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First-principles thermodynamics and experimental study of interface oxidation in Ni/Ni$_3$Al structures

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Anti-oxidation is one of the significant properties of Nickel-based superalloys for their potential applications in industry. However, previous researches mainly focused on single-phase compounds of NiAl or Ni$_3$Al. In the present study, first-principles density functional theory coupled with thermodynamics analysis are employed to investigate the atomistic oxidation behaviours of the Ni/Ni$_3$Al composites systematically. An oxidation experiment of DD6 alloy is conducted as well to further confirm the theoretical prediction. Initial surface formation energy analysis shows that the systems composed of Ni(111) and Ni$_3$Al(100)/(111) surfaces are more stable and therefore are selected for further investigations. Thermodynamics calculations indicate that the Ni$_3$Al phase is oxidized firstly, accompanied by Al-segregation on the top surfaces. Then it is followed by subsequent oxidation of Ni phase. Surface oxidation diagrams with respect to the surface formation energies show that oxygen adsorption could enhance Al-segregation to the surface and Ni$_3$Al(111) surfaces tend to be oxidized completely with slightly lower oxygen coverage. Oxidation at the interface is also investigated and shows that oxygen atoms bind with upper layers of Ni$_3$Al phase from the point of binding energy. The experimental results provide a reasonable explanation for the selective oxidation of Al atoms at the atomic-scale so as to form a dense anti-oxidation membrane. The present work could serve as beneficial references for subsequent investigations of oxidation or adsorption processes of two-phase composites.

1 Introduction

Nickel-based single crystal super-alloy has been extensively facilitated in high-temperature applications, especially as structure materials in aircraft turbine blades. These intermetallic materials possess many excellent properties, including low density, high melting point, good oxidation and corrosion resistance. The Ni$_3$Al phase is wrapped by Ni phase which accounts for 70% for its volume fraction in its micro-structure in engineering applications as the indispensable strengthener and anti-oxidation phase. The main reason for oxidation resistance is the formation of a dense and protective $\alpha$ – Al$_2$O$_3$ layer to hinder further oxidation. However, this formation process can constantly be hampered by competitive oxidation of Ni and Al which could produce less protective oxidation layers (e.g., Al$_2$O$_3$ and NiO). This is the major problem in investigations of oxidation mechanism of Nickel based single crystal super-alloy materials. In an oxidation environment, the excellent oxidation resistance of alloys induced by the selective growth of a dense protective oxide layer on their surfaces mainly depends on the local activities of the metallic elements and the oxides. Thus, a thorough understanding of the oxidation mechanism in Ni/Ni$_3$Al composite is of great necessity.

Previous experimental researches have found that the regions of emergent grain boundaries on the alloy surface oxidized faster than the grain centres. The formed surface oxide is Cr-rich with an enhancement of titanium in its outer regions. This is the situation at the grain boundaries and over the grain centres. Surface oxidation of aluminium was observed as well. The main oxides are Al$_2$O$_3$, NiO, NiCr$_2$O$_4$, and NiAl$_2$O$_4$ at 1100$^\circ$C in ambient atmosphere. By employing the wavelength dispersive spectrometer, Edmond et al. observed that oxidation was confined to the $\gamma'$ particles while $\gamma$ channels remained unoxidized. Then the in-situ process of $\gamma'$-$\gamma$ phase transformation during oxidation was investigated by Ding et al. and results showed the ordered $\gamma'$ phase (L1$_2$) gradually transforms to disordered $\gamma$ phase structure (fcc) and the main production is composed of $\gamma$-Al$_2$O$_3$ crystallites.

With regard to atomic-scale oxidation mechanism, the intermetallic compounds and interface have attracted less focus recently which may result from complicated nature of the inter-
metallic compounds and the relevant oxidation behaviour including oxygen selection of metallic elements, surface segregation, and multiple formation of possible oxides. In recent years, density functional theory (DFT) calculations plus ab initio thermodynamics method have been performed to study the oxygen adsorption of various Ni, Al compound surfaces, in which surface segregation was considered and the oxygen adsorption was found to enhance the Al segregation. Jennisson et al. and Lozovoi et al. adopted DFT calculations for the oxygen adsorption on the NiAl(110), (100) surfaces. They found the NiAl(110) surface would be stabilized by the segregation of Al antisites and Ni vacancies based on the obtained electronics structures, atomics geometry, and energetic properties. Wang et al. investigated Ni vacancies based on the obtained electronics structures, atomics geometry, and energetic properties. Wang et al. investigated surface phase diagrams of Ni3Al(100) and - (110) and concluded that Ni3Al(100) surface would be oxidized firstly. As far as two-phase composites are concerned, Liu et al. reported the oxidation of Nb/Nb5Si3 composite and found during the oxidation process the Nb(110) surface is oxidized first, followed by the segregation of Nb of the Nb5Si3(001) surface and subsequent oxidation of the Nb element of Nb5Si3. In addition, Reuter et al. and Bergermayer et al. studied oxygen molecules on Ru2O3(110), Fe2O3(0001), Ag2Pd(111), and Ti3Al surfaces and found the most stable configurations through energy analysis. However, detailed microscopic mechanism of the oxidation process of two-phase metal/intermetallic composites is still undiscovered.

In the present study, we firstly employ ab initio thermodynamics, which is a combination of first-principle DFT calculations and atomistic thermodynamics analysis, to investigate the oxidation mechanism of the two-phase Ni/Ni3Al composite. Specifically, we aim to research on the most stable structure through comparing surface formation energy. Then the surface phase diagrams for both phases are displayed through identifying the relative stable oxidized surfaces as a function of the chemical potential of Ni and O. The oxidation order is decided by comparing the formation energy and oxygen binding energy between the interface. What's more, investigation of the role of interface and surface segregation with oxygen concentration is performed to achieve comprehensive understanding of the whole oxidation process. At last, experiments of high temperature oxidation dynamics and mechanisms of a typical single crystal superalloy DD6 are conducted to confirm the theoretical conclusions.

2 Methods

2.1 Computational methods

The ab initio calculations are performed within density-functional theory (DFT) using the Vienna ab initio simulation package (VASP) code. The exchange-correlation energy functionals are treated with the PW91 generalized gradient approximation (GGA). A plane-wave cutoff energy of 500 eV is used for all DFT calculations. Optimization of the atomic structure is performed for each supercell via the conjugate-gradient technique through setting threshold values on the total energy and the Hellmann-Feynman forces on atoms. All the structures are fully relaxed until the force on each of the atom is less than 0.01 eV/Å. The (4×4×1) Monkhorst-Pack mesh in the Brillouin zone is employed for all (2×2)Ni3Al surfaces unit cell, while 5×5×1 k-point mesh for (2×2)Ni surface.

For bulk Ni3Al, it is an ordered cubic (L12) structure with the space group Pn3m while bulk Ni has the Fm3m space group. The lattice constants of bulk Ni3Al and bulk Ni are obtained from the energy minimization of both bulk unit cells using the 15×15×15 and 17×17×17 Monkhorst-Pack mesh for Ni3Al and Ni, respectively. The lattice constant of Ni3Al is 3.568 Å which is in good agreement with the experimental value of 3.57 Å and previous DFT calculations. Meanwhile, the calculated lattice constant of Ni is 3.518 Å, which agrees well with the experimental value of 3.52 Å and other DFT-GGA consequences.

The Ni3Al and Ni structural models with various surface terminations are constructed by cleaving supercells made from bulk Ni3Al and Ni. The slab surface models consisted of five metal layers are separated by a vacuum region of 15 Å. Each layer contains four atoms which are three Ni atoms and one Al atom if there is no defect. The atoms in the two bottom layers of slabs are fixed, while the other three layers are free to move so as to reduce the time of calculations without impacting calculation results. Besides, oxygen atoms are added on the top surface of the slab. Here, we define the oxygen coverage Θ as the ratio of the number of the oxygen atoms to that of the atoms in the substrate surface layer. The unit of the oxygen coverage is the monolayer (ML), and 1 ML is defined as four oxygen atoms per (2×2) surface cell. The oxygen coverage varies from 0 to 1 ML in 1/4 ML steps in this paper. Schematic top views of Ni3Al(100) and Ni3Al(111) surfaces with antisite defects are illustrated in Fig. 1. Fig. 2 shows all possible sites for oxygen atoms on Ni3Al(100) and Ni3Al(111) surfaces: eight and twelve bridge sites on Ni3Al(100) and Ni3Al(111) surfaces (labeled as B), four hollow sites on both surfaces (labeled as H) as well as four top sites (labeled as T). Since Ni surfaces have the same geometries and structures as Ni3Al, the details will not be repeated here.

Additionally, the oxidation of Ni/Ni3Al interfaces is also considered, which are demonstrated in Fig. 3. The interface is modeled by stacking 7-layer Ni phase on the substrate of 7-layer Ni3Al phase with a vacuum region of 15 Å. Seven layers are chosen because we want to calculate more data of O atom binding energy to obtain more accurate regularity and conclusions. Meanwhile, the computational costs should also be considered. In this article, only Ni(100)/Ni3Al(100) and Ni(111)/Ni3Al(111) are calculated due to little lattice mismatch, and the misfit between both planes is only 1.04%. To better diminish the influence of interfacial mismatch, atoms in Ni phase are slightly stretched to be compatible with Ni3Al phase. And the finally optimized lattice constant of Ni phase becomes 3.568 Å, which is in good agreement with Ni3Al phase. The single O atom is added in bridge site (B) on each layer of both interfacial phases (see Figs. S1 and S2 in Supporting Information). 4×4×1 k-point meshes are utilized for both calculations concerning interfaces through Monkhorst-Pack setting and Gamma setting, respectively. All atoms are free to move until reaching the converging threshold of 0.01 eV/Å and 1e-5 eV.

The thermodynamic stability of a given surface is decided by its
Fig. 1 Schematic top view of the Ni₃Al(100) and Ni₃Al(111) surfaces with possible antisite defects for five cases: (a)(f) the pure surface, (b)(g) the surface with one Al antisite defect [denoted by Ni₃Al(100)-1Al, Ni₃Al(111)-1Al], (c)(h) the surface with two Al antisite defects [denoted by Ni₃Al(100)-2Al, Ni₃Al(111)-2Al], (d)(j) the surface with one Ni antisite defect [denoted by Ni₃Al(100)-1Ni, Ni₃Al(111)-1Ni], (e) the surface with two Ni antisite defects [denoted by Ni₃Al(100)-2Ni], (i) the surface with three Al antisite defects [denoted by Ni₃Al(111)-3Al]. Blue and pink atoms represent Ni and Al elements in the surface layer, respectively. Blue and pink balls at hollow sites represent Ni and Al atoms in the second (subsurface) layer.

Fig. 2 Schematic top view of Ni₃Al(100) and Ni₃Al(111) surfaces with the possible adsorption sites for oxygen. Big and small black spheres represent multiple B,H,T sites while light grey spheres represent atoms in the second (subsurface) layer.
surface formation energy. The following formulations employed in this study literally follow the scheme of previous investigations [19-22,24,35,37]. The surface formation energy of O/Ni3Al, \( \gamma \) can be given as

\[
\gamma = \frac{1}{S_0} [G(T, p) - N_A \mu_A - N_B \mu_B - N_O \mu_O] 
\]

\[
= \frac{1}{S_0} [E_{\text{slab}} - N_A \mu_A - N_B \mu_B - N_O \mu_O + PV + E_{\text{vibration}} + TS],
\]

where \( S_0 \) is the surface area, \( G(T, p) \) is the Gibbs free energy, \( E_{\text{slab}} \) is the total energy of the slab; \( N_A, N_B, \) and \( N_O \) denote the numbers of Ni, Al, and O atoms in the slab, respectively; the chemical potential of Ni, Al, and O are denoted by \( \mu_Ni, \mu_A, \) and \( \mu_O, \) respectively. Contribution from \( PV(P \) and \( V \) represent pressure and volume, respectively), \( E_{\text{vibration}}(\text{vibrational energy}), \) and \( TS(T \) and \( S \) are temperature and entropy, respectively) terms are neglected because their impacts are very tiny [21,23]. In our study, for Ni3Al(100) with antisite defects or not and Ni(111),O/Ni(111), their surface formation energies can be rewritten as

\[
\gamma_d = \frac{1}{S_0} [E_{\text{slab}} - N_A \mu_{Ni} - N_B \mu_{Al}], 
\]

\[
\gamma = \frac{1}{S_0} [E_{\text{slab}} - N_A \mu_{Ni} - N_B \mu_{Al}], 
\]

\[
\gamma' = \frac{1}{S_0} [E_{\text{slab}} - \frac{1}{4} N_O \mu_{Ni}^{\text{bulk}}], 
\]

\[
\gamma'' = \frac{1}{S_0} [E_{\text{slab}} - \frac{1}{4} N_O \mu_{Ni}^{\text{bulk}} - N_O \mu_O],
\]

where \( \gamma_d \) denotes the surface formation energy of the slab with antisite defects; \( N_{Ni}^{d}, N_{Al}^{d} \) represent the numbers of Ni and Al atoms in slabs with antisite defects; \( \mu_{Ni}^{\text{bulk}} \) denotes the chemical potential of bulk Ni.

Based on Eqs. (2) and (3), in particularly, we define the segregation energy \( E_{\text{seg}} \) or relative surface formation energy \( \gamma_f \) of the Ni3Al slabs with the defect relative to that of the pure Ni3Al slab as

\[
E_{\text{seg}} = \gamma_d - \gamma_f = \frac{1}{S_0} [E_{\text{slab}} - \frac{1}{2} N_O \mu_O].
\]

The most stable oxygen adsorption site is achieved through comparing binding energy of oxygen on different sites. The binding energy per oxygen atom is given by [23]

\[
E_b = \frac{1}{N_0} [E_{\text{slab}} - E_{\text{slab}} - \frac{1}{2} N_O \mu_O],
\]

where \( N_0 \) is the number of oxygen contained in a slab. \( E_{\text{slab}} \), \( E_{\text{slab}} \), and \( E_{\text{slab}} \) represent the total energy of O-contained, clean surface of Ni/Ni3Al systems without any oxygen, and a free \( O_2 \) molecule, respectively. Note that the oxygen binding energy defined by Eq. (7) includes the change of the surface free energy when a surface defect is involved.

The surface phase diagram of the Ni/Ni3Al surfaces are calculated by surface formation energy

\[
\gamma_f = \frac{1}{S_0} [E_{\text{slab}} - N_O \mu_{Ni} - N_A \mu_{Al} - N_O \mu_O].
\]

Meanwhile, Ni/Ni3Al interface formation energy \( \gamma \) is taken into account to evaluate the stability of different structures as [38,40]

\[
\gamma = \frac{1}{S_0} [E_{\text{interface}} - N_{Ni} \mu_{Ni}^{\text{bulk}} - N_{Al} \mu_{Al} - N_{Ni} \mu_{Ni} - N_{Al} \mu_{Al}],
\]

where \( S_0 \) is the interface area. \( E_{\text{interface}} \) is the total energy of the interface system and \( \mu_{Ni}^{\text{bulk}} \) represents the number of Ni atoms in Ni phase of interface.

At equilibrium, the chemical potential of a given species is equal in all contacting phases. In order to avoid formation of bulk Ni and Ni3Al phases, the chemical potentials of Ni and Al must follow \( \mu_{Ni} \leq \mu_{Ni}^{\text{bulk}} \) and \( \mu_{Al} \leq \mu_{Al}^{\text{bulk}} \). Particularly, we assume that the equilibrium of chemical potentials in bulk Ni3Al, that is \( 3 \mu_{Ni} + \mu_{Al} = \mu_{Ni}^{3\text{Al}}. \) Thus, the chemical potentials of Ni and Al satisfy the constraints \( 3 \mu_{Ni} + \mu_{Al} = \mu_{Ni}^{3\text{Al}} \leq \mu_{Ni} \leq \mu_{Ni}^{\text{bulk}} \) and \( \mu_{Al} = \mu_{Al} = \mu_{Al}^{\text{bulk}}. \) The chemical potential of oxygen varies with an upper limit determined by \( O_2 \) molecules which is \( \mu_O = \frac{1}{2} E_{O_2}. \) With the results of DFT calculations of bulk Ni3Al, bulk Ni, bulk Al and molecular \( O_2 \), the ranges of the chemical potentials are determined to be \( -5.971 eV \leq \mu_{Ni} \leq -5.415 eV, \) \( -3.656 eV \leq \mu_{Al} \leq -3.698 eV \) and \( \mu_O \leq -4.89 eV. \)

2.2 Experimental details

The material used in the experiment is the second generation Ni-based single crystal superalloy DD6. Samples with the dimensions of 10 mm × 10 mm × 4.5 mm are cut from the aeroengine's blades and isothermally oxidized at 1000 °C in air for 1800 min.
X-ray diffraction (XRD) is employed to analyze the types of oxides formed on the surface of oxidized samples. Optical microscopy and electron scanning microscope (SEM) are used to measure the oxide layer thickness and identify the morphology of the layer structures.

3 Results and discussion

3.1 Clean surface of the Ni/Ni₃Al composite

We first investigate the relative stability of clean surface of the Ni/Ni₃Al composite. The surface formation energies of Ni(100), Ni(110), and Ni(111) are calculated to be 0.278 eV/Å², 0.291 eV/Å², and 0.243 eV/Å² just as shown in Fig. 4. Hence, Ni(111) is the selected surface with the lowest surface formation energy for Ni phase. On the other hand, the surface formation energies of Ni₃Al(100), Ni₃Al(110) and Ni₃Al(111) change with \( \mu_{Ni} \). It can be seen from the Fig. 4 that the Ni₃Al(100) is the lowest when \( \mu_{Ni} \leq -5.55 \) eV, indicating it is rather stable during Al-rich stage. While the surface formation energy of Ni₃Al(111) is the minimum when \( \mu_{Ni} > -5.55 \) eV when it is the Ni-rich stage. Thus, the preferred exposed surfaces of the Ni/Ni₃Al composite would be Ni(111) and Ni₃Al(100)(Al-rich), Ni₃Al(111)(Ni-rich). In addition, it can be noted that throughout the entire range of chemical potential of Ni, surface formation energy of Ni₃Al is always lower than that of Ni(111), revealing that Ni₃Al is the dominant phase.

![Fig. 4 Surface formation energies of Ni(100), Ni(110), Ni(111), Ni₃Al(100), Ni₃Al(110) and Ni₃Al(111) as functions of the chemical potential of Ni.](image)

In the next step, we firstly consider the relative stability of Ni₃Al(100) surfaces with and without the presence of antisite defects (Figs. 1(a)-(e)) in their configuration. It should be noticed that there is a full layer of Al and Ni atoms in the surface layer for Ni₃Al(100)-2Al and Ni₃Al(100)-2Ni surfaces. Fig. 5(a) shows the absolute surface formation energies of the perfect surface and four Ni₃Al(100) surfaces with different surface antisite defects as a function of chemical potentials of Ni. It can be observed that Ni₃Al(100) perfect surface has the lowest surface formation energy when \( \mu_{Ni} \) is greater than -5.9 eV while Ni₃Al(100)-1Al is the lowest in the remaining time. In other words, the perfect Ni₃Al(100) surface is thermodynamically stable in most time and Ni₃Al(100)-1Al is stable when Al is highly rich, which indicates that Al atoms would probably segregate to the surface from the bulk naturally under Al-rich condition. On the other hand, it can also be found out that the surface formation energies of Ni₃Al(100)-1Ni and Ni₃Al(100)-2Ni are always higher than that of perfect Ni₃Al(100) surface, implying that the segregation of Ni atoms to the surface is thermodynamically unstable.

Similarly, the relative stability of various atomic configurations of the clean Ni₃Al(111) surfaces and four other antisite surfaces (Figs. 1(f)-(j)) are investigated. Also, the top surface layers of Ni₃Al(111)-3Al and Ni₃Al(111)-1Ni are both composed by single Al and Ni atoms. It is depicted in Fig. 5(b) about the absolute surface formation energies of clean Ni₃Al(111) surface and four antisite defect surfaces as functions of chemical potential of Ni. It can be observed directly that Ni₃Al(111), Ni₃Al(111)-1Al and Ni₃Al(111)-2Al represent the most stable configuration successively in three domains of \( \mu_{Ni} \) from Ni-rich range to Al-rich range, which indicates the segregation of Al atoms to the top surface layer gradually. Particularly, with higher chemical potential of Al it would promote the segregation of Al atoms under Al-rich condition. The stability of Ni₃Al(111)-2Al can only be achieved under extremely Al-rich condition. Still, the surface formation energies of Ni₃Al(111)-1Ni is constantly larger than Ni₃Al(111) surface, suggesting that the Ni segregation is not favored under any circumstances.

3.2 Binding energy of Oxygen

The compromise between the tendency to lower the surface formation energy by segregating more metal species to the surface, and the tendency to lower the surface formation energy by achieving stronger adsorbate bonding at surfaces enriched with the more reactive metal species is still not clear. In order to further qualify these two competing trends we define a fundamental quantity to describe the adsorbate bonding, the average oxygen binding energy \( E_b \). Following the investigation of the clean surface of the Ni/Ni₃Al composite, calculations for adsorption of oxygen atoms on Ni₃Al(100), Ni₃Al(111), and Ni(111) surfaces are carried out with the oxygen coverage ranging from 0 to 1 (0 < \( \Theta \) ≤ 1, here \( \Theta \) represents the ratio of the number of the oxygen atoms to that of the atoms in the substrate surface layer). Possible oxygen atoms adsorption sites are shown in Fig. 2(b) which is also applicable for Ni(111) and various surfaces with antisite defects, including bridge, fcc hollow and top sites (denoted as B, H, and T in Fig. 2). Apart from that, some extra possible sites have been eliminated considering the symmetry of crystal lattice. The binding energies per oxygen atom at the most stable sites on several surfaces as the functions of oxygen coverage are illustrated in Fig. 6. In this work, the surface configurations with and without antisite defects are investigated sequentially under different oxygen coverages, and the most energetically stable surface configuration from the low oxygen coverage is subsequently used as a starting structure to determine the next stable configuration from the higher oxygen coverage. To achieve a better comparison, the result of Ni(111) is also shown in both charts of Ni₃Al(100) and Ni₃Al(111). It can be directly judged from
both pictures that the binding energy of oxygen on Ni(111) is constantly larger than that on most Ni$_3$Al(100) and Ni$_3$Al(111) surfaces, regardless of the oxygen coverage, indicating that the Ni$_3$Al phase should be selected to be oxidized firstly during the oxidation process of Ni/Ni$_3$Al composite. Meanwhile, the binding energy of oxygen atoms on Ni$_3$Al surfaces with Ni antisite defects is significantly higher than the perfect Ni$_3$Al surfaces and surfaces with Al antisite defects, which implies that Ni$_3$Al surfaces with 1Ni and 2Ni antisite defects are both unfavorable from energy perspective in initial oxidation process.

For the most stable configuration surfaces of Ni$_3$Al(100) which should be the Ni$_3$Al-2Al due to its lowest bonding energy, with the increase of oxygen coverage the difference between Ni$_3$Al(100)-2Al and Ni$_3$Al(100)-1Al becomes larger. According to Fig. 5(a), the pure Ni$_3$Al(100) is the most stable condition in most period compared with other surfaces with antisite defects. However, in the process of oxidation, Ni$_3$Al(100)-2Al becomes much more stable, suggesting that adsorption of oxygen at high coverage could enhance the surface segregation of Al, resulting in the formation of the top surface layer with all Al atoms. The absolute value of the oxygen binding energy decreases slightly with the increase of oxygen coverage, which can be attributed to the repulsive interaction between oxygen atoms. On the other hand, in Fig. 6(b) it can be observed that the curve of Ni$_3$Al(111)-1Ni is similar to Ni(111). This is mostly owing to single element atoms on the top layer of surface and nearly the same crystal structure. Similarly, Ni$_3$Al(111)-3Al is the most favorable surface throughout the process and the gap between the binding energy of Ni$_3$Al(111)-2Al and Ni$_3$Al(111)-3Al gets huge when the oxygen coverage is beyond 0.75, indicating that higher oxygen coverage promotes further surface segregation of Al atoms on the Al-segregated Ni$_3$Al(111) surface to get more stable compared to original stable situation obtained from Fig. 5(b). Above results are close to the surface segregation of Ti and Al on the surface of Nb-Ti(110) and Nb-Al(110) under oxygen adsorption$^{37}$.

### 3.3 Phase diagrams of oxidation

In order to further understand the oxidation characteristics of the Ni$_3$Al surfaces from the thermodynamics point of view, we construct three-dimensional surface phase diagrams of relative surface formation energies as functions of the chemical potentials of both O and Ni for oxygen adsorption on different Ni$_3$Al(100), Ni$_3$Al(111), and Ni(111) surfaces. Projecting the lowest surface free energies of the different Ni$_3$Al(100), Ni$_3$Al(111) and Ni(111) systems in the two-dimensional surface phase diagram onto the two-dimensional ($\mu_O - \mu_Ni$) plane, the corresponding two-dimensional surface phase diagrams could be obtained, which are given in Fig. 7 respectively.

For Ni$_3$Al(100) surface system, under the O-poor conditions (low \(\mu_O\)), it can be observed that clean Ni$_3$Al(100) surface and Ni$_3$Al(100)-1Al occupy the lower part of phase diagram with Ni$_3$Al(100) taking up the most area, which is consistent with the stable configuration shown in Fig. 5(a) and only one Al atom could segregate to the top surface layer under Al-rich condition. With the increase of the chemical potential of O under Al-rich condition, both 2O/Ni$_3$Al(100)-2Al and 1O/Ni$_3$Al(100)-1Al structures become stable for a rather short period. This is also the evidence for the fact that oxygen adsorption induces the segregation of Al atoms on the top surface until to a full Al layer. Ultimately, under a higher chemical potential of O, the final most stable configuration is 4O/Ni$_3$Al(100)-2Al surface (corresponding to oxygen coverage of 1 ML) no matter how chemical potential of Ni changes, suggesting that all the Al atoms could be oxidized totally during the oxidation process. It can be concluded that more Al atoms could be oxidized to form dense Al$_2$O$_3$ layer to prevent the oxidation going further, which could be a microscopic evidence to explain why Ni$_3$Al phase is a compound with good anti-oxidation$^{15,21}$.

For the Ni$_3$Al(111) system, likewise, the clean Ni$_3$Al(111) surface is stable under the O-poor and Ni-rich collective condition. On the opposite side, the Ni$_3$Al(111)-2Al surface is the stable one when the chemical potential of Ni is rather low. In the remaining part the Ni$_3$Al(111)-1Al is favored. Since the space occupied by the Ni$_3$Al(111)-1Al configuration is larger than the rest...
two parts, the former is thermodynamically more stable, which is also identical with the result shown in Fig. 5(b). Under the higher oxygen coverage condition, the surface diagram is occupied by $4\mathrm{O}/\mathrm{Ni}_3\mathrm{Al}(111)$-3Al, regardless of chemical potential of Ni. This phenomenon also demonstrates that the oxygen accelerates the Al segregation from the substrate to the top surface layer. It also leads to the sustained complete selective oxidation of Al on $\mathrm{Ni}_3\mathrm{Al}(100)$ and $\mathrm{Ni}_3\mathrm{Al}(111)$ surfaces under O-rich conditions.

For the Ni(111) oxidation process, it is gradually oxidized with the increase of oxygen coverage from Ni(111) to $4\mathrm{O}/\mathrm{Ni}_3\mathrm{Al}(111)$ configuration. Since it has only one type of atom, it is independent of the chemical potential of Ni.

In order to compare our numerical consequences with the experimental data in more detail, we calculate the chemical potential of oxygen as a function of the temperature ($T$) and the oxygen partial pressure ($p$) with

$$\mu_O(T, p) = \frac{1}{2}E_{\text{ox}}^{\text{tot}} + \mu_O(T, p^0) + \frac{1}{2}k_B T \ln \left( \frac{p}{p^0} \right),$$

where $E_{\text{ox}}^{\text{tot}}$ is the total energy of a free oxygen molecule, $k_B$ is the Boltzmann constant and $\mu_O(T, p^0)$ is the chemical potential of oxygen at temperature $T$ and pressure $p^0$, which can be attained from the available experimental data: $\frac{1}{2}E_{\text{ox}}^{\text{tot}} = -4.89 \text{ eV}$, $\mu_O(T = 1300 \text{ K}, p^0 = 1 \text{ atm} = 1013.25 \text{ mbar}) = -1.49 \text{ eV}$. Hence, the chemical potential of oxygen under experimental conditions of $T=1000 \text{ °C}=1273 \text{ K}$ and $p=1.0 \times 10^{-7} \text{ mbar}$ can be calculated to be, namely, $\mu_{O}^{\text{exp}} = -7.64 \text{ eV}$. This value indicates that experiments are carried out under a relatively high oxygen concentration condition. Judged from Fig. 2, it can be distinguished from surface phase diagrams that $4\mathrm{O}/\mathrm{Ni}_3\mathrm{Al}(100)$-2Al and $4\mathrm{O}/\mathrm{Ni}_3\mathrm{Al}(111)$-3Al surfaces are thermodynamically stable, leading to selective oxidation of Al at the first stage of oxidation process. Moreover, multiple pressure scales under the same temperature and different temperature scales under the same pressure are shown in Fig. 7 using Eq. (10).

Hence, from the analysis above, the initial stage of oxidation among Ni/Ni$_3$Al composite occurs in the Ni$_3$Al phase. This result can be further confirmed through the thermodynamics analysis as the oxidation sequence of the Ni/Ni$_3$Al composite can be determined by comparing the surface formation energies of the O/Ni$_3$Al and O/Ni(111) systems. To achieve this purpose, a three-dimensional surface phase diagram for the oxygen-adsorbed Ni/Ni$_3$Al composite system's surface formation energies is constructed as functions of chemical potentials of Ni and O. The surface formation energies of the most stable O/Ni$_3$Al(100), O/Ni$_3$Al(111), and O/Ni(111) systems are shown in Figs. 5(a) and (b). Obviously, both surface formation energies of the O/Ni$_3$Al(100) and Ni$_3$Al(111) are higher than that of the O/Ni(111) system under O-rich and Ni-rich circumstances, indicating that the Ni$_3$Al phase is selected firstly during the oxidation process, which is consistent with results before, leading to formation of initial Al$_2$O$_3$ surface at the top layer of the Ni/Ni$_3$Al composite.

Besides, the most stable surface formation energies of O/Ni$_3$Al(100), O/Ni$_3$Al(111), and O/Ni(111) systems as functions of chemical potential of O under extreme Ni-poor ($\mu_{Ni}=-5.971 \text{ eV}$) and extreme Ni-rich ($\mu_{Ni}=-5.415 \text{ eV}$) conditions are illustrated in Figs. 5(c) and (d), respectively. Under O-poor condition, only a few of Al atoms segregate on the top layer when the chemical potential of Ni is rather low in Fig. 5(c) while they are all much more stable than Ni(111) surface. Under the O-rich and extreme Ni-poor condition, the most stable configurations turn to be Al-terminated Ni$_3$Al(111) and Ni$_3$Al(100) surfaces. And it can be seen that $\gamma_{(111)} < \gamma_{(100)}$, which means that Ni$_3$Al(111) should be oxidized earlier slightly. Similarly, under Ni-rich condition, the most stable configurations are still the Al-terminated Ni$_3$Al surfaces. Both two figures suggest that O does promote Al segregation of Al on the top layer surfaces compared with pure surfaces without oxygen atoms. Likely, in this situation, $\gamma_{(111)} > \gamma_{(100)}$ can still be found, it can be concluded that the oxidation sequence is Ni$_3$Al(111)$>$Ni$_3$Al(100)$>$Ni(111).

Then, we calculate the oxidation starting chemical potentials ($\mu_{O}^{\text{Al-rich}}$ and $\mu_{O}^{\text{Ni-rich}}$) corresponding to the onset of bulk oxide binding energy to be -9.51 eV and -8.33 eV, respectively in Figs. 5(c) and (d). The Al-rich condition is largely similar compared to the situation at Al(111), where a p(2$x$2) structure with 0.25 ML...
on-surface oxygen adatoms in fcc hollow sites becomes stabilized at oxygen chemical potentials that are significantly higher than the onset of bulk oxide binding energy (-9.32 eV). The reason for such difference is the high cost of segregating the Al atoms in Ni$_3$Al matrix to the surface that is not a necessity at Al-rich or Al(111) systems. On the other hand, the oxygen binding energy computed at 0.25 ML coverage with the Ni-rich surface termination when it is the most stable configuration at the lowest $\mu_D$ is only -2.52 eV/atom, which can not be comparable to computed binding energy of -4.43 eV/atom at pure Al(111) surface in Fig. 9. Only by segregating Al atoms to the first layer can the $E_b$ of corresponding Ni$_3$Al come into the same level as that of Al(111). However, stabilizing such configurations involves the cost of Al segregation on the upper layer and thus delays the critical $\mu_D$ when bulk oxide formation is about to set in.

### 3.4 Oxidation at the Ni/Ni$_3$Al Interfaces

To further confirm our prediction that the Ni$_3$Al phase is the initial selection object during oxidation process, multiple interface composites are included to investigate the preferences of oxygen atoms at the Ni/Ni$_3$Al interfaces. To avoid excessive lattice mismatch, both Ni and Ni$_3$Al phases have the same lattice orientation. In this study, as shown in Fig. 3, different interface structures can be constructed for (100), and (111) orientations. For each particular lattice orientation interface structure, antisite defects are considered as well and structures are represented by Ni/Ni$_3$Al, Ni/Ni$_3$Al-1Al, Ni/Ni$_3$Al-2Al, Ni/Ni$_3$Al-1Ni, and Ni/Ni$_3$Al-2Ni. After the structural relaxation, interface energies of two types of Ni/Ni$_3$Al interfaces are calculated as functions of $\mu_{Ni}$ to determine relatively stable configurations for the subsequent calculation targets. Fig. 10 gives detailed curves of formation energies change with respect to the chemical potential of Ni. During the whole interval, it can be seen that different interface configurations have the lowest energy values depending on different values of $\mu_{Ni}$. In the Ni-poor stage, Ni(100)/Ni$_3$Al(100)-2Al($\mu_{Ni} \leq -5.83$ eV) and Ni(111)/Ni$_3$Al(111)-3Al($\mu_{Ni} \leq -5.88$ eV) become more stable. Under the Ni-rich condition, Ni(100)/Ni$_3$Al(100) and Ni(111)/Ni$_3$Al(111)-1Al exhibit more stability in particular areas.

Fig. 11 shows the binding energies per oxygen atom at the most stable site in the Ni(100)/Ni$_3$Al(100) and Ni(111)/Ni$_3$Al(111) interface configurations as functions of the distance between oxygen atoms and the boundary layer of interfaces through Eq. 7. The dashed line in Fig. 11 denotes the location of boundary surface between two phases, which represents the upper layer of Ni$_3$Al phase in the present study. It can be seen from both Figs. 11(a) and (b) that the relatively lower oxygen binding energies occur inside the Ni$_3$Al phase, and the distances of oxygen atoms from the interface boundary fall in a range of 0-7.5 Å from the boundary. This phenomenon has also been captured experimentally which is oxygen concentration of interface near sample edge is higher than the inner part. The binding energies per oxygen atom on the Ni$_3$Al side are lower than those on the Ni side, indicating that oxygen prefers to be bonded to Ni$_3$Al phase in the Ni/Ni$_3$Al interfaces at the initial oxidation stage. Then a bunch of oxygen atoms would diffuse into the subsurfaces to continue the oxidation process. The results discussed above are consistent with aforementioned conclusions, which could be a beneficial explanation for experimental phenomenon from the point of energy.

Additionally, through comparing binding energy values of different terminations of interfaces, it can be found that oxygen tends to bind with Ni(100)/Ni$_3$Al(100) at the first place under the same circumstance. It should be noted that the (111) surface of Ni$_3$Al phase is a close-packed surface of FCC lattice. Therefore, the O atom is rather hard to move through the interface into the sub-layers, and the needed binding energy is much higher than that of (100) surface.

In general, the adhesion work at the interface can be used to characterize the effect of interface strain/stress. In other words, lower interface strain/stress signifies higher adhesion work. Based on the viewpoints of thermodynamics, for the crystal's growing on an effective heterogeneous nucleation substrate, the interfacial strength and stability have to be larger than the crystal growing on itself. According to the formula:

$$W_{ad}A/B = \gamma_{A} + \gamma_{B} - \gamma_{int}A/B,$$  \hspace{1cm} (11)

where the work of adhesion ($W_{ad}$) equals the surface forma-
Fig. 8 Three-dimensional surface phase diagram for the oxygen-adsorbed two-phase composite system, O-Ni/Ni$_3$Al, as functions of $\mu_O$ and $\mu_{Ni}$, respectively. It contains the surface formation energies of the most stable (a) O/Ni$_3$Al(100) and O/Ni(111) systems, (b) O/Ni$_3$Al(111) and O/Ni(111) systems. Two-dimensional surface phase diagram for the oxygen-adsorbed two-phase composite system under (c) Ni poor condition and (d) Ni rich condition. 1O, 2O, 3O, and 4O represent adsorption of one, two, three, and four oxygen atoms on the Ni$_3$Al or Ni surfaces, corresponding to the oxygen coverage of 0.50, 0.75, and 1.0 ML, respectively.
tion energies $\gamma_{A/B}$, and $\gamma_{A/B}$ minus the interface formation energy $\gamma_{A/B}$. We totally calculate the adhesion work of 6,10,14,18-layer Ni/Ni$_3$Al interface, the results are list in Table. for (100) and (111) interface terminations, respectively. The results are consistent with Fig. 10 that the (111) termination interface structures have relatively lower formation energy as well as the stronger interface stability (higher adhesion works). Fig. 11 shows the significantly different oxygen binding energies for the two different interface configurations, which can also be explained by the fact that higher adhesion work hinders the oxygen adsorption. That is the interface strain/stress is beneficial for oxygen adsorption. In addition, it can be seen that works of adhesion of 14-layer interface configurations are the lowest of all, which is also the evidence of choosing 14-layer as interface models so that oxygen atoms could bind within the interface more easily. The rest values almost maintain the same with changes of Ni layers, indicating that the thickness can hardly impact the interface strain/stress.

### Table 1 Calculated adhesion works of various layers of Ni/Ni$_3$Al interfaces.

| Number of layers | Adhesion works (eV/Å$^2$) |
|------------------|---------------------------|
|                  | (100)                     |
| 6                | 0.153                     |
| 10               | 0.160                     |
| 14               | 0.146                     |
| 18               | 0.157                     |

### 3.5 Experimental results

DD6 is a typical Ni-based superalloy in industry and the Ni/Ni$_3$Al structure is the basic unit cell of this kind of superalloy. It has great thermal-mechanical and anti-oxidation properties. However, until now the micro-mechanism of $\alpha$ – $\gamma$ phase formation on the sample surface is not clear. To further confirm our theoretical outcomes, the DD6 alloy is chosen as an example to perform oxidation test and characterization. Fig. 12 shows the SEM morphologies of the oxide on the surfaces perpendicular to [001] direction after 1800 min oxidation of the sample and the X-ray diffraction (XRD) analysis results of surface oxide scales. Judging from Fig. 12, it can be found that the main oxide on the surface should be $\alpha$-Al$_2$O$_3$, which is an evidence to support the previous conclusions. According to the cross-sectional morphology of the sample and the energy spectra lines of the related elements in Fig. 13, a single Al-rich oxide layer is mainly formed on the surface, especially the interface composed of matrix and Al$_2$O$_3$ layer. These results provide similar points with other experimental reports that the $\gamma$-/$\gamma$ phase formation during oxidation is introduced by Al depletion in $\gamma$ phase and our theoretical results that oxidation process is accompanied by Al-segregation on the top surfaces. The underlying mechanism can be well explained in the present DFT calculation and analysis. On the other hand, the DFT calculations reveal the mechanism of reaction driving force of the oxidation process. Actually, we could find the increasing trend of Al content up to 80% from sample surface to the interface composed of Al$_2$O$_3$ and matrix, indicating oxygen could bind with Al atoms firstly and keep Al-segregation from matrix continuously. Furthermore, the Al content beyond 10 μm stays around 15% lower than original 25%, implying that Al atoms segregate from the matrix to the surface.

### 4 Conclusions

In conclusion, we have combined DFT and classical thermodynamics to investigate the initial oxidation behaviours and thermodynamic stabilities of two-phase Ni/Ni$_3$Al composite. For the pure Ni/Ni$_3$Al composite, the Ni(111) and Ni$_3$Al(100)/(111) terminations are selected by energy calculation. For the oxidation of the Ni/Ni$_3$Al two-phase composite, we have constructed three-dimensional and two-dimensional surface phase diagrams for O/Ni$_3$Al and O/Ni systems with various antisite defects under different oxygen coverages. The main conclusions of this study are listed as follows:

1. The pristine composites are found to comprise Ni(111) and Ni$_3$Al(100)/(111) surfaces. During the oxidation process, O/Ni$_3$Al system is always more stable than O/Ni system in oxygen-rich stages through comparing surface formation energies, leading to selective oxidation of Ni$_3$Al phase at the first place. The binding energy of oxygen implies that oxygen atoms tend to bind with Al-terminated surfaces.

2. The surface diagrams depict that oxidation process is accompanied by Al-segregation on the top surfaces, which can further explain the experimental observation that oxidation layer is almost composed of Aluminium oxide. And Ni-terminated surfaces are not favored thermodynamically. Segregation of Al atoms on the surfaces stabilizes the whole structures by comparing binding energy of bulk oxide. At the Ni/Ni$_3$Al interfaces, oxygen atoms prefer to bond with Ni$_3$Al phase under the same circumstance.

3. The experimental results show the sample surface is mainly composed of Al oxide due to Al-segregation on the surface under oxygen atmosphere, especially at the interface of oxides and matrix.
Fig. 10 Interface formation energies of Ni/Ni₃Al with different lattice terminations and antisite defects as functions of the chemical potential of Ni: (a) Ni(100)/Ni₃Al(100), (b) Ni(111)/Ni₃Al(111).

Fig. 11 Oxygen binding energies (per oxygen atom) in the (a) Ni(100)/Ni₃Al(100) and (b) Ni(111)/Ni₃Al(111) interface configurations as functions of the distance between oxygen atoms and the boundary layer of interfaces. The vertical dashed lines represent the corresponding boundaries in interfaces.

Fig. 12 (a) SEM morphologies of the surface parallel to [001] direction after 1800 min oxidization at 1000 °C, (b) X-ray diffraction (XRD) analysis result of oxide scales on the surface of the sample after 1800 min oxidation at 1000 °C. (a: α-Al₂O₃, b: TaO₂/NiTa₂O₆, c: NiCr₂O₄, d: Cr₂O₃, e: NiO, f: Co₃O₄/CoCo₂O₄/CoWO₄, g: γ'-Ni₃Al, h: γ-Ni)
trix. The present finding is consistent with aforementioned theoretical calculations that oxygen atoms tend to bind with Al-rich surfaces, oxygen causes Al-segregation on the surface.

Furthermore, the findings of our work could provide more beneficial references for subsequent investigations of oxidation or adsorption processes of two-phase composites.

**Conflicts of interest**

There are no conflicts to declare.

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