ELECTRONIC THEORY FOR GRAIN BOUNDARY SEGREGATION AND EMBRITTLEMENT OF INTERMETALLIC COMPOUND Ni₃Al

K. Masuda-Jindo

To cite this version:

K. Masuda-Jindo. ELECTRONIC THEORY FOR GRAIN BOUNDARY SEGREGATION AND EMBRITTLEMENT OF INTERMETALLIC COMPOUND Ni₃Al. Journal de Physique Colloques, 1988, 49 (C5), pp.C5-557-C5-562. 10.1051/jphyscol:1988568. jpa-00228065

HAL Id: jpa-00228065
https://hal.archives-ouvertes.fr/jpa-00228065
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ELECTRONIC THEORY FOR GRAIN BOUNDARY SEGREGATION AND EMBRITTLEMENT OF INTERMETALLIC COMPOUND Ni₃Al

K. MASUDA-JINDO

Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Abstract. The cleavage strength of grain boundaries in L1₂ type of intermetallic compounds (Ni₃Al) is investigated using the tight-binding (TB) electronic theory of s, p and d-basis orbitals. The two-center hopping integrals are determined by using the Harrison's universal TB theory and atomic energy levels are taken from the atomic structure calculations by Herman and Skillman. The local charge neutrality condition is used for both host metal and solute atoms. It is shown that cleavage strength of the grain boundaries depends strongly on the segregation of impurity atoms (boron) at the grain boundaries, in agreement with experimental results: The stoichiometry effect of the L1₂ compound is also discussed.

1. Introduction

It is now well established that introduction of small amount of impurity atoms can drastically improve the ductility of polycrystalline intermetallic compounds. Recently, Aoki and Izumi [1] have found that the grain boundary embrittlement of Ni₃Al (L1₂ structure) is improved significantly by an addition of boron and about 30% elongation can be attained in as-cast Ni₃Al sample. Similar experimental results have also been obtained using samples by thermomechanical processing [2] and rapid solidification [3]. In particular, Liu and coworkers [2] have found that boron increases the ductility only in Ni-rich Ni₃Al samples; the best ductility is achieved in samples with 24 atomic percent Al. These authors interpreted the experimental results qualitatively on the basis of impurity segregation to grain boundaries (or the peculiarity of the grain boundary structure).

In contrast to the experimental works on the grain boundary strength of intermetallic compounds, there has only been a few theoretical works on the subject [4-6]. In general, theoretical works so far presented are in a primitive stage and fundamental understanding on the grain boundary strength of intermetallic compounds has not been given yet. It is the purpose of the present paper to investigate the strength of grain boundaries of intermetallic compounds like Ni₃Al with L1₂ structure using a microscopic electronic theory. Particular attention is focused on the effect of impurity (boron) segregation on the cleavage strength of the grain boundaries.

To investigate the cleavage strength of the grain boundaries in the Ni₃Al crystal, we perform the total energy calculations for single crystal as well as for bi-crystals including a symmetric tilt grain boundary (with and without impurity segregation): The total energies of the system are calculated as a function of the separation distance Rsep between the two crystallites. This type of cleaving test of crystals can be done quite efficiently and accurately within the present TB electronic theory. One can then calculate the cleavage force during the cleaving process. From these calculations, we can discuss the grain boundary strength of the Ni₃Al crystal and understand theoretically the effect of impurity segregation on the strength of the grain boundary.
2. Principle of Calculations

To calculate the structure and total energy (enthalpy) of the grain boundaries, we use the well established TB (or LCAO) electronic theory for lattice defect problems [7]. The total energy of the system is assumed to be given by sum of the band structure energy $E_B$ and the pairwise repulsive potential energy $E_{rep}$ between atomic sites $i$ and $j$. Recently it has become possible to justify this type of division of the total energy from first principle electronic theory [8]. The TB hopping parameters are taken from Harrison's universal theory [9] and atomic energy levels are from the atomic structure calculations by Herman and Skillman [10].

The band structure energy $E_B$ are calculated for $s$, $p$ and $d$-subbands by using the recursion method [11, 12]. For the sake of numerical calculations of $E_B$, we use the following expression for the local density of states (DOS)

$$\rho_1^\lambda(E) = \frac{1}{\pi} \frac{b_1 b_2 \ldots b_n / D_{2n}^\lambda (E)}{\sqrt{4b_{\infty} - (E - a_{\infty})^2}} / 2b_{\infty},$$

where all the recursion coefficients $(a_n, b_n)$ after $n$-level are assumed to be equal to their infinite values $a_{\infty}$ and $b_{\infty}$. $\lambda$ specifies the nine valence orbitals $s$, $p_x$, $p_y$, $p_z$, $xy$, $yz$, $zx$, $x^2-y^2$ and $3z^2-r^2$.

In equation 2, the expansion coefficients $A_0^\lambda$ for $D_{2n}^\lambda (E)$ are simple functions of the recursion coefficients $(a_1, \ldots, a_n, a_{\infty})$ and $(b_1, \ldots, b_{n-1}, b_{\infty})$. For instance, within the approximation of $n=3$ (6-th moment approximation) $A_0^\lambda$ are given as

$$A_1^\lambda = 1 - b_3 / b_{\infty},$$
$$A_2^\lambda = -2(a_1 + a_2 + a_3) + (b_3 / b_{\infty}) (2a_1 + 2a_2 + a_3 + a_{\infty}),$$
$$A_3^\lambda = a_1^2 + a_2^2 + a_3^2 + 4(a_1 a_2 + a_1 a_3 + a_2 a_3) - 2(b_1 + b_2),$n
$$-(b_3 / b_{\infty}) (a_1^2 + a_2^2 + a_3^2 + 4a_1 a_2 + 2(a_1 - a_2) (a_3 - a_{\infty}) - 2b_1 - b_2 - b_3).$$

The similar expressions are also given for $A_4^\lambda$, $A_5^\lambda$, $A_6^\lambda$ and $A_7^\lambda$. The asymptotic recursion coefficients $a_{\infty}$ and $b_{\infty}$ are related to the bandwidth and center of the band, and can be determined by the method proposed by Beer and Pettifor [13]. Using equations (1) and (2), the local DOS functions are now given by the form

$$\rho_1^\lambda(E) = \sum_j \frac{C_j / (E - E_j)}{\sqrt{4b_{\infty} - (E - a_{\infty})^2}} / 2b_{\infty},$$

where $E_j$ denotes the $j$-th (complex) root of the equation $D_{2n}^\lambda (E) = 0$, and $C_j$ the weight of the partial fractions $1 / (E - E_j)$. Then, the integration of the DOS can be evaluated analytically in terms of elementary integrals [12], and results for $E_B$ are much more accurate compared to those obtained by using a direct Numerical integration method.

For the repulsive potential between atomic sites $i$ and $j$, we take three kinds of power law dependence:
where $\Phi_{AA}(R_{ij}) = C_{AA} \cdot (R_0/R_{ij})^{n_{AA}}$, $\Phi_{BB}(R_{ij}) = C_{BB} \cdot (R_0/R_{ij})^{n_{BB}}$, $\Phi_{AB}(R_{ij}) = C_{AB} \cdot (R_0/R_{ij})^{n_{AB}}$, $R_0$ is the nearest-neighbour interatomic distance of the perfect crystal. We have chosen this type of power law dependence, since within the TB formalism a repulsive contribution falls off as the square of the TB hopping integrals [14]. It is known that such repulsive potentials are quite successful for the studies on the structural trends of p-d bonded AB-compounds [15].

In view of the success in Refs. 14 and 15, the spatial dependence of the repulsive potentials are chosen such that $n_{AA} = 8$, $n_{AB} = 6$ and $n_{BB} = 4$. $C_{AA}$, $C_{BB}$ and $C_{AB}$ are determined so as to satisfy the equilibrium condition and to reproduce the experimental values of elastic constants (bulk modulus or usual elastic constants $C_{ijkl}$), using the condition of $\Phi_{AB} = \sqrt{\Phi_{AA} \Phi_{BB}}$. We have also consulted the experimental data on the change in the lattice constant of the intermetallic compounds due to deviation of stoichiometry.

The repulsive potential parameter between an impurity (boron) and host atoms is determined by taking into account the atomic volumes of the impurity and host atoms: For this determination, we use the formula of volume change $\Delta V$ due to the solute atom [16]

$$\Delta V = \frac{1}{3} \sum_i \left( R_i \cdot F_i \right)/K,$$

where $R_i$ and $F_i$ denote the position and force vectors for host atomic site $i$ around the solute atom, respectively, and $K$ the bulk modulus of the crystal. In the lack of the reliable experimental results on the $\Delta V$ for boron in Ni$_3$Al, we simply take the atomic volume of boron as $V_0(B) = (0.833)^3 \cdot V_0(Al)$, $V_0(Al)$ being the atomic volume of Al (for details see Ref. 17).

3. Numerical Results and Discussions

The present numerical calculations on the grain boundaries in the intermetallic compound Ni$_3$Al are performed using the two-center hopping integrals proposed by Harrison [14]. The atomic energy levels $E_s$, $E_p$ and $E_d$ for $s$, $p$ and $d$-basis orbitals are taken from atomic structure calculations by Herman and Skillman [10]; $s$, $p$ and $d$-basis orbitals are used for the transition metal atoms and $s$ and $p$-basis orbitals are used for the sp-valence metal atoms (Al and B in the present calculation). Charge neutrality conditions are imposed for each atom.

In order to assess the reliability of the present (sp$^{3d}$) basis TB scheme for the intermetallic compounds like Ni$_3$Al, we have calculated the shear elastic constants $C_{44}$ and $C' = (C_{11} - C_{12})/2$ both for Ni and Ni$_3$Al and presented the results in Table 1. One can see in Table 1 that calculated values of $C_{44}$ and $C'$ both for Ni and Ni$_3$Al are in good agreement with the corresponding experimental values. It is interesting to note that the calculated elastic anisotropy ratio $\Lambda$ for Ni$_3$Al is much larger than that of Ni: Recent experimental results on
the elastic constants for Ni-Al system clearly show this trend, i.e., the anisotropy ratio \( A \) increases quite significantly with increasing the content of Al up to 25 atomic percent of Al [18]. Furthermore, we have checked that anti-phase boundary (APB) energy of \((111)\) plane is about 150 mJ/m\(^2\) and about 1.4 times larger than that of \((100)\) plane (stability of \(L1_2\) structure relative to \(D0_{22}\) structure). We also note that the present TB scheme gives a reasonable description for the one-electron properties of the \(Ni_3Al\) compound. In Fig.1, we present the local DOS for \(Ni_3Al\) crystal calculated by the sp\(^d\)\(^f\) basis recursion method [7]. These DOS curves are similar to those obtained by using much more elaborate calculational schemes such as ASW or LMTO method [19].

Experimental values for Ni are taken from J. P. Hirth and J. Lothe, "Dislocation Theory", (John Wiley & Sons, 1982).

The calculation of the cleavage strength of grain boundary is performed as follows: The two halves of the ordered alloy lattice with surface index \((l,m,n)\) are separated in the \(l,m,n\) direction with no surface relaxation and no reconstruction. This is based on the fact that for transition metal systems the energy reduction due to the surface relaxation or reconstruction is generally small (less than a few percent) compared to the surface energy [20], and not of primary importance for the present problem. Actual numerical calculations are performed for the symmetric tilt \([001]\) grain boundaries with \(l=5\) (210) and \(l=13\) (320) structures in the \(L1_2\) \(Ni_3Al\) crystals. The stable atomic structure of the grain boundary is calculated by using a direct total energy minimization procedure [21], from unrelaxed initial atomic configurations proposed by Takasuugi and Izumi [22] and Farkas and Ran [23].

In Fig.2, we present the calculated atomic configurations in the core of the tilt grain boundaries with \(l=5\) (210) (a) and \(l=13\) (320) (b) structures in \(Ni_3Al\) crystal. Symbols \(\bigcirc\) and \(\Box\) represent Ni and Al atoms, respectively. One can notice in Fig.2 that the distances between (210) atomic planes or between (320) atomic planes are changed

---

**Table 1.** Calculated shear elastic constants \(C_{44}\) and \(C'\) for Ni and \(Ni_3Al\), in units of \(10^{10}\) Pa.

<table>
<thead>
<tr>
<th></th>
<th>(C_{44}) (cal.)</th>
<th>(C_{44}) (exp.)</th>
<th>(C') (cal.)</th>
<th>(C') (exp.)</th>
<th>(A) (cal.)</th>
<th>(A) (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>11.43</td>
<td>12.47</td>
<td>5.74</td>
<td>4.96</td>
<td>2.00</td>
<td>2.52</td>
</tr>
<tr>
<td>(Ni_3Al)</td>
<td>12.60</td>
<td>11.80</td>
<td>4.14</td>
<td>3.57</td>
<td>3.05</td>
<td>3.31</td>
</tr>
</tbody>
</table>

---

**Fig.1** Local DOS for \(Ni_3Al\) crystal, (a) Ni-site and (b) Al-site. Recursion coefficients are calculated up to \(n=11\) levels and energies, relative to the Fermi energy, are given in units of eV.
strongly near the grain boundaries. These characteristic grain boundary structures are not so much changed from those reported in Ref. 4.

In Fig. 3a, we present the calculated cleavage strength $f$, as a function of the separation $R_{sep}$ between a pair of the crystallites, for $\Sigma = 5$ tilt grain boundary in Ni$_3$Al crystal. The corresponding result of the cleavage strength for $\Sigma = 13$ tilt grain boundary is shown in Fig. 3b. In Figs. 3a and 3b, solid curves represent the cleavage strength for the (single and bi-) crystals, without impurity segregation, while symbols ▲ represent the cleavage strength for the boron segregated grain boundaries. The cleavage strength for the Ni enriched grain boundary is shown by symbols ⬤, in both Fig. 3a and 3b. In the boron segregated or Ni enriched grain boundaries, all of the Al-sites at the boundary Ni/Al layer are substituted by boron or Ni atoms: Cleavage plane is chosen to the boundary plane (dashed line in Fig. 2). We can discuss, from these cleavage force calculations, the strength of the grain boundaries in the L1$_2$ Ni$_3$Al crystal (more directly than the calculations of the grain boundary energy). The importance of the cleavage strength calculation has been discussed by Tyson [24] and Kelly et al. [25], in relation to the fracture toughness of crystalline materials.

![Fig. 2](image_url)  
**Fig. 2** Calculated atomic configurations of the tilt grain boundaries in Ni$_3$Al crystals, with (a) $\Sigma = 5$ (210) and (b) $\Sigma = 13$ (320) structures.

![Fig. 3](image_url)  
**Fig. 3** Cleavage force $f$ ($10^{10}$Pa), as a function of $R_{sep}$ for the $\Sigma = 5$ (210) (a) and $\Sigma = 13$ (320) tilt grain boundaries in Ni$_3$Al crystal.
One can see in Figs. 3a and 3b that the cleavage strength of the tilt grain boundaries in Ni$_3$Al reduces significantly (about 80%) compared to that for the perfect single crystal. This result can be understood qualitatively from the local DOS on the atoms near the grain boundaries. The local DOS on the Ni atom (at the first Ni layer) around $\Sigma = 5$ (210) tilt grain boundary in Ni$_3$Al crystal is shown in Fig. 4. One can see that local bandwidth decreases substantially and this gives rise to the reduction of grain boundary strength. On the other hand, cleavage forces in Fig. 3 give us other important information: One can see in Fig. 3 that segregated boron atoms considerably increase the cleavage strength of the grain boundary. It is most interesting that the effect of Ni enrichment on the grain boundary strength is fairly important and much stronger than that of boron. This indicates that the increase of d-electron bonding strongly enhances the grain boundary cleavage strength of Ni$_3$Al crystal. These theoretical findings (we have obtained the similar results for interstitial boron) are in good agreement with the experimental results of Refs. 1 and 2 (stoichiometry effect) and also with Ref. 26 (grain boundary strengthening due to solute atoms with unfilled d-shell).

References