Advances in *ab initio* thermodynamic studies on metal/oxide interfaces

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We provide a brief overview of the advances in *ab initio* thermodynamic studies on metal/oxide interfaces in this paper. Firstly, the development in interface modeling is briefly outlined. Secondly, the fundamentals of *ab initio* thermodynamic method are described. Thirdly, *ab initio* thermodynamic studies on several typical interfaces between alumina and metals including alloys are presented, especially for the interfaces between α-Al_2O_3 and Nb, Ni, Cu, and β-$Ni_{1-x}Al_x$

alloy. Finally, through analyzing electronic structure, chemical bonding, and adhesion of the interfaces between α-Al_2O_3 and a series of metals, including Al, Ni, Cu, Au, Ag, Rh, Ir, Pd, Pt, Nb, and β-NiAl, a formally unified model is derived for evaluating the works of separation of the representative aluminum-rich, oxygen-rich, and stoichiometric metal/α-Al_2O_3 interfaces. This model is also expected to be valid for studying other metal/oxide interfaces.

1 Introduction The study of metal/ceramic interfaces is of an interdisciplinary nature as well as a typical area covering physics, chemistry, and materials science [1, 2]. Among various heterogeneous interfaces, metal/oxide interfaces are particular because metals and oxides usually differ extremely in most materials properties. Metal/oxide interfaces play an important role in such applications as electronic packaging systems [3], wettability and adhesion of metals and ceramics [4], internal and external oxidation or reduction of materials [5], thermal barrier coatings (TBCs) for high-temperature gas-turbine engines [6], heterogeneous catalysis [7].

The structure, chemical bonding, and mechanical adhesion of a metal/oxide interface are key factors in determining the performance of the metal/oxide system, which has stimulated a considerable amount of experimental and theoretical researches. There have been some reviews summarizing the state of studies on the metal/oxide interfaces [4, 8–12], mostly referring to particular fields. For example, Finnis (1996) [9] reviewed various physical models and modeling methods for computer simulations to understand related experimental phenomena; Rühle (1996)

[10] introduced the electron microscopy technologies for the study of the microstructures of ceramic/metal interfaces; Saiz et al. (2008) [4] focused on analyzing the data of wetting and works of adhesion on metal/oxide systems at high temperatures. In the last decade, *ab initio* thermodynamic approach, which combines *ab initio* calculations with thermodynamic concepts [13–18], has been developed and frequently employed to predict the stability of metal/oxide interfaces which depends on thermodynamic variables, such as chemical potential, oxygen partial pressure, and metal activity at finite temperature. However, there is no systematic summary of the recent advances in *ab initio* thermodynamic studies on metal/oxide interfaces.

Different from most early reviews, this work focuses on a particular field and is to illustrate how *ab initio* calculations in conjunction with thermodynamics can be effectively used to study metal/oxide interfaces. The current paper is organized as follows. Firstly, the tendency and approaches of the computational simulations of metal/oxide interfaces are briefly introduced in Section 2. Secondly, the fundamentals of *ab initio* thermodynamics method are outlined in Section 3. Then results about several typical metal/alumina

and alloy/alumina interfaces as well as other heterogeneous interfaces are introduced in Section 4, which also illustrates the progress of the applications of *ab initio* thermodynamic method to interface modeling. Finally, a formally unified model is introduced to evaluate the adhesion of the metal/α-Al$_2$O$_3$ interfaces, covering three representative aluminum-rich, oxygen-rich, and stoichiometric cases.

2 Background We start from a brief summary of the progress in theoretical studies on metal/oxide interfaces. In the past years, various physical models have been provided to interpret related experimental observations. For interfacial geometry, the earlier coincidence site lattice (CSL) model [19] was used to describe matchings of metal/oxide phase boundary. In addition, the "lock-in" criterion proposed by Fecht and Gleiter was also applied to interface matchings [20]. Although some experimental phenomena could be explained by these two models, there were still considerable observations unclear. Afterward, in order to figure out the interaction at metal/oxide interfaces, some phenomenological models were proposed to explain interfacial adhesion mechanism [21–24], such as image charge theory [21]. The above models could partly provide some information about chemical bonds at metal/oxide interfaces, but hardly give in-depth understanding of many types of heterogeneous interfaces and evaluate the relationship between interfacial stability and thermodynamic environment in a systematic way.

As the computer improves, computer simulation becomes an effective way to explore the interfacial atomic and electronic structures. Among the various simulation methods, the molecular dynamics (MD) [25] and electronic structure calculations [26] were often used. The MD method critically depends on interatomic potentials which empirically describe interatomic interactions. MD simulations for metal/oxide interfaces require a complex and systematic way to obtain a set of interatomic potentials including metal–oxygen, metal–metal, and oxygen–oxygen potentials, which are usually very difficult to derive. Unlike MD, electronic structure calculations were widely accepted as an effective and reliable way for interface simulations. Initially, Johnson and Pepper (1982) [27] used an X-alpha-scattered-wave method to study metal/alumina interfaces in a cluster model. It could only give a qualitative description of the chemical bonding at the interfaces. Afterward, a series of semi-quantitative tight-binding approaches were used to investigate the bonding and adhesion for the interfaces between transition metals and alumina [28, 29]. Because tight-binding methods require some semi-empirical parameters and sometimes cannot carry out the relaxation of atom positions, their predictions are not as accurate and reliable as those from *ab initio* simulations directly based on the self-consistent electronic structure calculations.

Since 1990s, *ab initio* calculations based on density functional theory or Hartree–Fock approximation have been widely used to study the complex metal/oxide interfaces. There have been considerable amount of modeling of interfaces between oxide and a series of metals including Li, K, Y, Nb, Pd, Pt, Ag, Au, Al, Cu, etc. [30–37]. The *ab initio* approaches without dependence on the input of empirical parameters, can provide valuable information about the detailed atomic and electronic structures, as well as adhesion of interfaces.

Ab intio calculations alone cannot provide a complete picture about interfacial stability, especially when the interface has intrinsic nonstoichiometry problem in composition and dependence on external environment. Usually, interfacial structure predictions were only confined to predict relative sites of atoms in both metal and oxide slabs for some given metal/oxide interfaces through total energy calculations. For example, Siegel et al. [37] modeled the stoichiometric and oxygen-rich Al(111)/α-Al$_2$O$_3$(0001) interfaces, but whether the stoichiometric and oxygen-rich oxygen interface is more stable was not discussed. In order to identify the relative interfacial stability among various configurations, interfacial energies are needed to be calculated for both stoichiometric and nonstoichiometric interfaces. However, the absolute interface energy of a nonstoichiometric interface cannot be determined directly only by the outputs from *ab initio* total energy calculations as addressed in Ref. [38]. To solve that problem, Zhang et al. and Finnis and coworkers developed the so-called *ab intio* thermodynamic method which could be applied to investigate both the stoichiometric and nonstoichiometric interfaces [13–18, 39].

In 2000, Zhang and Smith [13] and Batyrev et al. [14] independently combined *ab initio* calculations with thermodynamic concepts to build a relationship between the stability of Nb/α-Al$_2$O$_3$ interface and chemical potentials of interfacial elements. In recent years, the metal activity and alloy composition were also introduced to analyze the environment-dependent stability of the interfaces between metals and alumina, *e.g.*, Ni, Cu, and β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces [16, 18]. It should be mentioned that the relationship between *ab initio* total energy calculation and chemical potentials was originated from those work on the polar surfaces of semiconductors and oxides, such as GaAs(111) [40], α-Fe$_2$O$_3$ (111) [41] and RuO$_2$(110) [42], and then was expanded naturally to interfaces and other systems of non-stoichiometry issue [39]. The fundamentals of *ab initio* thermodynamic for interfaces and surfaces are in principle the same. For surface studies, relationship to the partial pressure of environment is mostly addressed. For interfaces, relationships to both partial pressure of gas species and elemental activity, such as in metallurgical systems, should be equally addressed.

3 *Ab initio* thermodynamic approach for interface modeling The core of the *ab initio* thermodynamic approach is to introduce thermodynamic concepts into *ab initio* interface modeling. For an interface ensemble in thermodynamic equilibrium state, the chemical potential of each type of constituent atoms is identical in the whole ensemble. In this case, the interfacial energy, γ_{int}, of an equilibrium interface ensemble can be expressed as a function of chemical potentials of the constituents

by [39, 43–45]

$$\gamma_{\text{int}} = \left(G_{\text{total}} - \sum_i N_i \mu_i(T, p) \right) \Big/ S, \qquad (1)$$

where G_{total} is the total free energy of an ensemble that contains an interface which has a cross-sectional area S. μ_i ($i = 1, 2, 3, \ldots$) is the chemical potential of the constituent i at temperature T and pressure p, and N_i is the corresponding number of atoms of species i in the interface ensemble.

To combine *ab initio* calculations with thermodynamic concepts [43–45], Eq. (1) is rewritten as

$$\gamma_{\text{int}} = \left[G_{\text{total}} - \sum_i N_i \mu_i^0(0\,\text{K}, p) - \sum_i N_i \Delta\mu_i \right] \Big/ S, \qquad (2)$$

where $\mu_i^0(0\,\text{K}, p)$ is the chemical potential of constituent i in *ab initio* standard state at absolute zero temperature. For a solid, because the effect of pressure on the potential can be ignored [43, 45, 46], the chemical potential is defined as $\mu_i^0(0\,\text{K})$ and is just the total energy per atom of the corresponding crystal solid. For a solid, in *ab initio* thermodynamic method, there exists a relationship between the real potential and the *ab initio* standard state potential, *i.e.*,

$$\Delta\mu_i = \mu_i(T) - \mu_i^0(0\,\text{K}), \qquad (3)$$

where $\Delta\mu_i$ is the effective chemical potential difference between real-state value at the experimental standard state and that in *ab initio* standard state. Furthermore, the effective chemical potential difference $\Delta\mu_i$ can be directly linked to the thermodynamic variable elemental activity a_i, *i.e.*,

$$\Delta\mu_i = \Delta_i^0(T) + kT\ln a_i. \qquad (4)$$

Here, quantity $\Delta_i^0(T)$ is defined as the connection energy as discussed and tabulated in Ref. [39]. k is Boltzmann constant. Note that the above discussion is only outlined for reference state at the solid state. Readers can refer to Ref. [39] for the definition and equations when the reference state is gas.

When thermodynamic equilibrium exists between a heterogeneous interface and environmental atmosphere, by taking the metal/α-Al$_2$O$_3$ interfaces as an example, the activity of element, *i.e.*, a_{Al} for Al, can be related to environmental partial pressure of O$_2$ (p_{O_2}) by

$$\ln p_{\text{O}_2} = \frac{2}{3kT} \Delta G_{\text{Al}_2\text{O}_3}^0(T) - \frac{4}{3}\ln a_{\text{Al}}. \qquad (5)$$

Here, $\Delta G_{\text{Al}_2\text{O}_3}^0$ is the experimental standard Gibbs reaction energy corresponding to the formation of α-Al$_2$O$_3$ [47].

By using Eqs. (1)–(5), the calculated interface energies and their dependence on measured quantity are firmly established within *ab initio* framework. Based on the *ab initio* thermodynamic approach, the thermodynamic factors, such as chemical potentials, oxygen partial pressure, and metal activity, are all linked to *ab initio* calculations for analyzing both stoichiometric and nonstoichiometric interfaces. In fact, surface structures, defect stability, and doping of semiconductors can also be investigated by *ab initio* thermodynamics [39–45].

4 Applications to interface modeling This section mainly introduces the applications of *ab initio* thermodynamic method to the studies of metal/α-Al$_2$O$_3$ and alloy/α-Al$_2$O$_3$ interfaces focusing on the stability/environment and structure/adhesion relationships. For metal/α-Al$_2$O$_3$ (0001) interfaces [16, 17], there may exist three typical configurations, *i.e.*, the aluminum-rich, oxygen-rich, and stoichiometric cases, which correspond to metals adhered to α-Al$_2$O$_3$ (0001) surfaces terminated by two Al atom layers [labeled as M/(Al$_2$O$_3$)$_{\text{Al}_2}$], one O atom layer [M/(Al$_2$O$_3$)$_{\text{O}}$], and one single Al atom layer [M/(Al$_2$O$_3$)$_{\text{Al}_1}$], respectively.

4.1 Interfaces between metals and α-Al$_2$O$_3$ A considerable amount of *ab initio* thermodynamic calculations have been performed to investigate the metal/α-Al$_2$O$_3$ interfaces [13–17]. Initially, the difficulties associated with calculating interfacial energies for nonstoichiometric interfaces were overcome through introducing the effective chemical potential difference. Afterward, thermodynamic parameters such as gas partial pressure and metal activity were introduced to describe the environmental dependence of interfacial energies, and the relationship between environmental gas partial pressure and metal activity was also built.

Zhang and Smith (2000) [13] first calculated the interfacial energies of stoichiometric and nonstoichiometric Nb/α-Al$_2$O$_3$ interfaces as a function of the *ab initio* effective chemical potential difference $\Delta\mu_{\text{O}}$, using the equations described above [Eq. (2)]. They noticed that the chemical potentials of atoms at an interface closely related to the imposed oxygen partial pressure. The most important results they obtained were that the oxygen-rich Nb/(Al$_2$O$_3$)$_{\text{O}}$ interface becomes most stable as oxygen partial pressure increased (see Fig. 3 in Ref. [13]), consistent with the earlier experimental observations [48]. Almost in the same time, Finnis and coworkers (2000) [14] also adopted a similar approach to study Nb/α-Al$_2$O$_3$ interfaces including the aluminum-rich, oxygen-rich, and stoichiometric cases, and got similar conclusion.

In practice, an interface may be in metallurgical as well as gas-interaction environment [43, 44]. Therein, the important thermodynamic parameters not only refer to gas partial pressure, but also include the metal activity. By taking Ni/α-Al$_2$O$_3$ and Cu/α-Al$_2$O$_3$ interfaces as examples, Zhang and Smith et al. (2002) established the reliable relationship between interfacial energy and Al activity as well as oxygen partial pressure (see Fig. 1). All the theoretical results about interfacial stability and adhesion agreed well with available
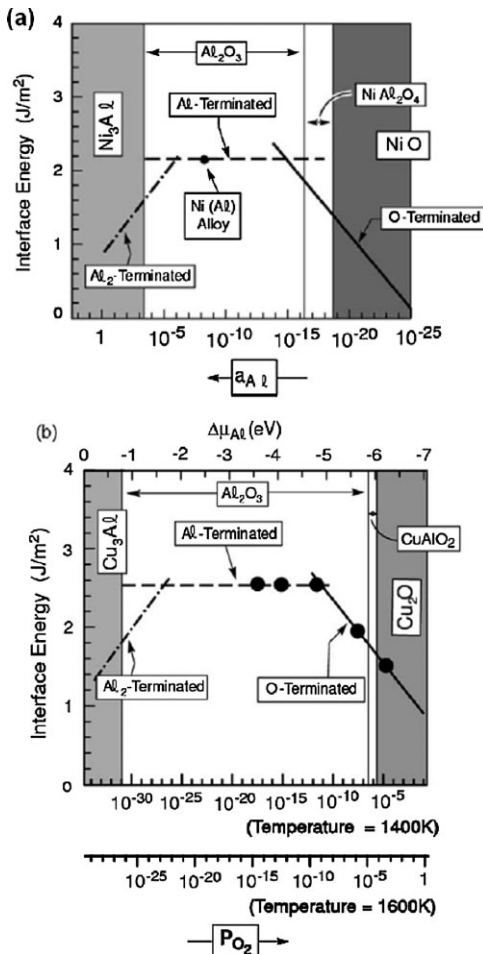
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Figure 1 Interfacial energies for (a) Ni/α-Al$_2$O$_3$ at 1300 K, and (b) Cu/α-Al$_2$O$_3$ at 1400 and 1600 K. The pictures are taken from Ref. [16].

experimental measurements [4, 49, 50]. For example, they reproduced the experimental observations that the energies of Ni/α-Al$_2$O$_3$ and Cu/α-Al$_2$O$_3$ interfaces were a function of oxygen partial pressure in sessile drop measurements [4], and the oxygen-rich Cu/α-Al$_2$O$_3$ interfaces should exist corresponding to the experimental conditions as reported in Refs. [49, 50]. This was an important progress in *ab initio* thermodynamic studies on metal/α-Al$_2$O$_3$ interfaces because the connection between the *ab inito* calculations and experimental measurements was firmly established. Afterward, this *ab initio* thermodynamic method were also successfully applied to analyzing Ag/α-Al$_2$O$_3$ and Au/α-Al$_2$O$_3$ interfaces [17], and the predicted stability and adhesions were also in reasonable agreement with experimental observations.

4.2 Interfaces between metal alloys and α-Al$_2$O$_3$ There are many complicated metal alloy/oxide interfaces in practice, in which the alloy is often two-component AB compound, such as Ni–Al or Fe–Al alloys. Usually, the binary alloy of a specific structure is only stable

within a certain composition range of alloy, such as $0.31 < x < 0.58$ for β-Ni$_{1-x}$Al$_x$ alloy [51]. So the interfacial energy of an alloy/oxide interface is also subject to the chemistry of the alloy. For an A$_{1-x}$B$_x$/BO$_y$ interface, the general expression for interfacial energy is [18],

$$\gamma_{\text{int}} = \left\{ G_{\text{total}} - \frac{1}{1-x} N_A \mu_{A_{1-x}B_x} - \frac{1}{y} N_O \mu_{BO_y} \right.$$
$$\left. - \left(N_B - \frac{x}{1-x} N_A - \frac{1}{y} N_O \right) \mu_B \right\} \Big/ S. \quad (6)$$

Note that the typical β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interface has been used as an example (A = Ni, B = Al). Given that the interface is also in thermodynamic equilibrium with β-Ni$_{1-x}$Al$_x$ alloy, an extra basic relationship is used in deriving Eq. (6), *i.e.*,

$$\mu_{\text{Ni}_{1-x}\text{Al}_x} = (1-x)\mu_{\text{Ni}}^{\text{bulk}} + x\mu_{\text{Al}}^{\text{bulk}} + \Delta H_{\text{Ni}_{1-x}\text{Al}_x}, \quad (7)$$

where $\mu_{\text{Ni}_{1-x}\text{Al}_x}$ is the chemical potential of Ni–Al alloy, $\mu_{\text{Ni}}^{\text{bulk}}$ ($\mu_{\text{Al}}^{\text{bulk}}$) is the energy per Ni (Al) atom in the fcc Ni (Al) state, and $\Delta H_{\text{Ni}_{1-x}\text{Al}_x}$ is the formation enthalpy of the β-Ni$_{1-x}$Al$_x$. A linear relationship between $\Delta H_{\text{Ni}_{1-x}\text{Al}_x}$ and alloy composition was adopted based on the experimental data [52] and theoretical calculations [18].

In order to calculate the total energy G_{total} of the interface ensemble which depends on alloy composition, the concept of *interface representative layers* was introduced to describe a few atomic layers close to the virtual interface plane, which separates oxide from substrate Ni–Al alloy as shown in Fig. 2. The underlying point is that the structure of *interface representative layers* is insensitive to the alloy composition for various β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces, primarily due to the fact that the composition of the stable Ni–Al alloy deviates slightly from the stoichiometric case ($x = 0.5$). The *interface representative layers* contain the most important information of possible interfacial structures. In searching for all possible configurations, those representative layers
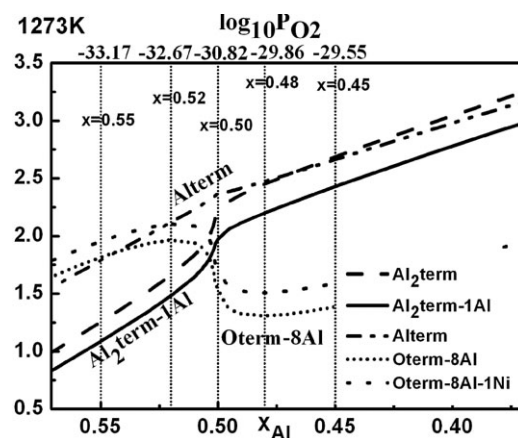

Figure 2 Interfacial energies for several typical β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces as a function of alloy composition x_{Al} and p_{O_2} at 1273 K. The picture is taken from Ref. [18].
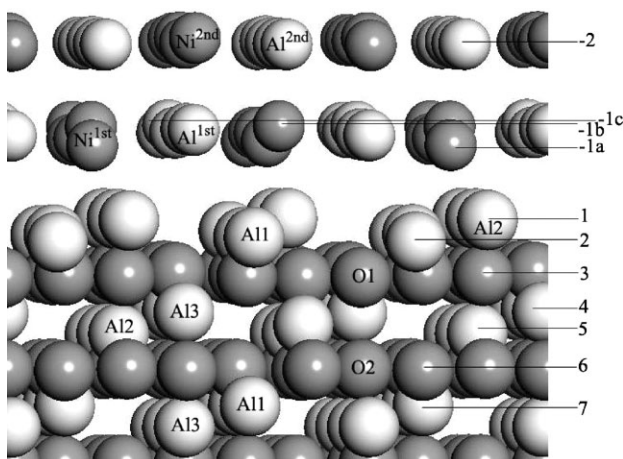
Figure 3 Structure of Al$_2$*term*–1Al interface. The picture is taken from Ref. [18].

are systematically modified through removing, inserting, and exchanging of interfacial atoms.

After establishing the relationship between Al activity, chemical potential μ_{Al}, and alloy composition [53], the stability of the interface and the associated dependence on alloy composition could be determined for β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces. The final results predicted that there should be two types of stable configurations for the β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces, *i.e.*, the Al$_2$*term*–1Al and O*term*–8Al interfaces as shown in Fig. 2. The Al$_2$*term*–1Al could be formed by joining Al-rich alloy with Al$_2$-terminated Al$_2$O$_3$ surface as shown in Fig. 3. The O*term*–8Al could be formed by adhering Ni-rich alloy to O-terminated Al$_2$O$_3$ surface, with some atom migrations and interchanges (see Fig. 7 in Ref. [18]). Both types of interfaces exhibited Al accumulation on top of oxide scale, while an adjacent Ni-rich layer should exist at the O*term*–8Al interface. Through the calculations of interfacial works of separation, it was found that the adhesion of the two types of stable β-Ni$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces are quite similar (see Table IV in Ref. [18]). In practice, this approach is also valid for investigating other interfaces between binary alloys and alumina, *e.g.*, Fe$_{1-x}$Al$_x$/α-Al$_2$O$_3$ and Ti$_{1-x}$Al$_x$/α-Al$_2$O$_3$ interfaces.

4.3 Generalization of the *ab initio* thermodynamic approach *Ab initio* thermodynamic method has also been successfully applied to studying many other heterogeneous interfaces [54–58]. For example, Siegel et al. [54] presented the stability analysis of polar Al(111)/WC(0001) interfaces and found that the optimal interface geometry was the W-terminated one within the physically acceptable range of carbon chemical potential; Liu et al. [55] studied the dependence of the interfacial energy of Al/TiN interface on nitrogen chemical potential, and concluded that the stability of Al/TiN interface could be changed by N$_2$; Some others [56–58] applied the *ab initio* thermodynamic approach to study the film growth on compound surfaces and

its dependence on environmental conditions, especially the gas partial pressure in growth chamber.

For *ab initio* studies of interfaces, interface mismatch remains as an intrinsic challenge. Very few of heterogeneous interfaces give perfect match or very small mismatch [16, 59]. For interfaces of mismatch, not very small but also not very big, a feasible approach is to study a few interface models which introduce different strains for different slabs, and only the conclusions insensitive to the introduced strains are trusted [16, 59]. For those interfaces with large strains, probably a large interface supercell could be adopted but computational demands become heavy. So far, only a few model systems were studied, such as Si/Cu [60]. However, this will certainly be an interesting direction in this field. It should also be pointed out that the absolutely Gibbs energy of a surface or an interface could be determined when the surface or the interface owns a specific symmetry in the direction normal to the interface plane, such as the Al$_2$O$_3$ (0001) surfaces and metal/α-Al$_2$O$_3$ (0001) interfaces [13–17] with inversion symmetry. In case of surfaces or interfaces of low symmetry, strictly speaking, there may be no way to construct a system with two equivalent surfaces/interfaces for *ab initio* calculations. In that case, only the relative stability among surfaces/interfaces of different terminations, could be determined by using the above approach. Readers may refer to Meyer's work for O-terminated ZnO (0001) surface [61]. In this aspect, Chetty and Martin [38] proposed a scheme to calculate the local surfaces energies with different slab terminations by introducing an energy density rather than directly calculating total energy. Employing this method, Kohyama and Tanaka [62] studied the polar interfaces of grain boundaries in SiC. This is certainly be very interesting to see if there is a way to combine the calculated surface/interface energy density with the above-discussed *ab initio* thermodynamic concepts.

Even though the relationship between the calculated chemical potential and elemental activity could be established from theory, the connection to doping concentration of one element into the host materials, *i.e.*, ppm Al into fcc Ni, to Al activity, or to the alloy composition is not established from the bottom of theory. Recent work by Jiang et al. [63] reported the calculated Al activity and its dependence on doping concentration as well as temperature in dilute γ-Ni(Al) solid solutions through combining the *ab initio* approach and thermodynamic concepts. In principle, the activity coefficient of Al in fcc Ni, could be estimated by

$$\gamma_{Al}(T, x) = a_{Al}(T, x)/x$$
$$\gamma_{Al}(T) = [\Delta H(T)\text{-}T\Delta S_{n\text{-}c}(T)]/kT. \tag{8}$$

Here, ΔH and $\Delta S_{n\text{-}c}$ are, respectively, the formation enthalpy and non-configurational entropy difference between an isolated solute Al atom in bulk γ-Ni and pure fcc Al, which could be determined independently from *ab initio* approach. With the activity coefficient obtained from theory, the adhesion of γ-Ni(Al)/α-Al$_2$O$_3$ interface, at a given doping concentration or solution condition, could be

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evaluated completely from theory, without the necessary of any experimental input. This is an important step toward a complete and independent theoretical design of interface. More work should be done along this direction in the future.

5 A formally unified model for evaluating the adhesion of metal/α-Al₂O₃ interfaces Work of separation, W_{sep}, of an interface is usually used to evaluate the adhesion of the interface, which is defined as the energy needed to separate the interface into two free surfaces [9]. *Ab initio* thermodynamic studies [13–17] have proved that there should exist aluminum-rich, oxygen-rich, and stoichiometric interfaces for most of the metal/α-Al₂O₃ interfaces, depending on external environment. Those calculations also showed that the works of separation for interfaces with different stoichiometries are quite different from each other.

In our recent work [64], interfacial stoichiometry, atomic relaxation, electronic structure, chemical bonding, and adhesion of interfaces between α-Al₂O₃ and a series of metals, including Al, Ni, Cu, Au, Ag, Rh, Ir, Pd, Pt, and Nb were comprehensively analyzed. The similarities and changing tendency of interfacial bonding for the metal/α-Al₂O₃ interfaces were revealed. In a generalized way, a formally unified model was reasonably proposed to evaluate the works of separation for the metal/α-Al₂O₃ interfaces, *i.e.*,

$$W_{\mathrm{sep}} = a n_{\mathrm{ws}} + b|\mathrm{EOF}| + c. \qquad (9)$$

Here, n_{ws} is the empirical electron density parameter at the boundary of Wigner–Seitz atomic cell of the adhered metal, which was estimated for the pure element in a metallic state [65] before. |EOF| is the enthalpy of formation |EOF| of the corresponding metal oxide [45, 66]. For the aluminum-rich interfaces with predominantly metallic bonds, the electron density parameter n_{ws} could be employed to estimate the interfacial adhesion. In terms of the ionic-covalent bonding of the oxygen-rich interfaces, the enthalpies of formation (|EOF|) of metal oxides are used alone to characterize their adhesion. Because both ionic-covalent and metallic bonding exists at the stoichiometric interfaces, the interfacial W_{sep} could be expressed as a function of the combination of n_{ws} and |EOF|. After a careful analyses of the calculated and measured data, we found that, one group of (a,b,c) coefficients could be extracted to describe the interfacial adhesion for metal/α-Al₂O₃ interfaces at a given termination [64]. In other words, three groups of (a,b,c) coefficients will be good enough to describe the adhesion trend of the interfaces between α-Al₂O₃ and a series of metals. It seems that the coefficients are mainly Al₂O₃-related and insensitive to the types of adhered metals. Figure 4 shows that the model describes well the adhesion tendency of the stoichiometric interfaces for α-Al₂O₃-related systems with different metals. Results for interface of the aluminum-rich, and oxygen-rich cases will be discussed in Ref. [64].

In contrast to earlier phenomenological models [21–24] valid only for the stoichiometric interfaces, our model covers
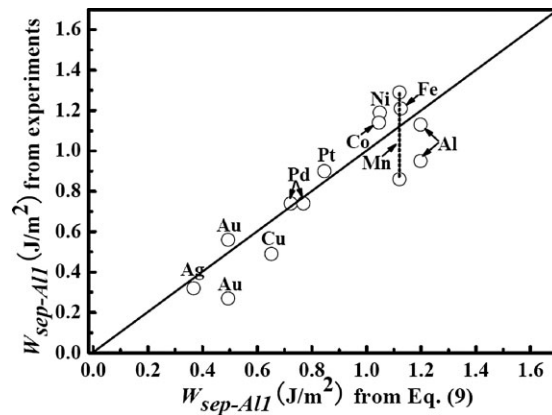

Figure 4 $W_{\mathrm{sep\text{-}Al_1}}$ for the stoichiometric metal/alumina interfaces. The picture is taken from Ref. [64].

the interfaces of different stoichiometries. It gives a general understanding of interfacial bonding for a variety of metals adhering to Al₂O₃. This model should also be valid for other metal/oxide interfaces. In principle, a general model describing oxide-metal adhesion is expected, which covers more than Al₂O₃. Work along this direction is also very interesting.

6 Conclusions and outlook We provide a brief overview of the advances in *ab initio* thermodynamic studies on metal/α-Al₂O₃ interfaces, covering the fundamental methodology and their related applications. By using the *ab initio* thermodynamic approach, various metal/ceramic interfaces have been studied. The theoretical results show clearly the stoichiometry-dependent interfacial stability and reveal the dependence of stability on thermodynamic environment. It has been testified that the results agree well with experimental observations. Recently, work on the complicated β-Ni₁₋ₓAlₓ/α-Al₂O₃ interface also revealed a relationship between interfacial stability and alloy composition. Based on the calculated adhesion data, a formally unified model was reasonably proposed to evaluate the works of separation for α-Al₂O₃-related interfaces with different metals.

Ab initio thermodynamic approach has been well established in recent years through the detailed studies of interface and surface structural stability, which was recognized as one of the most important progress in the field of interface simulations in recent years [11]. In principle, the approach is quite general, and can be applied to any system as long as non-stoichiometry issue in chemical compositions exist, which has been discussed in our earlier work [39]. It is highly expected that the approach is used to model other interfaces with increased complexity as well as many other systems with environment-dependent stoichiometry.

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