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EFFECTS OF B AND S ON Ni₃Al GRAIN BOUNDARIES

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INTRODUCTION

In many materials, the mechanical behavior is controlled by the grain boundary (GB) properties. An extreme example is the ordered alloy Ni₃Al, which, as a single crystal, is ductile, while as a polycrystal, pure Ni₃Al exhibits severe intergranular brittleness, making it useless as a technological material. However, it has been found[1] that doping Ni₃Al that is slightly Ni-rich (76% Ni) with small amounts of boron (~ 1-2 atomic%) restores the ductility almost to the level of the single crystal. While it is known experimentally that B segregates to grain boundaries[1], the mechanism by which ductilization occurs is not known. We present here results of our initial investigation into the effects of impurities on Ni₃Al grain boundaries, using interatomic potentials of the embedded atom[2,3] form, coupled with molecular statics techniques.

Theoretical studies of grain boundaries in homonuclear systems have been reported by many authors [4,5]. Both molecular statics and molecular dynamics techniques have been employed. As a result of these studies, the general structural features and, to a lesser extent, the energetics, of pure element GBs are now understood. More recently, studies of alloy GBs have appeared [6,7,8]. In the present work, we study Ni₃Al grain boundaries with B and S impurities. The S impurity is of interest because it is known to have the opposite effect from B on GBs: it promotes intergranular fracture.

The next two sections describe the procedure used to fit embedded atom style potentials to the pure elements Ni, Al, B and S, and the cross potentials necessary for treating alloys and segregants. Parts of this have appeared in detail elsewhere,[3] but are included here because an emphasis on interatomic potentials is appropriate for the present proceedings. It should be of interest that the potentials for B and S, and their cross potentials with Ni and Al, were fit almost exclusively to results from electronic band structure calculations. The last section presents and discusses results from molecular statics simulations using the potentials.

INTERACTION POTENTIALS FOR Ni, Al, B, AND S

The interatomic potentials employed here have the same form as the embedded atom method of Evis and Baskes,[2] though the method of parameterization is different [3]. In the embedded atom approach, the energy of an *n*-particle homonuclear system is written as

$$E = \frac{1}{2} \sum_{i,j=1}^n \phi(r_{ij}) + \sum_{i=1}^n E_{\rho_i}(\rho_i)$$

where r_{ij} is the distance between atoms i and j , ϕ is a pairwise interaction potential, F is the embedding function, and $\bar{\rho}_i$ is the density at atom i due to all its neighbors.

$$\bar{\rho}_i = \sum_{j(\neq i)}^n \rho(r_{ij}) \quad (2)$$

The pairwise potential is taken to be a Morse potential,

$$\phi(r) = D_M \{1 - \exp[-\alpha_M(r - R_M)]\}^2 - D_M \quad (3)$$

The three parameters, D_M , R_M , and α_M , define the depth, distance to the minimum, and a measure of the curvature at the minimum, respectively. The density function, $\rho(r)$, is taken as

$$\rho(r) = r^6 [e^{-\beta r} + 2^9 e^{-2\beta r}] \quad (4)$$

where β is an adjustable parameter. This is the density (ignoring normalization) of a hydrogenic 4s orbital with the second term added to ensure that $\rho(r)$ decreases monotonically with r over the whole range of possible interaction distance (2^9 is the relative normalization factor for a 4s orbital with a doubled exponent). This was originally chosen for describing first-row transition metals, but has been found to work well for a number of fcc metals.

Rose *et al.* [9] have shown that the cohesive energy of most metals can be scaled to a simple universal function, which is approximately

$$E_V(a^*) = -E_0(1 + a^*)e^{-a^*} \quad (5)$$

where a^* is a reduced distance variable and E_0 is the depth of the function at the minimum ($a^* = 0$). Following Foiles *et al.* [10], $F(\rho)$ is specified by requiring that the energy of the fcc crystal obeys Eq. (5) as the lattice constant is varied. The appropriate scaling is obtained by taking E_0 as the equilibrium cohesive energy of the solid (E_{coh}), and defining a^* by

$$a^* = (a/a_0 - 1)/(E_{coh}/9B\Omega)^{1/2} \quad (6)$$

where a is the lattice constant, a_0 is the equilibrium lattice constant, B is the bulk modulus, and Ω is the equilibrium atomic volume. Thus, knowing E_{coh} , a_0 , and B , the embedding function is defined by requiring that the crystal energy from Eqs. (5) and (6) match the energy from Eq. (1) for all values of a^* . By fitting E_V in this way, the potential should be appropriate for a large range of densities. Note that because a^* cannot be expressed neatly as a function of ρ , the construction of $F(\rho)$ is performed numerically once $\phi(r)$ and $\rho(r)$ are known.

To be suitable for use in molecular dynamics and molecular statics simulations, the interatomic potential and its first derivatives with respect to nuclear coordinates need to be continuous at all geometries of the system. This is accomplished by forcing $\phi(r) = \phi'(r) = \rho(r)$ and $\rho'(r)$ to go smoothly to zero at a cutoff distance by defining

$$f_{smooth}(r) = f(r) - f(r_{cut}) + \frac{r - r_{cut}}{m} \left(1 - \left(\frac{r - r_{cut}}{r_{cut}} \right)^m \right) \left(\frac{df}{dr} \right)_{r=r_{cut}} \quad (7)$$

where $f(r)$ denotes $\phi(r)$ or $\rho(r)$ and $m = 20$. The cutoff distance, r_{cut} , is used as a parameter in the fitting procedure. So that $F(\rho)$ is properly defined, $E_V(a^*)$ is also modified to go smoothly to zero when the expanded crystal has a nearest neighbor distance equal to r_{cut} .

Having specified the functional forms for $\phi(r)$, $\rho(r)$, and $F(\bar{\rho})$, we now describe the fitting procedure. Because of the way $F(\bar{\rho})$ is determined, the potential always gives a perfect fit to the experimental values of a_0 , E_{coh} , and B for any choice of $\phi(r)$ and $\rho(r)$. The remaining five parameters, R_M , D_M , α_M , β , and r_{cut} , are determined by minimizing the root-mean-square deviation (χ_{rms}) between calculated and experimental thermodynamic data. This is accomplished using a simplex procedure [11].

For Ni and Al, the experimental data consists of the three cubic elastic constants (c_{11} , c_{12} , and c_{44}), the vacancy formation energy (ΔE_{fv}^f) and the bond length (R_e) and bond energy (D_e) of the diatomic molecule. In addition, the search was constrained by the requirement that the fcc crystal structure be more stable than either bcc or hcp with ideal c/a ratio. As can be seen in Ref. 3, the fit is excellent for Ni ($\chi_{rms} = 0.75\%$) and quite good for Al ($\chi_{rms} = 3.85\%$).

For B and S, because experimental thermodynamic data are less readily available and the native crystal forms are more complex, we employed a different approach. Local density band structure calculations were performed on B and S in hypothetical crystal structures using the linearized muffin tin orbital (LMTO) method [12]. The thermodynamic properties calculated using LMTO for three different crystal structures (fcc, bcc, and fcc with a periodic vacancy structure obtained by removing one of the four cubic sublattices) were then used in the parameter searches. The only experimental information guiding the fits were the diatomic data for B_2 and S_2 . These fits are shown in Table I.

TABLE I. Best fit to LMTO and experimental data for B and S. The values of a_0 , E_{coh} , and B for the fcc phase match exactly due to the way $F(\bar{\rho})$ is determined.

Source	Property	B		S	
		<u>"Expt."</u>	<u>Calc.</u>	<u>"Expt."</u>	<u>Calc.</u>
LMTO	fcc a_0 (Å)	2.91		4.143	
LMTO	fcc E_{coh} (eV)	5.33		2.18	
LMTO	fcc B (10^{12} erg/cm ³)	2.02		7.55	
LMTO	bcc a_0 (Å)	2.34	2.33	2.23	3.29
LMTO	bcc E_{coh} (eV)	4.95	5.31	2.40	2.18
LMTO	bcc B (10^{12} erg/cm ³)	2.11	2.12	1.00	0.75
LMTO	3/4 fcc a_0 (Å)	2.78	2.65	3.97	3.94
LMTO	3/4 fcc E_{coh} (eV)	5.78	5.66	2.60	2.12
experiment	diatomic R_e (Å)	1.59	1.62	1.89	1.83
experiment	diatomic D_e (eV)	3.02	3.06	4.41	4.35

CROSS POTENTIALS FOR Ni/Al WITH B AND S

For a general alloy system, the energy expression becomes

$$E = \frac{1}{2} \sum_{i,j}^N \phi_{ij}(r_{ij}) + \sum_i^N U_i(\bar{\rho}_i) \quad (1)$$

where

$$\bar{\rho}_i = \sum_j^N \rho_{ij}(r_{ij}) \quad (2)$$

and the subscript i indicates the type of atom i . For the present work, we construct potentials for alloys with up to 3 components (we do not put B and S into Ni₃Al simultaneously). Most of the alloy functions required by Eq. (8) are already known from the pure element fits (ϕ_{NiNi} , ϕ_{AlAl} , ϕ_{BB} , ϕ_{SS} , ρ_{Ni} , ρ_{Al} , ρ_B , ρ_S , F_{Ni} , F_{Al} , F_B , F_S), leaving ϕ_{NiAl} , ϕ_{NiB} , ϕ_{AlB} , ϕ_{NiS} , and ϕ_{AlS} to be determined. Just as for the pure elements, these pair functions are taken as Morse potentials. In addition to optimizing the pair potentials, there are two other types of variation that can be utilized to improve the fit to alloy properties. Examination of Eq. (1) shows that the energy of a homonuclear system is invariant under two types of transformation: scaling $\rho(r)$ and adding a linear term to $F(\bar{\rho})$. For an atom of type A, the ρ -scaling transformation is

$$\rho_A(r) \rightarrow s_A \rho_A(r) \quad (10)$$

$$F_A[\bar{\rho}] \rightarrow F_A\left[\frac{\bar{\rho}}{s_A}\right] \quad (11)$$

and the linear embedding term transformation is given by

$$F_A[\bar{\rho}] \rightarrow f_A[\bar{\rho}] + g_A \bar{\rho} \quad (11a)$$

$$\phi_{AA}(r) \rightarrow \phi_{AA}(r) - 2g_A \rho_A(r) \quad (11b)$$

While these transformations do not affect the pure element energy, they do affect the energy of an alloy system. We thus use these additional g and s parameters in optimizing the fits to alloy properties. For an n -component alloy, there are $n - 1$ independent scaling transformations [Eq. (10)] and n independent linear term transformations [Eq. (11)]

We first fit the Ni-Al cross potential [$\phi_{NiAl}(D_M, R_M, \alpha_M, r_{cut})$, s_{Al} , g_{Ni} , g_{Al}], using experimental thermodynamic data on Ni₃Al and B2 phase NiAl, as shown in Ref. 3. Special attention was required to obtain positive energies for the antiphase boundaries (APBs) and the superlattice intrinsic stacking fault energies. Since the time this fit was originally performed, new experimental values have been determined for the 100 and 111 APBs (90 mJ/m² and 111 mJ/m², respectively [13]), which actually agree better with the calculated values (82 mJ/m² and 142 mJ/m², respectively). To obtain the cross potentials with B and S, we utilized LMTO properties of the hypothetical alloys L1₂ phase Ni₃B, Al₃B, Ni₃S, and Al₃S, and B2 phase NiB, AlB, NiS, and AlS, as shown in Table II. The fit for B is seen to be better than the fit for S. The optimized parameters from all the fits are shown in Table III.

TABLE II. Results of fit to LMTO data for Ni-B, Al-B, Ni-S, and Al-S cross potentials using L1₂ phase Ni₃B, Al₃B, Ni₃S, and Al₃S and B2 phase NiB, AlB, NiS, and AlS. For the Ni-B potential, an estimated bond length for diatomic NiB ($R_e=1.60\text{\AA}$) was also included in the fit.

Property	Ni-B		Al-B		Ni-S		Al-S	
	LMTO	Calc	LMTO	Calc	LMTO	Calc	LMTO	Calc
L1 ₂ a_c (Å)	3.39	3.39	3.81	3.91	3.59	3.66	4.19	4.19
L1 ₂ E_{coh} (eV)	4.80	4.80	3.72	3.92	3.96	4.18	3.60	2.89
L1 ₂ B (10 ¹⁷ erg/cm ³)	2.56	2.56	0.93	0.92	2.16	3.15	0.44	0.43
B2 a_c (Å)	2.55	2.58	2.96	2.96	2.97	2.98	3.22	3.59
B2 E_{coh} (eV)	5.30	5.30	4.24	4.27	3.50	3.78	3.90	2.59

TABLE III. Optimized parameters for embedded atom potentials for Ni-Al-B and Ni-Al-S.

	D_M (eV)	R_M (Å)	α_M (Å ⁻¹)	β (Å ⁻¹)	r_{cut} (Å)	s (Å)	g (eVÅ ³)
Ni	1.5335	2.2053	1.7728	3.6408	4.7895	1.0000	6.5145
Al	3.7760	2.1176	1.4859	3.3232	5.5550	0.61723	-0.22050
B	0.7182	1.6517	3.1915	2.0108	4.3716	0.0034936	-0.078785
S	0.5976	0.2495	2.0445	4.7632	5.0795	11.9960	2.1058
Ni-Al	3.0322	2.0896	1.6277		5.4639		
Ni-B	0.2822	2.3149	2.4852		2.8181		
Al-B	0.1295	2.8876	1.3904		3.0000		
Ni-S	0.9479	2.4498	2.9784		8.0382		
Al-S	0.7422	2.1196	1.1299		5.2622		

Despite the fact that the various crystal structures of B and S used here are not naturally occurring forms, potentials that give a reasonable description of these higher energy structures are perhaps as well suited to the task at hand, that of describing B and S as minority alloy constituents at Ni₃Al GBs, as potentials that are fit to the most stable structures. Two possibly more important questions are (a) how accurate are the LMTO results to which the potentials are fit, and (b) how well can the embedded atom method be expected to do in describing systems containing B and S. Regarding question (a), we note that using the same LMTO method to calculate thermodynamic data for the known crystals Ni, Al, and Ni₃Al leads to deviations from experiment of at most 10% and often significantly less. We thus feel that using the LMTO results instead of experimental data is justified. As for question (b), we note that the embedded atom potential does not have any terms that can describe angular effects arising from directional covalent bonding. Directional bonding is certainly more important for both B and S than for either Ni or Al. It is possible that when B or S are placed into the highly coordinated metallic environment, the importance of directional bonding is reduced, though we have no direct evidence of this. The results presented in the following section should thus be viewed with an awareness of this limitation of the interatomic potentials.

GRAIN BOUNDARY SIMULATIONS

The potentials described above have been used for simulations of surfaces^[14] and of grain boundaries in Ni, Al, and Ni₃Al, and Ni₃Al with either B or S segregants^[6,15,16]. We summarize the salient features of the GB results here. All simulations were performed using molecular statics techniques, in which a steepest descent search was used to find the minimum energy geometry. Energies thus correspond to T=0K. Periodic boundary conditions were employed in the GB plane, while the simulation block was terminated with free surfaces in the direction normal to the GB.

Properties of pure Ni, Al, and Ni₃Al [001] symmetric tilt GBs are presented in detail in Refs. 6 and 15. As expected, the GB energy (the energy increase relative to bulk per unit area of the planar GB defect) varies with both the tilt angle and the local composition (excess Al or Ni) of the GB, with the Al rich GB usually highest in energy. GB energies correlate strongly with the local volume expansion of the boundary. The GBs in pure Al are found to be much lower in energy than in pure Ni. The average GB energy in Ni₃Al is very similar to pure Ni, implying that the difference in ductility between the two probably arises from either the difference in yield stress of the surrounding matrix^[17] or from a reduced mobility of dislocations in the Ni₃Al GB region^[18].

When B is introduced into Ni₃Al, it is found to prefer interstitial sites, with typical binding energies as follows: (relative to B atom at infinity) interstitial binding site at GB: 5.7-6.9eV, bulk: 6.0eV (octahedral interstitial site, favored over tetrahedral); 4.6eV, interstitial site near free surface: > 5 eV, surface adsorption site: 5.5eV. These results are consistent with the experimental observation that B segregates to GBs^[1,2,19].

Ni_3Al that is slightly Ni rich (the common experimental stoichiometry is 76% Ni); excess Ni atoms exist as antisite defects. Moving an antisite Ni defect from the bulk to the (210) GB is favorable by 0.14 eV, while moving a B from an octahedral interstitial site to this GB is favorable by 1.9 eV. Moving both a Ni and B to the (210) GB is favorable by 2.5 eV, representing a favorable cosegregation effect of 0.46 eV. Because excess Ni at the boundary disrupts the L1_2 ordering, it is likely that dislocation mobility is also enhanced [18]. Ni cosegregation may thus be an important component of the B ductilizing effect.

While we have not yet performed simulations of dislocations near a GB, we have investigated the effect of B on the boundary cohesion. This was done in a simple fashion: by pulling apart the optimized GB with clamps four lattice constants away on either side. At successive strain increments of 2%, the system was allowed to relax to the lowest possible energy. With this approach the system may not break at the same position or in the same way as it would in a slowly strained, thermalized system, but the results are qualitatively instructive nonetheless. The resulting stress-strain curves are shown in Fig. 1 for the Ni_3Al (210) GB with segregated Ni and/or B (more detail can be found in Refs. [16 and 20]). (Note that both the stress and the strain are much larger than typical experimental values for a macroscopic stress-strain curve. This is because the present simulations give local GB properties.) The addition of B and Ni is seen to significantly enhance both the maximum stress the GB can accommodate and the total work done on the GB (given by the area under the stress-strain curve) before failure. In this case, B alone has only a small effect on the GB cohesion; for the (310) GB, B alone has a large effect. We thus conclude that boron may play two roles in enhancing the ductility of polycrystalline Ni_3Al : by promoting segregation of Ni to the GB, it disrupts the local order and increases the cohesive strength of the GB.

Figure 1. Stress-strain relationship for Ni_3Al [001] symmetric tilt (210) grain boundary. The computational method is described in the text.

In contrast to B, which prefers to bond to GBs, S bonds most favorably to the surface (8.4 eV), in agreement with experimental observations [19]. In the bulk or at the boundaries, S occupies substitutional sites, preferentially displacing Al (bulk Al substitution = 3.0 eV, bulk Ni substitution = 2.2 eV, GB Al

substitution $\approx \sim 0.5\text{eV}$) while interstitial binding is repulsive (3.4eV for bulk interstitial). If S is placed at the GB, it has a pronounced weakening effect, as shown in Fig. 1. This is consistent with experimental observations of sulfur embrittlement in other materials [22].

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