ATOMISTIC STUDIES OF GRAIN BOUNDARIES IN ALLOYS AND COMPOUNDS

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ABSTRACT

Atomic structure and atomic level properties of grain boundaries in binary alloys have been studied theoretically using computer modeling techniques. Both ordered and disordered alloys were investigated and the aim of these studies was to elucidate those structural, chemical and electronic features of grain boundaries in binary alloys that are responsible for different physical and mechanical properties of alloys when compared with pure metals. An integral part of this project was the development of appropriate descriptions of atomic interactions. The first are the many-body potentials akin to the embedded atom method. The most important was the development of the potentials for the Cu-Bi system which combined the use of empirical data and results of *ab initio* electronic structure calculations to construct reliable potentials. A major effort was devoted to the development of the LMTO based tight-binding method which has now been fully developed for pure metals while further advancement of this techniques towards alloys will be a subject of our future research. The structural studies were carried out for disordered Cu-Bi and ordered Ni₃Al and Cu₃Au alloys. In the former case the investigation was closely linked with high-resolution electron microscopic studies and the major result is the solution of the structure of the $\Sigma = 3$ (111)/(11 $\bar{1}$) facets containing Bi which were formed during segregation from originally curved boundaries. In the latter case the effect of the strength of ordering and deviations from stoichiometry on the boundary structure and its properties was investigated. The most interesting finding is a very different behavior of nickel rich and aluminum rich Ni₃Al which may explain why only nickel rich compounds can be ductilized by boron. In both cases the surplus element segregates to the boundaries. However, while in the former case this leads to the compositional disordering of the boundary region, in the latter case a two-dimensional ordered structure is formed in the grain boundaries.

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1. INTRODUCTION

The goal of this research project is to ascertain those structural, chemical and electronic features of grain boundaries in binary alloys that are responsible for different physical and mechanical properties of alloys when compared with pure metals. Both ordered and disordered alloys are studied and the most important phenomena followed are segregation of alloying elements and related structural changes in the boundary region. The approach adopted is theoretical investigation of the atomic structure and atomic level properties of grain boundaries employing computer modeling as the principal research tool. The modeling techniques utilized in these studies are molecular statics and Monte Carlo. The former is used to obtain relaxed, minimum energy structures at zero temperatures, and the latter the relaxed structures at non-zero temperatures which may also possess concentration gradients of alloying species. The atomistic studies are closely linked with experimental studies of grain boundary segregation and associated structural transformations and, in particular, with direct observations of the interfacial structures using the high resolution electron microscopy (HREM).

Since the essential precursor of any atomistic studies is a usable and realistic description of atomic interactions a large effort has been devoted in this project to the development of such descriptions. Two approaches have been advanced: Many body potentials of the Finnis-Sinclair type (Finnis and Sinclair 1984), akin to the embedded atom method (EAM) (Daw and Baskes 1984), and a quantum mechanical tight-binding technique based on the linearized muffin-tin method (LMTO) (Andersen 1975; Andersen, Jepsen and Glötzel 1985; Andersen, Jepsen and Sob 1987; Andersen, Methfessel, Rodriguez, Blochl and Potaglou 1989). While the methods for construction of many-body potentials were formulated in our previous research (Ackland, Tichy, Vitek and Finnis 1987; Ackland and Vitek 1990; Vitek, Ackland and Cserti 1991), the tight-binding method represents a new major development in the quantum mechanics based approaches suitable for studies of extended defects in crystals. In this framework electronic and chemical aspects of the interfacial structures and properties can be rationalized. The major problems encountered in this treatment are associated with incomplete self-consistency and deviations from local spherical symmetry. Approximate but physically justified solutions of these problems represent one of the main results of this research. This method is at present fully developed for pure metals but further advancement of this techniques towards studies of alloys will be a subject of our future research.

Two types of studies of segregation phenomena in disordered alloys have been made. The first is an investigation of general features of grain boundary segregation, especially its dependence on the solute size and on the grain boundary structure. For this purpose, model potentials describing atomic interactions in A-B alloys with different solute sizes, have been utilized. The second are studies of segregation and structures formed during the segregation in specific alloys. The system chosen for these studies is Cu-Bi. The corresponding many-body potentials reproducing experimental data and also data obtained from ab initio electronic structure calculations, were constructed for these alloys. In fact the use of ab initio calculations in construction of the many-body potentials is an important new development which was instrumental for the construction of reliable Cu-Bi potentials.

Copper-bismuth is also a very suitable model system for investigation of new boundary phases formed because of segregation. The reason is that bismuth segregation leads to boundary faceting (Blum, Menyhard, Luzzi and McMahon 1990; Donald and Brown 1979; Ference and Balluffi 1988; Menyhard, Blum and McMahon 1989; Michael and Williams 1984; Powell and Woodruff 1976) and associated formation of two-dimensional ordered phases (Luzzi 1991a, b; Urdaneta, Luzzi and McMahon 1992) the understanding of which may be the clue to comprehending intergranular embrittlement. Our recent research concentrated on investigation of the structure of $\Sigma = 3$ (111)/(11 $\bar{1}$) facets formed during segregation from boundaries which were originally curved. These facets, which in pure copper correspond to coherent twins, contain a high concentration of bismuth in spite of the fact that no segregation takes place to coherent twins if they are present in the sample prior to segregation. At the same time the $\Sigma = 3$ (111)/(11 $\bar{1}$) facets are ideally suited for high resolution electron microscopy (HREM) and provide an excellent opportunity to carry out a combined experimental and theoretical investigation of their structures. Such an analysis which reveals in detail the structure of the two-dimensional ordered phase formed in these facets, is one of the principal results of our research (Luzzi, Min Yan, Sob and Vitek 1991; Min Yan, Sob, Luzzi, Vitek, Ackland, Methfessel and Rodriguez 1992).

In the case of ordered alloys we explored grain boundaries in Ni₃Al and Cu₃Au with the aim to study the relationship between the ordering tendency, which is quantitatively very different in these two alloys, and grain boundary structure and properties. We have performed extensive Monte-Carlo calculations of grain boundaries at finite temperatures for both stoichiometric and non-stoichiometric

bulk concentrations. The most interesting finding is a very different behavior of nickel rich and aluminum rich Ni_3Al which may explain why only nickel rich compounds can be ductilized by boron (Aoki and Izumi 1979; Izumi and Takasugi 1988; Liu 1991b; Liu and White 1987; Liu, White and Horton 1985).

In the following section we summarize the most important results of the research performed in the framework of this project. More detailed descriptions of these studies and analyses of the results can be found in the publications listed in this report and in the doctoral thesis of Ms. Min Yan [Min Yan 1992].

2. DEVELOPMENT OF THE DESCRIPTIONS OF INTERATOMIC FORCES

2.1. Many-body central force potentials

The many-body potentials employed and developed in this research have been constructed in the framework of the Finnis-Sinclair (FS) scheme (Ackland, Finnis and Vitek 1988; Ackland, et al. 1987; Finnis and Sinclair 1984). This approach is analogous to the embedded atom method (EAM) (Baskes, Foiles and Daw 1989; Daw 1989a; Daw 1989b; Daw and Baskes 1984) and, as shown by Johnson (Johnson 1988a; Johnson 1988b), the two schemes are practically equivalent. The potentials are of the central force type, i.e. no orientational bonding is taken into account, but have a many-body character in that the energy of a system is not a sum of pair interactions between individual atoms.

The total energy of a system of N atoms is written as (Ackland, et al. 1987; Ackland and Vitek 1990; Vitek, et al. 1991) :

$$E = \sum_{i=1}^N \left[\frac{1}{2} \sum_{j \neq i} V_{s_i s_j}(R_{ij}) - \sqrt{\rho_{s_i}} \right] \quad (1a)$$

where

$$\rho_{s_i} = \sum_{j \neq i} \Phi_{s_i s_j}(R_{ij}) \quad (1b)$$

The suffices i and j refer to individual atoms and the suffices s_i and s_j refer to the species of the atoms involved. Both V and Φ are empirically fitted pair potentials and the summation over j extends over those neighbors of the atom i for which R_{ij} is

within the cut-off radii of these potentials. The analytic forms of these functions have been taken as cubic splines.

The first term in Eq.(2.1a) represents the summation of pair potentials describing a direct interaction between two atoms and the second term is the many body attractive part of the cohesive energy. The square root dependence of the latter term is justified when developing this scheme from a tight-binding approach which incorporates orbital charge conservation at individual atoms and utilizes the approximation of the second moment of the density of states; the potentials Φ are then identified with the squares of the corresponding hopping integrals (Ackland, et al. 1988; Finnis and Sinclair 1984).

For a binary system which is composed of type A and type B atoms, the semi-empirical pair potentials are denoted V_{AA} , V_{BB} , V_{AB} , Φ_{AA} , Φ_{BB} and Φ_{AB} . Functions V_{AA} , V_{BB} , Φ_{AA} and Φ_{BB} are identified with those for the pure metals and are fitted to known properties of the corresponding materials. The function Φ_{AB} is chosen as a geometrical mean of Φ_{AA} and Φ_{BB} , i.e.

$$\Phi_{AB} = \sqrt{\Phi_{AA} \Phi_{BB}} \quad (2)$$

which is consistent with its interpretation in terms of the hopping integrals (Ackland and Vitek 1990). Hence in principle only the pair potential term V_{AB} needs to be fitted to alloy properties. However, in some cases potentials V_{BB} and Φ_{BB} need to be re-scaled. For example, this has been done when fitting the potentials for copper-bismuth alloys as described below.

2.1.1 Cu-Bi and model potentials for study of segregation behavior

Potentials for Cu, constructed in earlier studies (Ackland, et al. 1987; Ackland and Vitek 1990) reproduce the experimental values of the lattice constant a , the cohesive energy, E_c , the elastic moduli, C_{11} , C_{12} and C_{44} , the upper bound of the unrelaxed vacancy formation energy, E_V^f , and the $1/6\langle 112 \rangle / (111)$ stacking fault energy, γ . Unfortunately, the same type of experimental data is not available for bismuth. At room temperature and atmospheric pressure bismuth crystallizes in a body-centered trigonal structure (Hultgren, Orr, Anderson and Kelley 1973; Pearson 1967). This phase is semi-metallic and, therefore, the essential assumption made in the construction of many-body potentials, i.e. charge conservation at individual atoms, may not be valid (Ackland, et al. 1988). However, the bismuth potentials are to be used for defect calculations in copper-bismuth alloys in which bismuth is effectively subject to a very high pressure because its atomic volume is about three times larger than that of copper. At the pressure of 90 kbar the trigonal bismuth

transforms into a metallic b.c.c. structure (Donohue 1973). Nevertheless, the only directly measured quantity for the b.c.c. bismuth is the lattice parameter while the cohesive energy and the elastic constants have only been measured for the trigonal phase (Pearson 1967; Simmons and Wang 1971). Therefore, the cohesive energy and the elastic moduli of the cubic phase have been estimated on the basis of the corresponding quantities of the trigonal phase. This is described in detail in the enclosed preprint (Min Yan et al. 1992) and in [Min Yan 1992].

Model potentials corresponding to different solute sizes but to the same enthalpy of mixing have been constructed in order to investigate the effect of the solute size on segregation behavior. First the Cu-Cu and Bi-Bi potentials described above were used to represent the A-A and B-B interactions; Φ_{CuBi} is then defined by Eq. (2). The model pair potential, V_{CuBi} , was fitted so that the enthalpy of mixing of an isolated solute atom B in the host lattice of A equals 0.8 eV/atom (approximately equal to the enthalpy of mixing in dilute Cu-Bi alloys (Maeda, Vitek and Sutton 1982)). Clearly, this potential characterizes an A-B alloy in which the mixing of A and B is energetically unfavorable. To construct model potentials which correspond to smaller solute sizes, the potentials for pure bismuth were first scaled by a factor f ($f < 1$), so that the lattice parameter of the b.c.c. bismuth, a_{Bi} , changes to fa_{Bi} . Such scaling corresponds to rigidly shifting potentials V_{BiBi} and Φ_{BiBi} towards smaller values of r . Using the scaled Bi-Bi potentials to describe B-B interaction and the original Cu-Cu potentials to describe A-A interactions, the V_{AB} potential was then adjusted so as to reproduce the enthalpy of mixing, 0.8 eV/atom.

Since copper and bismuth do not form any ordered structures and the solubility of bismuth in copper is only about 0.003 at% at 800°C (Hultgren, et al. 1973; Voce and Hallows 1947), there are virtually no experimental data to be fitted for the copper-bismuth system. In order to obtain more reliable fitting parameters, a metastable Cu_3Bi compound with $L1_2$ structure was investigated using the all-electron self-consistent full-potential ab initio linearized-muffin-tin-orbital method (LMTO) within the local-density approximation (Methfessel 1988; Methfessel, Rodriguez and Andersen 1989). The total energy of this structure was calculated as a function of the volume per atom and as a function of the applied tetragonal and trigonal shear strains. As a result, the equilibrium lattice parameter, the bulk modulus, the tetragonal shear modulus, $G = \frac{1}{2}(C_{11} - C_{12})$, and the trigonal shear modulus, C_{44} , for this metastable compound were obtained. These calculated quantities were then used as 'empirical' data for fitting the copper-bismuth alloy potential V_{CuBi} .

The lattice parameter and the bulk modulus of the metastable Cu_3Bi compound were fitted exactly and the shear moduli approximately (C_{44} practically exactly and G within 30%). The cohesive energy could also be fitted since it is determined in ab initio calculations. However, its absolute value is notoriously overestimated in the framework of the local-density approximation and, therefore, it was not utilized in the fitting. Instead, the enthalpy of mixing for the liquid copper-bismuth solution at 1200K, which was measured by Lomov and Krestovnikov (Lomov and Krestovnikov 1964), was fitted as precisely as possible. The latter part of the fitting utilized a Monte-Carlo simulation of the liquid Cu-Bi alloy. At this stage of fitting the Bi-Bi potentials were scaled such that the equilibrium lattice parameter of the b.c.c. bismuth is smaller than originally. This scaling corresponds to rigidly shifting the potentials V_{BiBi} and Φ_{BiBi} towards smaller values of r . Physically, the scaling leads to a reduction of the size of the bismuth atoms which will be smaller when embedded in copper than in the pure form. The Cu-Cu potentials were not changed. The details of the fitting are described in the enclosed preprint (Min Yan, et al. 1992).

2. 1. 2 Potentials for Cu_3Au and Ni_3Al

The many-body potentials for both Cu-Au and Ni-Al systems were constructed using the scheme proposed by Ackland and Vitek (1990). The Cu potentials are the same as those employed in studies of the Cu-Bi system. The Au potential, constructed in (Ackland, et al. 1987), was again fitted to the equilibrium lattice constant, the cohesive energy, the elastic constants, a lower bound of the unrelaxed vacancy formation energy, the stacking fault energy, and the pressure-volume relationship. The potential $V_{\text{Cu-Au}}$ was fitted to reproduce the alloying energy in disordered substitutional alloys and the lattice parameter for Cu_3Au alloy in the L1_2 ordered structure. For these potentials the L1_2 (Cu_3Au) and B2 (CuAu) ordered structures are favored at low temperatures over the disordered phase (Ackland and Vitek 1990). Hence, these potentials reproduce the basic features of the phase diagram of this alloy system (Hultgren, et al. 1973) without any further adjustment.

The potentials for Ni and Al were constructed using the same method as in the case of Cu and Au. The physical quantities fitted are the cohesive energy, the equilibrium lattice constant for the f.c.c. structure, the elastic constants and the vacancy formation energy. It should be noted, however, that these potentials do not reproduce the stacking fault energies in Ni and Al, respectively. Furthermore, while the constructed many-body potentials for Al may be appropriate for use in

alloys with low concentration of Al they should not be employed for pure Al and in the case when the Al concentration in the alloy is high since they do not reproduce the long range oscillations typical for the aluminum interactions which are responsible for the high stacking fault energy in this metal (Dagens, Rasolt and Taylor 1975; Taylor 1981). $V_{\text{Ni-Al}}$ is fitted such as to reproduce for $L1_2$ (Ni_3Al) and B2 (NiAl) structures the alloying energies and the lattice parameters as well as, approximately, the elastic constants for the $L1_2$ structure (Vitek, et al. 1991). For these potentials the $L1_2$ and B2 structures are more stable relative to other possible structures, as well as with respect to the disordered phase.

The validity of the potentials was tested by calculating a number of physical properties:

(a) The calculations of the energies of anti-site defects in Cu_3Au and Ni_3Al clearly demonstrated that the ordered phase is favored over the disordered one. For both Cu-Au and Ni-Al the $L1_2$ (A_3B) and B2 (AB) ordered structures are favored at low temperatures over the disordered phase. Hence, these potentials reproduce the basic features of the phase diagram of this alloy system (Hultgren, et al. 1973) without any further adjustment.

(b) The potentials reproduce very closely the measured values of the anti-phase boundary energies on $\{111\}$ planes in the $L1_2$ structure. For Cu_3Au the calculated value is 54mJm^{-2} and the measured one $40\text{-}60\text{mJm}^{-2}$ (Sastry and Ramaswami 1976); for Ni_3Al the calculated value is 226mJm^{-2} and the most recent measured value is $205\text{-}269\text{mJm}^{-2}$ (Baluc, Schaublin and Hemker 1991).

(c) The Monte Carlo calculations of the long range order parameters as functions of temperature predict the order-disorder transition temperature for Cu_3Au between 650K and 670K and for Ni_3Al about 1600K. In the former case the experimental value is 653K (Haasen 1986) and Ni_3Al remains ordered in the $L1_2$ structure until the melting temperature of 1658K (Hultgren, et al. 1973).

From the above analyses, it can be concluded that the potentials for Cu-Au and Ni-Al alloys give very good representation of their ordering strength. Hence, these potentials are well suited for investigation of the impact of the ordering strength upon grain boundary structure and chemistry which is one of the main goals of this research project.

2.2 LMTO based tight-binding method

The quantum mechanical method which we are developing follows the spirit of parametrized tight-binding methods which have been used in condensed matter physics for a long time (Cyrot-Lackmann 1967; Ducastelle and Cyrot-Lackmann 1970; Harrison 1980; Pettifor 1983; Pettifor 1992) and have recently been successfully applied in studies of crystal defects (Chadi 1989; Finnis, Paxton, Pettifor, Sutton and Ohta 1988; Paxton and Sutton 1989a; Paxton and Sutton 1989b; Sutton, Finnis, Pettifor and Ohta 1988; Thomson and Chadi 1984). The approach we have taken is based on the first principles tight-binding LMTO method (Andersen, et al. 1985). The main advantage of this approach is that s-, p-, d- and f- electrons are all treated on the same footing. When determining the electronic and atomic structure of an interface we do not perform fully self-consistent electronic structure calculation. Rather we use, similarly as in the parametrized tight-binding schemes, the Hamiltonian in which certain parameters have been determined on the basis of self-consistent calculations for simpler cases and by fitting certain experimental data.

The Hamiltonian in the orthogonal representation is

$$H_{RL,R'L'} = C_{RL}\delta_{RR'}\delta_{LL'} + \Delta_{RL}^{1/2}\{S^0(1-\gamma S^0)^{-1}\}_{RL,R'L'}\Delta_{R'L'}^{1/2} \quad (3)$$

where R labels the atomic site and $L = (l,m)$ is the angular momentum index (in our studies $l \leq 2$, i.e. we use sp^3d^5 orbitals at each site). The atomic sphere approximation (ASA) is employed, i.e. we assume spherically symmetric potentials in overlapping atomic spheres with the same volume as Wigner-Seitz polyhedra. The LMTO crystal potential parameters X_{RL} ($X = C, \Delta, \gamma$) are diagonal with respect to indices R and L and they characterize the scattering properties of atoms at individual sites; for example, C_{RL} represents the effective center of the l-like band ($L = (l,m)$) at the site R. S^0 is the canonical structure matrix, which is determined solely by the geometrical arrangement of the atoms.

The potential parameters, which are functions of the atomic volume, are obtained from first-principles self-consistent calculations in the local density approximation (LDA) for perfect crystals of varying densities. When studying defective structures, the volumes associated with individual atoms are identified with the volumes of the corresponding Voronoi polyhedra, and the potential parameters C, Δ and γ are re-scaled in accordance with the local atomic volumes.

The matrix

$$S^\gamma = (S^0(1 - \gamma S^0)^{-1}) = -\gamma^{-1} + \gamma^{-1}(\gamma^{-1} - S^0)^{-1}\gamma^{-1} \quad (4)$$

appearing in the Hamiltonian (3), is calculated for each atom by direct inversion, using a cluster containing typically 80-90 neighboring atoms with the atom considered in the center of the cluster. The inversion in Eq. (4) need not be performed completely. For each atom R we calculate only blocks $S_{RL,R'L'}^\gamma$, where R' are the interacting neighbors of the atom at R . Thus, in the spd LMTO basis, we calculate only first 9 lines of the matrix S^γ . Then the whole matrix S^γ is constructed by adding all the blocks, $S_{RL,R'L'}^\gamma$ together. Since, in general, the neighborhood of the atom R is different from the neighborhood of the atom R' we symmetrize the block $(RL, R'L')$ to maintain the symmetry $S_{RL,R'L'}^\gamma = S_{R'L',RL}^\gamma$.

The total energy of the system is then written as

$$E_{\text{tot}} = E_{\text{bs}}^{\text{LMTO-ASA}} + E_{\text{AS}}^{\text{EMT}} + E^{\text{rep}} \quad (5)$$

where $E_{\text{bs}}^{\text{LMTO-ASA}}$ is the band-structure energy evaluated within the LMTO in ASA, $E_{\text{AS}}^{\text{EMT}}$ is the correction for the ASA and E^{rep} is a short rang repulsive term. Both $E_{\text{AS}}^{\text{EMT}}$ and E^{rep} are fitted to reproduce experimental data as described below.

The band-structure energy is calculated by the standard k-space method. However, for this reason the supercell geometry has to be employed in the real space. This implies that a periodic array of interfaces or other crystal defects is always studied rather than an isolated defect. Owing to this periodicity a sufficiently large unit cell must always be chosen so that the interaction of periodically repeating defects is negligible.

The atomic sphere correction is constructed as in the effective medium theory in the framework of which the analytic expression for $E_{\text{AS}}^{\text{EMT}}$ has been derived (Häkkinen and Manninen 1989; Jacobsen, Nørskov and Puska 1987). This expression is devised such that $E_{\text{AS}}^{\text{EMT}}$ does not change if any hydrostatic deformation involving only the volume change is applied, but it corrects the band-structure energy when shape and symmetry are changed, for example, when shear deformation is applied. The detailed expression for $E_{\text{AS}}^{\text{EMT}}$ can be found in Refs. (Häkkinen and Manninen 1989; Jacobsen, et al. 1987) and in a forthcoming publication. These formulas contain a number of parameters which were evaluated for pure metals by Puska (Puska 1990). However, in our approach which is rather

different from the effective medium theory, some of these parameters are fitted so as to reproduce certain experimental quantities.

The repulsive term E^{rep} is represented by a sum of short-ranged pair-potentials. This approximation has been commonly used in parametrized tight-binding theories and, recently, it has been put on a sound basis in the framework of the Harris-Foulkes density functional scheme (Foulkes and Haydock 1986; Foulkes 1989; Foulkes and Haydock 1989; Harris 1985; Sutton, et al. 1988). The pair potential is represented in our approach by a polynomial function with adjustable parameters which, together with the parameters of the ASA correction, are chosen so as to reproduce as closely as possible the equilibrium lattice parameter, the bulk modulus and the shear moduli of the material studied. However, at this point we encounter the following problem related to non-uniquely defined zero level of the band-structure energy.

In self-consistent electronic structure calculations the first estimate for the crystal potential is usually the superposition of potentials of free atoms. The energy zero, V_0 , is then well defined and corresponds to the potential of free atoms at infinity; one usually sets $V_0 = 0$. After calculating the charge density, the crystal potential is determined via the Poisson equation up to an arbitrary additive constant. Therefore, the band-structure energy, E_{bs} , is also determined up to an additive constant. The electron energies are often measured relative to the average Hartree potential in the interstitial region; this leads to a variable energy zero (dependent on the atomic configurations) when evaluating for E_{bs} which may become repulsive in this treatment. It does not matter in the fully self-consistent ab initio calculations since only the total energy and its zero level are relevant quantities. However, to couple the first-principles band-structure energy with a semi-empirically described remainder of the total energy, we need a fixed energy zero, V_0 , for E_{bs} . In this case, if atoms come closer together, the average value of the crystal potential, as well as E_{bs} , decrease relative to V_0 and the E_{bs} is always attractive.

Therefore, in the present approach we first perform self-consistent LMTO-ASA electronic structure calculations for a metal (mostly in the fcc or bcc structure) at various volumes and align all the energies to the same position C_d^0 of the center of the d-band. C_d^0 is the value of the parameter C_{RL} for $l=2$ in Eq. (3) corresponding to a reference volume, usually the experimental one. Further, we assume that the center of the d-band depends on the local density as

$$C_d - C_d^0 = f(s) - f(s_0) \quad (6)$$

with respect to a fixed energy zero, V_0 . Here s_0 and s are the Wigner-Seitz (atomic-sphere) radii in the reference structure and in the configuration studied, respectively, and $f(s)$ is an appropriate function of the Wigner-Seitz radius. It is taken, following the suggestion of Andersen, et al. (1985, 1987) as $h \ln(s/s_0)$ with h being one of the adjustable parameters used to fit the above mentioned experimental data. In order to obtain $E_{bs}^{LMTO-ASA}$ measured with respect to V_0 , we shift $E_{bs}^{LMTO-ASA}$ by

$$\Delta E_{bs}^{LMTO-ASA} = W[f(s) - f(s_0)] \quad (7)$$

where W is the number of valence electrons per repeat cell.

This approach can be applied, at least in principle, to any single component material with the exception of ferromagnetic materials. At the present stage we have developed the scheme numerically for copper and tungsten. The former is a noble metal with filled d-shell in which s electrons play an important part in the bonding while the latter is a transition metal with unfilled d-shell in which the d electrons are likely to dominate the bonding.

Since the purpose of developing this method is to investigate structure and properties of extended defects, in particular, interfaces, it is important that the ground state structure of the material considered is stable not only with respect to small strains but also relative to structures produced by large deformations. This is not always checked when constructing interatomic potentials and as a result configurations corresponding to unphysical structures may be attained in studies of lattice defects (Vitek and DeHosson 1986). Furthermore, variation of the energy with large strains should also be well reproduced. The reason is that in the cores of lattice defects the deviation away from the ideal lattice structure is well beyond the linear response. While this cannot be examined generally, specific tests can be carried out. Results of such calculations cannot be, of course, compared with any experimental data but ab initio self-consistent electronic structure calculations may be used to play the role of experiments.

An example of such testing is presented in Fig. 1 which shows the calculated total energy of tetragonally deformed copper as a function of the tetragonal distortion, c/a . The solid curve corresponds to the calculation carried out using the full-potential LMTO (FP-LMTO) method (Methfessel 1988; Methfessel, et al. 1989) and the dashed curve to the calculation performed using the tight-binding method. The fcc lattice corresponds to $c/a = 1$ and the bcc lattice to $c/a = 1/\sqrt{2}$. Clearly the results of the ab initio calculations are well replicated by the present scheme. The reason why

the curve calculated by the tight-binding method lies in the vicinity of $c/a=1$ under the curve calculated by the FP-LMTO is that the FP-LMTO method in the LDA gives somewhat higher value of the corresponding shear modulus than the experimental value which is imposed in our scheme. The same test has also been carried out for tungsten and the results are very similar.

Fig. 1. The energy of the tetragonally deformed fcc copper as a function of the c/a ratio.

The second test of the validity of the present scheme was the calculation of the frequency for the Brillouin zone boundary phonon with $k = 2\pi/a(001)$. In the calculation the method of frozen phonons was employed. For tungsten we obtained $f=6.06$ THz and for Cu to $f = 7.81$ THz. The experimental values are 5.5 THz and 7.3 THz, respectively (Rebonato and Broughton 1987).

In the studies of defect configuration the total energy (or free energy) of the system must be minimized with respect to the positions of the atoms. This could be achieved by minimizing numerically the energy given by Eq. (5). However, a better

approach is to calculate analytically the forces acting on individual atoms (i. e. the derivatives of the energy with respect to atomic positions) and employ techniques, such as conjugate gradients, to minimize the energy. The ℓ -th component of the force acting on an atom i is

$$F_i^\ell = -\nabla_i^\ell [E_{\text{bs}}^{\text{LMTO-ASA}} + E_{\text{AS}}^{\text{EMT}} + E^{\text{rep}}] \quad (8)$$

The differentiation of the $E_{\text{AS}}^{\text{EMT}}$ and E^{rep} is straightforward as both these functions are given analytically. The most time-consuming and complex is the evaluation of the gradients of $E_{\text{bs}}^{\text{LMTO-ASA}}$. Following the Hellman-Feynman theorem

$$F_{i,\text{bs}}^\ell = -\sum_{L,L'} \sum_{j,k,T} A_{jL,(T+k)L'} \nabla_i^\ell H_{jL,(T+k)L'} \quad (9)$$

where i, j and k correspond to the atoms within the unit cell (i. e. the supercell), T is the translation vector of the system studied and L is the angular momentum index. The coefficients

$$A_{jL,(T+k)L'} = \sum_{n\vec{k}} (C_{n\vec{k}}^{jL})^* C_{n\vec{k}}^{kL'} \exp[i\vec{g} \cdot (\vec{T} + \vec{k} - \vec{j})] \quad (10)$$

where $C_{n\vec{k}}^{jL}$ are the expansion coefficients of the eigenstates, $|n\vec{k}\rangle$, of the tight-binding Hamiltonian into the Bloch functions

$$|k,j,L\rangle = \frac{1}{\sqrt{N}} \sum_T \exp[i\vec{k} \cdot (\vec{T} + \vec{j})] |T,j,L\rangle \quad (11)$$

where $|T,j,L\rangle$ is the muffin-tin orbital centered at the atom at $T+j$. The coefficients $C_{n\vec{k}}^{jL}$ are obtained as the result of the band structure calculations.

Only the Hamiltonian matrix elements are differentiated in Eq. (9) with respect to the atomic positions and the main components of these derivatives are the derivatives of the structure constant matrix S^j . This differentiation is carried out numerically and represents, together with the diagonalization of the Hamiltonian, the most time-consuming part of the calculation. This procedure was tested by displacing atoms in the ideal lattice arbitrarily away from their equilibrium positions. Within several iterations the displaced atoms always returned to their equilibrium positions. Employing this tight-binding scheme, the structures of symmetrical tilt $\Sigma=5$ (210) boundaries and $\Sigma=5$ twist boundaries in tungsten and copper are being studied at present. These calculations represent the first studies of grain boundaries in transition and noble metals in which the complete quantum mechanical nature of the interatomic bonding is taken into account. Comparison

with simpler schemes, in particular the central many-body potentials, will reveal the significance of directional bonding in determination of interfacial structures.

The present scheme appears to be equally applicable to transition metals with unfilled d-shells (W) and noble metals (Cu) where the s electrons contribute very significantly to bonding. This is an important aspect of the scheme, in particular when considering its application to alloys composed of transition and simple or noble metals. However, the development of this tight-binding method for binary alloys represents another major step and it is one of the goals of our future research.

3. A MODEL STUDY OF SEGREGATION: DEPENDENCE ON SOLUTE SIZE AND BOUNDARY STRUCTURE

A study of the dependence of the segregation propensity upon the size of the solute atoms and grain boundary structure was carried out using the model many-body potentials described in section 2. 1. 1. These calculations were carried out using a molecular statics relaxation technique. Starting from the equilibrium grain boundary structure, the segregation process in an A-B disordered alloy, where B is the solute, was modeled as follows. Initially, one B atom was placed successively at various sites in the vicinity of the boundary plane, and the segregation energy E^s , calculated for each of these sites. The site which has the largest negative value of E^s is the most favorable place for segregation. Keeping then this site occupied by the B atom, the process described above was continued by placing the second B atom on various sites in the vicinity of the boundary plane. The site found to be the most favored for the second B atom was then kept occupied by the B atom and the process repeated until no segregation sites could be found. At this stage the grain boundary is saturated with B atoms. Details of these studies are presented in (Min Yan 1992) and here we only summarize the main results.

The first noticeable observation is that the segregation occurs only on sites which have more open space associated with them than inside the bulk and the segregation is limited to a very narrow region in the boundary core. Secondly, the segregation energy was found to vary substantially at each stage of segregation, with a tendency to increase with increasing coverage of the solute. The reason for this behavior is two-fold: First, the local atomic volume increases with the solute concentration, and secondly, there is attractive interaction between the solute atoms. At saturation an ordered grain boundary structure is formed due to the periodicity of the boundary.

The segregation process modeled here can be discussed in the framework of the Fowler's isotherm in the framework of which the equilibrium segregation is described by the equation:

$$\frac{X_{gb}}{1 - X_{gb}} = \frac{X_b}{1 - X_b} \exp\left(\frac{-E^0 + \alpha X_{gb}}{RT}\right) \quad (12)$$

where X_{gb} is the grain boundary and X_b the bulk concentration of the solute, E^0 the segregation energy when $X_{gb} = 0$ and α is the parameter characterizing the interaction between solute atoms at a grain boundary. A positive value of α indicates an attractive interaction between solute atoms and a negative value of α indicates a repulsive interaction. The values of E^0 and α can be determined from the relation $E^s(X_{gb}) = E^0 + \alpha X_{gb}$ using the calculated values of $E^s(X_{gb})$. The concentration, X_{gb} , at each stage of the segregation has been measured with respect to the saturation level which, for example, for the $\Sigma 5\{310\}$ grain boundary corresponds to one $\{310\}$ layer fully occupied by B atoms. Taking the concentration of B in the bulk, X_b , as 50 at ppm, the relation between X_{gb} and T , established by Eq. (12), is plotted in Fig. 2.

Fig. 2. The solute concentration predicted according to Eq. 12 for the $\Sigma 5\{310\}[001]$ symmetrical tilt boundary at different temperatures and solute sizes characterized by different parameters f (a) $f=1.0$, (b) $f=0.9$, (c) $f=0.84$.

The segregation process follows the same path independently of the model potentials used. This, to some extent, indicates that it is the structure of the grain boundary that plays a dominant role in controlling the segregation process. As long as the atomic size of the solute is larger than that of the host and the interaction between solute and the host is repulsive, segregation is favored at those sites which have more open space associated with them than in the bulk. Furthermore, an ordered structure is very likely to be formed if the grain boundary possesses a periodic structure. However, the segregation energy depends on the atomic size of the solute very sensitively. This is reflected in the fact that for smaller solute atoms the segregation occurs at lower temperatures, as seen in Fig. 2. For example, for the $\Sigma=5(310)$ symmetrical tilt boundary the ratios of the solute radii 1:0.9:0.84 lead to the ratio of the corresponding values of E^0 1:0.78:0.61. The interaction between solute atoms weakens even more rapidly with the decreasing solute size, as manifested by ratios of the corresponding values of α 1:0.86:0.07.

Using this approach, segregation was studied for a variety of short and long period boundaries. One common feature of all the results is that segregation is very selective with respect to the atomic sites. With the potentials which correspond to larger solute sizes than the host, the segregation occurs only at those sites which are located at boundary plane and have more open space associated with them than the sites in the ideal lattice. This implies that the solute size plays a dominant role in the segregation processes. Secondly, the sequence of segregation is determined by both the boundary structure and the interaction between solute atoms. Although the periodicity of a boundary structure may provide geometrically equivalent sites for segregation, the interaction between solutes may favor some of the sites over the others. This leads to certain well defined sequences of segregation. Notwithstanding, as saturation is reached, ordered structures formed correspond to periodicities of the grain boundaries.

However, besides these common features, segregation also exhibits characteristics which are different for different boundaries. The first noticeable distinction is that the propensity for segregation depends strongly on the specific boundary. Secondly, the segregation energy shows different dependences on the solute concentration at different boundaries. For some grain boundaries the dependence of the segregation energy on solute concentration can be described to a good approximation as $E^s(X_{gb}) = E^0 + \alpha X_{gb}$ but for others the dependence of E^s on X_{gb} is much more complex and cannot be approximated as a simple linear function. The

Fowler's isotherm then fails and the equilibrium segregation needs to be described by a more complex isotherm.

From the present results, it can be concluded that in order to study solute segregations in a more quantitative way, it is critical to use interatomic potentials which characterize correctly the size of the solute in the host lattice. Furthermore, the segregation propensity depends strongly on grain boundary type. It can, therefore, be expected that if equilibrium segregation of solute occurs in a polycrystal which contains many different grain boundaries, some of the boundaries will get saturated while others may contain only very little or no segregant. This implies that studies of a wide variety of grain boundaries need to be done in order to assess properly the segregation behavior in polycrystals.

Clearly, the potentials for the Cu-Bi system discussed in section 2. 1. 1 which lead to a very precise description of the structure of $\Sigma = 3$ (111)/(11 $\bar{1}$) facets containing a high concentration of Bi, as described below, are a prime candidate for the study of the segregation. Preliminary Monte-Carlo calculations show, however, that very large blocks of atoms need to be employed to obtain reliable results. The reason is that the current potentials which correspond to strong repulsive interactions between Cu and Bi, and strong attractive interaction between Bi-Bi, lead to extremely small solubilities of bismuth in copper and to precipitation at higher concentrations. This is in agreement with experiments as the experimentally determined solubilities of bismuth are about 0.0003 at% at 600°C and 0.003 at% at 800°C (Hultgren, et al. 1973). The block which can reproduce such results must contain at least 10^5 atoms. The corresponding simulation would be extremely time consuming considering that each atom participates in about 1000 MC steps if thermodynamic equilibrium is to be attained. The studies of segregation and associated boundary faceting in this system is one of the goals of our future research.

4. STRUCTURE OF THE $\Sigma = 3$ (111)/(11 $\bar{1}$) FACETS IN COPPER-BISMUTH

As mentioned above, the segregation of bismuth to the curved boundaries corresponding to the $\Sigma = 3$ misorientation induces formation of (111)/(11 $\bar{1}$) facets. The HREM analysis of these facets suggests the following model for these interfaces (Luzzi 1991a, b). In the framework of the 'ABC' description of the sequence of (111)

atomic planes in an f.c.c. crystal, the $\Sigma = 3$ (111)/(11 $\bar{1}$) twin in pure copper can be represented as

where the vertical lines mark the position of the boundary. The structure containing bismuth can be most appropriately represented as

where C' denotes a plane of copper atoms in which one third of the atoms were replaced by hexagonally arranged vacancies, and C(Bi) the plane of bismuth atoms positioned above these vacancies.

The atomistic modeling of the $\Sigma = 3$ (111)/(11 $\bar{1}$) boundary containing Bi was then performed using the structure described by (14) as a starting configuration. The relaxation calculation was carried out such that the total energy of the block had been minimized with respect to the positions of individual atoms as well as with respect to the relative rigid body displacement of the two adjoining grains. This displacement has components both parallel and perpendicular to the boundary so that there are neither any tensile nor compressive stresses normal to the boundary nor shear stresses parallel to the boundary present in the final configuration.

In the direction perpendicular to the boundary the block is effectively infinite but it was found that it was sufficient to limit the relaxation to twenty two {111} layers on each side of the boundary. In the directions parallel to the boundary periodic boundary conditions have been maintained throughout the calculation. The smallest possible repeat cell of this structure is $\frac{3}{2}[1\bar{1}0] \times \frac{1}{2}[11\bar{2}]$. However, reconstructions leading to larger unit cells may occur, similarly to what has been observed in the case of free surfaces. For this reason calculations were also carried out for larger repeat cells of the type $n\frac{3}{2}[1\bar{1}0] \times m\frac{1}{2}[11\bar{2}]$, where n and m are integers. However, the same structure were found for n=m=1, n=1 and m=2 as well as for n=2 and m=4.

The relaxed structure is shown in Fig. 3 where copper atoms are represented by small circles and the bismuth atoms by large circles. The shading distinguishes different (220) layers of atoms. In order to make a detailed comparison of the calculated and observed structures, a series of images, corresponding to the same defocus conditions and thickness as in the HREM study, were calculated for the

relaxed structure using the multislice formalism. The details of this calculation and comparison with experimental observations can be found in the enclosed preprint (Min Yan, et al. 1992) and, more briefly, in (Luzzi, et al. 1991). The calculated images reproduce the systematic contrast changes in the experimental image. Most importantly, the periodicities within the boundary plane along the $[11\bar{2}]$ direction are preserved as is the expansion of the structure in the $[111]$ direction, perpendicular to the boundary plane. Furthermore, the total calculated expansion ($1.88\text{\AA}$), i.e. the relative displacement of the two grains in the direction perpendicular to the boundary, is within the experimental limits of the accuracy in the HREM ($\approx 0.1\text{\AA}$), in a perfect agreement with the experiment.

Fig. 3. The low energy structure of the $\Sigma = 3$ $(111)/(11\bar{1})$ boundary.

The degree of match in the image series is strong evidence for the very high accuracy with which the structure has been predicted theoretically. These results demonstrate for the first time that HREM studies and theoretical structural analyses can be used synergistically to decipher with a great accuracy the structure of boundaries containing multiple atomic species. At the same time these results provide a firm evidence that the empirical N-body potentials are capable to describe

with a sufficient accuracy atomic interactions even in relatively complex systems such as copper-bismuth provided an appropriate and sufficient input is used in their construction. For this purpose the self-consistent ab initio electronic structure calculations are essential since they provide data corresponding to sampling of configurations which are not attainable experimentally.

5. ORDERED ALLOYS AND INTERMETALLIC COMPOUNDS

5.1. Motivation of the research

Intergranular brittle fracture is frequently one of the failure modes in ordered alloys and compounds. The most eminent example is Ni_3Al which crystalizes in L_{12} structure and fails by intergranular fracture although it is ductile in the single crystal form (for reviews, see e. g. (Izumi and Takasugi 1988; Liu 1988; Liu 1991a, b; Pope 1992; Takasugi and Izumi 1992). Contrary to the segregation-induced embrittlement in disordered metallic alloys, the grain boundary brittleness in Ni_3Al has been found to be an intrinsic property of this material and not associated with any impurity segregation. This is so in spite of the fact that the very recent experimental observations suggest that grain boundary fracture in Ni based L_{12} alloys may be related to the presence of hydrogen at boundaries (Liu 1991a; Liu 1992a, b; Liu and McKamey 1990; Liu and Oliver 1991; Takasugi, Nagashima and Izumi 1990). The reason is that the presence of hydrogen in the grain boundaries and its possible embrittling effect are also related to some intrinsic properties of grain boundaries in Ni_3Al .

Another important finding is that a small amount of boron doping can effectively suppress intergranular fracture in Ni_3Al (Aoki and Izumi 1979; Liu and White 1987; Liu, et al. 1985; White, Padgett, Liu and Yalisove 1984). But such beneficial effect of boron occurs only if the material is enriched with nickel (Izumi and Takasugi 1988; Liu 1988; Liu, et al. 1985; Takasugi, Masahashi and Izumi 1987). This suggests that the off-stoichiometry effects may be as important as the alloying effects in determining the interfacial mechanical properties.

In contrast some other alloys, most notably Cu_3Au , which also crystallize in the L_{12} structure, are ductile even as a polycrystals. This poses interesting questions: What is the reason for intrinsic propensity to fracture in Ni_3Al ? Why such fracture does not exist in, for example, Cu_3Au which possesses the same crystal structure?

How is the fracture propensity affected by the boundary structure and chemistry? To provide answers based on the atomic level understanding of grain boundary properties was the motivation for our research.

5.2 Molecular statics studies

It was found in earlier studies that in Cu_3Au , which is weakly ordered, the boundary structure is very similar to that in pure f.c.c. materials. On the other hand, in strongly ordered alloys, such as Ni_3Al , all the atoms can be regarded as uniquely attached to either the upper or the lower grain so that the ideal L1_2 structure is practically undisturbed on either side of the boundary up to the boundary plane (Kruisman, Vitek and DeHosson 1988; Vitek and Chen 1991; Vitek, Chen, Voter, Kruisman and DeHosson 1989). These features of grain boundary structures have been confirmed by our more recent calculations performed for a variety of short and long period boundaries (Min Yan 1992). The reason for these remarkable structural differences can be sought in differences in ordering energies. In the case of a high ordering energy (Ni_3Al), the chemical order is the principal controlling factor of the energy of the system. On the other hand, in the case of a low ordering energy (Cu_3Au) more relaxed grain boundary structures are energetically favored.

The preservation of the ideal L1_2 order up to the boundary plane leads to the presence of columnar cavities in the boundaries in Ni_3Al . These cavities may serve as suitable nuclei for intergranular cracks. Furthermore, when dislocations are being emitted from the crack tip a high energy APB has to be formed at the same time, making the crack blunting more difficult (Vitek 1991). The atomistic studies suggest, therefore, that in strongly ordered L1_2 alloys the grain boundary structures makes the nucleation and subsequent propagation of intergranular cracks easier than in weakly ordered L1_2 alloys, such as Cu_3Au .

5.3 Monte Carlo studies

The purpose of these investigations was twofold. The first was to investigate the effect of ordering energy on the interfacial structure and chemistry at finite temperatures. These calculations were carried out for stoichiometric Cu_3Au and Ni_3Al . The second was to study the effects of off-stoichiometry in the bulk upon the structure and chemistry of grain boundaries in Ni_3Al . In all cases studied, the starting configurations for MC simulations were the corresponding structures obtained from the static relaxations, except that the bulk composition was adjusted

to an appropriate chosen off-stoichiometry in the bulk. During the simulation, the bulk composition was kept constant by fixing the corresponding chemical potential difference between the two species, while the grain boundary composition approached its equilibrium value gradually.

The calculations have been made for a number of short and long period boundaries but the main features of the boundary structure were the same in all cases. Fig. 4 shows the concentration profile in the boundary region of the $\Sigma 29(520)$ boundary in Cu_3Au at two different temperatures. This profile has been obtained by plotting the excess Cu concentration at $\{10\ 4\ 0\}$ layers parallel to boundary which are positioned at different distances from the boundary center, defined as the zero layer. An important feature revealed by this figure is a substantial compositional deviation from the ideal $L1_2$ structure which occurs in the vicinity of the boundary plane. This is manifested by the positive peaks (indicating surplus of Cu) and the negative peaks (indicating surplus of Au) which imply extensive interchanges between Cu and Au atoms in the grain boundary. Thus the grain boundary region becomes chemically disordered even at room temperature (300K) which is much lower than the order-disorder transition temperature of Cu_3Au . As the temperature increases to 600K, the compositional disordering in the grain boundary region becomes more extensive and spreads further into the bulk. At 700K, which is above the order-disorder transition temperature of Cu_3Au , the MC calculations show that the whole block, including both the grain boundary and the bulk, becomes compositionally disordered. However, the segregation to the grain boundary still occurs and the local composition there deviates from that in the bulk.

The chemical character of grain boundaries in Ni_3Al is quite different than in Cu_3Au . There is virtually no compositional disordering of the boundaries even at very high temperatures, close to the melting temperature. Thus while the boundary regions in Cu_3Au are substantially disordered even at room temperature and are, therefore, structurally very similar to those in pure metals or disordered alloys, in Ni_3Al the ideal $L1_2$ order extends up to the boundary plane even at high temperature. Thus the MC calculations demonstrate that the conclusions regarding the order and/or disorder in the boundary region based on static calculations, are valid at finite temperatures.

(a)

(b)

Fig. 4. The excess concentration of Cu on $\{10\ 4\ 0\}$ layers parallel to the $\Sigma 29(520)$ boundary in Cu_3Au at (a) 300K and (b) 600K.

However, the situation is more complex in non-stoichiometric Ni_3Al . As an example we show here the results for the $\Sigma 29(520)$ grain boundary in the Ni-rich Ni-24%Al and Al-rich Ni-26%Al alloys at 600°K. Segregation of the excess element towards the grain boundary occurs in both cases but the effect on the boundary structure is very different. The concentration profile showing the surplus of Ni in the $\Sigma 29(520)$ grain boundary in Ni-24%Al alloy is presented in Fig.5a. As seen from this figure, segregation of Ni occurs and it is accompanied by exchanges between Ni and Al atoms in the boundary region. This is also seen in Fig. 6a which shows the atomic structure of this boundary projected onto the (001) plane, where shading represents the chemical nature of the atoms. The darkest shade corresponds to Ni and the lightest to Al. The additional three intermediate levels of shading then represent the probability that an atomic site is occupied by Ni; the darker the shade the higher the probability that Ni is positioned at the site. It is seen that while the Ni concentration in the boundary region has increased some sites which were originally occupied by Ni possess a non-zero probability to be occupied by Al. Hence, the grain boundary becomes chemically disordered as a result of the Ni segregation.

In contrast, in Al-rich alloy, Ni-26%Al, Al segregates only to certain well defined atomic sites and there are no interchanges between Ni and Al atoms. This is seen from both Figs. 5b and 6b which show, respectively, the concentration profile of Al surplus in the grain boundary and the atomic structure in which shading represents the chemical nature of the atoms. No significant compositional disorder develops in the vicinity of the boundary. On the contrary, since the segregation of aluminum is very selective, a narrow layer of a two-dimensional ordered Ni-Al compound with a high aluminum content is formed at the grain boundary. This is in fact similar to what occurs, for example, in the disordered Cu-Bi alloy.

The most probable reason for the segregation differences between Ni and Al is the different atomic size of these two elements. Aluminum, being a large atom, can only segregate to sites with large free volume and, therefore, its segregation is very selective. Once these sites have been filled the boundary becomes saturated. At this point a two-dimensional ordered grain boundary structure has been formed. On the other hand, nickel is smaller and can, therefore, segregate to a number of sites in the grain boundary. Additionally, more favorable sites are formed if further disordering occurs in the boundary region.

(a)

(b)

Fig.5. Excess Ni (or Al) concentration on {10 4 0} planes parallel to the $\Sigma 29(520)$ boundary in Ni_3Al at 600K and bulk compositions (a) Ni-24at%Al, (b) Ni-26at%Al.

(a)

(b)

Fig. 6. Equilibrium structures of the $\Sigma 29(520)$ boundary at 600K at bulk compositions (a) Ni-24%Al, (b) Ni-26%Al.

The compositionally disordered region formed in Ni rich Ni_3Al is not of macroscopic dimensions but spans only a few lattice spacings. This may be, however, sufficient to affect the crack nucleation and propagation along grain boundaries. The grain boundary region becomes more akin to that found in weakly ordered alloys and, as discussed above, both the crack nucleation and propagation will be more difficult. In contrast, in Al rich Ni_3Al the two dimensional

compositionally ordered structure, formed due to the segregation of Al, may render the material even more brittle. This considerable difference between the structural changes invoked by segregation of Ni and Al, respectively, may be the principal reason why only in Ni rich alloys the intergranular brittleness can be inhibited by alloying with boron, in particular if co-segregation enhances the segregation of Ni in Ni-rich alloys (Chen, Voter, Albers, Boring and Hay 1990).

5. RECENT PUBLICATIONS BASED ON THE DOE SUPPORTED RESEARCH

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