Monte Carlo modeling of low-index surfaces in stoichiometric and Ni-rich NiAl

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The structure and chemical composition of low-index surfaces of NiAl are investigated by grand canonical Monte Carlo simulations. Atomic interactions in NiAl are modeled by an embedded-atom potential fit to experimental and first-principles data. The simulations are performed at the temperature of 1200 K for the stoichiometric and two Ni-rich bulk compositions. For the (110) surface, the top surface layer is slightly enriched in Ni relative to the bulk whereas deeper layers are slightly depleted in Ni, so that the overall Gibbsian surface adsorption is almost zero. For the (100) and (111) surface orientations, the Al termination is structurally stable but contains a certain percentage of Ni atoms, depending on the bulk composition. The Al (111) termination also develops a large amount of vacancies and adatoms. The Ni terminations of the (100) and (111) surfaces are both unstable and transform to the respective Al terminations. This transformation can take place by two different mechanisms. One mechanism is the development of a terrace surface structure with areas of Al termination separated by stoichiometric (110) facets. An alternative mechanism, observed only for the (100) surface, is the injection of an antiphase boundary into the bulk with a simultaneous switch of the surface termination to Al. It is demonstrated that this mechanism cannot work for the (111) surface.

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I. INTRODUCTION

The intermetallic compound NiAl crystallizes in the B2 (CsCl prototype) structure and has a homogeneity range of up to 10 at. % of either side of the stoichiometry. This compound has attracted much attention as a subject of fundamental research because of the existence of structural vacancies in Al-rich compositions, as well as its potential as a high-temperature structural material for aircraft, space, and other applications.1 Among other properties, it is important to have a detailed knowledge of the surface structure and composition of NiAl. Such knowledge is essential for understanding its oxidation resistance, as well as the fracture process in which crack propagation exposes new surfaces to the environment.

The surface structure and composition may depend on the surface orientation and temperature, and in ordered compounds such as NiAl, also on the chemical composition of the bulk. Experimental data available in the literature are fragmentary and do not explore these dependencies in a detailed or systematic fashion. Chambers2 studied the chemical composition of the surface region in epitaxial NiAl grown on GaAs (100) at the temperature of 523 K and found it to be nearly stoichiometric. Mullins and Overbury3 and Roos et al.4 determined the top layer of the (100) surface to contain 22–24 at. % of Ni at temperatures above 1000 K. Noonan and Davis5 examined the composition of the NiAl (111) surface at about 1000 K and found it to be almost stoichiometric. Much attention was devoted to the effect of the rippled relaxation of the NiAl (110) surface, which was discovered experimentally6 and reproduced by first-principles7 as well as embedded-atom calculations.8 McCarty et al.10 recently studied the dynamics of steps on the NiAl (110) surface and made very interesting observations of the vacancy generation and annihilation mechanisms on the surface. Bozzolo et al.11 performed a Monte Carlo modeling of the NiAl (110) surface at several descending temperatures, attempting to simulate a cool-down process. They observed the formation of an Al surface layer at the expense of Al atoms located originally in planes close to the surface.

In this paper we report on a computer-simulations study of the surface structure and chemical composition in NiAl for three low-index surface orientations and three bulk compositions. We apply a grand canonical Monte Carlo method in conjunction with a reliable embedded-atom potential fit to a large database of experimental and first-principles data.12 The results of this study suggest that the chemical composition of the (110) surface is very close to the bulk composition, in agreement with experimental data.6 For the (100) and (111) surface orientations, the Al termination contains some percentage of Ni atoms in the form of antisites, and for the (111) orientation also a significant amount of surface vacancies and adatoms exist. The Ni terminations of both surfaces are unstable and transform to Al terminations. This surface transformation process can be accompanied by the formation of a terrace surface structure. For the (100) surface, it can also take place by the injection of an antiphase boundary into the bulk.

II. SIMULATION METHODS

A. Atomic interactions and surface geometry

Atomic interactions in NiAl were modeled by the embedded-atom potential constructed in Ref. 12. The potential was fit to experimental properties of NiAl as well as to first-principles energies of several real and hypothetical compounds of the Ni-Al system. This potential accurately reproduces lattice properties of NiAl, including elastic constants, thermal expansion, and phonon frequencies. It also gives reasonable values of the point-defect formation energies, planar fault energies, as well as surface energies, including the reproduction of the rippled relaxation of the (110) surface.12
This potential has recently been applied to model segregation and decohesion at grain boundaries in NiAl.\textsuperscript{13} A thin film of stoichiometric NiAl was constructed using a slab geometry so that (110), (100), or (111) surfaces were exposed to vacuum on opposing sides of the slab. Periodic boundary conditions were imposed in directions parallel to the surface of interest. Because (110) layers of NiAl contain equal amounts of Ni and Al atoms, both surfaces with this orientation are identical and have the stoichiometric composition in the initial state. In contrast, for the (100) and (111) orientations the film consists of alternating Ni and Al layers parallel to the surface that result in Al and Ni terminations on opposing sides of the film. The dimensions of the simulation block were chosen so that the repeat unit of the surface would be approximately square and each slab would contain over 1000 atoms (Table I). The resulting slabs were approximately 30-Å thick.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Surface & Number of surface atoms & Number of layers & Total number of atoms \\
\hline
(110) & 80 & 14 & 1120 \\
(100) & 64 & 20 & 1280 \\
(111) & 30 & 36 & 1080 \\
\hline
\end{tabular}
\caption{Geometrical details of the surface simulations.}
\end{table}

**B. Molecular static calculations**

Prior to starting Monte Carlo simulations the tendency of a surface to develop compositional disorder was evaluated by examining the antisite formation energy inside the film as a function of the distance to the surface. This was done by individually selecting an atom, switching its atomic species, and performing a static relaxation of the film. This calculation was performed for both the Ni\textsubscript{Ni} (Ni atom on the Al sublattice) and Al\textsubscript{Ni} (Al atom on the Ni sublattice) antisites. The average of the formation energies of the Ni\textsubscript{Al} and Al\textsubscript{Ni} antisites lying in the same plane for the (110) orientation or adjacent planes for the (100) and (111) orientations was also determined. This average represents an exchange defect in NiAl (see Refs. 12, 14, and 15) and is a useful measure of the resistance of this compound to compositional disorder.

As another measure of the resistance to surface disorder, the Frenkel pair formation energy was calculated for each surface. First, an adatom of a particular species, either Ni or Al, was placed on the surface of interest in a position of a regular atomic layer and the simulation block was statically relaxed. In a separate run, a vacancy of the same atomic species was created in the top surface, followed by static relaxation. The resulting energy changes were then summed to obtain the formation energy of a dissociated Frankel pair. This two-step process guarantees that the two defects do not interact with each other and the total number of atoms in the system is conserved.

Due to the appearance of antiphase boundaries during some of the Monte Carlo simulations (see Sec. IV), it became necessary to evaluate their energetics and mechanical stability. To this end, a perfect antiphase boundary (APB) parallel to the surface was created in the center of the film and the \( \gamma \) surface of the APB was computed using the technique proposed by Vitek.\textsuperscript{16,17} The \( \gamma \) surface method is an effective tool for evaluating the stability of planar defects in crystals.\textsuperscript{1,6,17} In this method, rigid-body translations are performed parallel to the fault plane (the APB, in this case) and the partially relaxed fault energy is computed as a function of the translation vector. During the partial relaxation, all atoms are allowed to move only in the direction normal to the fault plane while displacements parallel to the fault plane are prohibited, which typically gives a smooth function (\( \gamma \) surface). Local minima on the \( \gamma \) surface correspond to stable or metastable structures of the fault. In this work, the \( \gamma \) surface calculations were performed for the (100) and (111) APB’s and the results are reported in Sec. III. It should be mentioned that APB’s with these orientations can be of two types, with either two Ni or two Al atomic layers neighboring each other. The APB’s computed in this work were Ni-Ni type since it was this type that was prompted by the Monte Carlo simulations.

**C. Monte Carlo simulations**

The Monte Carlo (MC) simulations of NiAl surfaces were implemented in the modified grand canonical ensemble in which the temperature, the total number of atoms in the system, and the chemical-potential difference \( \Delta \mu \) between Ni and Al (\( \Delta \mu = \mu_{\text{Ni}} - \mu_{\text{Al}} \)) are held fixed, whereas the number of atoms of each species is allowed to vary.\textsuperscript{18,19} The volume of the system may or may not be allowed to fluctuate during the simulation. 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 the probability of one if

\[ \Delta G = \Delta E \pm \Delta \mu < 0 \] (1)

and with the probability of

\[ \exp(-\Delta G/k_B T) \] (2)

if \( \Delta G > 0 \). Here \( \Delta E \) is the energy change in the trial move, \( k_B \) is the Boltzmann constant, and \( T \) is temperature. The sign before \( \Delta \mu \) in Eq. (1) depends on whether a Ni atom is replaced by Al (+) or vice versa (−). If the volume fluctuates, Eqs. (1) and (2) are modified by including a preexponential factor depending on the volume change.\textsuperscript{18–20} This method allows both the compositional rearrangement of atoms and the relaxation of the atomic positions to occur simultaneously.

In this work all MC simulations were carried out at the temperature of \( T = 1200 \) K for the three values of the chemical-potential difference listed in Table II. The equilibrium bulk compositions corresponding to the chosen \( \Delta \mu \) values were determined separately in Ref. 13 and are given in Table II. Here and everywhere in this paper, the bulk chemical composition of NiAl is measured by the atomic fraction of Ni atoms. Table II shows that the bulk compositions modeled in this work include the (almost) stoichiometric compo-
sition 0.504 as well as two Ni-rich compositions 0.528 and 0.597. The bulk simulations were performed in Ref. 13 under variable-volume (zero-pressure) conditions and the resultant linear thermal-expansion factors are also included in Table II. The decrease in the thermal-expansion factor with the Ni concentration reflects the significant atomic size difference between Ni and Al.

The surface simulations were performed under constant volume conditions in order to accelerate the computations. Prior to beginning a MC simulation the film was subjected to a uniform expansion appropriate to the chosen \( \Delta \mu \) value (Table II). This a priori expansion takes into account, in an approximate manner, the thermal expansion that would take place naturally during the MC simulation.

All simulations were carried out in increments of \( 5 \times 10^4 \) MC steps per atom, with snapshots of the current structure taken at every \( 10^4 \) MC steps. The snapshots were continuously examined in order to track the progress of the simulation towards equilibrium. After each increment, the Ni concentration profile across the film was computed using the window scan method applied previously to NiAl grain boundaries. In the present work the windows were centered on atomic layers parallel to the surface and had the width of the interlayer spacing. Therefore, the concentration profiles calculated here simply represent the Ni concentration averaged over individual atomic layers parallel to the surface. The Ni concentration in each layer was calculated separately for the Ni and Al sublattices. The sublattice type of an atom was determined according to its location relative to the perfect lattice. The atomic coordinates and occupation probabilities used for the profile calculation were averaged over the entire increment of the simulation (\( 5 \times 10^4 \) MC steps per atom).

Besides concentration profiles, the Gibbsian surface adsorption \( \Gamma \) of Ni was calculated after each increment of the simulations. The Gibbsian adsorption is defined as the number of excess (relative to the bulk) Ni atoms in the simulation block per unit surface area. This was evaluated using the equation

\[
\Gamma = \frac{(c - c_b)N}{2S},
\]

where \( c \) is the average concentration of Ni in the simulation block, \( c_b \) is the nominal bulk composition (Table II), \( N \) is the total number of atoms in the block, and \( S \) is the cross-sectional area of the surface. The divider 2 in Eq. (3) reflects the presence of two surfaces in the simulation block. Note that in the case of two different surface terminations Eq. (3) gives a value averaged over both terminations. We chose to express the adsorption in terms of the effective number of monoatomic layers by dividing \( \Gamma \) by the number of surface atoms per unit area (cf. Table I). The Gibbsian surface adsorption is an important quantity in surface thermodynamics.

This paper focuses on stoichiometric and Ni-rich compositions of NiAl, in which the bulk off-stoichiometry is accommodated by antisites. Al-rich compositions of NiAl are known to be dominated by structural vacancies on the Ni sublattice. Our MC procedure only allows for atomic permutations but not for the formation or annihilation of vacancies as MC trial moves. This limitation makes MC studies of Al-rich compositions more difficult, although not prohibitive since it is possible for vacancies to penetrate into the bulk from the surface. Simulations of this type are the subject of our current work but lie beyond the scope of the present paper.

### III. MOLECULAR STATICS RESULTS

Figure 1 presents the antisite formation energies as functions of the coordinate across the film for three surface orientations. The dash-dotted lines in these and similar plots indicate the initial film surfaces, labeled according to their termination where appropriate. The exchange defect formation energy is also shown in these plots. It is observed that the antisite formation energies are decreased appreciably within a few atomic layers near the surfaces, especially near the Ni terminations of the (100) and (111) surfaces. The exchange defect energy follows the same trend, pointing to an enhanced antisite-type compositional disorder near the surfaces. In particular, it is expected that the Ni terminations should be more prone to compositional disorder than the Al terminations.

Table III summarizes the Frenkel pair formation energies (\( E_F \)) calculated for the surfaces and terminations in question. The high \( E_F \) values for the (110) surface (\( \sim 2 \) eV) indicate that this surface is very stable against Frenkel disorder. Both terminations of the (100) surface are much less stable against Frenkel pair formation (\( E_F < 0.6 \) eV). The small \( E_F \) value for the Al (111) surface (\( \sim 0.17 \) eV) indicates that it should develop a significant Frenkel disorder at elevated temperatures. The most striking result is the negative \( E_F \) value calculated for the Ni termination of the (111) surface, suggesting that this termination is totally unstable against Frenkel pair formation.

APB’s parallel to the (100) and (111) surfaces were created inside the film by switching chemical sorts of all atoms between a Ni layer in the center of the film and the Ni-terminated surface. This resulted in the creation of a Ni-Ni APB inside the film and switching the Ni termination of the surface to Al. The difference between the statically relaxed energies of the final and initial states was found to be \( -2 \) mJ/m² for the (100) surface and 266 mJ/m² for the (111) surface. In the first case the energy difference is essentially zero. However, it remains possible that the formation of an APB will be energetically favorable to having a Ni termination at high temperatures when the initially sharp APB is

### Table II. Calculated bulk compositions (atomic fraction of Ni) and linear thermal-expansion factors for selected values of \( \Delta \mu \) at \( T = 1200 \) K.

<table>
<thead>
<tr>
<th>( \Delta \mu ) (eV)</th>
<th>Composition</th>
<th>Thermal expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.6</td>
<td>0.597</td>
<td>1.0181</td>
</tr>
<tr>
<td>-0.8</td>
<td>0.528</td>
<td>1.0205</td>
</tr>
<tr>
<td>-1.0</td>
<td>0.504</td>
<td>1.0208</td>
</tr>
</tbody>
</table>
likely to smear over a few atomic layers and have a lower energy. In contrast, the well-positive energy cost of the creation of a \(~1\!\!\!1\!\!\!1\) APB suggests that this transformation is unlikely to be energetically favorable.

The mechanical stability of both the \(~1\!\!\!0\!\!\!0\) and \(~1\!\!\!1\!\!\!1\) APB's was evaluated by the \(g\) surface method discussed in Sec. II B. Both \(\gamma\) surfaces (which are not shown here) were found to have a unique energy minimum corresponding to the initial placement of the APB. This calculation proves that both APB's considered here have a unique structure and are mechanically stable at \(T=0\).

IV. MONTE CARLO RESULTS

A. (110) surface

Simulations of the (110) surface converged very rapidly. After only \(2.5 \times 10^5\) MC steps per atom (five increments), further simulations did not result in any significant changes in the Gibbsian surface adsorption or concentration profiles across the film. The rapid convergence implies a degree of structural stability inherent in the (110) surface. Figure 2 shows the depth profiles of Ni concentration on the Ni and Al sublattices, as well as the average concentration on both sublattices. Each point of the plot corresponds to the average Ni concentration in one atomic layer, the result of an average taken over the last three increments of the simulation. The profiles show that the top surface layer is slightly enriched in Ni relative to the bulk for all three bulk compositions. At the same time two to three deeper layers are slightly depleted in Ni. The enrichment and depletion effects cancel each other in the Gibbsian surface adsorption and the latter turns out to be practically zero (<0.01 ML) regardless of the bulk compo-

![Graph showing the energy distribution across the distances for (a) (110), (b) (100), and (c) (111) surfaces.](image)

![Graph showing Ni concentration profiles across the distances for (110) surface.](image)

![Table III. Calculated Frenkel pair formation energies on the surfaces of NiAl.](image)

<table>
<thead>
<tr>
<th>Surface</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic species</td>
<td>Ni</td>
<td>Al</td>
<td>Ni</td>
</tr>
<tr>
<td>(E_F) (eV)</td>
<td>1.715</td>
<td>2.157</td>
<td>0.589</td>
</tr>
</tbody>
</table>

The mechanical stability of both the (100) and (111) APB's was evaluated by the \(\gamma\) surface method discussed in Sec. II B. Both \(\gamma\) surfaces (which are not shown here) were found to have a unique energy minimum corresponding to the initial placement of the APB. This calculation proves that both APB's considered here have a unique structure and are mechanically stable at \(T=0\).
The near-stoichiometric composition of the NiAl (110) surface is consistent with experimental data.\textsuperscript{6}

B. (100) surface

The results obtained for the (100) surface depended on the surface termination as well as on the bulk composition. We report the results for the Al and Ni terminations separately.

I. Al termination

The Al termination was found to be relatively stable. Some Ni\textsubscript{Al} antisites were produced by the simulations in the top layer, with the second layer consisting almost exclusively of Ni atoms. The top layer contained on average 16\% of Ni atoms for the stoichiometric bulk and 25\% for the 0.528 bulk composition. Mullins and Overbury\textsuperscript{7} used low-energy ion scattering spectroscopy to find the top layer composition to be 22 at.\% Ni at $T\geq 1000$ K and the second layer consisting entirely of Ni. Roos \textit{et al.}\textsuperscript{4} determined the surface composition to be 24 at.\% Ni at $T\geq 1000$ K using low-energy helium scattering. Both surface compositions compare very well with our findings, especially considering that initially stoichiometric experimental samples of NiAl may become slightly Ni rich due to the selective evaporation of Al during their thermal treatment in vacuum. Figure 3 shows Ni concentration profiles across the (100) film calculated by averaging over the last eight increments of the MC process. For the strongly off-stoichiometric bulk composition of 0.597, the surface structure was found to be qualitatively the same as discussed above, except that it contained more Ni\textsubscript{Al} antisites as well as vacancies and adatoms arising from the Frenkel pair formation.

2. Ni termination

For the Ni termination, we first discuss the results for the stoichiometric (0.504) and moderately off-stoichiometric (0.528) bulk compositions. The Ni termination showed much more disorder at initial stages of the simulation and required over $10^6$ MC steps per atom to reach an equilibrium. Surprisingly, Fig. 3 shows that the obtained equilibrium surface concentration is very close to that of the Al termination. Furthermore, the surface clearly develops a new atomic layer on top of the initial surface, as evidenced by the appearance of the left-most points in Fig. 3. The examination of multiple MC snapshots revealed that the surface develops a terrace structure illustrated schematically in Fig. 4. Some of the Ni atoms forming the initial surface layer move on top of other Ni atoms to form a new layer and simultaneously switch their species to Al. The locations abandoned by those atoms expose the underlying Al layer. This structural transformation results in a two-level structure in which only Al (100) layers lying above and below the initial Ni layer are exposed to vacuum. In other words, the initial Ni layer is partly “dissolved” and partly buried under the newly formed Al overlayer. It was found that the areas of Al termination in the terrace structure are separated by stoichiometric (110) facets.

The transformed surface structure is illustrated by a MC snapshot shown in Fig. 5. A few antisites that were present in this particular snapshot have been removed to enhance its clarity. Also, only a few near-surface layers are shown in this figure. Similar surface structures were observed for the 0.528

\begin{table}
\caption{Gibbsian surface adsorption of Ni (number of equivalent monoatomic layers) on NiAl surfaces obtained by Monte Carlo simulations. The average values and error bars were determined from the eight last increments of the simulation.}\
\begin{tabular}{lccc}
\hline
Bulk composition & 0.504 & 0.528 & 0.597 \\
\hline
(110) surface & 0.0067±0.0004 & 0.006±0.001 & -0.029±0.002 \\
(100) surface & -0.069±0.003 & -0.028±0.003 & 0.007±0.016 \\
(111) surface & -0.046±0.005 & 0.089±0.01 & 0.012±0.01 \\
\hline
\end{tabular}
\end{table
bulk composition, except that they contained more Ni\textsubscript{Al} antisites.

These observations suggest that the Ni termination of the NiAl\textsubscript{100} surface is thermodynamically unstable at 1200 K and has to be replaced by an Al termination. In a truly open system this could probably happen by the elimination of the Ni layer or creation of a new Al overlayer by deposition from the vapor or by atomic diffusion from the bulk. The present simulations, however, were carried out under the constraint of a fixed total number of atoms in the system. Despite this constraint, the surface still found a way to transform to an Al termination, even though it had to pay a price by increasing the total surface area in the terrace structure. We should not exclude that terrace structures of this type can appear in experimental conditions under appropriate kinetic constraints. The latter appears to be especially plausible for the surfaces left behind a fracture crack propagating in NiAl at a high temperature.

For the strongly off-stoichiometric bulk composition of 0.597, the behavior of the Ni termination was very different. Namely, the Ni\textsubscript{100} surface induced a spontaneous creation of a Ni-Ni\textsubscript{100} APB inside the film at early stages of the simulation process. As discussed above, the creation of this APB is accompanied by switching the surface termination to Al, so that both terminations of the film become Al. Figure 6 shows the Ni concentration profiles on the Al sublattice after several increments of the MC process. The kink in the profile corresponds to the APB position, which tends to slowly wander across the central part of the film in a random manner in the course of the simulation. We did not pursue the kinetics of the APB wandering since the MC scheme applied here does not reflect the true dynamics of the system. This scheme is only suitable for finding thermodynamically stable or metastable states of the system.

For the strongly off-stoichiometric bulk composition of 0.597, the behavior of the Ni termination was very different. Namely, the Ni\textsubscript{100} surface induced a spontaneous creation of a Ni-Ni\textsubscript{100} APB inside the film at early stages of the simulation process. As discussed above, the creation of this APB is accompanied by switching the surface termination to Al, so that both terminations of the film become Al. Figure 6 shows the Ni concentration profiles on the Al sublattice after several increments of the MC process. The kink in the profile corresponds to the APB position, which tends to slowly wander across the central part of the film in a random manner in the course of the simulation. We did not pursue the kinetics of the APB wandering since the MC scheme applied here does not reflect the true dynamics of the system. This scheme is only suitable for finding thermodynamically stable or metastable states of the system.

Figure 7 shows a snapshot of the simulation block containing an APB. The significant compositional disorder both at the surfaces and in the bulk is observed, as well as the smearing of the APB over a few atomic layers. Even though the spontaneous formation of an APB did not occur at lower Ni bulk concentrations, the plausibility of
APB energy in the more disordered bulk environment. In particular, Ni-rich bulk compositions favor the APB injection mechanism, presumably due to the reduction in the transition. In particular, Ni-rich bulk compositions favor the APB dominant mechanism obviously depends on the bulk composition and the injection of a Ni-Ni~111~ termination: the surface transformation to a terrace structure thus concludes that the state of the film with an APB and two Al terminations is stable or at least metastable for all three bulk compositions.

This mechanism at all bulk compositions was also studied. To this end, an APB was deliberately created in the center of the (100) film prior to Monte Carlo simulations (thus making both surface terminations Al) and the simulations were implemented for the other two bulk compositions. In all cases the APB smeared over a few atomic layers and started to wander back and forth across the central part of the film, but no other changes were observed during long simulation runs. As an illustration, Fig. 8 shows Ni concentration profiles on the Al sublattice after about $5 \times 10^5$ MC steps per atom. We can thus conclude that the state of the film with an APB and two Al terminations is stable or at least metastable for all three bulk compositions at the chosen temperature.

Thus, we found two competing mechanisms by which the (100) NiAl surface can eliminate the inherently unstable Ni termination: the surface transformation to a terrace structure and the injection of a Ni-Ni (100) APB into the bulk. The dominant mechanism obviously depends on the bulk composition. In particular, Ni-rich bulk compositions favor the APB injection mechanism, presumably due to the reduction in the APB energy in the more disordered bulk environment.

3. Gibbsian adsorption

For the 0.504 and 0.528 bulk compositions, the Gibbsian adsorptions of Ni on the (100) surfaces are small and negative (Table IV), indicating that the surface regions are slightly enriched in Al relative to the bulk. Note, however, that these values represent an average of the flat and terraced Al-terminated surfaces. For the sake of completeness, the Gibbsian adsorption was also calculated for the 0.597 bulk composition to obtain a zero value within the simulation errors (Table IV). In this case, however, the film contains an APB and the adsorption characterizes an average over all three interfaces present in the film.

FIG. 8. Calculated Ni concentration on the Al sublattice across the (100) NiAl film at 1200 K for three bulk compositions. In all cases an antiphase boundary parallel to the surface was introduced into the film prior to Monte Carlo simulations and the concentration curves were calculated after a long Monte Carlo run. This plot demonstrates the stability (or metastability) of the antiphase boundary for all three bulk compositions.

FIG. 9. Calculated Ni concentrations on the Ni and Al sublattices (labeled as NiNi and NiAl, respectively) across the (111) NiAl film at 1200 K for three selected bulk compositions. Notice the formation of an Al-rich overlayer on top of the initial Ni termination.

C. (111) surface

The (111) surfaces proved to be the most unstable and difficult to analyze due to their significant disorder. The latter is not surprising given the low or even negative Frenkel pair formation energies established for these surfaces by molecular statics calculations (see Table III). Long MC runs (on the order of $10^6$ MC steps per atom) were required before trends of the surface evolution could be clearly revealed.

1. Al versus Ni termination

Figure 9 presents the Ni concentration profiles across the film for three bulk compositions. The profiles show significant oscillations of the Ni concentration on the Al sublattice near the surfaces. We also clearly observe the formation of an Al-rich layer on top of the initial Ni termination. Similar to the case with the (100) surface, the Ni termination of the (111) surface tends to develop a terrace structure. However, this terrace structure is not as clear and well defined as that for the (100) surface because of the larger amount of antisites, vacancies, and adatoms present in the surface region. Figure 10 shows a snapshot taken at a late stage of the simulation for the stoichiometric bulk composition. Despite the significant disorder, (110) planes separating disparate Al planes can still be identified. The level of surface disorder becomes higher for Ni-rich bulk compositions, but the trend to form a terrace structure can still be noticed.

In contrast to the (100) surface, no APB generation was observed for the (111) surface for any bulk composition. The plausibility of the APB mechanism was examined further by MC simulations even though all indications were that it was less favorable than the formation of a terrace structure. An Ni-Ni (111) APB was intentionally created inside the film prior to MC simulations, thereby creating a film with two Al terminations. During the subsequent MC simulations the APB was observed to gradually spread over a wide zone and...
energy is likely to decrease with temperature and bulk off-
stoichiometry, the APB generation remains totally unfavor-
able at the temperature of the present simulations.

2. Gibbsian adsorption

The Gibbsian adsorption on (111) surfaces is again very
small (Table IV) and has a negative sign (small Al segre-
gation) for the stoichiometric bulk, becomes positive for the
0.528 bulk composition, and finally reaches zero (within the
error bar) for the 0.597 bulk composition. This irregular be-
behavior may suggest that the system has not reached the com-
plete thermodynamic equilibrium despite the long simulation
time.

V. CONCLUSIONS

The atomic structure and chemical composition of the
(110), (100), and (111) surfaces of NiAl have been studied
using grand canonical Monte Carlo simulations and an
embedded-atom potential fit to experimental and first-
principles data. All simulations have been performed at the
temperature of 1200 K for the stoichiometric and two Ni-rich
bulk compositions. The results can be summarized as fol-
lows.

The top layer of the (110) surface is slightly enriched in
Ni relative to the bulk composition whereas a few deeper
layers are slightly depleted in Ni. Both effects are weak, so
that the surface region has essentially the bulk composition.
The (110) surface structure is very stable and resists the for-
mation of vacancies, and adatoms. These findings are in
agreement with experimental data.

The (100) and (111) surfaces can be created with either an
Al or Ni termination. The Al termination of the (100) surface
is structurally stable but develops a notable amount of anti-
sites, vacancies and adatoms. Depending on the bulk com-
position, it can contain 15%–25% of Ni atoms, which is in
good agreement with experiment. The Ni termination is
unstable and transforms to an Al termination. Two compet-
ing mechanisms of this transformation have been found. In one,
the surface develops a terrace structure with Al (100) regions
separated by stoichiometric (110) facets. In the other mecha-
nism, the Ni-terminated surface generates an APB into the
bulk while the surface atoms switch their chemical sorts to
Al. Although the second mechanism was only observed for
the strongly Ni-rich bulk composition, additional simulations
indicate that nothing prevents it from operating for the sto-
ichiometric bulk composition as well. It should be admitted
that our simulation scheme can only point to the existence of
these two mechanisms but does not allow us to predict which
one of them would dominate under real conditions. In reality
the formation of a terrace structure or an APB generation is
controlled by vacancy diffusion and other thermally acti-
vated processes whose kinetics are not captured correctly by
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method. It is not unreasonable to expect that both mecha-
nisms can occur in experiments, depending on the specimen
history, atmosphere, and other factors.

The Al termination of the (111) surface is also stable but
develops a large amount of vacancies and adatoms. It tends

FIG. 11. Calculated Ni concentration on the Al sublattice across
the (111) NiAl film at 1200 K for the bulk composition of 0.504. An
antiphase boundary parallel to the surface was introduced into the
film prior to the Monte Carlo simulation and the curves were ob-
tained at different stages of the simulation. The labels indicate the
number of Monte Carlo steps per atom times 10^5. This plot dem-
onis the instability of the antiphase boundary.

FIG. 10. Typical structure of the initially Ni-terminated (111)
surface of NiAl obtained by Monte Carlo simulations for the sto-
ichiometric bulk. Black and white atoms represent Ni and Al, re-
spectively. Despite the significant disorder the surface tends to de-
signate that nothing prevents it from operating for the sto-
ichiometric bulk composition as well. It should be admitted
that our simulation scheme can only point to the existence of
these two mechanisms but does not allow us to predict which
one of them would dominate under real conditions. In reality
the formation of a terrace structure or an APB generation is
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to contain a few percent more Ni atoms than the bulk. The Ni termination of this surface is again unstable and transforms to an Al termination with a terrace structure. The latter consists of Al (111) regions separated by stoichiometric (110) facets. Calculations show that the APB mechanism mentioned above cannot operate for the (111) surface. An APB deliberately introduced into the bulk prior to MC simulations quickly spreads out, while one of the surfaces develops a terrace structure.

Overall, with other parameters equal, the atomic order of the surfaces decreases in the rows (110), (100), and (111). Interestingly, this and some other trends revealed by the MC simulations could be anticipated based on simple molecular static calculations. From this stability trend, we expect that the (111) surface of NiAl should develop facets with (110) and/or (100) orientations, especially in Ni-rich bulk compositions. This kind of faceting was observed as a trend in our simulations but could not be studied on a full scale because of the limited size of the simulation block. However, the constrained simulations performed here may reflect the conditions at the tip of a rapidly growing crack and in other situations where large-scale faceting is suppressed by slow diffusion kinetics.

Our simulations also demonstrate that the surface behavior in NiAl is quite complex and can involve other defects, such as antisites, vacancies, and even APB’s. This observation allows us to conclude that reliable atomistic simulations of NiAl surfaces should be based on accurate atomic interaction models capable of reflecting the correct defect energetics. For example, an underestimation of the APB energy or overestimation of surface vacancy energies can easily bias the delicate balance between competing mechanisms of surface transformations and give misleading results. Given that these simulations were based on a highly reliable interatomic potential fit to first-principles data, we believe that they reflect the surface behavior correctly.

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