-rate and temperature of deformation.

It is discovered:

1. σ_f has minimum in the $Fe_{100-x}B_x$ system at the eutectic composition (x=17), in $Fe_{85-x}Co_x B_{15}$ system at the compositions with the ratio of Fe and Co atoms concentrations close to 3:1, 1:1, and 1:3 ;

2. Non-monotonous temperature dependencies of the $Pd_{84.5}Si_{15.3}$ and $Fe_{40}Ni_{40}P_{14}B_6$ AMA

   in the 4.2-0.5 K temperature interval;

3. Non-monotonous straine-rate dependences of σ_f in the $Fe_{80-x}Ni_x B_{20}$ AMA system;

4. Increasing of σ_f almost twicely for $Fe_{82}B_{12}Si_4C_2$ and $Fe_{71}Cr_{10}Si_7B_{12}$ AMA after the preliminary "overheating" of the melt above the critical temperature T_c before rapid quenching.

Established regularities find their explanation in the frame of the model [1]and corroborate it.

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The Structure of Grain Boundaries and the process of Failure in the Ferrite-Pearlitic Steals

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The influence of microstructure and a structure of internal division boundaries on mechanical properties and development of failure processes at low-cycle fatigue was studied on the bases of the widely used ferrite-pearlitic steels (St3 and 17GS).

It is revealed, that one can observe appearance of brittle component at impact rupture, when having "knife" boundaries inside of ferrite grains "Knife" boundaries are characterized by smooth bent, very thin and perfect boundaries. These boundaries make up very large (several dozens of degrees) misorientations of neighbouring regions,

It is shown by methods of scanning electron microscopy that in steel with "knife" boundaries at fatigue failure the width of fatigue furrows are essentially higher as compared to steel, where such boundaries are absent. This sestifies that the rate of fatique cracks in this case is higher.

The influence of dislocation structure, which forms during low-cycle fatigue, on changes of mechanical properties of ferrite-pearlitic steals was studied. It was shown that in case of appearance of "knife" boundaries in steels, values of yield stress and ultimate strength considerably increase. With all that values of maximum relative elongation and impact strength decrease.

In the present work there are discussing nature of the influence of "knife" boundaries. metallografic structure, a lobule of pearlitic component on development of failure processes.

It is suggested to take into consideration the mentioned above factors for calculations of residual sources of pipelines and tanks working in unsteady regimes.

ELASTIC ANALYSIS OF FINITE STIFFNESS BIMATERIAL INTERFACES: APPLICATION TO DISLOCATION-INTERFACE INTERACTIONS

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The mechanical properties of an interface are determined by the chemical bonding at the interface, which may be significantly different from that within the bulk. In continuum elasticity, an interface manifests itself through interfacial boundary conditions imposed upon the equations of elastic equilibrium. Typically, we assume that both the displacements and tractions are continuous across the interface (i.e., a "welded" interface). An effective interfacial viscosity may be defined as inversely proportional to the interface diffusivity. Hence, an interface may be viewed as liquid-like at high temperature. This liquid-like interface cannot support a shear. To capture this effect, the elastic boundary conditions are commonly modified such that normal tractions and displacements are continuous across the interface and the shear traction is zero (i.e., a "slipping" interface). The literature contains many studies of dislocation - inclusion interactions in this "slipping" interface limit.

While both the "welded" and "slipping" interface boundary conditions are rigorously defined and have found wide applications, the appropriate boundary condition for most real interfaces lies somewhere in between these two extremes. One approach to correcting this deficiency is to develop a phenomenological model that approximates the bonding at interfaces. For small shear, the jump in the displacement across the interface is proportional to the shear traction.

In the present paper, we propose a simple, analytical method for accounting for variations in interfacial properties on the elastic behavior of a two phase material. Our approach is based upon a linear shear traction-displacement jump condition [1] within a Green function framework. We apply this approach to determine the climb force acting on an edge dislocation and an array of such dislocations near a bimaterial interface. For the individual dislocation case, we found that an unstable dislocation-interface equilibrium separation exists, above which the dislocation is repelled and below which it is attracted to the interface, provided that the material containing the dislocation is more compliant than that across the interface.

When the two materials are misfitting with respect to each other, the misfit is relieved by the formation of a misfit dislocation array. When the interface is "slipping", the dislocations always reside at the interface. However, when the interface is "welded" and the material containing the dislocations is stiff, the misfit dislocations may stand-off from the interface, as seen experimentally. In the case in which the dislocations are repelled from the interface in the welded interface limit, the finite interfacial stiffness either decreases the equilibrium stand-off distance or results in no stand-off at all, depending on the relative elastic properties of the two materials. This stand-off distance decreases with decreasing interfacial stiffness. Even when a finite stand-off distance does exist, there is a dislocation/interface separation smaller than which the dislocation array is attracted into the interface.

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MECHANICAL PROPERTIES AND DEFORMATION BEHAVIOUR OF THE INTERFACES OF DISSIMILAR METALS

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Attainment of high strength properties of the interfaces obtained by advanced technologies based on plastic deformation at relatively low temperatures (mechanical alloying, cold pressure welding, cold sintering) is an actual problem of materials science. Bimetallic joints obtained by the special cold welding method, were used as a model analogue of phase boundaries to investigate their strength, deformation behaviour and fracture mode. Investigations were carried out at 77 and 293 K. The results showed marked adhesion for all bimetallic systems. However, mechanical properties of the interfaces were quite different. For most systems, such as Ni/Ag, Ni/Cu, Al/Cd, Al/Pb, etc. strengthening of the interface was observed. In this case ductile rupture inside the softer metal occurred. For some systems, such as Pb/Sn, Cd/Sn, Al/Sn, formation of an interface similar to an intraeutectic one was observed. Strength characteristics obtained for these interfaces represent effects of brittleness (Al/Sn, Zn/Sn) and superplastic interface sliding (Pb/Sn, Cd/Sn). Deformation behaviour of Pb/Sn and Cd/Sn interfaces showed features of viscous flow with viscosity coefficient of order 10^9 - 10^{11} P [1]. On the contrary, in the case of Al/Sn and Zn/Sn plastic flow along the interface is accompanied by pore accumulation and formation of cracks. That is the reason why these interfaces exhibit brittleness. It has been shown that differences in the mechanical behaviour of the interfaces are related to differences in phase boundary energy and other thermodynamic parameters as well as to mechanoactivation of both adhesion interaction and structure formation under non-equilibrium conditions.

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EFFECT OF GRAIN BOUNDARY SEGREGATION ON FRACTURE BEHAVIOUR
OF TWO BAINITIC STEELS

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An impurity effect on fracture behaviour was studied in two CrMoV and CrNiMoV bainitic steels of high purity used for applications in power industry. Scanning electron microscopy of fracture surfaces obtained by fracturing the standard notched specimens at low temperature revealed generally a transgranular fracture mode. Isolated islands of intergranular fracture were recognised at the cleavage initiation only (Fig.1). The study of chemical composition of these islands by Auger electron spectroscopy disclosed enhanced concentration of sulphur and phosphorus (several atomic percent, Fig.2). Presence of these impurities at grain boundaries is the primary cause of local decrease of intergranular cohesion. The effect of segregation and thus the portion of intergranular fracture decrease after increasing the test temperature.

These results were obtained in framework of the projects of European collaborative action COST 517 – „Cleaner Metals for Industrial Exploitation".
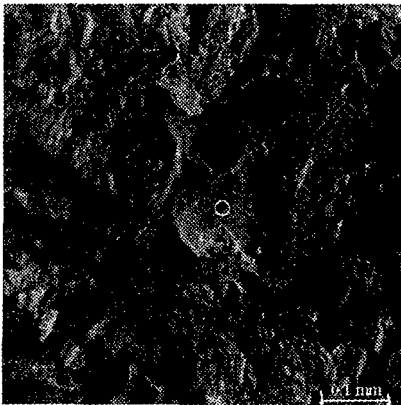
Fig.1: SEM image of the initiation of cleavage at low temperature.
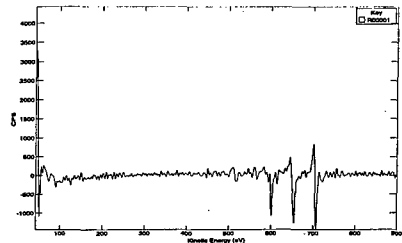
Fig.2: Typical AES spectrum of the intergranular fracture surface.

MODELS OF INTERGRANULAR FRACTURE

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When polycrystalline materials fail, intergranular fracture competes with several other mechanisms including transgranular cleavage and ductile fracture. The proportion of intergranular fracture which actually occurs in practice depends on many physical and material parameters including, for example, temperature, applied stress, grain size, grain shape, preferred orientation, the limited number of cleavage planes available, relative grain boundary and cleavage surface energies, the size and distribution of potential crack nuclei, such as precipitate particles, and prior damage, such as the presence of wholly or partially decohered boundaries.

Theoretical models have been developed to investigate the influence of these parameters. In some cases two-dimensional models are valuable and the polycrystal is then represented by an array of distorted hexagonal cells. The main limitation of this approach is that cleavage cracks in adjacent cells can always propagate directly across cell boundaries so that no boundary fracture need occur. The three-dimensional models which have been developed are based on arrays of regular tetrakaidecahedra, which have six square and eight hexagonal faces. In these models cleavage planes in adjacent grains do not meet in a line in their common grain boundary so that, if a cleavage crack is to propagate across such boundaries, an additional failure mechanism such as fracture of part of the grain boundary must occur. The models enable the extent of this partial grain boundary failure to be calculated and using a range of assumptions about, for example, crack nucleation sites, stress axes, and the orientations of grain boundaries and cleavage planes, the result has been consistently about 30 per cent. This figure is much larger than accepted experimental values, which for pure iron approaches 20 per cent but for C-Mn steels is less than 6 per cent. The discrepancies are in fact much worse than this as the experimental values include a large element of total failure of grain boundaries as well as the partial failures which are all that is considered in the theoretical work.

New experimental work, using high resolution scanning electron microscopy of fracture surfaces, has demonstrated that the discrepancies can not be explained by possible inadequacies in earlier experimental techniques and procedures. The assumptions used in the models would therefore appear to be questionable. In particular the assumption that cleavage occurs on a single plane in each grain appears to be untenable. Therefore the possibility of multiple-cleavage in at least some grains is being investigated. In an extreme case, for example if cleavage was possible on three distinct planes in each grain, the effective fracture plane could have any orientation and no intergranular fracture would be required. Experimental work is currently investigating this suggestion.

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"COMPETITION BETWEEN SENSITISATION AND ENVIRONMENTALLY INDUCED GRAIN BOUNDARY DAMAGE IN 304 STAINLESS STEEL : FROM AN INDUSTRIAL CASE TO A FUNDAMENTAL STUDY"

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Abstract

Grain boundary cracking has been recently observed in bimetallic welds which local composition is very closed to 304H stainless steel. This cracking was attributed to the stress relief heat treatment which is performed at around 600°C under oxidising environment.

The aim of this study was (i) to choose the relevant laboratory test to reproduce the intergranular damage on 304H stainless steel and (ii) to analyse the reasons of this phenomena in terms of microstructure evolution and environmental effect.

Slow strain rate tests ($\dot{\varepsilon} = 1$ à 5.5×10^{-7} s^{-1}) between 450 and 610°C either under oxidising environment or under secondary vacuum have been chosen to reproduce and analyse cracking. Tests have been done on cylindrical specimens, some of them were notched in order to assess the environmental effect.

It has been shown that slow strain rate test (10^{-7} s^{-1}, 610°C) results in intergranular surface cracking for plastic deformation as low as 2% and leads to fully intergranular fracture surface with no necking at total plastic deformation lower than 10%, with strong evidence for grain boundary sliding (GBS).

Furthermore, tests as a function of temperature (450 - 610°C) allowed to establish a clear correlation between intergranular damage and sensitisation, i.e. local de-chromisation and formation of $M_{23}C_6$ carbides. The presence of these carbides has been confirmed by TEM study.

Sensitisation induced grain boundary fracture was confirmed by liquid nitrogen testing which results in fully intergranular fracture in presence of $M_{23}C_6$ carbides, as opposed to the ductile fracture for non sensitised specimens.

The damaging effect of environment has been established out of sensitisation domain by comparing fracture surfaces after slow strain rate testing at 480°C either under secondary vacuum (fully ductile fracture) or oxidising environment (intergranular areas in the vicinity of a notch).

In conclusion :

1. The grain boundary cracking observed in bimetallic welds at around 600°C was successfully reproduced on 304H stainless steel using slow strain-rate testing under controlled environment,

2. This cracking is attributed to the combination of sensitisation and GB sliding,

3. At lower temperatures, intergranular damage is induced by oxidising environment,

4. High temperature slow strain-rate testing constitute a viable way to study interactions among several internal (sensitisation, grain boundary sliding) and external (environment) damaging factors.

DEPENDENCE OF DEVIATION ANGLE FROM Σ3(111) RELATION ON INTERGRANULAR FATIGUE CRACKING IN COPPER BICRYSTALS

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It has been established that GB-related phenomena such as the GB corrosion and the GB sliding show strong dependence on GB structure. One can expect that intergranular fatigue crack growth behavior also depends on the GB structure. Apart from the GB structure, the intergranular crack growth velocity has been reported to be influenced by slip system geometry of constituent grains [1]. Hence, both of the GB structure and the slip geometry should be taken into account in order to investigate intergranular fatigue crack growth. To diminish one of their effects, we paid attention to the Σ3(111) boundary that have large energy cusp in f.c.c. metals. Around this orientation relationship, the GB energy increases rapidly with increasing deviation angle from the Σ3(111) relation. Therefore, the slip geometry of constituent grains does not change significantly in spite of the rapid increasing of the GB energy. In this study, we prepared copper bicrystals that have several deviation angles from the Σ3(111) relation using the Bridgman method. The resultant deviation angles were less than 12°. Such deviation angles were determined with a computer-aided X-ray Laue method. The GBs in strip bicrystal specimens was located perpendicular to tensile axis. A notch was introduced along a single edge of the GB. Fatigue crack growth tests were carried out in air at room temperature in a servo-hydraulic machine.

Fatigue crack growth behavior depended significantly on the deviation angle from the Σ3(111) relation. In the specimens having the deviation angles less than 3°, no any intergranular crack growths were observed. The cracks propagated along one of several slip planes in zigzag ways. When the deviation angle increased up to about 4°, the fatigue cracks often propagated along the GBs. However at the deviation angles around 10°, the intragranular cracking became predominant again. The intragranular cracks propagated along well-developed slip bands.

The intergranular fatigue cracking in copper is reported to be related closely to a local GB damage due to ambient air [2]. The higher ratio of intergranular cracking at the deviation angle of 4° can be explained by the increasing local GB damage with increasing deviation angle. Near the deviation angle of 10°, the GB is no longer Σ3 boundary according to the Brandon's criterion, and has a higher GB energy than that of a smaller deviation angle. This seems to be inconsistent with the dominant intragranular cracking observed. This can be understood in terms of the development of a slip band. Since the tensile axes of the constituent grains become distant from <111> multiple-slip orientation with increasing deviation angle, the deformation should concentrate at one of slip systems in the specimen having a high deviation angle. This slip concentration at one slip system probably gives rise to preferential intragranular cracking along it. In conclusion, it can be suggested that the intergranular fatigue crack growth perpendicular to the tensile axis requires both of the high GB energy and the multiple slip of the constituent grains for the copper.

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BICRYSTAL STUDY ON A SIMPLE CRITERION FOR OCCURRENCE OF INTERGRANULAR FATIGUE CRACK PROPAGATION IN A FERRITIC STAINLESS STEEL

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An intragranular fatigue crack encountering a GB within a polycrystalline material has two possible further paths. One is a passage through the GB, and the other is a propagation along the GB. However, a criterion which determines the path is still unclear as far as we know. In the present study, the authors attempted to find one of the criteria using bicrystal compact tension (CT) specimens of a ferritic stainless steel. Especially, the relationships between preferential intragranular crack directions of constituent grains and occurrences of intergranular crack propagations were carefully investigated.

The bicrystal of an Fe-30%Cr alloy was produced by a diffusion bonding between oriented single crystals. We cut two bicrystal CT specimens (Bicrystals A and B) from the produced bicrystal. These specimens differed at an angle between the GB plane and a loading axis. The GB of Bicrystal A was perpendicular to the loading axis. On the other hand, the GB plane normal of Bicrystal B was inclined to the loading axis at about 22°. Notches in the specimens were introduced at one of the constituent grains.

In both bicrystal specimens, an intragranular fatigue crack propagated from the notch and encountered the GB during further cycling. The crack in Bicrystal A began to propagate along the GB as shown in Fig.1. On the other hand, the crack in Bicrystal B passed through the GB although the GBs of both bicrystals are same. Therefore, it is suggested that the GB structure is less important for the occurrence of the intergranular fatigue crack propagation at least under the present experimental condition. In the both constituent grains of Bicrystal A, the preferential growth directions of intragranular crack were oriented towards the GB, whereas that of one constituent grain in Bicrystal B was oriented so as to leave the GB. In the situation of Bicrystal A, the crack arrived at the GB can not leave the GB. This is because, if the crack passed through the GB temporarily, the passed crack should begin to propagate towards the GB again in both constituent grains. However, this propagation process is not operated in Bicrystal B. Accordingly, it can be proposed that the relation between the preferential crack directions of constituent grains is one of the criteria for the occurrence of the intergranular fatigue crack propagation.
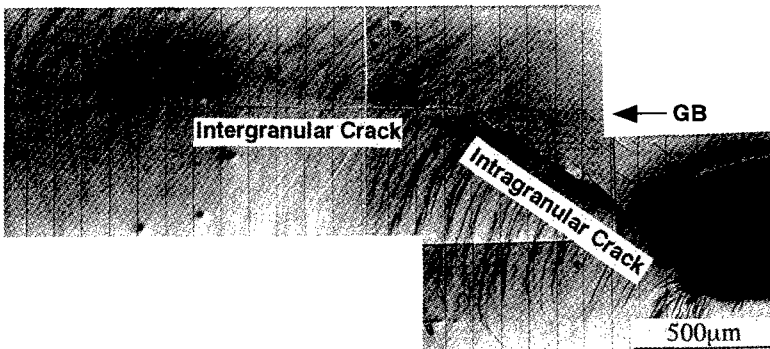
Fig.1 Optical photograph showing the intergranular fatigue crack observed at Bicrystal A.

CARBON (GRAPHITE) INTERFACES IN TRIBOLOGYCAL MATERIALS.

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Using new developments for identification of carbon phase state by Auger spectroscopy it was set up formation of multilevel undersurface carbon layers during friction in series of ceramics and steels. Self- generating carbon layers have thickness of 15 to 300 A and undergo amorphous carbon-graphite phase transformation during friction (under conditions of local shearing stresses). In this case Van der Waals bonding is oriental normally to slip direction of interacting bodies resulting in decrease of adhesion between surface oxide phases and base material. It results in peeling of oxide layers. This work sets up main physical processes leading to formation of undersurface carbon interfaces. The phenomenon of formation of such protective' carbon layers localizing fracture in this surface layers has also analogs in animate nature and may be described from synergetics positions.

IMAGE FORCE BETWEEN A DISLOCATION AND A GRAIN BOUNDARY IN HEXAGONAL MATERIALS

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Elastic interaction between a dislocation and a grain boudary is studied in the frame of anisotropic elasticity theory (1,2). Results have been obtained for cubic materials (3,4) and interphase boundaries (5).

The interaction energy is caculated for line dislocation parallel to the grain boudary plane and allows us to predict if the dislocation is repelled or attracted by the grain boudary. If we consider the distance between the dislocation and the the grain boundary we obtain the image force intensity exerted on the dislocation.

In the case of hexagonal materials, the results are analysed by taking account the dislocation character, the grain boundary crystallography and the material anisotropic coefficients.

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FATIGUE CRACK GROWTH ACROSS THE INTERPHASE BOUNDARIES IN TWO-PHASE BICRYSTALS

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Crystallographic fatigue cracks in polycrystals are microstructurally so sensitive that usually propagate in a complicated manner. Especially grain boundaries (GBs) have a considerable influence on transgranular fatigue crack growth. Some of bicrystal studies revealed that a retardation of crack growth at a GB was affected by various crystallographic characteristics, e.g. GB structures, slip behaviors near a crack tip, dislocation transfer across a GB, and so on. In the present study we examined the feature of crack growth across interphase boundaries (IBs) by using two-phase stainless steel bicrystals.

Two types of bicrystals, consisting of α- (Fe30Cr) and γ- (Fe11Cr19Ni) single crystals, were produced by a diffusion bonding method. In the bicrystal A, the elastic compatibility is satisfactorily fulfilled. The specimens notched in the α- or γ-phase are termed A-α or A-γ, respectively. Two specimens, B-α and B-γ, were made from the elastically incompatible bicrystal B. The IBs are located in the middle of the specimens. Fatigue crack propagation tests were performed at room temperature in air.

Figure 1 shows the fatigue crack growth rates. The a- and b-regions are so far from the IBs that are hardly affected by the IBs. In A-γ, B-α and B-γ, crack arrest at the IBs (c-region) occurs due to the prevention of dislocation emission from the crack tips. In the bicrystal B it may be hard for lattice dislocations to pass through the IB because of the crystallographic orientation. In the case of the bicrystal A crack arrest occurs only in A-γ. It is difficult for dislocations to transfer from the softer γ-phase to the harder α-phase, although the orientation of the bicrystal A is suitable for the primary dislocation transferring across the IB. In the bicrystal B, as the crack approaches to the IB, acceleration or deceleration of the crack growth takes place in B-α or B-γ, respectively (a'-region). However this effect is not observed in the bicrystal A which is elastically compatible. These features can be explained by the analytical calculation of the elastic incompatibility stresses in the bicrystal B. It was revealed that the behaviors of dislocation movement near the IBs and the stress fluctuation due to the incompatibility are the major factors controlling the complicated crack growth manner near the IBs.
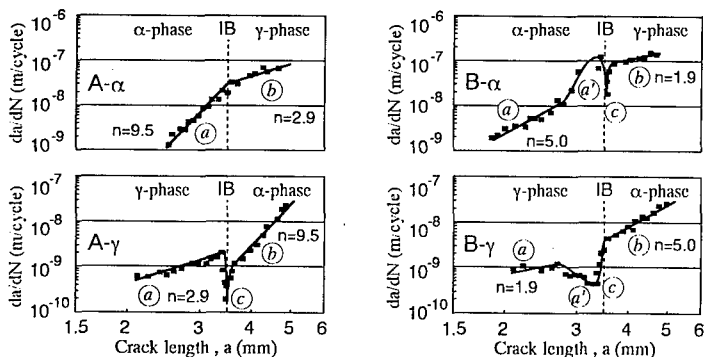
Fig.1. Change in the fatigue crack growth rates, da/dN, across the IBs of the four specimens tested. The slopes, n, of the log da/dN - log a plots far from the IBs have definite values and are intrinsic for the component single crystals in each bicrystal.

EFFECT OF GRAIN BOUNDARIES RECOVERY ON MICROCRYSTALLINE COPPER ELECTRIC RESISTANCE

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There are presented experimental investigations of electric resistance and electric resistance temperature dependence coefficient in microcrystalline copper containing different impurities: A) oxygen-free copper having the purity 99.99%; and B) technologically pure copper 99.98%. The subjects of inquiry had special microstructure with characteristic size of the structural elements ~100 nm. This structure was gained by the special methods of the intensive plastic deformation (ECAE-technology). (The samples were prepared by Dr. V.I.Kopylov.) Conductance was measured by the four-probe compensation method using the samples having a rectangular section 3x3x60 mm. The achieved accuracy of Cu resistance measurements is less than 1%. In the course of experiments the copper samples were being exposed to the consecutive annealing during the period of 60 minutes in the temperature range 70^0 to 220^0C. The measurement were carried out in the process of annealing, furthermore, after each hour-long annealing and quick cooling the measurements were carried out at room temperature and in liquid nitrogen. In parallel there were carried out the measurements of the hardness.

It is shown that in the process of isothermal annealing at the temperatures $T_i \geq 70^0$C it is observed the electric resistance decrease according to the law $\rho_i = \rho_{oi} \exp(-t/t_{oi})$ (i is the number of annealing). ρ_{oi} is the value of the resistance decrease after the i-th annealing, t_{oi} is the characteristic time of the resistance recovery depending on the temperature T_i according to the law $t_{oi} = t_o \exp(-Q_i/kT)$. Q_i is the recovery process activation energy during the i-th annealing. It was established in the work that the Q_i value is not stable, but increases together with the annealing number increase. In copper (A) the activation energy was changing depending on the value of $6kT_m$ at 70^0C up to the value of $9kT_m$ at 200^0C, in copper (B) from the value $5.5kT_m$ at 70^0C up to the value $8.5kT_m$ at 220^0C. In the work was built a theoretical model, in which the observed resistance changes are related to diffusion controlled processes of the grain boundary structure recovery, with the boundary transfer from non-equilibrium to the equilibrium state.

THE DYNAMIC PROPERTIES OF THE GRAIN BOUNDARY CORE AND ADJACENT LATTICE REGIONS IN POLYCRYSTALS OF 3d, 4d AND 5d METALS

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The dynamic properties of the grain boundary (GB) core and the two-dimensional lattice regions adjacent to the GB were studied using a new method [1], which combines the nuclear gamma resonance spectroscopy (NGRS) and the intercrystalline diffusion for delivery of the ^{57}Co atomic probe to polycrystals of the 4d and 5d metals. For the 4d (Rh, Pd) and 5d (Ta, W, Ir, Pt, Au) metals in the "intrinsic" range {subsequent to annealing at a temperature of $\cong (0.4 \div 0.7)T_{melt}$} the Debye temperature at the GB core (θ_1) is much lower than the Debye temperature in the bulk of these matrices (θ_2):

$$\theta_1 \cong 0.6\theta_2 .$$

This is a natural consequence of a low symmetry and a small atomic density at the GB core.

The dynamic properties of the GB core changed insignificantly when it was doped with residual impurities. The Debye temperature of the stationary region with a high concentration of point defects, which results from the segregation of residual impurities, dropped abruptly (compared to the volume Debye temperature) to the level of the Debye temperature at the GB core. This decrease in the Debye temperature is due to a high vacancy concentration, which is 10 orders of magnitude larger than the equilibrium concentration.

ORIGIN AND KINETICS OF GRAIN BOUNDARIES UNDER LOADING AND
RECRYSTALLIZATION

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The study of microplasticity in alkali halides, metals and
alloys, semiconductors and ceramics revealed the damping
character of dislocation (D) unpinning, motion and multi-
plication irrespective of test parameters.
Having covered the ultimate mean paths (UMP) determined by
test and sample history, the dislocations exposed to suc-
cessive acts of multiplication thus forming the slip lines
with a mean spacing of D [1]. It is the visible cross-
slip of D that causes the highest dislocation drag and re-
tardation. In the case of extremely small cross-slip heights
(which are invisible through the optical microscope) the
crucial role of stress-aided jogs in crystal work-hardening
for the motion and multiplication of individual D is con-
firmed by regular dislocation multiplications after their
start, motion and full stop.
The numerous sources of D in the matrix or due to D cross-
slip and climb are close to the first slip line.
They subsequently form the dislocation slip bands (SB),
walls and subgrains (mechanical poligonization),cell stru-
cture and low-angle grain boundaries (LAGB) under increa-
sing external stress. The rise of flow stress results in
the decrease of cell sizes and D spacings (increase of D
density) in slip bands, walls, LAGB, etc., as the hardeni-
ng of crystals is increased thus promoting grain sliding
and rotation and successively transforming the LAGB into
high-angle grain boundaries (HAGB) up to nanocrysalline,
amorphous structures and fracture.
The mobility of D, SB, L/HAGB depends on sample prehistory
and it is much lower than that of for lower density struc-
tures at the same stresses due to various damping prehisto-
ry of dislocation arrays. This explains the departures from
the Hall-Petch curve, the same kinetics of D, SB, L / HAGB.
The identity of mchanisms is confirmed by the same sequence
of microstructure transformations during forward (under lo-
ading) and reverse (recovery, recrystallization) motion of
D-arrays in different materials.
Again, the scaling behaviour of the reciprocal dependences
of grain sizes, individual mean dislocation paths and their
spacings in SB, walls, grain interior and L / HAGB, etc.
of heavily deformed crystals versus applied stress strongly
confirms the universality of dislocation mechanisms of all
deformation modes at atomic-, meso- and macroscopic scale
lengths for various crystal classes and tests.

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GRAIN BOUNDARY EFFECTS IN NANOCRYSTALLINE COPPER.

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The results of investigations of bulk nanostructured copper with a mean grain size of about 20 nm processed by severe plastic deformation via consolidation of powders after ball-milling are considered in the present work. Samples were fabricated by two steps: the first step - preliminary compacting in vacuum; the second step - severe plastic deformation on a Bridgmen anvil type device at 150°C.

The processed copper has a rather stable nanostructure and high strength properties. Heating of nanostructured copper to a temperature of 250°C does not results in a grain growth but significantly decreases the strength of the material. This effect is connected with grain boundary transformations at such temperature and a decrease of internal stresses in the nanostructured material. It was also revealed a strong influence of severe deformation temperature on grain growth and a decrease of a value of internal stresses. This is evidently attributed to the realization of recovery processes on grain boundaries and the onset of recrystallization processes already at low homological temperatures.

The obtained results show that a state of grain boundaries in the nanostructured copper is a very important parameter determining properties of nanostructured materials. A structural model was used for explanation of experimental data. According to this model a nanostructured material consists of ultra fine elastically distorted grains due to high density of grain boundary dislocations and disclinations, but during heating the recovery of these defects takes place.

RECOVERY MICROMECHANIZM IN
GRAIN BOUNDARIES OF STRAINED METALS

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In our works [1,2] there was proposed a semiphenomenological theory providing the possibility to describe the structure and characteristics of equilibrium and non-equilibrium grain boundaries (GB). In particular, there was proposed the model providing the possibility to calculate the changes of the grain boundary diffusive characteristics when lattice dislocations fall into the GB. There was shown that diffusion parameters in GB depend on the density of misfit orientational dislocations and their delocalization products accumulating in the boundaries. Accoding to the ideas developed in the works [1,2], after strain the defects are diffusively redistributed in the boundaries. During the annealing, the diffusion processes cause complete elimination of excessive defects as a consequence the recovery of equilibrium structure and characteristics takes place.

In the given work there are described the structure and characteristics of GB of a polycrystal being subjected to preliminary strain and there is developed the quantitative model providing the calculation of kinetics for the grain boundary structure change and their diffusive characteristics at various degrees of preliminary strain, annealing temperatures and material structure parameters.

There is shown that the recovery process and, correspondingly, the boundary diffusive characteristics depend on the initial grain size. When the grain size is fine the recovery process is limited by the misfit orientational dislocations "leaving" from the grain boundaries, and its kinetics has low dependence on the grain sizes. When the grain sizes are coarse the recovery kinetics is limited by the leaving of delocalized dislocation sliding components and its characteristics time depends strongly on the grain size.

There is presented in more detail the derived equations comparison with experimental data for polycrystalline aluminium recovery kinetics [3].

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THE FORMATION OF THE GRAIN BOUNDARY SRUCTURE, AGING BEHAVIOUR AND MECHANICAL PROPERTIES OF **Al-Zn-Mg-Cu** ALLOY WITH **Zr** AND **Sc** ADDITIONS

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Using methods of the transmition electron microscope, optical metallography, X-ray diffraction and mechanical testing methods, the influence of the small additions Sc and Zr on the stabilization of the deformation texture, kinetics of dynamic recrystallizations, phase transformations and mechanical properties of Al-Zn-Mg-Cu alloy after thermomechanical treatments, natural and artifical aging has been studied.

It was found that small additions of Zr and Sc affect on the formation of the grain boundaries and dislocation sell structure in deformed alloy. The character of the grain boundaries structure is connected with the density and distribution of the Al_3Sc, Al_3Zr and $Al_3(Sc_{1-x} Zr_x)$ dispersoids. Atoms of additions present in the solid solution stabilize the substructure.

The type of grain boundary structure and density of the dispersoids influence on the kinetics of the supersaturated solution decomposition: the precipitation of the metastable and stable phases $MgZn_2$ and their transformation.

The remaining of the texture of deformation, the increasing of the density of dispersoids and the features of nucleation and growth of the metastable and stable phases in the alloy Al-Zn-Mg-Cu with small additions, and particularly Sc and Zr are shown to increase the strength, while retaining a satisfactory ductility level.

Namely, the addition of Zr to an Al-Zn-Mg-Cu alloy already containing Sc somewhat decreases the strength properties of this alloy. This is due to the decreased precipitation density of the η' and η hardening phases. The increased plasticity of the alloy with Sc and Zr results mainly from the formation of more homogeneous (in size) grain structure.

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Study of the disclinations characteristics during FCC polycrystal annealings.

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The method of a defect structure of triple junctions (TJ) determination in polycrystals developed by us was applied for research of the evolution of this structure of a real polycrystalline material (transformer steel) during at plastic deformation [1]. The obtained results have confirmed an intuitive expected situation about the existing of defect TJ in an initial annealed real polycrystal material. These data also have revealed the increasing of quantity defect (i.e. containing junction disclinations (JD)) triple junctions and change of the quantitative characteristics of their Frank vectors.

In the present work the method was applied for the study of the changes of a defect structure of TJ during the annealing of polycrystalline Al. Specimens for experiment were cut from a sheet of 60% rolled steel and then were anealled. We concentrated on the analysis of two stages of annealing: 1) T=683 K, τ=0.5 h and 2) T=763 K, τ=1.2 h after the first stage. The same junctions after the first and the second annealing were analyzed. The matrices of orientations of the grains forming triple junctions were calculated from X-ray diffraction study of every grain. Then Frank vectors power were calculated according to the method mentioned above. The necessity of modifying of existing technique of calculation of Frank vectors power appeared during the work. It is connected with possible presence of special boundaries among the boundaries forming TJ. The additional operation connected with the mirror symmetry was introduced in calculation specially for such boundaries.

It was shown, that the average value of Frank vector power for the first and the second annealing is different. This value decreases in 1.5 times after the second anneal in comparison with the first. Standard deviation decreases in 1.75 times too. These facts point to leveling of average value of Frank vector power during of the annealings.

The possible mechanisms of the decreasing of plastic incompatibility during the annealings are discussed.

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GRAIN BOUNDARY CHARACTER DEPENDENCE OF
POTENTIAL BARRIER IN BARIUM TITANATE

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Positive temperature coefficient of resistivity (PTCR) in donor-doped barium titanate is a typical phenomenon caused by a potential barrier at grain boundaries. It was recently found by the present authors that the PTCR effect appears in random boundaries but not in small angle or low Σ boundaries. To describe more precisely the grain boundary character dependence of the PTCR effect, the resistance-temperature characteristics in donor-doped $BaTiO_3$ were examined using bicrystals prepared by solid-state sintering. Estimated PTCR effect differs from a grain boundary to boundary up to two-orders of magnitude depending on orientation relationship. A method based on the coincidence of reciprocal lattice points (CRLPs) analysis was employed to explain the change in the PTCR effect with the orientation relationship in random boundaries. The magnitude of the PTCR effect correlates well with the overlapped volumes of CRLPs, i.e., the effect becomes larger with an increase of the volumes. These results indicate that the potential barrier at a grain boundary is closely related to its character. This must be an example to demonstrate the usefulness of this method to analyze random boundaries

Effect of block boundaries on electrical conduction in mosaic crystals

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The experiments reveal an additional electron conductivity along block boundaries in mosaic single crystals $Hg_{1-x}Cd_xTe$ (MCT). One group of samples displays a two-dimensional block boundary conductivity, another group of more perfect crystals displays a bulk block boundary conductivity. Thus, the mosaic crystal has usual bulk p- or n-type conductivity and additional 2D or 3D electron conductivity along block boundaries. By the Shubnikov-de Haas oscillation analysis parameters of 2D and 3D channels have been determined: electron concentrations, cyclotron masses, relaxation times and mobilities. In the high magnetic field and at the helium temperature the bulk conductivity can be essentially reduced and in this case the current would mainly flow through a framework formed by randomly oriented block boundary channels. The resistance of such framework of 2D channels in the sample of 6x1.5x0.5 mm³ dimensions and with average block size of 200 mkm³ approximately equal 110 Ohm and it weakly depends on the temperature. This resistance is comparable with the bulk one in n-type sample – $R = 50$ Ohm. It is obvious that the framework resistance depends on an average block size. If it takes a lower value the resistance also decreases since the number of parallel connected channels become larger. For example, the resistance of framework composed by blocks of 100 mkm³ sizes will equal 39 Ohm.

THE ELECTRONIC PROPERTIES OF THE GRAIN BOUNDARY CORE IN METAL POLYCRYSTALS

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The electronic properties of the grain boundary (GB) core in 3d, 4d and 5d transition metals were studied using a new method, which combines the nuclear gamma resonance spectroscopy (NGRS) and the intercrystalline diffusion for delivery of the ^{57}Co atomic probe to polycrystals of the said metals [1]. In 4d and 5d transition metals the ^{57}Co atomic probe is a small-radius impurity and occupies interstitial sites in the GB core. For these matrices the information about the electron density in the GB core has been obtained only thanks to the shift of the Curie temperature $(T_C)_1$ of the GB core relative the Curie temperature $(T_C)_2$ of the adjacent lattice volumes. For all the 4d and 5d matrices

$$(T_C)_1 < (T_C)_2 , \qquad (1)$$

which suggests a low density of conduction electrons in the GB core of these matrices.

In chromium, iron and nickel the ^{57}Co atomic probe is not a small-radius impurity. Therefore it occupies interstitial sites in the GB core structure and does not experience volume changes in these positions. Different isomer shifts of the spectral components-1 of the radiation of ^{57}Co located in the GB core and the adjacent lattice sites reflect different densities of conduction s-electrons in the atomic probe localization regions. The density of conduction s-electrons (n_1) in the GB core is lower than the corresponding density (n_2) in the lattice regions adjacent to the GB in 3d matrices:

$$n_1 < n_2 . \qquad (2)$$

This fact is due to a low atomic density at the localization of the atomic probes in the GB core.

INTERFACIAL STRUCTURE AND ELECTRICAL PROPERTIES OF GRANULAR CERMET THICK-FILM RESISTORS

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Thick-film circuit are made by printin and firing pastes consisting of granular current conducting and dielectric phases on ceramic substrates.

The best operating characteristics are found in the resistance elements based on noble metals, in particular ruthenium compounds. Since cermet films are used on an increasing scale and the quality of electronic circuits has to be improved, the problem arises of devising cermet resistors with good operating characteristics not containing expensive metals. This problem cannot be solved without the use of modern methods of ivestigating the physicochemical interaction between the current conducting and the glass binding phases in the process of firing resistive composites, which affects the real microstructure and the electrophysical properties of resistive films. We investigated the interaction on the boundary by electron microprobe analisis with recording of the intensity of reflected electrons and of the intensity of the characteristic X-ray radiation of the elements composing the speciment on an X-ray microanalyser. As objects of the investigation we chose films containing hexaborides of rare-earth elements and of glass with cristallizing composition, and also films based on ruthenium oxide and glass. We also ivestigated transverse sections of model speciments consisting of alternative layers of current conducting phase and glass phase subjected to heat treatment by the regime of firing resistive pastes in vacuum and air. In resistive hexaboride films fired in air diffusion of chemical elements on the phase boundary is more substantial on account of oxidation of particles of the current conducting phase than diffusion in film fired in vacuum or in ruthenium films where there are no process of oxidation. This manifests itself on the working characteristics of the resistive films. The resistivity of films fired in vacuum is almost ten times lover, the resistance temperature coefficient and moisture resistance almost ten times poorer, then of those fired in air.

The performed studies have shown the differences in the structure of the zone of contact of current conducting and glass binding phases in film without noble metals and films on the base of ruthenium oxide as wall as a significance of the oxidation process of current-conducting phase in formation of high working characteristics of cermet resistors on the base of hexaborides of the rare-earth elements.

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ELECTRONIC STRUCTURE OF Σ5 [100] GRAIN BOUNDARY AND DOPING EFFECT IN α–FE

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ABSTRACT

Based on CSL model and MD relaxation, the atomic structure of Σ5 [100] grain boundary in α–Fe is obtained. By using the tight-binding bond recursion method, the electronic structure and boron doping effect on Σ5 [100] grain boundary in α–Fe are investigated. The calculated results indicate that the boron enhances the atomic interaction between the host atoms on grain boundary, as well as between the boron and host atoms. The calculation of the energy of impurity segregation to grain boundary shows that the boron has the tendency to segregate onto the grain boundary, and can improve the cohesion of grain boundary.

Electronic, optical and elastic properties calculations of the Zinc-Blende Nitrides GaN, AlN and BN

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Abstract

The isothermal elastic compliances, stiffnesses, and bulk moduli of a Tersof potential organised into an fcc crystal structure have been calculated as a function of testing temeprature. Tests conducted in pure shear were used to determine S_{44} and $C_{44} = G_{100}$, where 100 refers to crystallographic directions. Tests imposing axial elongation with fixed lateral dimensions established C_{11} and C_{12}. Axial deformation with zero lateral pressure (a tension test) was used to determinen S_{11}, S_{12}, E_{100} and v_{100}. This provided an independent set of results for comparison with the dilatation C_{11} and C_{12}. The bulk modulus K was obtained by independent triaxial tension testing. The moduli all decreased with increasing temeprature.

SIMULATION OF THE ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES

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There are a number of fundamental issues related to the electrical properties of grain boundaries and what controls the measured properties. Of these, two are of particular importance. One is whether there is any dependence of the charge density and current-voltage characteristics on the grain boundary misorientation. The other is what controls the value of the equilibrium charge density and whether this is set by all the available grain boundary states being filled or whether it is determined energetically. To address these questions, we have performed a series of Monte Carlo and molecular dynamics simulations, based on extending Read's ideas of the charge distribution along dislocations, to tilt grain boundaries. The simulations indicate that below a critical value of the grain boundary misorientation, the I-V characteristics are linear whereas above they are nonlinear. The degree of nonlinearity and the voltage onset of nonlinearity are both found to be dependent on the grain boundary misorientation. In addition, the equilibrium charge density increases monotonically with misorientation angle approaching a value given by a random distribution of charge in a sheet. The issue of whether the charge density is limited by the number of available states will be discussed in detail.

CORRELATION BETWEEN SUPERCONDUCTING TRANSPORT PROPERTIES AND GRAIN BOUNDARY MICROSTRUCTURE IN $YBa_2Cu_{3-x}O_y$ AND $YBa_2Cu_{3-x}O_y/Ag_x$ CERAMICS

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The superconducting properties (V-I, J_c-B and I_c-T) were correlated with a systematic characterization of the grain boundary microstructure, via TEM observation and local chemical analysis in STEM by EDX on $YBa_2Cu_{3-x}O_y$ (D samples) and $YBa_2Cu_{3-x}O_y/Ag_x$ (S samples) ($0 \leq x \leq 0.4$) ceramics prepared by the citrate gel process. In the attempt to substitute Ag for Cu, it turned out that the amount of silver incorporated into the lattice is always less than the nominal concentration x and its maximum value is limited to approximately 0.03 (for x=0.4). Ag was found to segregate mainly as small precipitates in boundaries and grains. The segregated Ag particles and nonsuperconducting phases appear to stop grain growth resulting in fine-grain microstructure for $x \geq 0.2$.

Micrograph of a clean boundary with Ag precipitates (arrows) in TEM for an S sample (x=0.4).

The TEM systematic characterization of grain boundaries showed an increase in proportion of clean boundaries in the Ag-doped samples compared to the Cu-deficient nondoped ones. Specific Ag precipitations of 2-5 nm in size on or near clean boundaries were found in S samples for x=0.4. This is the most likely reason for the improvement of the critical current density J_c in these samples by a factor of 3. The increase in J_c with x in D samples was observed and was probably associated with an increase in the proportion of faceted boundaries. $J_c(B)$ data showed that in samples of both type J_c is limited by weak links at grain boundaries. The measurements of $I_c(T)$ at temperatures close to T_c indicated SIS character of weak links in D and SNS character in S samples. It has been concluded from EDX analysis in STEM that the SNS behaviour of S samples is likely to result from a percolation path through 'clean' grain boundaries coated with an extremely thin film ($\cong 1$ nm).

SUPERCONDUCTIVITY IN CRYSTALS WITH VOIDS.

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One of the interesting results of material irradiation is appearance of vacancy and rare-gas voids in irradiated materials. Voids may appear either at irradiation of a metal by neutrons and ions, or as the result of technological processes of metal film preparation. Porous structure is the character feature of high-temperature ceramics. The size of voids depends mainly on material and temperature of the sample, dose and intensity of irradiation, subsequent thermal treatment. Void shape is nearly spherical, their radius may reach values up to 100 nm, typical concentration of voids equals to 10^{16} cm^{-3}, so the relative volume of voids can be as large as 10% or more. Thus, the summary area of void surface may significantly exceed the sample surface.

In definite cases the voids form a three-dimensional superlattice. The symmetry of voids superlattice coincides with the symmetry of material lattice, its lattice parameter equals from 2 to 7 void diameters. Voids forming a superlattice have nearly equal size. Such superlattice have been observed in different metals, including niobium and niobium alloys, which are II type superconductors.

Occurrence of voids changes the mechanical properties of a metal and causes some new superconducting properties in the region of magnetic fields larger and less than the second critical field H_{c2}.

- In strong magnetic field ($H \geq H_{c2}$) near voids a surface superconducting layer appears. The superconducting currents circulating around the voids in the magnetic field interval $H_{c2} < H < H_{c3}(R)$ give a diamagnetic contribution to magnetic susceptibility. At sufficiently high void concentration this diamagnetic contribution may be of several orders of magnitude larger than the intrinsic paramagnetic metal susceptibility.

- The porous superconductor in the presence of a strong magnetic field is a system of numerous regions with surface superconductivity which exists near voids. The superconductor with void superlattice has to exhibit Josephson effects caused by Cooper pairs tunneling between neighboring voids.

- Long-range strain field around voids can give rise to localized superconducting domains at temperatures T_c, higher than the bulk critical temperature T_{c0}. This effect is caused by the two facts: a large Laplacian pressure $p = -2\gamma/R$ is created around void surface, where γ is the coefficient of surface tension, R is the void radius, and the strong dependence of T_{c0} upon pressure. For voids with R=100 nm the pressure is $|p| \geq 10^8$ P. The strain-induced critical temperature T_c on voids is essentially enhanced in high-temperature superconductors due to small coherence length ξ, high T_{c0} and strong anisotropic pressure dependence of the T_{c0}.

- At $H < H_{c2}$ the critical current of superconductor increases because voids are pinning centers or captures for vortices. The interaction between voids and vortex lattice disturbs the equilibrium hexagonal configuration of vortex lattice, and in case of superconductor with void superlattice can occur the vortex structures with different symmetry.

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INFLUENCE OF THE INTERFACES ON THE OPTICAL AND MAGNETOOPTICAL PROPERTIES OF Fe/Al MULTILAYER SYSTEM

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Fe/Al multilayer structures (MLs) are insufficiently studied yet. They are characterized by existence of thick interfaces due to high mutual solubility of Fe and Al. In this report 6 samples of Fe/Al MLs with constant Fe layer thickness t_{Fe}=21 Å and varying t_{Al}=4-30 Å were investigated. Samples were fabricated by rf-sputtering. There were measured the effective optical conductivity spectra $\sigma_{eff}(\omega)$ in 0.25-7 mkm spectral range and equatorial Kerr effect (EKE). Applied in the framework of phenomenological theory analysis of data obtained showed the complicated structure of interfaces depending on t_{Al}. At $t_{Al} \leq 14$ Å all Al is in solution with Fe. Beginning from $t_{Al} > 14$ Å there is forming an interface layer of constant thickness representing nonmagnetic alloy with nearly equiatomic concentration. The interface layers at $t_{Al} < 14$ Å are heterogeneous in composition and in magnetic state. Absence of sharp interfaces is confirmed by coincidence of the numerical values of relaxation frequency γ for conduction electrons in Fe/Al MLs and in corresponding bulk alloys. The character of field dependence of EKE in MLs with t_{Al}=14,30 Å points to the formation of non-interacting magnetic clusters in nonmagnetic fraction of interfaces with quantity of Fe atoms equal to ~ 3800 and ~ 1500 respectively. The thickness dependence anomaly of $\sigma_{eff}(\omega)$ (1) and of EKE (2) (Fig.1) at t_{Al}=6 Å is found in wide spectral range. This anomaly correlates with the exchange coupling energy maximum (3), found earlier [1] in Fe/Al/Fe sandwiches.
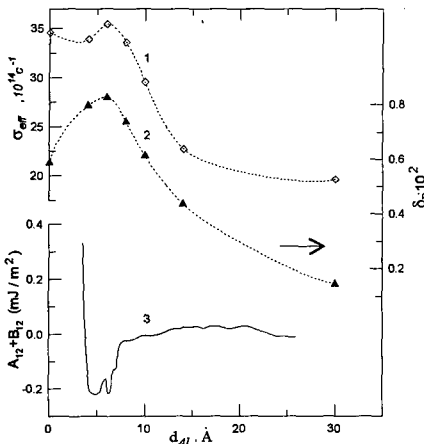
Fig.1
Dependence of $\sigma_{eff}(\omega)$ - 1, EKE - 2, and parameter $A_{12} + B_{12}$ - 3 on t_{Al}.

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PREDOMINANT ROLE OF THE INTERBOUNDARY PHENOMENA IN A MAGNETORESISTANCE OF POLYCRYSTALLINE MANGANITES $La_{1-x}Ca_xMnO_3$

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Intrinsic electroresistance of granulas, length of a contact layer between granulas and its influence on electro- and magnetoresistance in polycrystalline perovskite manganites $La_{1-x}Ca_xMnO_3$ (x = 0-0.3) are defined from researches on direct current (dc) of electroresistance ρ_0 and magnetoresistance MR from temperature and strength of an impulse electrical field, and also microwave electroresistance ρ_{MW} on 9 and 32 GHz in a temperature interval 77-300 K and in magnetic fields up to 1.6 (5) T.

The investigated samples had properties, typical for manganites: a maximum of ρ_0 and peak of a negative magnetoresistance MR (up to -0.5 in magnetic field H = 1.6 T) near Curie temperature. The temperature dependences of electroresistance on a microwave ρ_{MW} and on direct current ρ_0 are approximately identical. However the values of ρ_{MW} were on 2-3 orders less than the appropriate values of ρ_0 on direct current. The induction method of measurement of microwave electroresistance ρ_{MW} [1] in polycrystalls defines intrinsic electroresistance of granulas. It is shown, that for x = 0.3 the value ρ_{MW} is very small ($\cong$ 0.3-0.8 Ω cm at 77 K and 32 GHz) and approximately coincides with value of ρ_0 of a monocrystalline film $La_{0.7}Ca_{0.3}MnO_3$ [2]. These data show, that the values of ρ_0 and MR on direct current in the investigated polycrystalls are completely determined only by their intergranular properties.

It is revealed, that the Ohm law works up to an electric field strength $E \cong$ 3-20 V/cm. At higher values of E dc electroresistance decreases at the expense of increase of charge carriers concentration [3]:

$$\rho_0(E) = \rho_0(E = 0) \text{ x } \exp((-\sqrt{e^3 \cdot E / \varepsilon})/ kT),$$

where e is the electron charge, ε - dielectrical permeability. Changes of $\rho_0(E)$ are very large. For example, for x = 0.1 at 77 K the value of ρ_0 decreases 50 times in a field $E \cong$ 150 V/cm. The changes of $\rho_0(E)$ have repeating and unhysteresis character. At $E \cong$ 0.5 kV/cm switching of the samples in a more conducting state occurs.

The changes of $\rho_0(E)$ are stipulated by the fact that all voltage is enclosed in a thin intergranular contact layer and the effective field in it is great: $E_{eff} = E \cdot Lgr / Lc$, where Lgr is the size of granulas wich is about several microns. The length Lc of this layer which depends on temperature and magnetic field is evaluated: Lc =(1-3) $\cdot 10^3$ A$^\circ$. The researches of $\rho_0(E)$ and $\rho_0(T)$ in magnetic field show, that the decrease of ρ_0 with magnetic field and temperature occurs not due to the decrease of Lc, but owing to increase of volume of contacts between granulas.

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THE MAGNETIC PROPERTIES OF THE GRAIN BOUNDARY CORE AND ADJACENT LATTICE REGIONS IN POLYCRYSTALS OF 4d AND 5d METALS

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The magnetic properties of the grain boundary (GB) core and two-dimensional lattice regions adjacent to the GB were studied using a new method [1], which combines the nuclear gamma resonance spectroscopy (NGRS) and the intercrystalline diffusion for delivery of the ^{57}Co atomic probe to the metal polycrystals. Starting from a certain temperature, when the NGRS measurement temperature is decreased, the intensity of both paramagnetic components of the emission NGR spectra in 4d (Rh, Pd) and 5d (W, Ir, Pt, Au) metals does not rise but drops owing to the appearance of a line sextet. This sextet is caused by magnetic splitting of the nuclear levels of the atomic probes localized in the GB core and the lattice regions adjacent to the GB. The temperature-extended phase transition of the II kind reflects an inhomogeneous structure of the GB core.

In the "intrinsic" range the Curie temperature and the effective magnetic field at the atomic probe nucleus in the GB core are lower than their counterparts in lattice regions adjacent to the GB. This is explained by the fact that the density of conduction s-electrons in the GB core is lower than the electron density in the bulk of these matrices [2]. In the "impurity" range these characteristics of the two-dimensional regions diminish near the GB and become equal to the corresponding parameters of the GB core.

If Pd and Pt polycrystals are doped with a magnetoactive impurity (for example, iron), the Curie temperature of the localization regions of the occupied states increases and the critical temperature range is extended. The effective magnetic field at the atomic probe nucleus does not respond to the addition of magnetoactive impurities.

In niobium and tantalum lattices 3d atomic probes do not preserve their local magnetic moments. The local ferromagnetic ordering at the GB and in the two-dimensional lattice regions adjacent to the GB was not detected in these matrices.

In both regions of the atomic probe localization the magnetic ordering is realized thanks to the effect of "the vacancy enhancement of the local magnetic moment".

MAGNETIC PROPERTIES OF INTERPHASE BOUNDARIES IN CuO-Cu$_2$O-Cu SYSTEM

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Study of low-dimensional systems has gained widespread interest during recent year. Cupric monoxide fits into these materials. CuO having a monoclinic structure is the low-dimensional antiferromagnet with T_N=230K and the strong spin correlations of Cu^{2+} ions above T_N. There is much speculation that the observed anomalies of CuO properties are connected with the defects or CuO phase, having the NaCl structure. Attempts of creating many defects by doping and annealing have not been successful because of the narrow homogeneity region. The states in the contact layer between CuO and nonmagnetic compound can differ in their properties from bulk sample. Our interest is the investigation of interphase boundaries in systems on CuO base.

The heterophase systems CuO-Cu, CuO-Cu$_2$O, CuO-MgO were prepared and their magnetic properties were studied. The system CuO-Cu was made by mixture and annealing of CuO and Cu powders at 650°C in air to 3 min. The samples contained about 3% Cu$_2$O phase except the initial phases. The system CuO-Cu$_2$O was prepared by two ways-method of metal scattering and the hydrothermal method. The samples represent finely grained powder of CuO, Cu$_2$O and 3-5 % of metallic copper. The system CuO-MgO was prepared by annealing pellets pressed from CuO and MgO powder at 300°C in air for 40 h.

In the heterophase systems on CuO base paramagnetism of the form χ=C/T was revealed, which was absent without the thermotreatments. It is suggested that the reason of the paramagnetism is the imperfection of superficial CuO layer, intensified by the contact with the diamagnetic phase. The defects lead to frustration of antiferromagnetic interactions in the interphase boundaries and the occurrence of the paramagnetic Cu^{2+} ions.

THE INFLUENCE OF THE SEMI ISOLATING SUBSTRAET OF GaAs AND THE EPITAXIAL – SUBSTRAT INTERFACE LAYER AN THE MESFET GaAs PROPRIETIES

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The present contribution studies more deeply the increasing inclusions in the electronic circuits based on grid Schottky field components in the MESFET GaAs and their use in complex systems, leading to reliability, reproducibility and in addition to stability of conditions which can hardly be satisfied if the physics phenomena of the components are not well know. However, there is a deviation over a certain time of the dynamic and static parameters. Moreover, we can notice abnormal electric behaviour such as the dispersion of the electric abnormal tension of the conductance frequencies and the appearance of the hysteresis of the characteristic curves. It is quite clear that these phenomena make serious limitations to the users. Their origins are not well known and they can be explained by the surface phenomena at the interface or by the defects in the volume.

The interface phenomena have not yet been treated. In this paper the typical characteristics of the semi-isolators compensated by chromium are presented. The different physical phenomena related to the epitaxial layer and semi-isolating substrate interface experimentally showed the hysteresis and elbow effects as the outlet static characteristic curves as well as the influence of dispersion of the polarisation of the substrate and the dispersion of the conductivity in small signals of these systems are underlined.

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SIMULATION OF THE DIFFUSION PROCESS OF OXYGEN IN ZRO$_2$ GROWN ON ZR-2.5%NB

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Zr-2.5% Nb alloy Pressure tubes are used in the core of CANDU nuclear power reactors. During the operation, oxidation takes place. The oxide film, formed on the pressure tube surface is a good barrier against oxidation and hydrogen ingress. These processes have deleterious effect on the mechanical properties of the Zr-2.5% Nb alloy. It is known that the oxidation process in this alloy is controlled by inward diffusion of oxygen through the oxide grain boundaries.

In this paper, the oxide grain boundary character distributions and grain boundary densities are calculated based on simulated oxide texture and microstructure. The results show that the oxide grain boundary character distribution and grain boundary density is affected by the alfa-Zr grain boundaries and beta-Zr impurities. These complex microstructural characteristics affect the diffusion process of oxygen through the oxide. The predicted oxidation kinetics has been compared to the experimental data and good agreement has been obtained.

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INTERGRANULAR OXIDATION OF ALLOY 600 IN PWR ENVIRONMENTS

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Alloy 600 steam generator tubes can suffer intergranular stress corrosion cracking when exposed to Pressurised Water Reactor primary side coolant. The cracking can be inhibited or prevented by thermal stabilisation that generates chromium carbides on the grain boundaries. An alternative solution to primary water stress corrosion cracking (PWSCC) is to use alloy 690, which has a higher chromium content than alloy 600.

As yet, no definitive explanation of the mechanism of PWSCC has been agreed by the scientific community, although the internal oxidation mechanism proposed by Scott and Le Calvar and by Shen and Shewmon appears a strong candidate. The present paper presents metallographic evidence, via back scattered electron imaging and energy dispersive X-ray analysis, supporting an internal oxidation mechanism for the intergranular cracking of alloy 600 and alloy 690. The findings are supported by mechanical tests that indicate that grain boundaries containing higher oxygen and chromium than the matrix have been embrittled relative to other grain boundaries in the alloys.

Interfacial properties of α-SiC in contact with molten metals and alloys.

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Wetting experiments performed on α-SiC/Sn and α-SiC/Ni systems in an argon atmosphere with a 700vpm moisture content showed that wettability and reactivity at the ceramic-liquid metal interface is affected by the oxidation state of the α-SiC-surface. Under the specific experimental conditions thermochemical calculations have shown that the transition of the α-SiC-surface from a passive to an active oxidation state occurs at ~1600K. In the temperature range $505K \leq T \leq 1600K$ the wettability between α-SiC and liquid Sn is governed by the presence of passive SiO_2-layer overlaying the α-SiC-surface. At ~1600K the partial pressure of the reaction products CO and SiO, formed at the SiO_2/α-SiC interface, become high enough to overcome the ambient pressure. The removal of the gaseous products results in fragmentation of the passive SiO_2-layer and to an instability of the liquid Sn. Above 1600K the formation of a graphite layer is favoured on the α-SiC-surface, which results in higher contact angle values between α-SiC and liquid Sn. Between α-SiC and liquid Ni the fragmentation of the passive SiO_2-layer indicates the initiation of a reaction between the two components and the formation of a reaction zone, consisting of Ni-silicides and graphite. Further wetting experiments showed that the presence of Si at the ceramic-metal interface in the form of alloying element into both Sn or Ni decreases the temperature of transition from passive to active oxidation state of α-SiC-surface. With increasing Si-content the wettability between α-SiC and liquid Sn is improved. In the case of the α-SiC/liquid Ni system the presence of Si at the interface results in the suppression of the interfacial reaction. For a Si-content equal to 47.3at% no reaction takes place between α-SiC and liquid Ni while the system shows good wettability.

PENETRATION OF LIQUID Bi INTO Cu GRAIN BOUNDARIES

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Various physico-chemical processes can occur when a solid is in a liquid metal environment. In some cases, it results that the fracture stress of the material can be reduced. The processes by which the mechanical properties can be severely degraded are usually termed liquid metal embrittlement. This phenomenon has been recognized for a long time but the nature of the interactions which promote crack extension remains unclear. In particular, the mechanisms by which a liquid metal penetrates the grain boundaries of a solid metal are not well understood. To investigate these mechanisms, the penetration behaviour of liquid bismuth into copper grain boundaries has been studied.

The experimental work has been carried out on Cu polycrystals and bicrystals (40° <100> symmetrical tilt boundary) immersed in the liquid at various temperatures (ranging from 600 to 350°C) and for different times (ranging from several hours to a few minutes). The composition of the melt was either pure Bi or adjusted to the liquidus temperature given by the phase diagram. After the immersion, some samples were prepared to be examined by scanning electron microscopy in order to study the Bi penetration. Some samples were fractured for a surface examination. Then, samples were stressed so that cracks appear and the kinetics of penetration was studied by measuring the crack length as a function of immersion time. A surface analysis by Auger spectrometry was also performed.

This paper reports the results related to the phenomena which occur at the grain boundaries in the Cu_{solid}-Bi_{liquid} system. It is found that the results depend on various parameters (condition of saturation of the bath, grain boundary orientation...). At first, in some cases, very deep channels were observed at the grain boundary intersection with the solid-liquid interface. Such grooves indicate a high and rapid penetration of bismuth along the boundaries. Then, the samples were found to fail by an intergranular mode and brittle cracks were observed. Finally, the kinetics of the Bi penetration was determined.

MEASUREMENT OF GRAIN BOUNDARY CORROSION CURRENT ON COPPER [110]-TILT BICRYSTALS BY SCANNING VIBRATING ELECTRODE TECHNIQUE

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Localized corrosion often occurs at a grain boundary since the corrosion potential at the grain boundary differs from that at the grain interior. This potential difference is often due to chemical inhomogeneity such as precipitation and impurity segregation at the grain boundary. However, structural irregularity of the grain boundary itself intrinsically controls the grain boundary chemistry, and thus the intergranular corrosion at chemically clean grain boundary in high purity metals still appeals to the interest of electochemists and solid-state physicists. In this paper, intergranular corrosion at [110]-tilt boundaries of high purity copper bicrystals were investigated in an acid solution using scanning vibrating electrode technique (SVET).

Bicrystals with symmetrical [110]-tilt grain boundaries of 99.99998%-purity copper were grown from seed crystals using the Bridgman method under vacuum. Crystallographic orientations of the bicrystals determined by examining back-reflection X-ray Laue patterns showed that the bicrystals were characterized by the CSL orientation relationships. The bicrystals were immersed in a modified Livingston's dislocation etchant at $303 \pm 2K$, and then the grain boundary corrosion currents were measured by the SVET. The probe of the SVET was W wire with diameter of 0.1mm.

Anodic current peaks were observed at the grain boundaries. On the other hand, cathodic current peaks were measured at small regions in the grain interiors quite adjacent to the grain boundaries. Laser micrographs obtained at the grain boundaries showed that 10 μ m-wide terraced embankments parallel to the grain boundaries are present extremely close to the V-shaped corrosion grooves formed by the intergranular corrosion. This means that cathodic regions are localized adjacent to the grain boundaries which were preferentially dissolved anodic sites. These results could interpret the previously unexplained observation[1] that the grain boundary groove grows deeper but not wider with time thus resultantly crevice-like corrosion groove forms. The present SVET experiments revealed a kind of galvanic anode effect of the grain boundaries which protects grain interiors next to the grain boundaries.

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DYNAMIC EMBRITTLEMENT OF A Ni-BASED ALLOY BY OXYGEN

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It has long been known that low-cycle fatigue cracking of nickel-based alloys at elevated temperatures becomes time dependent and that the cracking mode becomes intergranular when the environment is switched from vacuum to air or water vapor. We have studied the cracking of IN718 under static loads in air and at various partial pressures of oxygen and have found that it undergoes oxygen-induced dynamic embrittlement in the same way as in steels with surface-adsorbed sulfur and bronze with surface-adsorbed tin. When the oxygen supply at the surface is plentiful, the intergranular fracture surface exhibits decohesion with no apparent plasticity, which is consistent with stress-induced oxygen penetration on the nanometer scale ahead of a sharp crack, the cracking rate being diffusion controlled. At low partial pressures of oxygen, they cracking is intermittent, and the rate is presumably controlled by the rate of surface delivery, with oxygen diffusing into the region of maximum stress ahead of the crack. Based on observations in other alloy systems, we would suggest that this kind of cracking can be inhibited by anything that retards the diffusion of oxygen along grain boundaries.

ANTIMONY, TIN AND SELENIUM SURFACE SEGREGATION ON NON ORIENTED ELECTRICAL STEEL SHEET

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Non-oriented silicon steel sheets are the base material for the generation and the transformation of electric power. Low loss, high permeability non-oriented steel sheets are needed for efficient power generation and transformation, which is relevant concerning energy conservation and environmental aspects. To attain the full potential of this important material the recrystallization texture must be improved.

It has been found that small additions of certain elements (Sb, Sn,Se,Te), and especially antimony, affect through the surface segregation the recrystallization, lead to an increase of the number of ferrite grains with favourable magnetic space orientation in the sheet plane and improve electrical properties [1-4].

The effect of surface active elements i.e. antimony, tin and selenium additions (from 0.05 to 0.1 wt. % of Sb, Sn or Se) into silicon steel, on the improvement of electrical properties of non-oriented steel sheet was investigated. Measurements of surface segregation of Sb, Sn and Se was made under UHV conditions in the temperature range from 450 to 900°C using high resolution AES and TDS. A maximum equilibrium of antimony, tin and selenium surface segregation was determined at 700 °C . At higher temperatures T> 800°C desorption of antimony from the surface was measured while a tin surface segregation decrease but there was no tin desorption, the phenomena was explained with a higher solubility of tin in ferrite.

The grain boundary segregation of antimony and selenium was negligible and we can conclude that the texture formation, rich in (100) grains results from orientation dependent surface segregation of Sb and or Se [5-7].

Sn grain boundary segregated layer was estimated to 0.2 of a monolayer. The surface Sb as well as Sn segregation causes differences in surface energies and stability of different grains. Controlled surface segregations promotes the selective grain growth and improves the electrical properties of non oriented steel sheet.

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GRAIN BOUNDARIES IN MONOLAYER LIQUID FOAMS

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A new technique is described with which grain boundaries are formed between two monolayer foam "crystals" of regular hexagonal bubbles. The misorientation θ between two "crystals" is varied continuously from 0° to the maximum angle (30°) and the topological defects in the transition zone are identificed. These are bubbles with 5 and 7 sides (exclusively), in equal numbers. At low θ the defects are in pairs (dislocations) but at large θ the structure consists of individual disclination defects.

With the device used to form the boundaries it is also possible to deform the samples in tension/compression along a direction roughly perpendicular to the boundary. The effect of deformation on the arrangement of the topological defects at fixed θ was studied.

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RADIATION-INDUCED GRAIN BOUNDARY SEGREGATION IN AUSTENITIC STAINLESS STEELS

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Radiation-induced segregation (RIS) at grain boundaries has received considerable interest over the last decade because of its potential influence on the irradiation-assisted stress corrosion cracking (IASCC) of Fe- and Ni-base stainless alloys. Segregation mechanisms are driven by the production of defects in the grain matrix and their subsequent migration to grain boundary sinks. Local composition changes occur because specific chemical species interact differently with these defect flows. Inverse-Kirkendal (IK) segregation results from differences in vacancy diffusion rates for alloy elements. Faster diffusing elements, such as Cr and Fe, become depleted at grain boundaries, whereas slower diffusing elements, such as Ni, become enriched. Minor alloying and impurity elements also segregate due to differential binding of solute atoms to self-interstitials. Species that have strong binding, such as Si, become enriched at grain boundaries after irradiation.

This paper evaluates the current ability to measure and model RIS in Fe-Ni-Cr stainless alloys. The nanometer-scale composition profiles of interest have been most effectively characterized using analytical transmission electron microscopy (ATEM) and scanning Auger microscopy (SAM). Extensive grain boundary composition measurements on materials irradiated by charged particles or neutrons have demonstrated boundary-to-boundary anisotropy, variability along individual boundaries, and the strong effect of irradiation temperature and dose on the interfacial composition. Temperature and dose effects on RIS have been systematically studied using charged-particle irradiations of controlled purity alloys. Grain boundary composition of Ni and Si increased, while Cr and Fe decreased, with increasing irradiation temperature (constant dose) or dose (constant temperature). No significant enrichment of phosphorus or sulfur is detected even in doped alloys consistent with results on neutron-irradiated steels. The extensive ion-irradiation data base is employed to quantify predictions of both temperature and dose effects. Model predictions are then assessed versus ATEM and SAM measurements on neutron-irradiated stainless steels. Good agreement is documented between measured Fe, Ni and Cr segregation and IK predictions. This is not the case for RIS of minor elements like Si and P, where the interstitial binding model sharply overpredicts measured grain boundary enrichment. Mechanisms limiting RIS are discussed, and model modifications made, to help quantify predictions. Results of this study are used to determine RIS development in light-water-reactor core components and if grain boundary composition changes play a primary role in IASCC susceptibility.

A STUDY OF MIXED DUMBBELL MIGRATION IN CONCENTRATED Fe-Cr ALLOYS

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The direct observation of segregation effects in irradiated materials often gives only the final result of irradiation-induced processes, both vacancy-induced and interstitial-induced unseparated, without specific details of defect interaction with material components. The knowledge of the details is desirable especially when analysing segregation phenomena in a row of concentrated alloys with varying content of one component. BCC Fe-Cr alloys are namely the case since they are used as a basis for many structural materials in a wide range of Cr concentration and known as highly resistive to void swelling.

According to positron annihilation studies [1] the onset of vacancy long-range migration is almost not affected by Cr alloying (near 220 K, like in pure iron), so alloying can change only the features of an interstitial atom (IA) migration. Two distinct cases of an IA migration in concentrated binary alloys should be considered: either mobile mixed dumbbells are formed in the alloys or not. To detect the mobile mixed dumbbell formation we have used the phenomenon of short-range ordering (SRO), typical for all concentrated alloys. The SRO is a diffusion-controlled phenomenon and can take place only if Fe and Cr atoms in the Fe-Cr alloy can exchange their positions during defect migration. In case of the IA migration such exchange is possible only if mixed dumbbell migration and dissociation takes place.

The variations in the SRO degree during the IA migration are easily seen by means of residual resistivity (RR) and their contribution to the RR recovery in the course of post-irradiation annealing has been detected through comparison of RR recovery in samples of the same alloy electron irradiated to different doses at low temperatures. Rather unusual alternative sign of dose effect was found in the alloys at different annealing temperatures probably pointing to an interchage of the SRO sign over different temperature intervals.

In all studied Fe-Cr alloys (2-16 at.% Cr) the manifestation of the SRO was found starting from 90-100 K up to the onset of the vacancy long-range migration. This evidences on a formation of highly mobile mixed dumbbells, what can be expected in the BCC structure where mixed dumbbells can migrate via the same mechanism as the self-IAs in contrast to the FCC systems [2]. The total RR recovery over investigated temperature interval of the Stage I (90-135 K) is suppressed with increasing Cr content while the SRO manifestation is not. Such features of the IA behaviour are compatible with the IA configuration trapping mechanism, found earlier in Ag-Zn concentrated alloys [3]. Such trapping may be strengthened with increasing Cr content and, if operative at high temperatures, can suppress the Cr atom migration via the interstitial mechanism [4], in spite of mobile mixed dumbbell existence in the Fe-Cr system.

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ON THE SEGREGATION REDISTRIBUTION IN THE Fe-Ni AUSTENITE UNDER THERMAL AND RADIATION EFFECTS

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Today a new process is finding ever increasing favor for modification of the structure and properties of alloys through a segregation redistribution of the solid solution under radiation or thermal effect. It was shown [1] that this redistribution in Fe-Ni alloys may take place in the high-temperature region: the dome of nickel redistribution at 450-700 °C was introduced in the Fe-Ni equilibrium diagram. However, up to the present there has been no unambiguous answer if this region is caused by an ordinary thermal effect or is due to the radiation-induced segregation of nickel at dislocation loops or helium-containing clusters. By this study we have attempted to determine more precisely the Fe-Ni equilibrium diagram in the austenitic range at 450-700 °C proceeding not from the nickel redistribution in the γ-phase during long-time annealings but, oppositely, from the analysis of the elimination kinetics of the preset microscalar redistribution of the γ-phase in this temperature region. The redistribution in the Fe alloys with 32.5 and 34 mass % Ni into low-. and high-nickel components was realized in the low-temperature two-phase $\alpha+\gamma$ range (300-450 °C) during the reverse martensitic $\alpha \rightarrow \gamma$ transformation under very slow heating (0.2-0.3 deg./min.). The Mössbauer analysis showed that FCC plates were enriched up to 40% in nickel, while the surrounding BCC martensite was simultaneously depleted in nickel to $\leq$25%. The similar microconcentration nonuniformity was observed in the single-phase FCC structure when the thin-plate $\alpha+\gamma$ mixture transformed to the globular austenite during fast heating to 650 °C. Annealing of the concentrationally nonuniform austenite for about 24 hours at 520 °C eliminates the nickel redistribution. This fact. calls into question the existence of the thermal redistribution dome in the high-temperature single-phase γ range of the Fe-Ni equilibrium diagram.

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THE EFFECT OF INTERPHASE BOUNDARIES ON THE RADIATION RESISTIVITY OF NEW LOW-ACTIVATED AND CHROMIUM-NICKEL STAINLESS STEELS.

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The study deals with the evolution of the phase composition and vacancy voids in new reactor stainless steels over the temperature interval of 500 to 700 °C under irradiation with krypton ions up to high damaging doses (200 dpa). The investigations were performed directly in an electron microscope while the foils were irradiated with 1.5-MeV Kr^+ ions from a special accelerator.

Subject to irradiation were both austenitic steels type 16Cr-15Ni-3Mo-1Ti with radiation-induced intermetallic aging and steels types 16Cr-9Ni-3Mo and 13Cr-7Mn-2W possessing a purposefully produced fine-plate austenitic-martensitic structure and a large number of point defect sinks in the form of dislocations and α/γ phase boundaries.

It is shown that when the 16Cr-15Ni-3Mo-1Ti austenitic steel undergoes irradiation, dislocations are pinned by disperse particles, this contributing, along with homogeneous precipitation of Ni_3Ti intermetallics, to a considerable delay of the vacancy swelling compared to the same process in close-composition non-aging steels (16Cr-15Ni-3Mo). It was found that under a high-dose irradiation an equilibrium redistribution of the dopants (chromium) takes place in the steel at 600-650 °C, an interval which was previously assumed to be a single-phase austenitic region.

It is shown that a lamellar austenitic-martensitic structure, which comprises alternating thin laths of martensite and reversed austenite, swells little if at all as distinct to a coarse-grain polyhedral austenite of the same composition.

THE REDISTRIBUTION OF ATOMS DURING RADIATION-INDUCED MARTENSITIC TRANSFORMATIONS IN Fe-Ni ALLOYS

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Depending on the initial state of the alloys prior to strain, different directions of radiation-induced martensitic transformations – the FCC (gamma) phase produced by water-quenching after a high-temperature (1300 K) annealing or the BCC (alpha) phase produced by quenching in the liquid nitrogen – were found in the Fe-(31-32%)Ni alloys, which are a heterogeneous mixture of the FCC and BCC phases formed under shear pressure.

A high-pressure (8 GPa) shear strain increases the temperature of the forward FCC→BCC transformation and reduces the temperature of the reverse BCC→FCC transformation. Subject to this treatment, binary Fe-Ni alloys develop a two-phase alpha/gamma structure having a nonequilibrium weight ratio of the phases and loaded with elastic stresses.

Large elastic distortions accumulated during strain affect the direction of the phase transformations under a low-temperature (400-500 K) irradiation by high-energy electrons (E = 5.5 MeV, the dose F = $5 \times 10^{18}/cm^{-2}$). Radiation point defects stimulate relaxation of elastic stresses after a strong plastic deformation. As a result, the alpha+gamma composition is stabilized. The NGR spectroscopic analysis showed that the amount of the strain-induced phase decreased under the low-temperature electron irradiation and the atoms redistributed in the austenitic (gamma) phase. The redistribution of atoms near the alpha/gamma phase boundaries, which act as sinks for radiation vacancies and interstitials, is an additional thermodynamic impetus to development of alpha↔gamma transformations under irradiation. The radiation-induced BCC-FCC transformations in binary Fe-Ni alloys have been classified as martensitic transformations controlled by diffusion transfer of atoms.

MODELING THE RADIATION-INDUCED SEGREGATION OF UNDERSIZED SOLUTES NEAR GRAIN BOUNDARIES.

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The system of diffusion equations is formulated for component and point defect concentrations near grain boundary (GB) in irradiated ternary alloy, in which a minor component has a small atomic size. A possibility of GB migration is taken into account. It is assumed that undersized atoms migrate via interstitial mechanism as nearly stable mixed dumbbells. Radiation-induced segregation (RIS) of Si near motionless and moving GBs in Fe-Cr-Ni alloys is modeled by numerical solving the system of equations. The results are compared with experimental data available and with analytical expressions obtained earlier for component profiles around point defect sinks. It is shown, that formation of strongly bounded mixed dumbbells consisting of undersized alloying atoms and major component atoms can significantly enhance RIS of alloying elements around point defect sinks.

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CALCULATION OF RADIATION-INDUCED SEGREGATION NEAR MOVING GRAIN BOUNDARIES IN Fe-Cr-Ni ALLOYS.

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A method of calculation of radiation-induced segregation (RIS) and segregation-induced bias (SIB) for a moving plane sink in ternary substitutional alloys is suggested. It is assumed that thermal equilibrium concentrations are maintained at the moving plane, which is transparent to component fluxes. Of various drift forces on point defects arising due to RIS, only Kirkendall ones are taken into account. RIS and SIB for a moving plane grain boundary in Fe-Cr-Ni alloys are calculated. It is shown that dose dependence of SIB is nonmonotonic with a maximum at some intermediate dose depending on sink velocity. Steady-state values of SIB decrease significantly with increasing sink velocity and can be negligible at the velocities corresponding to ones of climbing dislocations at high swelling rate. An opposite limiting case of a moving plane nontransparent for component fluxes is considered. In this case an additional velocity appears due to Kirkendall effect on moving sink. This additional velocity is calculated in dependence on initial one. The predictions of both models are compared with experimental data available on RIS near moving grain boundaries in irradiated Fe-Cr-Ni alloys.

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INTERFACES IN RAPIDLY SOLIDIFIED ZIRCONIA-YTTRIA

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Rapidly spread and solidified molten droplets (splats) are basic building units of thermal-sprayed coatings. Various interfaces of zirconia-yttria (7%wt. yttria) single splats produced by atmospheric plasma-spraying have been investigated using cross-sectional high-resolution transmission electron microscopy. The interface between the substrate and the rapidly solidified splats is of utmost importance for the adhesion of coatings formed by this method. Melting and resolidification of the substrate are commonly observed as a result of rapid heat transfer from molten droplets. Possible formation of a thin interfacial layer between the substrate and the splat depends on the substrate material and its temperature. The interfacial layer may be either nanocrystalline or amorphous and is composed of both the substrate and splat material. "Bond coat" layers of NiCrAlY prevent the formation this interfacial layer.

Rapid solidification, together with good contact at the splat/substrate interface favors copious nucleation followed by growth of narrow columnar grains through the splat thickness starting at the substrate interface. Possible relationships between resolidified grains in the substrate and columnar grains in the coating are being investigated. The zirconia grain width ranges from 30 to 100 nm, while their length is determined by the thickness of the solidified splat and is typically on the order of microns. Boundaries between the columnar grains are clean, without any second phases or amorphous regions, unlike the boundaries in conventionally prepared ceramic materials, although they are occasionally cracked. Certain misorientations between individual columnar grains are present more often than others, although the reasons for this are not yet entirely clear. Growth of narrow columnar grains in splats solidifying on previous splats is very often epitaxial.

MICROSTRUCTURE OF EPITAXIAL (InGa)As ON A BOROSILICATE GLASS-BONDED COMPLIANT SUBSTRATE

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The lack of substrate materials with suitably matched lattice parameters remains a central issue in nitride semiconductor technology. Early results of a new approach to fabrication of a universal compliant substrate for epitaxial growth of high-quality nitride and other materials with large lattice mismatches to available substrate materials will be presented. The compliant substrate consists of an ~10 nm thick GaAs template layer that is bonded to a layer of borosilicate glass that previously has been deposited on a handle wafer by chemical vapor deposition. The glass composition is controlled so that it can flow viscously to accommodate strain at the temperatures used for growth of the epitaxial layer on thin GaAs template. To test the approach, a 4μm thick film of $(In_{0.45}Ga_{0.55})As$ (3.1 % mismatch with GaAs) was deposited on the compliant substrate. Orientation Imaging Microscopy (OIM) showed that the large $(In_{0.45}Ga_{0.55})As$ islands that grew on the compliant substrate were all in the same crystallographic orientation over the 2 mm long section examined, thereby demonstrating that epitaxy was achieved between the template and the film. OIM showed variations of less than 0.5° in the handle wafer. The orientation variation within the $(In_{0.45}Ga_{0.55})As$ film was 0.5-1°. TEM investigations of the defect structure of the films are underway. The defect structures observed in the films grown on the compliant substrate will be compared to those in films grown on bulk GaAs under the same deposition conditions. This work is supported by the ONR MURI on Compliant Substrates at the University of Wisconsin-Madison. Partial support for electron microscopy facilities is provided by the NSF MRSEC on Nanostructured Materials at the University of Wisconsin-Madison.

COMPARATIVE STUDY OF SEVERAL TOTAL ENERGY TIGHT-BINDING MODELISATIONS APPLIED TO STACKING FAULT ENERGIES IN SILICON.

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One shortcoming of the otherwise rather good semi phenomenological potentials like Stillinger-Weber and Tersoff potentials is that they give zero interfacial energies for (111) stacking faults in silicon (or any cubic diamond material). Quantum total energy tight binding modelisations of semiconductors do not have this restriction and are yet less heavy than fully *ab initio* calculations. We present here a comparative study of stacking faults calculations via several total energy tight binding modelisations of silicon: Chadi, Goodwin-Skinner-Pettifor, Sawada-Kohyama and Torrent-Hardouin Duparc. Structural minimisation is taken into account. Accurate energies are calculated as sums of eigenvalues in the reciprocal space while minimisations are performed via the Li-Nunes-Vanderbilt N-order density matrix scheme. Möbius boundary conditions are used whenever useful.

THE GRAIN STRUCTURE OF VACUUM ARC DEPOSITED
Co THIN FILMS

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The Co coatings were produced with the aid of the vacuum arc deposition and studied by transmission electron microscopy and electron back-scattering diffraction (EBSD). At large distances from the cathode, the deposition rate R_d of Co is comparable with R_d values for vacuum arc deposited Mo and Ni–Ti alloys and exceeds the R_d values obtained in magnetron sputter deposition. The vacuum arc deposited coatings are formed from the multiply charged ion flux and microparticles. The Co film formed from ions consists of a hexagonal close-packed phase and possesses a dense microstructure with uniform and extremely small grains (5 nm). The Co microparticles solidified after collision of liquid Co droplets with the substrate, have a metastable face-centered cubic structure. Their grain structure was studied by EBSD. The EBSD method allowed to resolve the grains having a size about 100 nm in the largest droplets. These droplets are rather flat and have a thickness below 1 μm. The grain structure of such droplets contains thin circular grains. The triple junctions are practically absent. Such droplets can be used as a good object for studies of the mobility of individual grain boundaries in face-centered cubic Co.

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IMPURITY SEGREGATION AND INTERGRANULAR FRACTURES IN CONTINUOUSLY CAST PRODUCTS

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The segregation processes in steels are occuring during all steps of processing from crystallisation to final product. During the continuous casting of steel slabs, impurity segregation can occur during solidification or in solid state, too. The effect of impurity segregation, mostly Sn on the structure and the morphology of fracture surfaces is investigated for samples of the surface zone of continuously cast slabs after impact bending test. Low carbon steel with initial low level of impurities and same steel enriched by 0,134%Sn continuously casted on curve type plant were analysed. The results show, in the slab enriched by Sn, there was high enrichment of the subsurface region measured up to 0,42% Sn in the depth of approximately 6mm, Fig.1. Small surface enrichment by Sn was shown for the material with low mean concentration of Sn. The distance, where the Sn concentration peak occur, approximately corresponds to the onset of columnar dendrite zone. It was shown that Sn affected failure in surface zone of slabs by formation of the intergranular fracture due to segregation of Sn and other present impurities on austenite grain boundaries. The intergranular fractures were smooth or with dimple morphology. The large intergranular facets are mostly initiated on interface of fine grained surface skin with the zone of columnar dendrites where the concentration maximum of tin and other impurities exists. The observed macroscopic changes in impurity content at the slab cross-section are the result of microsegregation. They work as dendritic segregation and the solid state segregation. The crystallisation at the continuous casting is much faster than it was with the old casting methods. Due to this a larger portion of impurities is trapped in solid solution. It would be the impurities with a higher coefficient of equilibrium, as is the analysed Sn and Sb [1]. Moreover, their the diffusion coeficient is large [2]. These elements, since they are surface active, can consequently segregate to the austenite grain boundaries or to the free surfaces of the slab, or to the interface of very different structure zones such as the interfaces between fine-grained surface skin and the zone of columnar dendrites. Such segregation can occur at the change of cooling rate, as is the movement of the slab into the secondary cooling segment. Therefore, such microsegregation in solid solution is nonequilibrium and is based on segregation induced by faster cooling and stress-induced segregation due to some deformation of solid phase.
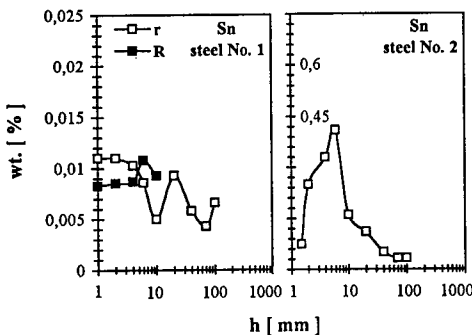
[1] Barthel,J. et al.: Kristallisation aus Schmelzen. Leipzig, VEB Deutscher Verlag für grundstoffindustrie 1983, 344 [2] Oikawa,H.: Tetsu to Hagané 68,1982,148
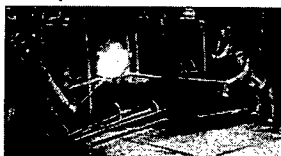
COST

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1830 *In VÍTKOVICE the iron was produced in a puddling furnace fired with hard coal for the first time in Europe except England.*

1847 *VÍTKOVICE Iron Works brought railway to the town of Ostrava.*

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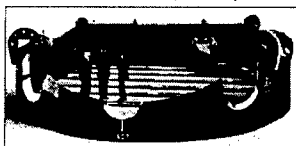
1928 *VÍTKOVICE Mining and Metallurgical Corporation was the biggest company in Czechoslovakia with agencies in sixty countries of the world.*

1952 *VÍTKOVICE built up steel making company Nová huť Ostrava with complete metallurgical equipment.*
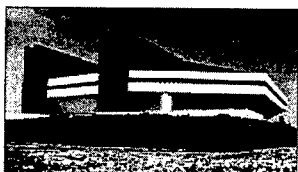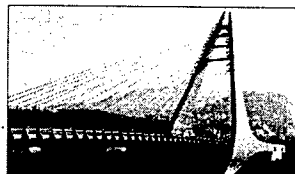
1986 *VÍTKOVICE opened the Palace of Culture and Sports.*

1991 *VÍTKOVICE completed TV tower in Žižkov, Prague*

1996 *VÍTKOVICE installed the oil tanking bay in Kralupy.*

VÍTKOVICE supply the steel structure of the bridge over the River Labe

1998

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