Interfacial Segregation of Early Transition Metals in Nickel Aluminide*

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Segregation behavior of Ti, V, and Hf impurities at antiphase boundaries (APBs) in Ni_3Al is computed and related to the site preference. The effect of relaxation of atomic positions is considered. Using a relationship between site preference and segregation behavior, the effect of other transition metals on APBs is predicted.

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Ni_3Al has the L_{12} structure¹⁾ that is derived from the fcc structure by ordering. In the L_{12} structure the cube corners are occupied by the Al species, and the face centers are occupied by the Ni species. Antiphase boundaries (APBs) are formed when a dislocation with a $[\frac{1}{2} \frac{1}{2} 0]$ Burgers vector moves through Ni_3Al with the L_{12} structure. The most important parameter which characterizes APBs is the APB energy (APBE). This property has been measured extensively, but the effect of composition and of substitutional impurities remains controversial,^{2,3)} with some authors claiming that the APBE can be very much increased by impurities.²⁾ Simulations have shown that impurities and other defects can strongly segregate towards APBs.^{3,4)} Here, the segregation of Ti at (111) and (100) APBs in Ni_3Al is examined using electronic total energy calculations and Cluster Variation Method (CVM) calculations. The CVM calculations were performed in the tetrahedron-octahedron (TO) approximation⁴⁾ with *ab initio* effective interatomic interactions. In an earlier report the relationship between site preference^{5,6)} and APB segregation was discussed for unrelaxed APBs.⁴⁾ Here, a more detailed discussion is given and the effect of positional relaxation near an APB is investigated through electronic total energy calculations.

Details concerning the cluster variation method (CVM) have been published in an earlier paper.⁴⁾ Total energies required for the cluster expansion of the internal energy were obtained with the LMTO-ASA method.⁷⁾ In order to evaluate how relaxation of atomic positions in the vicinity of APBs would affect the results, supercell calculations were carried out. Structural optimization in the ASA approximation is known to be unreliable, and therefore, for the supercell calculations, we used the plane-wave pseudopotential method with ultra-soft pseudopotentials⁸⁾ while employing the generalized gradient approximation⁹⁾ for the exchange-correlation potential. A cutoff energy of 242 eV was used and the reciprocal space integrations were carried out by summing over a $3 \times 3 \times 3$ grid of 'special' k-points.¹⁰⁾ Four cells were considered with translation vectors $\langle 1 - 1 0 \rangle$, $\langle 1 0 - 1 \rangle$, and $\langle 2.5 1.5 2 \rangle$, in terms of the fcc lattice parameter (0.3477 nm), making for a cell with 24 atoms, see Fig. 1. In these cells a (111) APB occurs once every 6 (111) planes. The basal plane

Fig. 1 Unrelaxed supercells for determining impurity—APB interaction. Small dark gray, small light gray, and big dark gray spheres represent Al, Ni, and impurity atoms. In (a) and (c) the impurity atom is located at the APB, whereas in (b) and (d) the impurity atom is two (111) planes away from the APB.

in Fig. 1 is a close packed (111) plane, and the APB occurs between the lowest and second lowest (111) plane. The second nearest neighbor Al—Al bonds are indicated, and across the APB no Al—Al second nearest neighbor bonds occur. By inserting impurity atoms in these cells both at, and two planes away from the APB, the interaction between impurity atoms and APBs can be examined. In cells (a) and (b), a Ni atom was removed from stoichiometric Ni_3Al and replaced with a Ti atom, creating the unfavorable situation in which a Ti atom occupies a Ni site. In cell (a), the Ti atom was located right at the APB, and in cell (b) the Ti atom was two planes away from the APB. In cells (c) and (d), an Al atom was removed from stoichiometric Ni_3Al and replaced with a Ti atom, creating the favorable situation in which a Ti atom occupies an Al site. In cell (c), the Ti atom was located right at the APB, and in cell (d) the Ti atom was two planes away from the APB.

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CVM calculations were carried out as described in an earlier study.⁴⁾ In that work a very low value for the (100) APBE was computed. This could be attributed to an inaccurate cluster expansion which underestimated the formation energy of the Ni_3Al L_{12} structure and overestimated the formation energy of the DO_{22} structure. The too small energy difference, as computed with the cluster expansion, between these structures, which differ from each other in terms of closely spaced (100) APBs, naturally leads to a too small (100) APB energy. Here, the same total energies are used to obtain the cluster expansion as in the previous work, but by giving large weights¹¹⁾ to the L_{12} and DO_{22} structures (value of $w_{\text{Ni}_3\text{Al}-\text{L}_{12}}$ and $w_{\text{Ni}_3\text{Al}-\text{DO}_{22}}$ in eq. 6 in Ref. 4) was set to 10) a much improved cluster expansion was obtained. The improved cluster expansion gave APBEs of 318 mJ/m^2 for the (111) plane and 176 mJ/m^2 for the (100) plane in binary Ni_3Al . These values are higher than has been obtained by other electronic structure calculations, which is reasonable because our values exclude the effect of relaxation near the APB. This relaxation is known to reduce the APB energies by about 20% in L_{12} structures.¹²⁾ The current cluster expansion also gives a much more reasonable ratio of (111) APBE over (100) APBE of about 1.8 which is close to the FLAPW value of 1.6.¹³⁾ On purely geometric grounds it can be argued that generally the (111) APBE should be greater than the (100) APBE. Across a (111) APB, the nearest neighbor shell is disturbed, so that the (111) APBE is proportional to the nearest neighbor effective pair interaction. At the (100) APB, however, the nearest neighbor shell is completely intact, and the second nearest neighbor shell is disturbed. As the nearest neighbor effective pair interaction generally is bigger than the second nearest neighbor effective pair interaction,⁵⁾ and this is also the case in Ni_3Al , it follows that the (111) APBE is larger than the (100) APBE.

It should be mentioned that the Ni_3Al order-disorder temperature as predicted with the CVM in the TO approximation is about 2500 K, or about 30% higher than has been surmised from experimental work.¹⁴⁾ As the TO-CVM gives rather accurate order-disorder temperatures, this indicates that the cluster expansion overestimates the temperature scale. Therefore, the theoretical temperature should be reduced by about 30% in order to make comparisons with experiment.

Total energy calculations, detailed in Table 1, reveal that irrespective whether Ti occupies the Ni or Al site, it favors to be located away from a (111) APB. The tendency to segregate away from the APB is most pronounced on the Al site for which Ti has a strong affinity. Ti favors the Al site by about

1 or 3 eV (site preference energy) depending on whether the alloy is Ni-poor or Al-poor.⁶⁾ It should be noted that the segregation energy is almost an order of magnitude smaller than the site preference energy, see Table 1. Relaxation reduces the segregation energy, on the Ni site as well as on the Al site. It is clear that the site preference of Ti is not affected much by the presence of APBs, and not affected much by relaxation either. The segregation of Ti away from APBs is reduced by as much as a third (from 0.321 to 0.205 eV). We should expect then that the segregation of Ti computed with the CVM, where relaxation is ignored, should be overestimated by about a third. Other elements which have been reported to much increase the APB energy have been considered as well. Hf has an even stronger site preference for the Al site than Ti,⁵⁾ and correspondingly the segregation energy is larger too. Hf, like Ti, strongly segregates away from the APB and thus according to the Gibbs absorption law¹⁵⁾ Hf increases the APBE. Therefore, Hf behaves like Ti at APBs but with greater intensity.

V has a weaker site preference for the Al site than Ti,⁵⁾ and the segregation energy is weaker as well. The weaker site preference means that the site occupancy of the V atoms is dependent on the composition.⁵⁾ In Al-rich material, some fraction of the V atoms will be forced onto the Ni sites. V on the Al sites will segregate away from the APB, but V on the Ni sites has a vanishing segregation energy. Thus, we might suspect that in Ni-rich alloys, V segregates away from the APB therefore raising the APBE, and in Al-rich alloys V does not interact with APBs and therefore does not affect the APB energy.

The difference between the relaxed and unrelaxed total energies is largest for Hf and smallest for V, as one would expect on the basis of their atomic sizes. The relaxation energy in every case is larger on the Ni sites than on the Al sites. The differences being 0.5, 0.3, and 0.2 eV, for Hf, Ti, and V, respectively. This means that relaxation somewhat weakens the Al site preference seen for early transition metals. The unrelaxed site preference energy for Ti and Hf is 1 eV or more in Al-rich alloys and 3 eV or more in Ni-rich alloys, so that the site preference of these elements is not changed by relaxation. In the case of V the site preference remains weakly in favor of the Al site.

In all cases, relaxation is seen to make the segregation energies less positive. This is not surprising given that Hf, Ti, and V atoms are all larger than the Ni and the Al atoms in Ni_3Al (Al atoms in pure Al are quite large on the other hand),

Table 1 Computed (pseudopotential) total energies of supercells shown in Fig. 1, both for the case of atoms at fcc lattice positions and for relaxed atomic positions.

Impurity	Relaxed	Energy				Segregation energy	
		a (eV)	b (eV)	c (eV)	d (eV)	a-b (eV)	c-d (eV)
Ti	no	-130.566	-130.646	-136.067	-136.388	0.080	0.321
Ti	yes	-131.113	-131.152	-136.339	-136.544	0.039	0.205
V	no	-134.588	-134.583	-133.825	-134.084	-0.005	0.259
V	yes	-134.968	-134.977	-134.036	-134.255	0.009	0.219
Hf	no	-130.987	-131.033	-137.217	-137.776	0.046	0.559
Hf	yes	-131.966	-131.985	-137.766	-138.089	0.019	0.323

and given that the interplanar spacing is greater near the APB because of the presence of unfavored (Al–Al) bonds. Again, as the interplanar spacing is increased more at (111) APBs, which have ‘wrong’ nearest neighbor bonds, than at (100) APBs, which have ‘wrong’ second nearest neighbor bonds only, relaxation will matter more at (111) APBs than at (100) APBs.

Results obtained with the CVM give insight in the behavior of Ti in Ni_3Al at finite temperature. As described in earlier work,⁴⁾ Ni_3Al with impurities with strong Al site preference can be compared to the binary case provided that the effective Al concentration is taken as the sum of the actual Al concentration and the concentration(s) of the Al site preferring impurities. This is especially evident in Fig. 2 which shows that at constant Ni concentration the Ti concentration has almost no effect of the amount of Ni that has segregated towards or away from the APB. This indicates that Ti itself does not affect segregation on the Ni sublattice. Of course, the amount of Al that is absorbed onto the APB is very sensitive to the Ti concentration. In Ni-poor materials, Al segregates towards an APB,³⁾ and the presence of Ti, that strongly segregates away from the APB, makes that Al segregates even more towards the APB when some Al in the alloy is replaced with Ti. In Al-poor materials, Ni segregates towards the APB, and Al segregates away from the APB. The presence of Ti, that segregates even stronger away from the APB than Al does, means that replacing Al with Ti reduces the Al segregation away from the APB.

Strong segregation of Ti away from the APB indicates that when Al is replaced with Ti, the APBE increases. This is borne out by the CVM calculations. In Fig. 3 the APBE is shown as a function of the Ni concentration for three concentrations of Ti. The (111) APBE rises by as much as 15 mJ/m^2 per atomic percent Al replaced with Ti in Ni-poor alloys, while in Ni-rich alloys the effect is weaker at about 10 mJ/m^2 per atomic percent Al replaced with Ti.

The (111) APBE in Ni_3Al has been determined experimentally with the weak beam method.¹²⁾ These measurements indicate that APBEs increase when early transition metals,¹²⁾ such as Ti, V, and Hf, are added to Ni_3Al . This implies that early transition metal impurities in Ni_3Al segregate away from the APBs. Our calculations for Ti and Hf are in complete agreement with these observations. On the other hand, for V we predict that an increase in the APBE occurs in Ni-rich alloys only.

The interaction between Ti, V, and Hf substitutional impurities with APBs in Ni_3Al was studied. Electronic total energy calculations at zero temperature showed that atomic species that have a strong preference for the Al type site, tend to strongly segregate away from the APB as was argued on the basis on previous CVM calculations.⁴⁾ Relaxation of atomic positions makes that large atoms like Hf and Ti have a lower energy near APBs, where ‘wrong bonds’ locally expand the lattice, than in the bulk. However, in the bulk, Hf(Ti) atoms located on Al sites have an ideal surrounding in that the number of attractive bonds with Ni is maximized and the number of repulsive bonds with Al is minimized.⁴⁾ This ideal surrounding makes for a very large site preference energy. Near APBs the local order is disturbed and unfavorable bonds occur, meaning that part of the site preference energy is relin-

Fig. 2 Amount of Ni segregated towards a (111) APB at a theoretical temperature of 2000 K (corresponding to an actual temperature of about 1400 K) as a function of the Ni concentration in a $\text{Ni}_x\text{Al}_{1-x-y}\text{Ti}_y$ alloy.

Fig. 3 (111) APBE at a theoretical temperature of 2000 K (corresponding to an actual temperature of about 1400 K) as a function of the Ni concentration in a $\text{Ni}_x\text{Al}_{1-x-y}\text{Ti}_y$ alloy.

quished. This makes positioning of Hf(Ti) atoms near an APB unfavorable. The difference of the relaxation energy associated with a Hf(Ti) atom at an APB and a Hf(Ti) atom in the bulk is much smaller than the site preference energy. Therefore, relaxation does not much affect the segregation behavior of Hf(Ti) at APBs. The strong segregation away from the APB makes that Hf(Ti) increases the APB energy. The same reasoning applies to any substitutional element that has strong Al site preference (Sc, Ti, Zr, Hf, Nb, Ta).

For elements that have a weak or no site preference such as V, Cr, Mo, W, the situation is more complicated. The site occupancy of these atoms depends on whether the alloy is Ni-rich or Al-rich. In Ni-rich alloys, V occupies the Al sites and there is a weaker segregation away from the APB. V then has a similar effect as Hf and Ti on the APB properties, weakly increasing the APBE. In Al-rich alloys, V occupies the Ni sites. As the site preference energy on these sites is much weaker, the relaxation energy is strong enough to cancel the interaction between V and the APB. Thus, V does not segregate toward or away from APBs and does not affect the APBE in Al-rich alloys.

In the case of Ti, CVM calculations confirmed that these

tendencies do not apply only at low temperatures but strongly persist at high temperature.

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