Segregation and structural transformations at $\Sigma = 3$ grain boundaries in NiAl: A Monte-Carlo study

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Abstract

Grain boundary structure and grain boundary segregation in stoichiometric and Ni-rich compositions of NiAl are studied by molecular statics and grand-canonical Monte-Carlo simulations in conjunction with an embedded-atom potential. Significant Ni segregation is found at the $\Sigma = 3(1 1 1)$ and $\Sigma = 3(2 1 1)$ grain boundaries, with segregation isotherms showing a saturation effect. The amount of Ni segregation increases and the excess free energy of the grain boundaries decreases with increased Ni bulk concentration. In strongly Ni-rich bulk compositions, both boundaries undergo transformations to new structures capable of accommodating more excess Ni atoms than the initial structures. The structural transformation is clearly manifested by a non-monotonic behavior of the segregation isotherm. In the $\Sigma = 3(2 1 1)$ grain boundary, the transformation is accompanied by a relative tangential translation of the grains.

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1. Introduction

The nickel aluminide NiAl crystallizes in the B2 (CsCl prototype) structure and has a homogeneity range of approximately 40–60 at.% Ni. This compound possesses unique physical, chemical and mechanical properties that make it a promising candidate for many high-temperature structural applications [1]. At room temperature, however, NiAl tends to fail at small strains by intercrystalline crack propagation. This brittleness is believed to be due to weak cohesion across grain boundaries (GBs), which causes their failure before stresses can activate sufficient slip systems in the lattice. A search for ways of alleviating the GB weakness in NiAl requires a fundamental understanding of GB structure and other GB properties in this material.

In partially ordered compounds, one of the components can segregate to GBs and alter their energy and cohesion, which in turn can affect fracture behavior of the material [2,3]. GB structure and segregation in NiAl have been studied by atomistic computer simulations using $\Sigma = 5$ symmetrical tilt boundaries as representative high-angle GBs in this material [4–8] ($\Sigma$ being the reciprocal density of coincidence sites [2,3]). Ni was found to segregate to the $\Sigma = 5$ GBs in both stoichiometric and Ni-rich bulk compositions. Furthermore, in one of the $\Sigma = 5$ boundaries, a structural transformation to a new structure was found to result from the Ni segregation [8]. It was determined that Ni segregation increases the ductility of $\Sigma = 5$ GBs in NiAl [8].

There has been little work on GBs beyond $\Sigma = 5$ [6,9]. Therefore, the goal of this paper is to perform atomistic computer simulations of structure and segregation at $\Sigma = 3$ GBs in NiAl. Such boundaries are very common in this material and can have a significant impact on its properties. For example, an increase in the fraction
of $\Sigma = 3$ and $\Sigma = 5$ GBs by an appropriate thermomechanical treatment improves the GB crack resistance of polycrystalline NiAl [10]. This observation suggests that fracture toughness of this material can be increased by shifting the GB character distribution towards low-$\Sigma$ orientations (GB engineering [11]). In this work, we apply molecular statics calculations and Monte-Carlo simulations to determine the atomic structure and chemical composition of $\Sigma = 3$ GBs in NiAl depending on the bulk composition. As with $\Sigma = 5$ GBs before, we observe Ni segregation and structural transformations at $\Sigma = 3$ GBs. This finding suggests that Ni segregation is likely to be general to all GBs in NiAl.

2. Atomic interactions and simulation block

Atomic interactions in NiAl were modeled using the embedded-atom potential constructed in [12]. This potential has previously been applied to model segregation and decohesion at $\Sigma = 5$ GBs [8] as well as surface structure and segregation in NiAl thin films [13,14]. The potential is fit to experimental and first-principles data and accurately reproduces lattice properties (including elastic constants, thermal expansion and phonon frequencies), point-defect formation energies, planar fault energies, surface energies and other properties of NiAl.

A $\Sigma = 3$ lattice misorientation is obtained by an appropriate rotation of two grains around the [0 1 1] axis. Various $\Sigma = 3$ tilt GBs can be produced by choosing different GB planes (inclinations) containing the [0 1 1] direction. There are two particular inclinations that are most commonly found in NiAl. The choice of the (1 1 1) inclination results in the $\Sigma = 3(1 1 1)[0 1 1]$ symmetrical twin boundary. In NiAl, crystal planes parallel to (1 1 1) represent alternating Ni and Al atomic layers. Therefore, this boundary can be centered on either a Ni or an Al layer. We denote the relevant GB structures by $\Sigma = 3(1 1 1)_{\text{Ni}}$ and $\Sigma = 3(1 1 1)_{\text{Al}}$, respectively. Both boundaries will be studied in this paper. We emphasize that both GBs are fully stoichiometric, i.e., there is no access of Ni or Al atoms in the boundary region. The second inclination is (2 1 1), which produces the symmetrical twin $\Sigma = 3(2 1 1)[0 1 1]$ GB. The centering of this boundary is unique since (2 1 1) layers are stoichiometric.

The chosen GBs were created by standard geometric constructions of the coincidence site lattice model [2]. The computational block had periodic boundaries in all three directions. Under such conditions, the grains are free to slide against each other to achieve equilibrium. Due to the periodicity in the direction normal to the GB plane, the block effectively contained two identical GBs. Their separation was set to be large enough to prevent their interaction. Namely, for the $\Sigma = 3(2 1 1)$ GB the block comprised 2400 atoms arranged in 48 (2 1 1) atomic layers parallel to the GB plane. For the $\Sigma = 3(1 1 1)$ GBs, the block contained 2160 atoms with 36 (1 1 1) layers parallel to the GB. The block was relaxed statically (temperature $T = 0$ K) by minimizing its total energy with respect to: (1) local atomic displacements and (2) block dimensions in all three directions. The GB energies were found to be 0.673 J/m$^2$ for $\Sigma = 3(1 1 1)_{\text{Al}}$, 2.072 J/m$^2$ for $\Sigma = 3(1 1 1)_{\text{Ni}}$, and 0.436 J/m$^2$ for $\Sigma = 3(2 1 1)$.

3. Molecular statics calculations

To probe the tendency of the GBs to develop compositional disordering, antisite formation energies were calculated as functions of distance from the GB plane. The calculations were implemented by selecting an individual atom, switching its atomic sort to opposite species (thus creating an antisite defect), and performing a static relaxation of the block. The change in the total energy gave us the formation energy of the antisite. This calculation was repeated for each atomic layer parallel to the GB. For the (1 1 1) GBs, the layers consisted of either Ni or Al atoms and the relevant antisites were $\text{Al}_{\text{Ni}}$ (Al atoms on the Ni sublattice) and $\text{Ni}_{\text{Al}}$ (Ni atom on the Al sublattice), respectively. For the $\Sigma = 3(2 1 1)$ GB, the energies of both antisites were computed within the same stoichiometric (2 1 1) layer. The average of the formation energies of opposite antisites within the same (2 1 1) layer or in neighboring (1 1 1) layers was also determined. For the (1 1 1) GBs, this average value was assigned to a median plane between two (1 1 1) layers. The average antisite formation energy equals half of the formation energy of the exchange defect in NiAl [12] and is useful as a metric of resistance of this compound to compositional disorder.

The results of the calculations for the $\Sigma = 3(1 1 1)_{\text{Al}}$ GB are shown in Fig. 1(a). Both antisite formation energies show a marked decrease in the GB region. The average antisite formation energy follows the same trend, indicating a tendency towards compositional disordering over a relatively wide ($\pm 0.5$ nm) region around the GB. Attempts to calculate antisite formation energies in the $\Sigma = 3(1 1 1)_{\text{Ni}}$ GB were unsuccessful: during the static relaxation, this boundary spontaneously transformed to the $\Sigma = 3(1 1 1)_{\text{Al}}$ GB containing an antisite. This extreme instability of the $\Sigma = 3(1 1 1)_{\text{Ni}}$ GB correlates with its very high energy and will be confirmed by Monte-Carlo simulations in Section 4.

The $\Sigma = 3(2 1 1)$ GB demonstrates a larger decrease in the antisite formation energy (Fig. 1(b)), suggesting a stronger compositional disordering in comparison with the $\Sigma = 3(1 1 1)_{\text{Al}}$ GB. In addition, this decrease is more strongly localized around the GB core.
4. Monte-Carlo simulations

4.1. Simulation methodology

The segregation and structural transformations at the GBs were studied by Monte-Carlo simulations. They were performed within the modified grand-canonical ensemble wherein the temperature $T$, the total number of atoms in the system $N$, and the chemical potential difference $\mu$ between Ni and Al ($\mu = \mu_{Ni} - \mu_{Al}$) were held fixed [15]. The number of atoms of each individual species was allowed to vary according to the value of $\mu$. The volume of the simulation block was also allowed to fluctuate at each Monte-Carlo step in order to simulate zero-pressure conditions. In effect, our simulated system contains a constant number of substitutional sites and is connected to an infinite reservoir of heat and Ni and Al atoms. At each step of the simulation, an atom is randomly selected and displaced by a relatively small random amount in an arbitrary direction. Simultaneously, its chemical sort is randomly chosen to either remain unchanged or switch to the alternate species. This trial move is accepted with a unit probability if

$$\Delta \Omega \equiv \Delta E + \mu \pm \frac{3}{2} k_B T \ln \frac{m_{Ni}}{m_{Al}} - N k_B T \ln \frac{V'}{V} < 0$$  \hspace{1cm} (1)

and with the probability of

$$\exp(-\Delta \Omega/k_B T),$$  \hspace{1cm} (2)

if $\Delta E > 0$ [16]. Here $\Delta E$ is the potential energy change in the trial move, $V$ and $V'$ are the block volumes before and after the move, $m_{Ni}$ and $m_{Al}$ are the atomic masses, and $k_B$ is the Boltzmann constant. The sign in Eq. (1) depends on whether a Ni atom is replaced by Al (+) or vice versa (−). This method allows both compositional rearrangements and relaxation of atomic positions to occur simultaneously.

Throughout all simulations, the temperature was held fixed at 1200 K. Several chemical potential differences were chosen, each corresponding to a different equilibrium bulk composition. The relevant bulk compositions were obtained by separate simulations using a cubic supercell without a GB. They range from a nearly stoichiometric composition of 0.501 to a strongly Ni-enriched composition of about 0.579 (in this work the chemical composition is measured by the atomic fraction of Ni atoms).

Statically relaxed GBs were used as starting configurations. The simulation block was brought to thermodynamic equilibrium at 1200 K by $10^4$ Monte-Carlo steps per atom, followed by an additional $6 \cdot 10^4$ steps for calculating the average distribution of the species. For highly Ni-rich compositions, two additional runs of $4 \cdot 10^4$ steps per atom were made to verify that equilibrium had indeed been achieved. The simulations delivered the average occupation of each atomic site. These average occupations, coupled with average atomic coordinates, were used to calculate the Ni concentration profile across the simulation block. The profile was obtained by averaging the Ni concentration over each atomic layer parallel to the GB.

The Gibbsian adsorption, $\Gamma$, was also computed in order to quantify the total amount of GB segregation [17]. This quantity is defined by the number of excess Ni atoms per unit GB area,

$$\Gamma = \frac{(\bar{c} - c_b) N}{2S},$$  \hspace{1cm} (3)

where $\bar{c}$ is the average Ni concentration in the simulation block, $c_b$ is the bulk composition, and $S$ is the cross-sectional area of the GB. The factor 2 in the denominator of Eq. (3) reflects the presence of two grain boundaries in the simulation block. As a matter of convenience, all $\Gamma$ values are reported here in the effective number of monolayers (ML). The latter is obtained by

Fig. 1. Antisite defect formation energy as a function of distance to the grain boundary. (a) $\Sigma = 3(1 1 1)_{Al}$ GB; (b) $\Sigma = 3(2 1 1)$ GB. The dashed line marks the boundary plane.

![Fig. 1](image-url)
dividing $\Gamma$ by the number of atoms per unit area of a perfect crystal plane parallel to the GB.

4.2. $\Sigma = 3\text{(1 1 1)}$ boundaries

Fig. 2 shows the isotherm of segregation, $\Gamma$ as a function of the bulk composition $c_b$, for the $\Sigma = 3\text{(1 1 1)}_{\text{Al}}$ GB. As was observed earlier for $\Sigma = 5$ GBs [8], Ni readily segregates to this GB ($\Gamma > 0$) and the amount of segregation increases with Ni bulk concentration and shows a saturation trend at high Ni concentrations. At $c_b \approx 0.57$, the boundary absorbs almost a complete equivalent monolayer of Ni. Notice a rapid increase in $\Gamma$ at $c_b \approx 0.52$, which is indicative of either a change in the segregation mechanism or a structural transformation in the boundary.

Representative Ni concentration profiles across the $\Sigma = 3\text{(1 1 1)}_{\text{Al}}$ GB are shown in Fig. 3. They reveal marked concentration peaks corresponding to regions of enhanced GB segregation. In agreement with the segregation isotherm (Fig. 2), the height of the peak increases with Ni bulk concentration. Notice, however, that the peaks are shifted away from the initial GB plane and that the direction of the shift varies from one bulk composition to another. This behavior indicates that Ni segregation destroys the initial mirror symmetry of the GB and probably alters its structure.

The structural evolution of the GB has been analyzed by examining multiple snapshots produced by Monte-Carlo simulations. In Fig. 4(a) and (b), we compare the ground-state GB structure at 0 K with the structure obtained at 1200 K for the stoichiometric bulk. In these and all subsequent plots of boundary structures, we show projections of all atoms onto the plane normal to the tilt axis. The latter is normal to the viewer while the GB plane is horizontal. To reduce the scatter associated with atomic vibrations, a short Monte-Carlo run was made on each snapshot without switching chemical sorts of atoms. The atomic coordinates were averaged over this run and used for plotting the structure. We emphasize that this averaging was only implemented for the structure representation and by no means affected our simulation results. Ni and Al atoms are shown in the plots by circles and triangles, respectively, and represent an instantaneous site occupation. All distances are in nanometers. The structural units of the GB are outlined by dashed lines. Fig. 4(a) and (b) demonstrate that the initial GB structure remains virtually unchanged at 1200 K except for its thermal expansion, which is especially noticeable within the GB core (the structural units become significantly wider in the [1 1 1] direction).

As the bulk deviates from stoichiometry towards Ni-rich compositions, the boundary develops an increasing structural disorder and eventually transforms to a new structure shown in Fig. 4(c). This structure is best described as an embedded Ni layer surrounded by “compressed” (1 1 1)-type layers, each obtained by merging two adjacent (1 1 1) planes. The “compressed” layers still maintain some small separation and develop a significant concentration of vacancies, which are left behind by atoms moving into the GB plane. The latter accommodates the excess Ni atoms and thus facilitates the Ni segregation. The former Al layer forming the center of the initial GB structure becomes incorporated into one of the “compressed” layers, which results in a shift of the new structure away from the initial GB plane. The direction of the shift is chosen by the boundary at random. The transformation to the new GB structure does not happen abruptly at a particular bulk composition.

Fig. 2. Isotherms of Ni segregation at $\Sigma = 3$ grain boundaries in NiAl at 1200 K. $c_b$ is the Ni bulk concentration and the Gibbsian adsorption is measured in the effective number of monolayers.

Fig. 3. Selected Ni concentration profiles across the $\Sigma = 3\text{(1 1 1)}_{\text{Al}}$ grain boundary in NiAl at 1200 K. Upper curves: Ni sublattice; lower curves: Al sublattice. The bulk concentrations are indicated in the legend.
but is smeared over a range of $c_b$ values around $c_b \approx 0.52$.

4.3. $\Sigma = 3(111)_{\text{Ni}}$ boundary

The $\Sigma = 3(111)_{\text{Ni}}$ GB was found to be unstable under our simulation conditions. During Monte-Carlo runs, this boundary quickly transformed to the Al-centered $\Sigma = 3(111)_{\text{Al}}$ GB with the new boundary plane located above or below the initial one. Thus, even though the $\Sigma = 3(111)_{\text{Ni}}$ GB is metastable at 0 K, its energy is too high and the energy barrier separating it from the $\Sigma = 3(111)_{\text{Al}}$ GB is apparently so small that it can easily be overcome at finite temperatures. Furthermore, as discussed in Section 3, the local distortions produced by an antisite defect are capable of triggering this transformation already at 0 K. The extremely poor stability of the $\Sigma = 3(111)_{\text{Ni}}$ GB is consistent with experimental high-resolution transmission electron microscopy observations by Nadarzinski et al. [18], who found the $\Sigma = 3(111)$ GB to be Al-centered.

4.4. $\Sigma = 3(211)$ boundary

The isotherm of Ni segregation at the $\Sigma = 3(211)$ GB is shown in Fig. 2. Its initially linear part suddenly turns to a strong saturation region, a behavior which is indicative of a structural transformation. This suggestion is further confirmed by the segregation profiles across this boundary shown in Fig. 5. As for the $\Sigma = 3(111)_{\text{Al}}$ GB (cf. Fig. 3), the profiles develop a sharp concentration peak shifted away from the initial GB plane. This peak is especially pronounced for Ni-rich bulk compositions. Notice that the segregation region is much more narrow than for the $\Sigma = 3(111)_{\text{Al}}$ GB, which is well consistent with the static calculations of antisite formation energies (Section 3).

Comparing the ground-state structure of this GB (Fig. 6(a)) with its structure in stoichiometric bulk at 1200 K (Fig. 6(b)), we observe that the structural units remain essentially the same up to small distortions. Along with distortions caused by thermal expansion, we notice a slight tangential displacement of the upper grain relative
to the lower one in the [1 1 1] direction. This displacement produces a shear deformation of the structural units which destroys the initial mirror symmetry of the GB structure. The sign of the tangential displacement is chosen by the system at random. The amount of the shear deformation increases as the Ni bulk concentration is increased. Simultaneously, an initially stoichiometric atomic layer immediately adjacent to the GB plane becomes increasingly more Ni-rich. As we reach bulk compositions corresponding to the plateau region on the segregation isotherm (Fig. 2), this layer turn to an almost pure Ni layer, as illustrated in Fig. 6(c) for $c_b \approx 0.533$. This layer is manifested by the sharp concentration peak in the GB segregation profiles (Fig. 5). Further growth of $c_b$ does not alter this GB structure except that the segregation profile becomes more diffuse and the Gibbsian adsorption slightly decreases.

It was interesting to find out if the transformed GB structure is only stabilized by the high temperature...
and the contact with non-stoichiometric bulk, or if it can also exist at 0 K. To test its stability, a stoichiometric atomic layer adjacent to the GB plane in the ground-state structure (Fig. 6(a)) was turned to pure Ni by switching all Al atoms in this layer to Ni. The “synthetic” GB structure thus obtained is designed to mimic the transformed structure shown in Fig. 6(c), except that it has no relative shift of the grains and the bulk is exactly stoichiometric. This boundary was then relaxed statically with respect to local atomic displacements and rigid translations of the grains, a procedure which was well documented in our previous work [5,8]. The relaxed GB structure, displayed in Fig. 7, is very similar to the transformed structure found by the Monte-Carlo simulations (Fig. 6(c)). Both structures have the same type of site occupation and are characterized by a significant shear deformation of the structural units. The only difference is that the Ni layer develops a marked rippled relaxation at 0 K, while the high temperature makes this layer nearly flat. We thus conclude that the transformed structure of the $R = 3(211)$ GB is metastable, i.e., can readily exist at 0 K.

5. Discussion and conclusions

We have shown that Ni segregates to $\Sigma = 3$ GBs in Ni-rich NiAl and that the amount of segregation increases with Ni bulk concentration. A similar segregation behavior was earlier observed for $\Sigma = 5$ GBs in NiAl [8]. Both findings validate the earlier prediction, based on considerations of chemical potentials and antisite formation energies [9,19], that Ni should always segregate to GBs in NiAl.

The thermodynamic driving force for Ni segregation is a reduction in the GB free energy $\gamma$. Using our Monte-Carlo results we are able to quantify this reduction by the procedure proposed in [8]. Namely, we integrate the Gibbs adsorption equation [17] at constant temperature and pressure between two chemical potential, $\mu_0$ and $\mu$, corresponding to nearly stoichiometric bulk and a particular Ni bulk concentration, respectively. This gives us the change in $\gamma$ due to GB segregation,

$$\Delta \gamma = -\int_{\mu_0}^{\mu} \Gamma(\mu') \mathrm{d}\mu'.$$

From the Monte-Carlo simulations, we know the segregation isotherm $\Gamma(c_b)$ (Fig. 2) and the bulk relation $c_b(\mu)$. These relations define the integrand $\Gamma(\mu)$ in Eq. (4). The integration was implemented numerically by applying a linear interpolation between the data points. Fig. 8 displays the $\Delta\gamma(c_b)$ relations obtained for the $\Sigma = 3(111)_{\text{Al}}$ and $\Sigma = 3(211)$ GBs. To put these $\Delta\gamma$ values in perspective, they can be compared with the relevant GB energies in the stoichiometric bulk at 0 K (Section 2). It follows that Ni segregation can reduce $\gamma$ by about 25% for the $\Sigma = 3(111)_{\text{Al}}$ GB and almost 45% for the $\Sigma = 3(211)$ GB. Both effects are quite significant.

Both $\Sigma = 3$ GBs studied in this work undergo structural transformations with increasing Ni concentration. These transformations break the initial mirror symmetry of the GB structure and can be expected to represent first order phase transformations [2,20].
However, in the finite-size systems studied here, the transformations actually occur in a continuous manner, although they produce a very distinct change in slope of the segregation isotherm. This change correlates with the bulk composition range at which the transformations are confirmed by direct structural observations. The GB free energy is also a smooth function of the bulk composition within the accuracy of our simulations (Fig. 8). We believe that simulations in a larger system could have revealed more sudden changes in GB properties accompanying the structural transformations.

One could expect that the transformed GB structures would be reminiscent of some bulk phases existing on the Ni–Al phase diagram. While thermodynamically unstable in a bulk form under our simulation conditions, such phases could be stabilized in Ni-rich GB regions. The Ni–Al phase diagram [21] points to the \( \gamma' \) phase with the Ni\(_3\)Al stoichiometry as the closest candidate for a GB structure. However, careful examination of the transformed GBs did not reveal any similarity with the L\(_{12}\) structure of Ni\(_3\)Al. The only distinct feature of the transformed GB structures that could be noticed was their ability to accommodate a significant amount of Ni atoms by forming new Ni layers.

We notice, finally, that the structural transformation in the \( \Sigma = 3(2 1 1) \) GB is accompanied by relative tangential translation of the grains. The periodic boundary conditions used in our simulations readily accommodated such translations as the grains were free to slide against each other. Under real conditions, however, because grain translations are constrained by other GBs and their triple junctions, the GB transformation can give rise to elastic stresses in the grains. The energy cost associated with these internal stresses can shift the bulk composition corresponding to the transformation or even suppress it. This effect can be studied in our future work by repeating the simulations under fixed boundary conditions. It would also be interesting to examine whether external shear stresses applied parallel to the GB plane can enhance the GB segregation and induce the GB structural transformation in nearly stoichiometric bulk compositions. These effects can be important in relation to processes such as creep where the material is exposed to sustained mechanical loads at high temperatures.

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References