First principles calculation of interfacial stability, energy, and elemental diffusional stability of Fe (111)/Al₂O₃ (0001) interface

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First principles calculation of interfacial stability, energy, and elemental diffusional stability of Fe (111)/Al₂O₃ (0001) interface

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ABSTRACT

First-principles calculation is widely used to study solid-solid interfaces, which provides insights into the atomic and electronic structure of an interface including the interfacial stability and adhesion strength. In general, the interface of the Fe/Al₂O₃ composite material is hardly wetted, and the aluminum oxide layer is firm and thin. It is difficult to observe the interface via an electron microscope. Thus, the changes at the interface were studied by first-principles calculations. Interfacial stability, energy of the Fe (111) surface, the Al₂O₃ (0001) surface, and Fe (111)/Al₂O₃ (0001) interfaces were studied using the first-principles calculation method. The work of adhesion (W_ad), interface energy (γ_int), and the electronic structure of Fe (111)/Al₂O₃ (0001) interfaces were studied. The results indicated that W_ad of the O-terminated interface was significantly larger than that of the Al-terminated interface. The O-terminated interface was the most stable interface. Furthermore, the O-terminated interface consisted of strong polar covalent bonds and weak metallic bonds, while the Al-terminated interface primarily consisted of covalent and metallic bonds. Furthermore, the segregation of Al atoms at the interface enhanced the stability of the interface structure, and interfacial bonding ability was increased with the increase in aluminum atoms. Only aluminum atoms diffused through the initial oxide layer forming intermetallic compounds on the iron side. The inclusion of Al₂O₃ significantly impacts the mechanical properties of steel, such as toughness and fatigue, underscoring that it is important to predict and control the inclusions in steel to obtain desired mechanical properties. The insights obtained from the study described here provide fundamental insights and guidelines into tailoring the steel/aluminum composite interface.

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I. INTRODUCTION

Interface between metal and oxide is present in engineering structures that involve dissimilar welding of metals, bimetal casting, thermal spraying, and coatings, which are responsible for promoting efficiency and stability. Fe/Al₂O₃ is one of the common metal-oxide interfaces when the ferrous alloy comes in contact with the aluminum oxide layer present on the surface. The bond strength and toughness of the Fe/Al₂O₃ interface largely determines the performance and reliability of a number of application systems. The application systems range from conventional large-size structural composites to small-size functional films and coatings to microsize nanoelectronic devices. This includes the interaction of ferroalloys with the solid or semisolid aluminum during welding, diffusion bonding, or the antioxidation process.

In general, the optical, magnetic, mechanical, or catalytic properties of metal–ceramic composites are strongly affected by the interface microstructure and chemical composition of the interface. In order to understand chemical bonding, adhesion mechanisms, and other phenomena that are specific to metal–ceramic interfaces, several fundamental studies have been recently carried out on interfaces formed by growing ultrathin metallic layers of different metals on
oxide substrates. In particular, an ultrathin iron film grown on an Al$_2$O$_3$ substrate has significant potential in the field of nanoscale magnetism, where the Fe/Al$_2$O$_3$/Fe system is used as a magnetic tunnel junction (MTJ). Arranz et al. presented a study of growth and electronic properties of Fe ultrathin films deposited on Al$_2$O$_3$ substrates at room temperature using soft X-ray photoelectron spectroscopy (SXPS) and resonant photoemission (RPE). They also analyzed the thermal stability of the interface up to 873 K. Heiba studied the effect of iron doping on structural, optical, and electronic properties of doped alumina. The results showed that the diffused reflectance increased with the increase in wavelength but decreased when the content of Fe doping was increased. The intensity also decreased with the introduction of Fe cations into the Al$_2$O$_3$ lattice. The lattice parameters were increased when some Fe atoms replaced the Al atoms in the Al$_2$O$_3$ matrix because of the difference in their atomic radius.

When the surface of the oxidized steel is subjected to thermal cycling and other external mechanical stress, the adhesion of the metal-oxide interface is weak, and the oxide layer tends to peel off. During the welding process, the appearance of brittle intermetallic phases or other undesired constituents induced by the reaction of iron and alumina at the interface can lead to poor adhesion and can impact the mechanical properties of the weld zone. Additionally, the initial oxide layer also affects the diffusion process and final properties of Al$_3$Fe/stainless steel laminate composites, which are fabricated by hot pressed iron and aluminum foils.

The interface of the Fe/Al$_2$O$_3$ composite material is hardly wetted and is only physically joint to the extent that the cracks are easily formed at the interface. Considering that the aluminum oxide film is very thin, it is difficult to observe via an electron microscope, and the effects of the changes at the interface were largely studied by calculations. First-principles calculation is widely used to study the solid-solid interface, which reveals the atomic and electronic structure of the interface as well as the interfacial stability and adhesion strength.

The first-principles and interface geometry theory can characterize the atomic structure, calculate the energy of the metal-oxide system, acquire the work of adhesion and interface energy, and obtain the effect of oxide on the interface adhesion behavior by using first-principles calculation of heat of segregation. Dong et al. used the first-principles calculation method to discuss the effect of additives on Fe (111)/Cr$_2$O$_3$ (0001) interfacial adhesive strength in austenitic stainless steels. They considered that Fe crystallizes as an fcc structure, and the interface was parallel to the cubic (111) and hexagonal (0001) faces where the direction of Fe (111) is parallel to the direction of Cr$_2$O$_3$ (0001). Using the first principles to calculate the adhesion energy and interface bond strength, the key properties of the interface and the effect of the bond on the interface can be further researched from a microscopic perspective. They studied the segregation of different alloying elements X (X = Si, Al, V, Ti, Mo, W, Nb, Y) at the Fe (111)/Cr$_2$O$_3$ (0001) interface and systematically determined the effect of additives on interfacial adhesion using the first-principles method. The results suggested that the dissolved W, Mo, and Nb were easily segregated at the Fe/Cr$_2$O$_3$ interface, which weakened the adhesive strength of the interface through weak-electron effects. Y, Al, Si, Ti, and V were difficult to segregate at the interface. Zhukovskii et al. performed a study on the Ag/Al$_2$O$_3$ interface for both Al-terminated and O-terminated interfaces ab initio, including the dependence of adhesion energy on the interfacial distance and interface bond strength. It was shown that adhesion on the Al-terminated and O-terminated corundum substrate varied significantly. For the Al-terminated interface, they observed smaller adhesion energy, while for the O-terminated interface, there was significantly large binding energy.

However, the Fe/Al$_2$O$_3$ interface is one of the most widely used interfaces in engineering and is rarely studied. Zhang studied the effect of active elements (HF and Y) on the adhesive behavior of the Fe (110)/Al$_2$O$_3$ (0001) interface by using the first-principles method. In the calculations, the surface stability and the number of surface convergence layers were not elucidated. Instead, they directly used (110) the surface of Fe as the stability interface for calculation. In general, the crystal structure of ferrous alloys such as austenitic stainless steel is fcc with (111) as the close-packed plane. Thus, it is reasonable to select the cubic (111) surface of fcc-Fe and the (0001) surface of hexagonal Al$_2$O$_3$ as the test surface to study the stability of the surface and the number of convergent layers on the surface.

In the study described here, we systematically studied the properties of the Fe/Al$_2$O$_3$ interface by using first-principles calculation. The interface was considered parallel to the cubic (111) and hexagonal (0001) facets, where the [110] direction in Fe (111) is parallel to [1010]. The bulk and surface properties of fcc-Fe and a-Al$_2$O$_3$ are described via simulation of interfacial interactions and the analysis of simulation results. The interfacial energy, electronic structure, and bond of the Fe/Al$_2$O$_3$ interface were calculated for obtaining a stable interfacial state. The stabilities of aluminum atoms at the interface of Fe/Al$_2$O$_3$ and Al/Al$_2$O$_3$ were calculated based on the stable interfacial model and was experimentally confirmed.

II. THEORETICAL CALCULATION METHOD

The calculations were performed with the Cambridge Serial Total Energy Package (CASTEP) code. The first-principles calculation, which is based on plane wave expansion technology, was used in the reciprocal space. The exchange-correlation interactions in the present calculations considered the Perdew-Burke-Ernzerhof (PBE) function in the generalized gradient approximation (GGA) of the plane wave pseudopotential method. Ultra-soft pseudopotential was used to calculate the interactions between the ionic nucleus and valence electrons. In order to further optimize the structure, the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm was used for geometry optimization. Furthermore, $3s^23p^63d^44s^2$ for Fe, $3s^23p^6$ for Al, and $2s^22p^4$ for O were selected as the valence electrons of the atoms. The value of cut-off energy was set at 380 eV, and the value of k-point was set to $10 \times 10 \times 10$ for a bulk. For a slab, a $10 \times 10 \times 1$ k-point mesh was employed, and the cut-off energy was set as 400 eV for all the slabs.

A vacuum layer of 15 Å is selected for each surface and interface structure to eliminate the interactions between the surface atoms. The BFGS convergence parameters are set in the calculations as follows: the total energy and the maximum force tolerance is set to $1.0 \times 10^{-5}$ eV/atom and 0.03 eV/Å, respectively.
According to Eqs. (1)–(3), the following equation is obtained:

\[
\sigma = \frac{1}{2A} \left[ E_{\text{slab}} - \frac{1}{2} N_{\text{Al}} \mu_{\text{Al}}^{\text{bulk}} - \frac{2}{3} N_{\text{O}} \mu_{\text{O}}^{\text{bulk}} \right] - \left( N_{\text{Al}} - \frac{2}{3} N_{\text{O}} \right) \left( \mu_{\text{Al}}^{\text{slab}} - \mu_{\text{Al}}^{\text{bulk}} \right),
\]

where \( E_{\text{slab}} \) is the total energy of the fully relaxed surface model, \( A \) is the surface area of the slab, \( N_{\text{Al}} \) and \( N_{\text{O}} \) are the number of Al and O atoms in the slabs, respectively, and \( \mu_{\text{Al}}^{\text{bulk}} \) and \( \mu_{\text{O}}^{\text{bulk}} \) denote the chemical potential for Al and O, respectively. The terms PV and TS can be neglected at 0 K and atmospheric pressure.

In fact, the \( \text{Al}_2\text{O}_3 \) (0001) slab and bulk \( \text{Al}_2\text{O}_3 \) could reach equilibrium when the surface structure is fully relaxed. Therefore, the chemical potential of the \( \text{Al}_2\text{O}_3 \) (0001) slab is equal to the chemical potential of the bulk and is defined by

\[
\mu_{\text{Al}_2\text{O}_3}^{\text{bulk}} = 2\mu_{\text{Al}}^{\text{bulk}} + 3\mu_{\text{O}}^{\text{bulk}},
\]

\[
\mu_{\text{Al}_2\text{O}_3}^{\text{bulk}} = 2\mu_{\text{Al}}^{\text{bulk}} + 3\mu_{\text{O}}^{\text{bulk}} + \Delta H_{\text{Al}_2\text{O}_3},
\]

where \( \mu_{\text{Al}_2\text{O}_3}^{\text{bulk}} \) is the total energy of bulk \( \text{Al}_2\text{O}_3 \), and \( \mu_{\text{Al}}^{\text{bulk}} \) and \( \mu_{\text{O}}^{\text{bulk}} \) represent the single atomic energy.

According to Eqs. (1)–(3), the following equation is obtained:

\[
\sigma = \frac{1}{2A} \left[ E_{\text{slab}} - \frac{1}{2} N_{\text{Al}} \mu_{\text{Al}}^{\text{bulk}} - \frac{2}{3} N_{\text{O}} \mu_{\text{O}}^{\text{bulk}} \right] - \left( N_{\text{Al}} - \frac{2}{3} N_{\text{O}} \right) \left( \mu_{\text{Al}}^{\text{slab}} - \mu_{\text{Al}}^{\text{bulk}} \right),
\]

where \( \Delta \mu_{\text{Al}} = \mu_{\text{Al}}^{\text{slab}} - \mu_{\text{Al}}^{\text{bulk}} \leq 0 \) and \( \Delta \mu_{\text{O}} = \mu_{\text{O}}^{\text{slab}} - \mu_{\text{O}}^{\text{bulk}} \leq 0 \). Considering the stability of the compound at equilibrium, it cannot spontaneously decompose into a single substance. The chemical potential of each component is less than the chemical potential of its corresponding bulk and is described by the following inequalities:

| Composition | This work (Å) | Other (Å) | Expt. (Å) | \( V_0 \) (Å\(^3\)) | B (GPa) |
|-------------|---------------|-----------|-----------|----------------|---------|
| fcc-Fe      | \( a = b = c = 3.447 \) | \( a = b = c = 3.430 \) | \( a = b = c = 3.447 \) | 40.970 | 309.786 |
| \( \text{Al}_2\text{O}_3 \) | \( a = b = c = 4.759 \) | \( a = b = c = 4.792 \) | \( a = b = c = 4.758 \) | 263.798 | 246.023 |

FIG. 1. Surface model of \( \alpha-\text{Al}_2\text{O}_3 \) (0001) surface relaxation: red is an oxygen atom, and pink is an aluminum atom; (a) Al-terminated, (b) O-terminated, and (c) \( \text{Al}_2\text{O}_3 \)-terminated.
Combining Eqs. (2), (3), (5), and (6), the range of Al chemical potential is given by
\[
\Delta H_{\text{Al,O}_3} + \mu_{\text{Al}}^\text{slab} - \mu_{\text{Al}}^\text{bulk} \leq 0. \tag{7}
\]

The heat of the formation of bulk Al\(_2\)O\(_3\) is obtained from\(^{30,31}\)
\[
\Delta H(M_s N_s) = [E_{\text{tot}}(M_s N_s) - xE_{\text{bulk}}(M) - yE_{\text{bulk}}(N)] / (x + y), \tag{8}
\]
where \(\Delta H(M_s N_s)\) and \(E_{\text{tot}}(M_s N_s)\) are the formation enthalpies of the formation and the total energy of Al\(_2\)O\(_3\), respectively, \(E_{\text{bulk}}(M)\) is the cohesive energy of Al, and \(E_{\text{bulk}}(N)\) is the cohesive energy of O.

The range of variation of \(\mu_{\text{Al}}^\text{slab} - \mu_{\text{Al}}^\text{bulk}\) is known. Thus, the surface energy can be obtained using Eq. (4) and has a certain variation. However, when the surface energy is determined in a certain direction, the surface energy can be obtained using Eq. (4) and has a certain variation. Moreover, when the surface energy is determined in a certain direction, it should be constant. In order to deal with this situation, the calculation of the chemical potential of each component in the compound is solved as follows:

There is a compound composed of 1 mol of regular solution and \(T = 0\) K; the chemical potential of Al and O are given as follows:
\[
\mu_{\text{Al}} = 0 \ G_{\text{Al}} + (1 - x_{\text{Al}}) \ G_{\text{Al,O},}\tag{9}
\]
\[
\mu_{\text{O}} = 0 \ G_{\text{O}} + (1 - x_{\text{O}}) \ G_{\text{Al,O},}\tag{10}
\]
Interaction energy is defined as \(I_{\text{Al,O}} = z N_0 \ (u_{\text{Al-O}} - u_{\text{Al,O}})\), where \(z\) is the coordination number, \(N_0\) is the Avogadro constant, and \(u_{\text{Al-Al}}, u_{\text{Al,O}},\) and \(u_{\text{Al-O}}\) represent the bond energies of three chemical bonds, Al–Al, O–O, and Al–O, respectively. From thermodynamics, the narrowly defined normal solutions and the system’s free energy calculation expression are as follows:
\[
G = X_{\text{Al}} G_{\text{Al}} + X_{\text{O}} G_{\text{O}} + RT (X_{\text{Al}} \ln X_{\text{Al}} + X_{\text{O}} \ln X_{\text{O}}) + X_{\text{Al}} X_{\text{O}} I_{\text{Al,O}}, \tag{11}
\]
For \(T = 0\) K,
\[
G = X_{\text{Al}} G_{\text{Al}} + X_{\text{O}} G_{\text{O}} + X_{\text{Al}} X_{\text{O}} I_{\text{Al,O}}, \tag{12}
\]
where \(X_{\text{Al}}\) and \(X_{\text{O}}\) are the atomic fractions of Al and O components, respectively, and \(G_{\text{Al}}\) and \(G_{\text{O}}\) are the Gibbs free energies of Al and O components, respectively. Based on these normal solution energies, the chemical potential of the aluminum and oxygen components in alumina are calculated as \(-62.05\) eV and \(-435.93\) eV, respectively.

The ideal work of adhesion \((W_{\text{ad}})\) is used to describe the bond strength of interface atoms, which is reversible work. It can be calculated by the following equation:\(^{32,33}\)
\[
W_{\text{ad}} = (E_{\text{Fe/Al,O}_3} - E_{\text{Fe/Al,O}_3}^{\text{total}})/A, \tag{13}
\]
where \(E_{\text{Fe/Al,O}_3}^{\text{total}}\) and \(A\) are the total energy and interface area of the Fe/Al\(_2\)O\(_3\) interface, respectively, \(E_{\text{Fe/Al,O}_3}\) represents the total energy of Fe (111) with five layers, and \(E_{\text{Fe/Al,O}_3}^{\text{total}}\) represents the total energy of Al\(_2\)O\(_3\) (0001) with 15 layers.

The interface energy \((\gamma_{\text{int}})\) is an important parameter to evaluate the stability of the interface; \(\gamma_{\text{int}}\) can be defined as\(^{32,34}\)
\[
\gamma_{\text{int}} = \sigma_{\text{Fe}} + \sigma_{\text{Al,O}_3} - W_{\text{ad}}, \tag{14}
\]
where \(\sigma_{\text{Fe}}\) and \(\sigma_{\text{Al,O}_3}\) are the surface energies of the Fe (111) and Al\(_2\)O\(_3\) (0001) respectively, and \(W_{\text{ad}}\) is the work of adhesion of the Fe/Al\(_2\)O\(_3\) interface.

\(\text{FIG. 2.}\) Total and partial density of states (DOS) of (a) Fe and (b) Al\(_2\)O\(_3\), respectively; the black vertical dash lines denote the Fermi level.

III. RESULTS AND DISCUSSION

A. Bulk calculations

Figure 2 shows the calculated density of states (DOS) of Fe and Al\(_2\)O\(_3\), and the black vertical dash lines of the DOS represents the Fermi level. From Fig. 2(a), it can be noted that the bond peak is between \(-5\) and \(2.5\) eV and the metal bond strength between Fe atoms is mainly generated by d-orbital electrons. From Fig. 2(b) of the DOS of Al\(_2\)O\(_3\), it can be seen that the \(-7\) to \(0\) eV energy range is the main bond distribution area and the bond electronic states of \(\alpha\)-Al\(_2\)O\(_3\) are mainly distributed in this region. The strong interaction between p electrons of O and s and p electrons of Al in this range is the main manifestation of the bond peak of the density of states, especially the interaction between p-electrons of Al and p-electrons of O.

B. Surface convergence and surface energy

Before performing Fe/Al\(_2\)O\(_3\) interface calculations, determination of the thickness of each side is essential to ensure a bulk-like
TABLE II. Surface energy $\sigma$ vs slab thickness for Fe (111).

| Atom layers, n | 3 | 5 | 7 | 9 | 11 |
|----------------|---|---|---|---|----|
| Surface energy ($\sigma$) ($J/m^2$) | 2.51 | 2.64 | 2.65 | 2.63 | 2.64 |

TABLE III. Interlayer relaxation of the Fe (111) surface as a function of slab thickness.

| Interlayer | Slab thickness, n |
|------------|------------------|
|            | 3 | 5 | 7 | 9 | 11 |
| $\Delta 12$ | -3.75 | -4.09 | -4.04 | -4.43 | -4.81 |
| $\Delta 23$ | 1.52 | 1.54 | 1.57 | 1.57 |
| $\Delta 34$ | 1.44 | 1.43 | -1.46 |
| $\Delta 45$ | 0.87 | 0.97 |
| $\Delta 56$ | -0.19 |

TABLE IV. The surface energy calculations and theoretical values of different terminated $\alpha$-Al$_2$O$_3$ (0001) surfaces.

| Surface | Present ($J/m^2$) | Other ($J/m^2$) |
|---------|------------------|-----------------|
| O-terminated | 5.215 | ... |
| Al-terminated | 1.561 | 1.590(26) |
| Al$_2$-terminated | 5.708 | ... |

However, as the accuracy increases, it may result in long computational time. Fe (111) and Al$_2$O$_3$ (0001) are the most densely arranged faces of the cubic structure and hexagonal structure, respectively. Therefore, convergence tests of Fe (111) and Al$_2$O$_3$ (0001) should be reasonably performed to select the number of layers.

The surface energy of the Fe (111) slabs in the range of 3–11 atomic layers (Table II) were calculated, and the results show that the surface energy is well converged by a five layer thick slab. Interlayer relaxation of the Fe (111) surface as a function of slab thickness is listed in Table III, where $\Delta ij$ represents the increased or decreased percentage of layer spacing compared with the bulk material, and $n$ represents the number of layers. $^{35,36}$ It can be concluded from Table III that for 9-layer and 11-layer interlayer tests, the interlayer relaxation between the first layer and the second layer does not converge, but the rest are convergent, and the calculation of the surface energy indicates that when $n \geq 5$, results are convergent such that the five layered Fe (111) surface was selected for further calculations.

Substituting the chemical potentials given in Eq. (4), the obtained surface energy of O-terminated, Al-terminated, and Al$_2$-terminated structures are shown in Table IV. The Al-terminated structure with a lower surface energy is the most stable in the system, while the Al$_2$-terminated structure with the highest value is unstable. For determining the suitable number of atomic layers in the Fe and Al$_2$O$_3$ slabs, the interlayer relation was continually measured with identical layer spacing calculation, which is given in Sec. III B. Table V lists the calculation of the first five interlayer relaxation of two $\alpha$-Al$_2$O$_3$ (0001) terminated (O-terminated and Al-terminated) surfaces for different thicknesses. The calculation results are compared with the literature where the slab containing 15 or more atomic layers is convergent, which reveals that the accuracy of subsequent calculations for interface construction can be improved by using 15 or more atomic layers.

In summary, we have shown that our calculated values of the bulk and surface properties of Fe and Al$_2$O$_3$ are consistent with other first-principles results and available experimental results, thereby validating the application of this methodology to the calculation of interfacial properties.

C. Properties of the Fe (111)/Al$_2$O$_3$ (0001) interface

1. Interface structure

According to the above calculations, Fe (111)/Al$_2$O$_3$ (0001) interfaces were simulated with supercell structures, while combining five layers of the Fe (111) slab and 15 layers of the Al$_2$O$_3$ (0001) slab with orientation relationship: Fe (111)/Al$_2$O$_3$ (0001) and Fe [110]/Al$_2$O$_3$ [1010]. According to the lattice mismatch rule that the

TABLE V. Interlayer relaxation of the Al$_2$O$_3$ (0001) surface as a function of slab thickness.

| Termination | Slab thickness, n | Other |
|-------------|-------------------|-------|
| O-terminated | $\Delta 12$ | 18.4 | 18.7 | 17.5 | 17.6 |
|              | $\Delta 23$ | -19.1 | -18.3 | -17.8 | -17.9 |
|              | $\Delta 34$ | 2.4 | 2.3 | 2.2 | 2.4 |
|              | $\Delta 45$ | -0.9 | -0.8 | -0.3 | -0.2 |
|              | $\Delta 56$ | 4.2 | 3.6 | 3.6 |

| Al-terminated | $\Delta 12$ | -91.6 | -89.1 | -87.2 | -87.3 |
|              | $\Delta 23$ | 4.5 | 1.6 | 3.2 | 3.2 |
|              | $\Delta 34$ | -51.8 | -38.6 | -42.2 | -42.9 |
|              | $\Delta 45$ | 25.3 | 18.4 | 19.3 | 19.2 |
|              | $\Delta 56$ | 5.9 | 4.8 | 4.8 | 6 |

Reference 37 Reference 38 Reference 39
percentage of mismatch should not be greater than 5%, the obtained lattice parameter of the Al₂O₃ (0001) surface (a = 4.809 Å) is close to the supercell of the Fe (111) surface (a = 4.875 Å), and the lattice mismatch of the Fe (111)/Al₂O₃ (0001) interface is 1.37%. Moreover, the two end surface slabs are separated by a 15 Å vacuum. The obtained structural model is shown in Fig. 3. From the above results of surface energy, it can be seen that for the Al₂O₃ (0001) surface, the Al-terminated structure is most stable and easy in forming a stable interface. When the Al₂O₃ surface is Al-terminated, there are many different combinations of atoms on both sides of the interface.

![FIG. 3. Top view of Fe (111)/Al₂O₃ (0001) models with different stacking sites: (a) top-site, (b) bridge-site, (c) center-site, and (d) O-terminated. The different colors denote oxygen (red), aluminum (pink), and iron (blue).](image)

According to the relative location between Al atoms on the outermost surface of the Al₂O₃ (0001) surface and the position of the Fe (111) surface, three possible stacking sites (top-, bridge-, and center-sites) can be obtained [as shown in Figs. 3(a)–3(c)] for simplicity. The interface formed by the O-terminated structure is also shown in Fig. 3(d).

2. Work of adhesion and interface stability

Table VI shows the calculated \( W_{ad} \) and interfacial optimal separation (\( d_0 \)) of different Fe/Al₂O₃ interfaces. For the Fe (111)/Al₂O₃ (0001) interface, the average \( W_{ad} \) from the three models (top, bridge, and center) of the Al-terminated interface is 2.40 J/m², and \( \gamma_{int} \) is 1.82 J/m². The \( W_{ad} \) of the O-terminated interface is greater than that of the Al-terminated interface, and \( \gamma_{int} \) of the O-terminated interface is less than that of the Al-terminated interface, indicating that the O-terminated interface is more stable. However, the O-terminated interface needs to be formed from the O-terminated surface, which is unstable because of its higher surface energy, as calculated in Sec. III B. Comparing \( W_{ad} \) and \( \gamma_{int} \) of the three models of the Al-terminated surface, the bridge model with a higher \( W_{ad} \) and lower \( \gamma_{int} \) is relatively stable.

3. Electronic structure and bond

To further explain the bond characteristics of the Fe (111)/Al₂O₃ (0001) interface, the density of states (DOS) and partial density of states (PDOS) of the Al-terminated (top, bridge, and center) and O-terminated interface were calculated, and results are shown in Figs. 4(a)–4(d). Among them, the black solid line represents the summation state, the blue solid line represents s-states, the red solid line represents p-states, the green solid line represents d-states, and the black dotted line denotes the Fermi level. For the four different interfaces, it can be seen from the figure that there are significant peaks at the Fermi level. This indicates that these interfaces have certain metallic properties. In addition, the s, p, and d orbitals contribute to the total density to some extent, but p and d orbital contributions are more significant. This reveals that the hybridization between p and d orbitals determines the adhesion strength and stability of interfaces. The DOS values at the Fermi level of the top, bridge, center, and O-terminated interfaces are 38.66, 35.48, 35.67, and 35.18 electron/eV, respectively. The stability of the interface increases with the decrease in the DOS value of the Fermi level. Therefore, the O-terminated interface has the best stability among the four kinds of models, and the bridge model is relatively stable in three Al-terminated models, which is consistent with the above results.
The calculated bond peaks of the Al and O-terminated interface are $-10.18$ to $1.67$, $-11.56$ to $1.59$, $-10.97$ to $1.59$, and $-11.15$ to $1.61$ eV.

In order to understand the influence of the interface on the atoms near the interface, the Al-terminated (bridge) interface and the O-terminated interface system model was used as an example to analyze the PDOS in different layers of the interface system model. It can be seen from Fig. 5 that the density of atomic states in the first layer of the interface is relatively different from the atoms in the matrix. For the Al-terminated (bridge) interface, interfacial atoms are significantly different from the interior layers. Considering the hybridization between the interfacial Fe-d orbit and Al-sp orbit, one obvious peak in the range of $-4.5$ to $1.25$ eV was observed, which indicated that the interface bond had a covalent characteristic [Fig. 5(a)]. In addition, the iron atoms at the interface have large DOS values near the Fermi level, which revealed the formation of the metallic bond. In summary, there is a mixture of covalent bonds and metallic bonds in the Al-terminated (bridge) interface. For the O-terminated interface [Fig. 5(b)], there is obvious orbital hybridization between the interfacial Fe-3d,4s,4p and O-2p states in the range of $-10$ eV to $1.25$ eV, which indicates that a strong covalent bond is obtained at the interface. These observations suggest the formation of strong covalent bonds (p-d hybridization) in the O-terminated interface, which also explains the calculated largest $W_{ad}$ of the O-terminated interface in Sec. III C 2.

To further compare the different interface bonding between the Al-terminated and O-terminated interfaces, the charge density distributions and the charge density differences are calculated and shown in Figs. 6 and 7, respectively. It can be seen that chemical bonds with different strengths are formed between interfacial Fe, Al, and O atoms in the interface model. As shown in Fig. 6(a), a weak covalent/metallic bond is formed in the Al-terminated (bridge) interface, while as shown in Fig. 6(b), there is a charge accumulation region between iron and aluminum atoms at the interface, indicating that a covalent bond is formed at the O-terminated interface. Figure 7(a) shows that the Al-terminated (bridge) interface has localized features at the interface. A charge depletion region exists on the Al side and extends to the Fe atoms of the Fe side, implying that these two atoms form a metal bond at the interface. As shown in Fig. 7(b), the charge depletion region exists in the interfacial Fe atom, and this region has

![FIG. 4. Density of states (DOS) and partial density of states (PDOS) for (a) Al-terminated (top), (b) Al-terminated (bridge), (c) Al-terminated (center), and (d) O-terminated.](image-url)
FIG. 5. PDOS for the (a) Al-terminated (bridge) interface and (b) O-terminated interface.

FIG. 6. Charge density for the (a) Al-terminated (bridge) interface and (b) O-terminated interface.

FIG. 7. Charge density difference for the (a) Al-terminated (bridge) interface and (b) O-terminated interface.
obvious directionality. The charge transfers lost to the interfacial O atoms lead to the charge accumulation region around the interface, which indicates that the covalent bond is formed at the interface.

To further clarify the bonding characteristics of the two Fe\textsubscript{Al}O\textsubscript{3} interfaces, the Mulliken population analysis was analyzed. Table VII lists the Mulliken population analysis results of Fe, Al, and O atoms at the interface. It can be seen from Table VII that for the Al-terminated (bridge) interface, the interfacial Fe atom gains charge from the Al atom, which indicates the formation of an Fe–Al metallic bond. It may also be noted from the table that the interface O atoms obtain a lot of charges, which may be obtained from iron atoms and aluminum atoms near the interface. Thus, it can be judged that Fe–O ionic bonding exists between the interfacial Fe atom and O atom. For the O-terminated interface, the interfacial Fe and Al atoms lose charge, while the interfacial O atom gains a small amount of charge.

Table VIII also summarizes the Mulliken bond population analysis results of the interface systems. The overlap population of the Fe–O bond in the Al-terminated (bridge) interface is 0.06, which proves that a covalent bond is formed at the interface. The bond overlap population of the Fe–Al bond 0.16, which indicates that the metallic bond exists between interfacial Fe atoms and Al atoms. The bond overlap population of the Fe–Al bond is 0.10. From the molecular orbital theory point of view, it can be explained as the electrostatic repulsion between a charged Fe atom and Al atom, which suggests a formation of a metallic bond between Fe–Al. However, for the Fe–O bond in the O-terminated interface, the bond overlap population 0.31 confirms the covalent bond formed at the interface, which corresponds to the results from the density of states and charge density difference analysis.

### Table VII. Mulliken population analysis results of interfacial atoms for different Fe\textsubscript{Al}O\textsubscript{3} interface models.

| System          | Atom | s   | P   | d   | Total  | Charge |
|-----------------|------|-----|-----|-----|--------|--------|
| Al-terminated   | Fe   | 0.91| 0.60| 6.71| 8.22   | -0.22  |
| (bridge)        | Al   | 0.50| 0.89| 1.39| 1.61   |        |
|                 | O    | 1.85| 5.20| 7.05| 1.05   |        |
| O-terminated    | Fe   | 0.74| 0.51| 6.67| 7.92   | 0.08   |
|                 | Al   | 0.53| 0.90| 1.43| 1.57   |        |
|                 | O    | 1.84| 5.00| 6.83| -0.83  |        |

### Table VIII. Mulliken bond population analysis results between interfacial atoms for the Fe\textsubscript{Al}O\textsubscript{3} interfaces.

| System          | Bond    | Population | Length (Å) |
|-----------------|---------|------------|------------|
| Al-terminated   | Fe–Al   | 0.16       | 2.79       |
| (bridge)        | Fe–O    | 0.06       | 2.90       |
| O-terminated    | Fe–Al   | −0.10      | 2.60       |
|                 | Fe–O    | 0.31       | 1.99       |

### 4. The stabilities of aluminum with different occupation

The calculated stable interface of Al\textsubscript{2}O\textsubscript{3} and Fe is the O-terminated Fe (111)/Al\textsubscript{2}O\textsubscript{3} (0001) interface which can be used to study the stability with a different occupation behavior of the aluminum atom at the Fe/Al\textsubscript{2}O\textsubscript{3} interface from a microscopic point of view.

Based on Fe/Al diffusion during the welding process, a model of the diffusion welding interface is built. The model consists of Al along with the initial Al\textsubscript{2}O\textsubscript{3} layer on the Al surface in contact with Fe, as shown Fig. 8. The model can be individually considered as the Fe/Al\textsubscript{2}O\textsubscript{3} and the Al/Al\textsubscript{2}O\textsubscript{3} interface. The occupation behavior of a single aluminum atom at the Fe/Al\textsubscript{2}O\textsubscript{3} and Al/Al\textsubscript{2}O\textsubscript{3} interface was first calculated from a theoretical point of view, and then, the effect of different contents of aluminum atoms on the interfacial bond and occupation behavior was elucidated. Based on the above-mentioned study, close packed surface Fe (111), Al\textsubscript{2}O\textsubscript{3} (0001) were selected, and, according to the literature, the Al (111) surface was selected. Figures 9(b) and 9(c) illustrate the possible location of aluminum atoms at the Fe/Al\textsubscript{2}O\textsubscript{3} interface occupation, where (b) shows the structure of the interface with the Al atom replacing the Fe atom in the Fe bulk and (c) is the structure of the interface with an Al atom providing an Fe atom at the interface; while (a), (c), and (d) show an aluminum content of (0%), (50%), (100%), respectively, (e) shows the structure of the clean Al/Al\textsubscript{2}O\textsubscript{3} interface. (f) shows the structure of the interface with an Al atom replacing one O atom in the Al\textsubscript{2}O\textsubscript{3} bulk.

The effect of different sites of aluminum atoms on the interfacial bond ability can be described by the interface ideal adhesion energy. The equation of the ideal adhesion energy $W_{ad}$ of the interface is consistent with the equation given above. In addition, the effect of aluminum atom occupation on the interfacial properties can also be expressed as heat of segregation. The equation for heat of segregation is as follows:

$$
\Delta E_{seg} = \frac{1}{n} \left( E_{\text{Fe/Al}_2\text{O}_3,n\text{Al}} - E_{\text{Fe/Al}_2\text{O}_3} + nE_{\text{Fe}} - nE_{\text{Al}} \right),
$$

$$
\Delta E_{seg} = \frac{1}{n} \left( E_{\text{Al}_2\text{O}_3,n\text{Al}} - E_{\text{Al}_2\text{O}_3} \right),
$$

where $E_{\text{Fe/Al}_2\text{O}_3,n\text{Al}}$, $E_{\text{Al}_2\text{O}_3,n\text{Al}}$, $E_{\text{Fe/Al}_2\text{O}_3}$, and $E_{\text{Al}_2\text{O}_3}$ are the total energies of the interface with and without n aluminums. $E_{\text{Fe}}$ and $E_{\text{Al}}$ are the energies of the Fe and Al atom, and $n$ is the number of occupied Al atoms.

FIG. 8. A model of the interface in diffusion welding.
Table IX lists the calculated heat of segregation and work of adhesion of four configurations with different sites and coverage of aluminum atoms at the Fe/Al$_2$O$_3$ interface. By comparing the work of adhesion, it is noted that when an Al atom is exited at the Fe/Al$_2$O$_3$ interface, the model had the lowest work of adhesion (1.98 J/m$^2$), which means that the state is the initial state of the Al segregation process. Furthermore, when the aluminum atom is inside the Fe cubic structure [as shown in Fig. 9(b)], the highest work of adhesion (2.02 J/m$^2$) is observed, indicating that this state is the final state of the Al segregation process. The calculated heat of segregation also shows that aluminum atoms near the Fe/Al$_2$O$_3$ interface will pass through the Fe/Al$_2$O$_3$ interface into the Fe layer. The calculated values of ideal adhesion energy show that as the segregation of aluminum atoms progresses, the bond ability of the Fe/Al$_2$O$_3$ interface increases from 1.98 J/m$^2$ to 2.02 J/m$^2$.

To reveal the impact of aluminum occupation sites and concentration on the interfacial properties, the work of adhesion is illustrated in Fig. 10. It is interesting to note that for an aluminum atom, no matter which site the aluminum occupies, the adhesion of the interface is improved compared to the clean interface. In particular, the bonding ability of the interface can be increased as the interfacial work of adhesion is increased to 0.23 J/m$^2$ when an aluminum atom takes the place of an iron atom at the interface. Compared with the clean interface of (0%) Al, it was found that the interfacial binding ability of Fe/Al$_2$O$_3$ was greatly improved with increase in aluminum content, and when the aluminum atom content reached 100%, the interface structure was most stable.

In order to reflect the effect of aluminum content on structural stability, the interface density of states for different aluminum contents at 0%, 50%, and 100% are plotted in Fig. 11. From Fig. 11(a), it can be seen that for 0% aluminum atoms at Fe/Al$_2$O$_3$, the bond electrons are mainly contributed by the 3d electron of Fe, the 3s electron and 3p electron of aluminum, and the 2p electron of O and were mainly distributed in the range of $-10.2$ to $1.25$ eV. The structure shows the highest peak of 39.49 electrons/eV at $-1.4$ eV energy, indicating the density of states as the Fermi level approaches 29.74 electrons/eV. Figure 11(b) shows the density of interface states corresponding to 50% aluminum atoms. The bonding electrons

| Fe/Al$_2$O$_3$ Construction | $E_{tot}$ (eV) | $\Delta E_{seg}$ (eV) | $W_{ad}$ (J/m$^2$) |
|-----------------------------|----------------|---------------------|-----------------|
| Model a (clean interface)   | $-18\,130.582\,0$ | $\ldots$ | 1.79 |
| Model b (one Al in Fe)      | $-17\,322.594\,8$ | $-0.7738$ | 2.02 |
| Model c (one Al on the interface) | $-17\,302.243\,6$ | $-0.4226$ | 1.98 |
| Model d (two Al on the interface) | $-17\,727.897\,4$ | $-0.8457$ | 2.72 |
of this structure are mainly contributed by 3d electrons of Fe, 3s and 3p electrons of Al, and 2p electrons of O. Considering the diffusion of Al at the interface, the position of the maxima peak shifts to −1.5 eV, and the peak value also decreases to 34.40 electrons/eV. The decrease in the density of states at the Fermi level reduces from 29.74 electrons/eV without Al to 26.47 electrons/eV; at a 50% Al content at the Fe/Al₂O₃ interface, the addition of an aluminum atom makes the electronic structure of the Fe/Al₂O₃ interface model more stable. When the aluminum atom content is increased to 100%, as shown in Fig. 11(c), the highest peak value is reduced to 33.15 electrons/eV compared to the structural density of states with a 50% aluminum atom content, implying that the interface structure becomes more stable with an increased number of aluminum atoms.

The positive value of interfacial segregation represents segregation from the substrate to the interface (and vice versa). Comparing the segregation energies of identical elements at different positions of the interface, the segregation path of the element can be determined. From the previously calculated values of heat of segregation, the aluminum atoms near the Fe/Al₂O₃ interface will pass through the Fe/Al₂O₃ interface into the Fe layer. Next, the segregation value of aluminum atoms at the Al/Al₂O₃ interface was calculated to be 1.75 eV, while the value of the Fe atom at the Fe/Al₂O₃ interface was only 0.48 (Table X). This suggests that it is almost impossible for Fe atoms and aluminum atoms to segregate from the substrate to the interface. In summary, from first principles calculation, the aluminum atoms will pass through the initial oxide layer into the iron layer.

The primary advantage of molecular dynamics (MD) is that it gives a direct view of dynamic conformation of molecular structures, which elucidates the relationship between molecular structure and diffusion. In order to verify the dynamic stability, we conducted a preliminary study by finding the migration path and transition state of the atoms in the crystal lattice. Also, using molecular dynamics, we can obtain the lowest energy position and diffusion path of atoms.
in the crystal lattice to determine the most stable position of atoms. We selected a stable interface model after optimizing Al$_2$O$_3$ bulk and Fe bulk through the cutting surface. The approach and parameters that were set for the calculation work are as follows: first, the time step to 2 fs was set, and the system was allowed to relax by 5000 steps so that it reaches the lowest energy state. After the energy is minimized, the simulation of diffusion was carried out. Simulating the diffusion at a temperature of 927 K by NVT (constant number of atoms, volume, and temperature), the time step was 1.0 fs, the number of steps was 500 000, and the dynamics time was 500 ps. We recorded the configuration of the system and the change in the position of the labeled yellow aluminum atoms. Figure 12 is a simulated cross-section perpendicular to the diffusion interface at a temperature of 927 K, at different times of dynamics, to dynamically describe the diffusion of atoms. As shown in Fig. 12, the red circle represents the position of atomic diffusion, yellow circle represents the labeled atom, and the direction of the arrow represents the direction of atomic diffusion. From the cross-sectional view, we can see that atomic diffusion occurs, and aluminum atoms diffuse into the iron atom layer. Thus, it is reasonable to believe that Al atoms will move

![Figure 12](image-url)
from the $\text{Al}_2\text{O}_3$ side to the Fe side, which makes it logical to calculate the stability of $\text{Al}$ occupation at the $\text{Fe}/\text{Al}_2\text{O}_3$ interface and $\text{Fe}$ occupation at the $\text{Al}_2\text{O}_3$/Fe interface.

The calculation results show that only Al atoms can diffuse through the $\text{Al}/\text{Al}_2\text{O}_3$/Fe interface, and the diffusion direction is from the Al side to the iron side. The calculation results are consistent with the experimental observation reported in the authors’ previous study, where the effect of the initial $\text{Al}_2\text{O}_3$ oxide layer on interdiffusion of Al with pure Fe was studied. The microstructural evolution of intermetallic compound layer nucleation and growth at the Al/Fe diffusion couple was studied by chemical analysis via EDS and crystallography by EBSD. It was observed that aluminum diffuses through the initial oxide layer ($\text{Al}_2\text{O}_3$) to form a thin (1.5 nm) $\text{Al}_3\text{Fe}_2$ phase (87 at. % Al and 13 at. % Fe by EDS analysis). The intermetallic compound nucleated and grew on the Fe side across the interface rather than on the Al side, and Al diffused through the $\text{Al}/\text{Al}_2\text{O}_3$/Fe interface, whereas Fe was not able to diffuse to the Al side of the $\text{Al}_2\text{O}_3$ initial oxide layer. Interdiffusion of Al and Fe started with the fragmentation of the oxide layer, which allows the intermetallic compound to grow more rapidly, as observed experimentally. Moreover, Al atoms diffused across the $\text{Al}_2\text{O}_3$/metal interface and were also observed experimentally, where the presence of the initial oxide layer hinders the diffusion of other metal atoms (Ti or Ni) through the layer. In summary, the calculation results are supported by previous experimental studies and are useful in describing the impact of the initial oxide layer of $\text{Al}_2\text{O}_3$ on the nucleation and interdiffusion in Al/Fe diffusion bonded systems.

IV. CONCLUSIONS

First-principles calculations were carried out to study the interfacial properties of the $\text{Fe}/\text{Al}_2\text{O}_3$ interface. Four $\text{Fe}$ (111)/$\text{Al}_2\text{O}_3$ (0001) models with different terminations, Al-terminated (with different stacking sites, namely, top, bridge, and center) and O-terminated interfaces, were adopted. The work of adhesion ($W_{\text{ad}}$), interface energy ($\gamma_{\text{int}}$), and partial density of states (PDOS) were calculated. The interfacial atomic configuration, adhesion strength, and nature of bonding are discussed. The conclusions are as follows:

1. The Fe (111) slab with 5 layers and the $\text{Al}_2\text{O}_3$ (0001) slab with 15 layers can represent bulklike interior characteristics. The Al-terminated surface is more stable.
2. The $W_{\text{ad}}$ of the Al-terminated (top, bridge, and center) and O-terminated interface was 2.39 J/m², 2.43 J/m², 2.40 J/m², and 7.05 J/m², respectively, and the $\gamma_{\text{int}}$ was 1.83 J/m², 1.79 J/m², 1.82 J/m², and 1.53 J/m², respectively. The O-terminated interface was greater than the Al-terminated interface; hence, the bridge model was relatively stable in three Al-terminated models.
3. The DOS values at the Fermi level of the top, bridge, center, and O-terminated interfaces were 38.66, 35.48, 35.67, and 35.18 electron/eV, respectively. The lower is the DOS value at the Fermi level, and the superior is the stability of the interface. Therefore, the O-terminated interface had the best stability among the three kinds of models, and the bridge model was relatively stable among the three Al-terminated models, which is consistent with the analysis.
4. The O-terminated interface consisted of a combination of strong polar covalent bonds and weak metallic bonds and exhibited the strongest interfacial interaction, while the Al-terminated interfacial bond was primarily covalent and metallic and exhibited a relatively weaker adhesion strength.
5. With segregation of Al atoms at the interface, the stability of the interface structure was enhanced, and with the increase of aluminum atoms, the interfacial bond ability was increased. From the experimental and computational aspect, only aluminum atoms diffused through the initial oxide layer forming intermetallic compounds on the iron side.

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