Surface Stoichiometry and the Initial Oxidation of NiAl(110)

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Selective oxidation of the surface of an ordered alloy requires redistribution of the atomic species in the vicinity of the surface. This process can be understood in terms of the formation and movements of point defects in the compound. On the basis of \textit{ab initio} density-functional calculation we found both the creation of exchange defects near the NiAl surface and segregation of Ni vacancies to the top layer to be extremely favorable in the presence of oxygen. Scenarios for the initial oxidation of NiAl are suggested which demonstrate the appearance of an additional energy barrier on the Ni-rich side compared to the Al-rich side. The expulsion of Ni from the oxide layer as it forms is the driving force for its stability.

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The oxidation of metal surfaces is relevant to many fields in which the metal-oxide interface occurs, including heterogeneous catalysis and corrosion. Understanding the microscopic processes which govern the \textit{initial} stages of oxidation has been the focus of much research recently, using both experimental and theoretical \textit{ab initio} techniques. The oxidation of \textit{pure} metal surfaces such as Al(111) is comparatively well understood [1,2]; however, the situation in metallic \textit{compounds} is much less clear, even though the latter are of great practical importance. For example, the intermetallic NiAl, which is prototypical of highly ordered metallic compounds, easily oxidizes, forming a continuous coherent Al$_2$O$_3$ film (about 5 Å thick) (see Ref. [3] for a review). This property is widely used in growing well-ordered alumina films for experimental investigation; for that purpose NiAl is better suited than pure Al, as the low melting temperature of the latter makes it impossible to obtain films of well-ordered alumina in its stable configuration [3]. In particular, Al$_2$O$_3$/NiAl(110) is considered to be one of the most convenient model systems for experimental studies of alumina supported metallic nanoclusters [4].

The structure of the oxide film on the NiAl(110) surface is described as follows: at low temperatures the film is amorphous (locally ordered), at higher temperatures (about 1300 K) it becomes globally ordered and takes on the structure of two O-Al bilayers, terminated with an Al layer on the interface and with an O layer from vacuum [5–7]. According to [7], the NiAl-Al$_2$O$_3$ interface is atomically sharp without any intermediate phases. The possibility of Ni-O bond formation in either low-temperature or high-temperature oxide is doubted [6–8]. The presence of “metallic” Ni at the oxidized surface at low temperatures has not been ruled out, but during the higher temperature annealing Ni atoms are suggested to be expelled from the oxidizing oxide overlayer [6].

In the absence of an atomic-scale mechanism of the film formation, one cannot explain the observed oxygen uptake curves [8], nor resolve whether the oxidation \textit{injects} additional vacancies into the NiAl crystal by extracting Al atoms [9], or, on the contrary, \textit{absorbs} vacancies by destroying a few surface layers of NiAl with subsequent dissolution of Ni atoms in the bulk [6].

Here we present the first detailed \textit{ab initio} study of the oxidation of NiAl(110), and show that qualitatively new phenomena occur, when compared to pure metal surfaces, in the oxidation process. These are related to the additional thermodynamic degree of freedom available, namely the composition of the surface. We show that the thin oxide film is hugely stabilized by the introduction of \textit{point defects} at the surface, in particular, Al antisites and Ni vacancies. Based on these observations, we develop scenarios involving segregation of point defects to the surface as a result of the oxidation. An implication of this is that the change of point defect thermodynamics in the \textit{bulk} in crossing the stoichiometric composition, significantly affects the oxidation at the \textit{surface}. As a result, the kinetics of the oxidation process for Ni-rich and Al-rich alloys will be different. Such an effect should be present in the oxidation of any ordered compound that requires redistribution of the species [10].

Calculations were performed using the plane wave pseudopotential method within the framework of the finite-temperature density functional theory [11]. The surface of NiAl was modeled by a slab consisting of four layers separated with four interlayer spacings of vacuum; atoms of the two bottom layers of the slab were held fixed at their bulk positions. Each layer contained four nonequivalent atomic positions, as shown in Fig. 1. For the Brillouin zone integration the $4 \times 4 \times 2$ Monkhorst-Pack mesh was employed. We used soft kinetic-energy-filtered pseudopotentials for Ni and O [12] (for Al, we used the Troullier-Martins pseudopotential [13]) and the electronic orbitals were expanded up to a cutoff of 50 Ry.

Geometry optimizations were performed until the maximal force component dropped below 1 mH/a.u. As a rule, atomic arrangements with which we dealt had a complicated energetic surface rich with local minima. Therefore, we found it strictly necessary to perform molecular dynamics (MD) simulation as a prelude to final optimization of atomic positions in cases where the final atomic arrangement was not obvious or constrained. Typically, we
The study of the adsorption of one O atom per supercell (1/3 ML) [22] reveals the preferred position of the oxygen at the (2Al + Ni) hollow site above the top layer (Table I). Adsorption of O at the Al-Al bridge site is close in energy. The distances between the adsorbed O and the nearest Al atoms ($I_{O,Ai}$) and between the oxygen and aluminium subplanes ($\Delta d$) are a little larger than those reported for the adsorption of an O atom at the Al(111) surface (1.79 Å and 0.7 ± 0.1 Å, respectively; see references in [2]). The LDA and GGA energies listed in Table I demonstrate the same ranking preference of O atoms to have Al rather than Ni as a nearest neighbor. It is indicative that if placed at the Ni-Ni bridge site, the O atom pushes two Ni neighbors away, while two neighboring Al atoms move closer to it. As a result, the distances $I_{O,Ai}$ and $I_{O,Ni}$ become almost equal (Table I).

TABLE I. The 1/3 ML oxygen coverage: surface energy $\Delta \gamma$ (in eV/cell) relative to the energy of configuration $\alpha$, and distances (in Å) between an O atom and the nearest Al ($I_{O,Ai}$) and Ni atoms ($I_{O,Ni}$), and between the outermost O and Al subplanes $\Delta d$. As the number of atoms for each species is the same for all configurations, $\Delta \gamma$ on Ni- and Al-rich sides are equal.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Adsorption site</th>
<th>$I_{O,Ai}$</th>
<th>$I_{O,Ni}$</th>
<th>$\Delta d$</th>
<th>$\Delta \gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>2Al + Ni hollow</td>
<td>1.84</td>
<td>1.98</td>
<td>0.95</td>
<td>0</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Al-Al bridge</td>
<td>1.81</td>
<td>2.42</td>
<td>0.97</td>
<td>0.20 (0.05)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Al + 2Ni hollow</td>
<td>1.80</td>
<td>1.95</td>
<td>0.93</td>
<td>0.59 (0.74)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Ni-Ni bridge</td>
<td>1.98</td>
<td>1.97</td>
<td>0.67</td>
<td>0.59 (0.81)</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Al-Ni bridge</td>
<td>1.78</td>
<td>1.88</td>
<td>1.08</td>
<td>0.99 (1.02)</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Al top</td>
<td>1.71</td>
<td>1.71</td>
<td>1.53</td>
<td>2.59 (2.17)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Ni top</td>
<td>1.77</td>
<td>1.77</td>
<td>1.33</td>
<td>3.02 (3.00)</td>
</tr>
</tbody>
</table>

values (in brackets), though we stress that the picture that emerges for both sets of calculations is the same.
obtained O-Al bilayer could be considered as the precursor of the γ-Al2O3-like oxide phase. The structure of the bilayer closely resembles the lower bilayer of the alumina film in the structural model, suggested by Yang et al. [7].

Because configuration $E$ requires a vacancy to be absorbed in the top layer, the actual bulk composition of the NiAl becomes important. The composition in Ni-rich and Al-rich NiAl is maintained by different constitutional defects (by nickel antisites $V_{Ni}$ and by nickel vacancies $V_{Ni}$, respectively), which give rise to different oxidation kinetics as discussed below.

Consider possible pathways for the system to arrive to configuration $E$ starting from configuration $A$. The pathways involving single events are depicted in Fig. 3, together with their energies. After chemisorption of 1 ML of O atoms at the perfect surface (configuration $A$), the system can proceed by segregating a Ni vacancy in the second layer ($A \to B$), which then may jump to the surface layer ($B \to C$), and the creation of an exchange defect ($C \to E$) completes the path $ABCE$. Alternatively, having a Ni vacancy in the second layer the system can first create an exchange defect ($B \to D$) and then either allow the Ni vacancy to jump to the first layer immediately ($D \to E$) or first convert $V_{Ni}^{(2)}$ and $V_{Al}^{(2)}$ defects [23] into Al vacancy $V_{Al}^{(2)}$ (i.e., the Ni antisite atom returns to its own sublattice, filling a Ni vacancy there), which is filled afterwards with a nearest-neighbor Ni atom from the first layer ($D \to F \to E$). Another family of pathways arises if we suppose that the system starts by creating an exchange defect ($A \to G$). Then a Ni vacancy arrives to the second layer either on the Ni sublattice ($G \to D$) or to the Al sublattice ($G \to F$), and the rest is the same as described above.

In Ni-rich alloys vacancies are not constitutional defects. Their creation is energetically costly, and this results in the appearance of an additional energetic barrier which enters the calculations of $\gamma$ via $\mu_{Ni}$. Indeed, on the Al-rich side each subsequent step lowers the energy of the system, with the exception of the $G \to D$ (LDA and GGA) and $G \to F$ (LDA) transitions, which are slightly uphill. On the contrary, on the Ni-rich side the transition $A' \to B$ already requires noticeable energy. The situation is even worse if the system starts with an antisite defect formation ($A' \to G'$), because this requires an even larger amount of energy to proceed further or to return to $A'$. Overall, on the Ni-rich side an additional 0.5 eV barrier appears for all the paths in comparison to the Al-rich case.

How can we rationalize the cascade of energies we find for the metastable surfaces depicted in Fig. 3? We first compared their structural parameters such as the number and length of Al-O bonds, thinking with a simple pairwise argument that a large number of Al-O bonds might favor a particular structure, or perhaps a short average Al-O bond length. These parameters gave no indication of the ranking at all. We then considered the argument (see, e.g., Ref. [24]) that a large distance between the two top layers of ions might indicate an unstable surface. The thinking here is that a neutral plane would be more characteristic of a low energy surface, whereas a bilayer of charged species, a dipole layer, would be unstable. However, this argument also fails to indicate the ranking of surface energies here; it is inappropriate to think of oxygens and metal atoms at a surface as carrying nominal charges [25]. Indeed, our
lowest energy surface is a clearly resolved bilayer, with an O plane outside an Al plane, and it is certainly not the thinnest of the O-Al bilayers we are considering. Finally, the best indicator of the surface energy turns out to be the extent to which Ni has been excluded from the layer of oxide which is bonded to the substrate metal. This information is summarized in Table II, which shows how decreasing surface energy (columns 4–6) is associated with expulsion of Ni from the oxide layer into the bulk (column 3).

In conclusion, we have studied the initial stages of oxidation of the NiAl(110) surface up to 1 ML oxygen coverage. After the initial chemisorption of oxygen, significant reduction of the energy could be achieved by the co-adsorption of V_{Ni} in the first layer and by the exchange of Al and Ni atoms between the first two layers. Therefore, at the start of the oxidation process the surface must absorb vacancies rather than inject them. A change of oxidation kinetics is predicted in crossing the equiatomic composition of the species in the bulk NiAl.

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[10] A similar phenomenon is the possible switch of the species type which segregates to the surface in ordered alloys on either side of stoichiometry [A.V. Ruban (private communication)].
[22] We define 1 ML of adsorbed O atoms to correspond to three O atoms per each cell of the slab [four atomic sites in a NiAl(110) layer], which agrees with the structural models of the NiAl(110)/Al/2O3 interface, suggested in Refs. [6,7].
[23] X_{i} denotes species X on sublattice Y in layer i, counting from the top layer of the NiAl(110) surface.