Research Progress of First Principles Studies on Oxidation Behaviors of Ti-Al Alloys and Alloying Influence

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Abstract: Ti-Al alloys have good prospects in the aerospace, automobile, and other fields because of their excellent mechanical properties. However, the lack of high temperature oxidation resistance limits their practical applications. Various ways have been used to study their oxidation behaviors. Besides numerous experimental studies focused on the oxidation resistance properties of Ti-Al alloys, theoretical research based on first principles calculations has been carried out on the oxidation mechanisms on the atomic and electronic scales. In recent years, these theoretical studies have provided strong support for understanding the oxidation mechanisms and designing anti-oxidation modification measures. This review will focus on the surface oxidation reactions, element diffusion behaviors and interface bonding properties. The influencing mechanisms of alloying elements on the oxidation properties will be discussed in detail.

Keywords: Ti-Al alloys; oxidation; alloying elements; ab-initio calculations

1. Introduction

Ti-Al intermetallic alloys show promising applications in the aerospace, vehicle, and other fields. Due to their high contents of aluminum, their weight reduction effects are extremely remarkable. Furthermore, Ti-Al alloys have high specific strength, good high-temperature fracture toughness, and strong creep resistance, providing obvious advantages over traditional high temperature alloys. In elevated temperature environments (600 °C to 800 °C), the specific strength of Ti-Al based alloys is close to that of nickel-based alloys. One of the tendencies in aero-engine materials design is to introduce intermetallic alloys, metal matrix composites and polymer matrix composites to gradually replace high temperature steels and nickel alloys. Ti-Al intermetallics are suitable for the preparation of the rotor blades and integral blade rings of the compressor, low pressure shafts, high/low pressure turbine blades and other parts [1,2].

However, there are also some obstacles that hinder the applications of Ti-Al alloys, among them their oxidation behavior is one of the most critical problems. Titanium and aluminum both are easily passivated metals, they will spontaneously form dense oxide films in an air environment at room temperature. The dense oxide films will help to protect the matrix from further oxidation or corrosion. Low electrode potential and high chemical activity endow them with the ability of self-protection in severe environments. Nevertheless, for the Ti-Al alloys, the affinity energy difference between oxygen and metal elements in oxides TiO_2 and Al_2O_3 is very small [3], which leads to bonding competition between Ti and Al with oxygen at high temperature. Therefore, the mixed oxides, e.g., TiO_2 and Al_2O_3 will often appear in the oxide scale during the Ti-Al alloy oxidation process, due to the similar formation energies of the oxides. The mixed oxides are not always dense and uniform, and are often accompanied by large nodular-like or needle-like TiO_2 oxides. Such irregular oxide layers are mixed with a large number of vacancies, crystal boundaries, and other defects, which provides diffusion paths for oxygen atoms into the alloy matrix and accelerates the progress of Ti-Al alloy oxidation.

In the initial stage of oxidation progress, both the TiO_2 and Al_2O_3 oxides form simultaneously and have the same growth orientation. The activation energy for TiO_2 grain growth is much lower than that of Al_2O_3, so the surface of the Ti-Al matrix will be quickly become covered by titanium oxide. An aluminum-rich zone caused by the Ti consumption will be formed between the titanium oxide layer and the matrix, and Al_2O_3 scale will be produced due to the element diffusion behaviors. By the end of the oxidation process, the final oxidation products can be divided into the titanium oxide, the aluminum oxide, the mixed oxide layers, and the oxygen-affected zone. A large amount of mass transfer can take place between TiO_2 grains and irregular oxide grain boundaries, which may weaken the bonding between the oxides and the matrix. Therefore, the oxidation may damage the mechanical properties of Ti-Al and even leads to the failure of the materials. In recent years researchers have also focused on applying new Ti-Al alloy manufacturing methods such as electron beam melting (EBM), spark plasma sintering (SPS), and so on. Nevertheless, the poor high temperature oxidation resistance problem always remains, as the formation of mixed oxides and the rapid weight growth at high temperature can hardly be avoided and this may bring risks to the performance of the materials [4–6].

At present, many experimental and theoretical studies focus on the oxidation behaviors of Ti-Al alloys. In this paper, the experimental studies on the oxidation properties of Ti-Al are briefly introduced, and first principles calculations of the oxidation mechanism of Ti-Al alloys and the effects of alloying elements on their oxidation resistance properties will be emphasized.

2. Alloying Methods

There are two main pathways to improve the high-temperature oxidation resistance properties of Ti-Al alloys: one is to change the composition through element doping in order to improve the overall performance of the alloys; the other is through surface modification by forming an anti-oxidation film to protect the material matrix from oxidation, such as laser cladding and micro-arc oxidation. This paper will mainly focus on the alloying methods, which are closely related to the current research progress of the theoretical studies.

Alloying is a widely used method to improve the oxidation resistance of Ti-Al alloys, which can be realized in the material preparation stage without subsequent surface treatments. Although there is a high content of Al element in Ti-Al alloys, a single Al_2O_3 layer cannot be formed in the oxidation process, mainly because of the close equilibrium oxygen partial pressure of Al/Al_2O_3 and Ti/TiO_2 and the similar formation energies of the Al_2O_3 and TiO_2 oxides [7]. The core idea of the alloying method is to promote the formation of stable oxide films on the surface. The protective oxide films should possess good thermodynamic stability in a high temperature environment, inhibition of mutual diffusion of oxygen and metal ions, low saturation vapor pressure of oxygen, certain self-healing ability, good combination and thermo-mechanical compatibility with the matrix. Introducing alloying elements can help to improve oxidation resistance through the following ways: (1) Valence control mechanism, that is, inhibiting the formation of titanium oxide and promoting the formation of aluminum oxide; (2) Diffusion barrier effect, forming a dense and protective film on the alloy surface to prevent oxygen atoms from further invading into the matrix; (3) Selective formation of initial oxides, making aluminum oxide selectively generate in the initial stage of oxidation [8]. The influence mechanics of representative elements on the oxidation properties of Ti-Al alloys such as Nb, Si, Cr, Mo, Zr, and so on will be discussed in the following sections.

As rutile TiO_2 is a non-stoichiometric compound, a lot of defects such as oxygen vacancies and Ti ion vacancies will be easily produced in this oxide. Replacing tetravalent Ti with pentavalent Nb can reduce the aggregation of interstitial Ti ions, reduce the concentration and mobility of cracks, decrease the diffusion rate of oxygen and metal ions, and thus inhibit the formation of titanium oxide [9]. Other high cation valence elements like Mo, Ta, and W also share a similar role [10,11]. In addition, Nb can weaken the interactions between Al and other elements in the Ti-Al system and strengthen the combinations of Ti

with the surrounding environment. Therefore Nb can improve the activity of Al relative to Ti, promote the formation of Al$_2$O$_3$, and reduce the necessary Al content for the formation of protective oxides [8]. Doping a small amount of Nb in Ti-Al alloys can also reduce the solid solubility and diffusion coefficient of oxygen, thus inhibiting the formation of oxides. Nb has been proved to be effective in enhancing the formation of titanium nitrides, the stabilized nitrides can hardly be converted to titanium oxides, therefore controlling the rate of oxidation [12]. When alloying with Si element, a dense and continuous SiO$_2$ oxide layer can be formed on the surface of the Ti-Al alloys and the Ti$_5$Si$_3$ can be formed by the reactions between the Ti and Si. Therefore, the Si element can reduce the activity of Ti ions and control their outward diffusion [13]. Si doping can cause the formation of the titanium nitride layer or isolated nitride particles between the oxide layer and the matrix, which prevents the further inward diffusion of oxygen atoms, and reduces the weight gain rate in oxidation experiments [14]. With the increase of Si content, the thickness of the oxide layer gradually decreases. Furthermore, the Si can even improve the oxidation resistance of the alloys at 1200 K [15]. By comparing the weight change and the morphologies of the oxidized surfaces of the TiAl alloys with and without Si element, when the content is not enough for segregate and form a separate SiO$_2$ layer, the Si alloying can still reduce the thickness of the oxide scales [16]. Cr doping offers a combination of valence, initial oxide control, and diffusion barrier effects. Although the substitution of Ti^{4+} with low cation valence Cr^{3+} can increase the defect concentration in TiO$_2$ and lead to an increased growth rate, a higher Cr content can reduce the necessary aluminum content for the formation of protective aluminum oxide layer by promoting the formation of Al$_2$O$_3$ [17]. Moreover, Cr element itself will form Cr$_2$O$_3$ in an air environment under high temperature, which is even more compact, playing a positive role in protecting the alloy matrix and isolating the external environment. Mo element mainly promotes the formation of Al$_2$O$_3$ between the oxide layer and the matrix, and at the same time participates in the reaction to form Ti$_2$AlMo. These two products hinder the further diffusion of oxygen atoms into the alloy matrix, and therefore they will improve the high-temperature oxidation resistance, however, the extent of compressive residual stress and strain may increase with the growth of Al$_2$O$_3$ and lead to oxide spalling [18]. Mo can reduce the solubility and diffusion rate of oxygen in Ti-Al alloys by occupying Ti^{4+} sites with Mo^{6+}, hindering the formation of the outer TiO$_2$ layer, which depends on the outward diffusion of Ti^{4+} and inward diffusion of oxygen [19]. Some experimental results show that some elements can optimize the structure of the oxide, for instance, doped Sn element can react with Ti to form a Ti$_3$Sn phase, which promotes the formation of Al$_2$O$_3$ pegs, leading to the formation of a single and continuous Al$_2$O$_3$ layer, the Ti$_3$Sn phase impedes inward diffusion of oxygen and the outward diffusion of Ti ions, relatively contributing to the diffusion of Al. Zr can control the grain size of oxide by increasing the nucleation rate of the oxides at the initial stage of oxidation, improve the compactness of the oxide and hinder the inward diffusion of oxygen atoms [8,20].

As the effect of single element substitution on the oxidation resistance is still relatively limited, numerous studies on mixed doping with multiple elements have been carried out. For example, the oxidation kinetics curve of Ti$_2$AlNb alloy doped with Mo, Zr, and Si through isothermal oxidation experiments from 650 °C to 800 °C can always maintain a parabolic shape, only becoming a little bit faster at 800 °C. Compared with the traditional titanium alloy, the weight gain rate and the thickness of oxygen-rich α layer are significantly decreased. The main role of these alloy elements is to reduce the diffusion rate of oxygen atoms and inhibit the formation of brittle oxides, and therefore they can improve the high temperature oxidation resistance [21]. In Ti-Al alloys with high Nb content, Sn doping can reduce the thickness of the oxide film, change the structure of the oxide film and inhibit the formation of cracks in the oxide layer. The Sn and Nb segregate in the transition layer between oxide film and substrate, forming a barrier layer to hinder the oxygen diffusion. At the same time, the addition of Sn stabilizes the TiN in the alloy and prevents the diffusion of Ti ions from the matrix to the oxide layers, thus reducing the thickness of the oxide

film and improving the oxidation resistance of the alloy [22]. The Ti-Al-Nb-Mo-X(TNM) alloy, which has already been used by GE (America) for producing low pressure turbine (LPT) blades for PW1100G™ engines [1], also benefits from the combined effect of Nb and Mo elements. A continuous and dense Al_2O_3 oxide film can be formed and can prevent oxygen atoms from spreading inward and reduce the oxidation rate [23]. There are also methods that use elements with positive effects to balance the negative influence of other elements, for instance, Mn can diffuse rapidly in Ti-Al alloys at high temperature and be oxidized to Mn_2O_3, which finally incorporates with TiO_2, weakening the strength of the bonds between the oxides and the matrix. By Mn-W co-alloying, the selective oxidation of Al is promoted by the W element and that of the Mn element is suppressed [24].

Combined with different processing and heat treatment methods, the alloyed Ti-Al alloys present corresponding micro-structures which may greatly alter the oxidation resistance. For instance, in Ti-48Al-2Cr-2Nb alloys, samples with lamellar structures show better oxidation resistance than ones with duplex microstructures. The smaller the grain size is, the more compact the oxide layer will be. Furthermore, Ti-Al alloys with smaller grain size have better high temperature oxidation resistance [25]. Boron addition with 0.5 at. % B can refine the microstructure of the Ti-45Al-8Nb alloy, reduce the lamellar structure size from 400 μm to 70 μm. The refinement behavior reduces the thermal stress inside the oxides and prevents spalling. The grain refinement also provides more Al_2O_3 oxide pegs, enhancing the strength between the oxide layer and the matrix [26]. By doping Co element into a Ti-48Al-2Cr-2Nb alloy, Co-rich phases of $CoAl_2Ti$ form along the grain boundaries, and a Co-rich layer also forms between the oxide layer and the matrix, such structures can hinder the diffusion of oxygen and metal ions, thereby suppressing the growth of the oxides and preventing spallation [27].

3. Theoretical Study

The adsorption and dissolution properties of oxygen on the surface of the Ti-Al alloys are the key factors that control the initial stage of high temperature oxidation behavior. After the adsorption process, the diffusion properties of oxygen and metal ions through the oxides and alloy matrix further affect the oxidation process. Furthermore, the stability and strength of interfaces between the phases and oxides in Ti-Al alloys also affect the oxidation resistance properties. However, these processes involve the reactions and interactions on an atomic scale, which are difficult to analyze or test by experimental methods. For the anti-oxidation protection of the alloys, alloying methods are some of the most effective ways, which not only improves the oxidation resistance of the alloys but also provides comprehensive properties such as mechanical properties, such as Si and Zr element can improve the creep resistance of the alloys. The multiple-elements alloying is one of the development directions of the Ti-Al alloys, it is worth predicting the role and influence mechanics of various alloy elements in the oxidation process. However, it is hard to provide more information on them using experimental methods.

With the rapid development of chip technology, high-performance computing clusters have been greatly developed and widely used at present. Different kinds of computation methods are used to simulate the physical and chemical properties of materials, and to understand the phenomena and characteristics of materials from micro to macro scale appeared one after another. Among them, first principles computation methods based on density functional theory (DFT) can help to explore the geometry, electronic structure, magnetic, optical, and mechanical properties of materials. In recent years, researchers have employed first principles calculation methods to study the chemical and physical properties of various materials in different environments, including the oxidation process of Ti-Al alloys. For instance, as shown in Figure 1, the oxygen adsorption properties of surface, interface, and bulk systems can be studied by applying first principles calculations. The research progress will be introduced from three aspects.
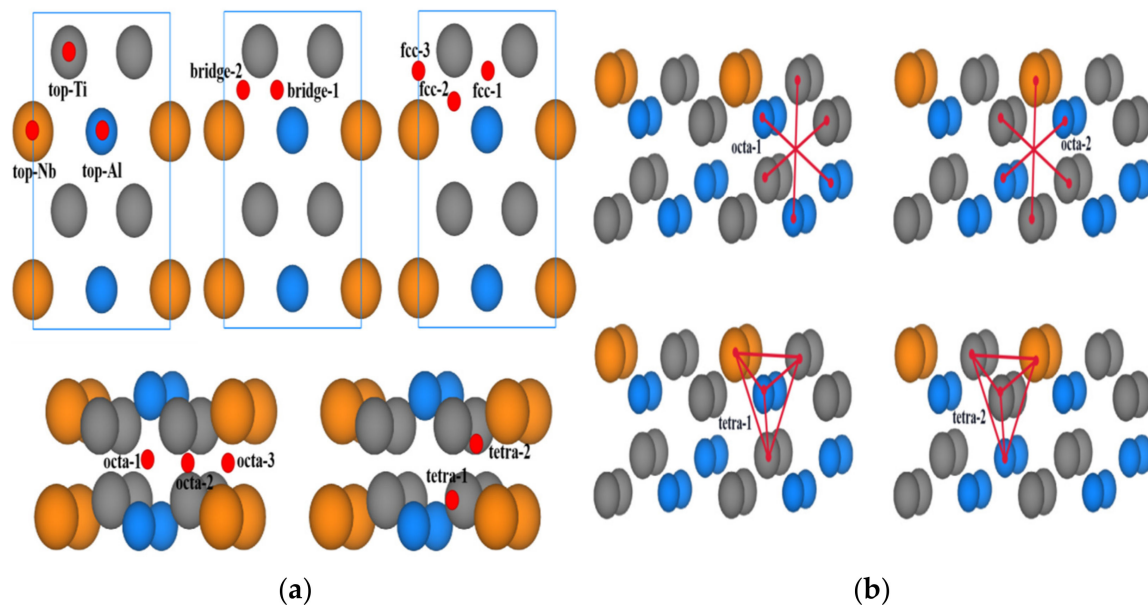
Figure 1. Schematic of the adsorption sites of the Ti$_2$AlNb alloy (**a**) On the (010) surface and inside the bulk (top views), (**b**) Interstitial sites at the O(1$\bar{1}$0)/B2(21$\bar{1}$) interface (side views), red, blue, orange, and gray balls denote O, Al, Nb, and Ti atoms, respectively.

3.1. Surface Oxidation Properties

The oxidation process always takes place firstly on the surface, and the surface properties of materials, e.g., the terminal elements and atomic arrangement determine the oxygen adsorption properties. For Ti-Al alloys, due to the very similar formation energies of TiO$_2$ and Al$_2$O$_3$, the competitions between Al and Ti will inevitably lead to the failure of protective oxide layer formation. With the increase of oxygen coverage, the oxygen adsorption on the surfaces tends to be saturated, then the surface structures are destroyed and reconstructed, which will cause the subsequent diffusion behaviors of oxygen and metal ions.

Our group has studied the adsorption behaviors of oxygen on the low indexes surfaces of γ-TiAl. When performing DFT calculations, the chosen surfaces generally obey the following rules: Firstly, the surface like γ-TiAl (111) has been proved by experiments that can form interface with Al$_2$O$_3$, the related lattice mismatch between the surfaces of the oxide and the matrix is small. In addition, by applying calculations, the surfaces with low surface energies can be found, which provides the possibility of the adsorption behavior during the oxidation process. The surface energies are significantly affected by the bonds between the metal atoms, once the surface has been cleavaged, the chemical environment of the surface has been decided and that may greatly influence the oxygen adsorption and the formation of oxides. The stabilities of (100), (001), (110), and (111) surfaces were compared firstly [28], and it was found that the surface energy of (100) with 1:1 stoichiometric distribution of Ti and Al was the lowest. The co-existence of the two elements indicated that there might be a competition between TiO$_2$ and Al$_2$O$_3$ in the initial oxidation process. By comparing the adsorption energies of different adsorption sites, the results show that oxygen atoms tend to be adsorbed in the titanium-rich regions. The adsorption energy is defined as follows, where $E_{(x)}$ stands for the total energy of the system X:

$$E_{ads} = E_{(O-TiAl)} - (E_{(TiAl)}^{slab} + \frac{1}{2}E_{(O_2)}) \tag{1}$$

Table 1 shows the adsorption energies of an oxygen atom for the considered surfaces (the (001) and (110) surfaces are divided into Al-terminated surfaces and Ti-terminated ones). The adsorption energies for the (111) surface agree with the results that estimated by Li et al [29], the fcc-Al site is the most stable with the adsorption energy of −5.18 eV; the

A2 site is the most favorable site of the (100) surface, followed by the T2 site, the energies are −4.51 eV and −4.39 eV; in the Ti or Al terminated surfaces, except for the (001) surface with Al-terminal, the oxygen adsorption behaviors of other cases are all controlled by O-Ti bonds, which indicates that TiO_2 is easy to form on these surfaces.

Table 1. Adsorption energy of an oxygen atom on the considered surfaces. (For (001) and (110) surfaces, B, T, and C stand for bridge site, top site, and center site, respectively. On the (100) surface, the oxygen atoms are on top of the Al and Ti atoms in the topmost (A1 and T1) and second (A2 and T2) layer.).

Surface	Site	$E_{(O-TiAl)}$ (eV)	E_{ads} (eV)
Al-(001)	B	−285.454	−3.94
	T1	−283.557	−2.04
	T2	−285.133	−3.62
Ti-(001)	B	−286.506	−5.08
	T1	−287.196	−5.78
	T2	−284.938	−3.51
Al-(110)	T1	−140.811	−0.92
	T2	−142.212	−2.32
	C1	−144.114	−4.22
	C2	−143.654	−3.76
Ti-(110)	T1	−143.911	−3.86
	T2	−145.203	−5.15
	C1	−145.015	−4.97
	C2	−145.401	−5.36
(100)	A1	−287.049	−2.00
	A2	−289.560	−4.51
	T1	−288.023	−2.97
	T2	−289.548	−4.39
(111)	fcc-Al	−150.912	−5.18
	hcp-Al	−150.815	−5.08
	fcc-Ti	−149.918	−4.18
	hcp-Ti	−149.871	−4.14

The oxidation properties are also greatly affected by the surface type. For γ-TiAl (100) surface, in the absence of oxygen, the segregation energy of Al is lower than that of Ti, thus being easier to form, but oxygen atoms are more easily adsorbed near Ti atoms, and the strength of O-Ti bond is higher than that of O-Al bond. The oxygen adsorption behaviors promote the segregation of Ti and even leads to the formation of a pure Ti-terminal surface, which may lead to the selective oxidation of Ti [30]. With the increase of the coverage of oxygen atoms, not only the sites on the surfaces but also interstitial sites between surface and subsurface are occupied by oxygen, which may lead to further oxidation [31]. The γ-TiAl (111) surface is found to be stable only when the chemical potential of oxygen is very low, otherwise, it will become unstable, so it is easy to absorb oxygen atoms and it reaches high coverage quickly. The adsorption in the interstitial sites can also be observed on the γ-TiAl (111) surface with the high coverage of oxygen. However, different from the (100) surface, the oxide-like structure on the surface become dense after relaxations and hinder the subsequent oxygen adsorption, benefiting to the oxidation resistance [29,32]. For γ-TiAl (110) and (001) surfaces, the interaction between O-Ti is much stronger than that between O-Al. The Ti-terminal surfaces with oxygen adsorption are more stable, as only titanium oxides may appear under such conditions. Compared with γ-TiAl, Al_3Ti based alloys have higher Al content and therefore they own different adsorption properties of oxygen atoms. Among Al_3Ti(110) surfaces, the Al-terminal one has the lowest surface energy. When oxygen atoms adsorb on this surface, the Al-Al bridge sites are the most preferable. According to the analysis of the state density, the *p*-orbital electrons of oxygen atom have obvious bonding interactions with the *d*-orbital electrons of Ti atoms and *p*-orbital electrons of Al atoms. The Al-O interaction is stronger compared to the Ti-O one, indicating that

oxygen atoms tend to bond with aluminum atoms, which is obviously different from the γ-TiAl system situation. Therefore, it is easier to form the protective aluminum oxide layer in Ti-Al alloys with high Al content [33].

We have studied the adsorption behaviors of oxygen on the surfaces of orthorhombic (O) phase Ti_2AlNb to clarify the interaction mechanisms between oxygen and Ti_2AlNb. The stoichiometric (010) surface of O phase was found to be the most stable low index surface evaluated by the surface energy. Oxygen atoms prefer to adsorb at fcc-hollow and hcp-hollow sites. The electronic structures of adsorption systems containing the charge difference distributions and the densities of states of the hcp site are shown in Figure 2.
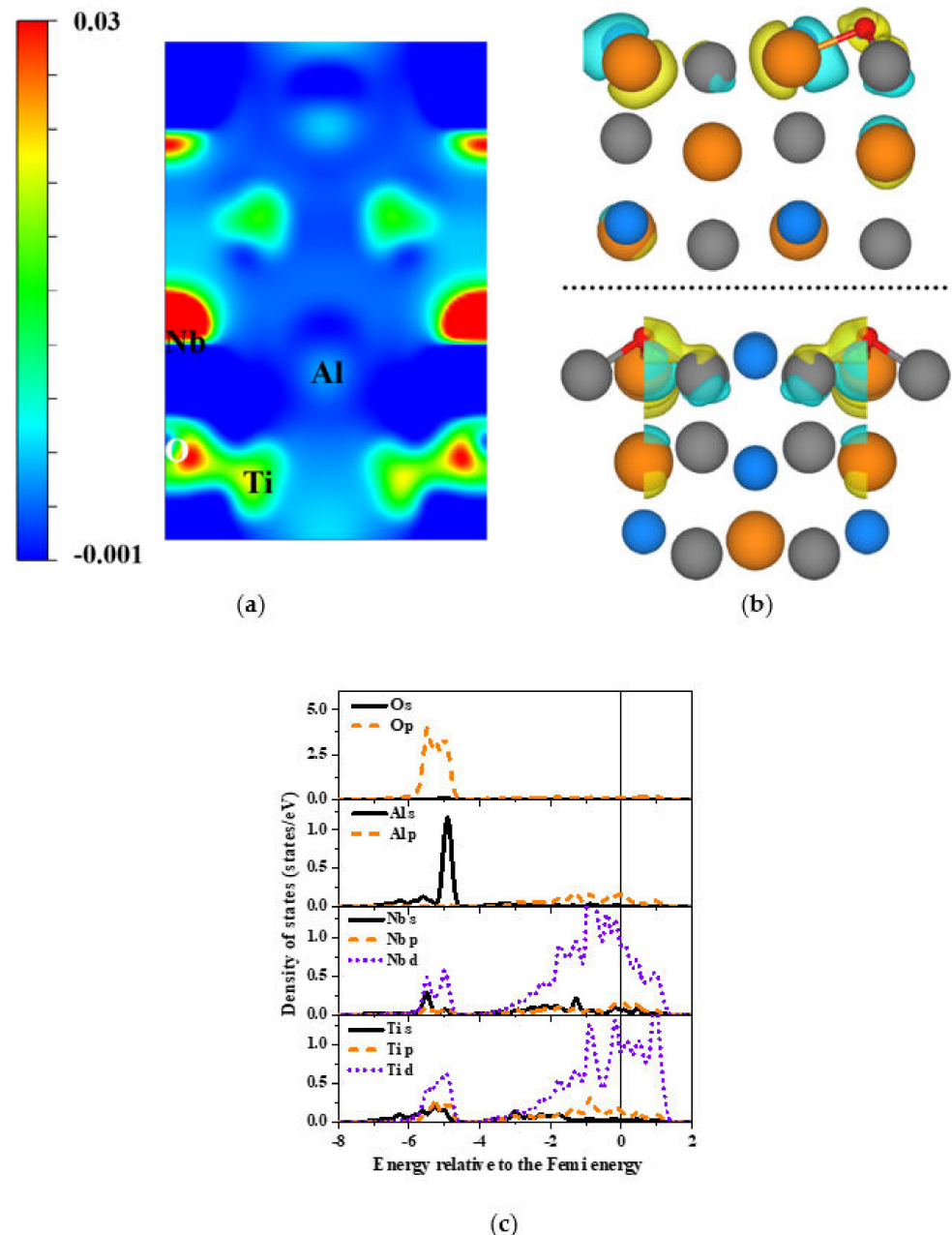
Figure 2. (**a**) charge densities, (**b**) charge difference distributions (side views), and (**c**) densities of states of oxygen adsorbed on the hcp site, red, blue, orange, and gray balls denote O, Al, Nb, and Ti atoms, respectively, blue isosurface stands for loss of electrons and yellow isosurface stands for capturing electrons.

The charge transfer from Ti and Nb atoms to the adsorbed oxygen as well as the overlaps between O p, Nb d, and Ti d orbitals indicate that O-Ti and O-Nb bonds are stronger than the O-Al bond. At the initial oxidation stage under high temperature, the O phase of Ti_2AlNb could not form protective alumina but instead Ti and Nb oxides [34]. The coverage of oxygen atoms is another main factor that may influence the adsorption progress, which not only has an obvious effect on the adsorption energies of oxygen atoms, but also significantly impact the surface morphology, oxide nucleation, oxygen atom diffusion, and the interaction between elements. A clearer understanding can be obtained through the surface phase diagram, which is also clearly reflected in the calculations of other materials [35,36].

In addition to the clean surfaces of the Ti-Al alloys, recent studies began to focus on the changes of oxidation resistance caused by the alloying elements. The segregation of alloying elements has a significant impact on the oxygen adsorption and changes the oxidation kinetics. Because such a phenomenon only occurs on the atomic scale during the oxidation reaction processes, the DFT-based calculation method is very suitable for this kind of study, and here are some typical results. The investigations on the influence of Si-segregation on the oxygen adsorption properties on the γ-TiAl (111) surface are carried out. Si atoms do not easily appear inside the bulk, but rather tend to replace Ti atoms then segregate on the surface, which improves the Al/Ti ratio on the surface. According to the comparison of the oxidation properties, oxygen atoms on the primary surface are more easily adsorbed around Ti atoms, and the oxygen atoms are mutually exclusive. However, the interaction between O-Al on the alloyed surface becomes stronger and the oxygen atoms attract each other, promoting the formation of aluminum oxide [37,38]. The element B, which prefers to segregate on γ-TiAl (111) surface, can also make a contribution to improve the oxidation resistance. B addition can decrease the coverage of oxygen and the binding energy of oxygen at the surface, and hinder the growth of Al_2O_3 and TiO_2 [39]. Cl is effective to prevent the adsorption of oxygen on γ-TiAl (111) surfaces. The computation results show that the adsorption of the Cl atoms will weaken the bonding interactions between the oxygen and metal atoms on the alloy surface. On the other hand, the adsorption competition between Cl and oxygen atoms will reduce the overall coverage of O on the surface, thus weakening the oxidation [40]. The influence of transition metal elements with $4d$ valence electrons as well as the third and fourth main group elements on the oxidation resistance of γ-TiAl (100) surface have been analyzed. When the transition metal replaced the Ti atoms on the surface, the adsorption energies of the oxygen atoms on HCP positions increases compared to the original surface. However, if Al atoms are replaced, the condition will be opposite. Furthermore, the effect of Al-replacing on adsorption energies is smaller than that of Ti. When doping with $4d$ transition metal elements, the competition and the change of hybrid state among the ions are the main factors that affect the adsorption energies. When the third and fourth main group elements are doped, the reduction of hybrid energy makes the adsorption energies of oxygen atoms decrease accordingly [41]. The Ta-W co-alloying on the γ-TiAl (111) surface changes the favorable adsorption sites of the oxygen atoms, decreases the formation rate of Ti-O bonds, and the electronic structure analysis also indicates that the existence of $5d$ orbital electrons significantly reduces the activity of the Ti $3d$ orbital electrons, the combination of Ti and O has been greatly reduced, these results agree with the experimental conclusions that the high cation valence elements doping may inhibit the formation of titanium oxide [10,11]. The parallel experimental results also show that the Ta-W co-alloying can improve the high temperature oxidation resistance of the γ-TiAl by inhibiting the diffusion of oxygen [42]. The elements like Y and Hf may segregate on the surfaces of γ-TiAl, then weaken the interaction between oxygen atoms and the surfaces. Therefore, the Y and Hf are helpful to slow down the oxidation rate and inhibit the growth of the oxide layer. The bonding between oxygen atoms and γ-TiAl surfaces can be an ionic bond or a covalent bond, while Y and Hf elements mainly weaken the covalent bonding. In addition, Cr, Mo and other

elements also have positive effects on improving the oxidation resistance and affecting the oxygen adsorption behavior when doping on different surfaces [43,44].

3.2. Stability and Adhesion Properties of the Interfaces

As the oxidation reaction is happening, the oxide layer begins to form and the oxidation behaviors of the alloys are no longer controlled by the original crystal surfaces. The interfaces between the oxide and the matrix provide channels for the internal diffusion of oxygen atoms. At the same time, the bonding strength determines whether oxide spalling occurs. On the other hand, Ti-Al alloys are two-phase or three-phase alloys with a lot of phase boundaries. The mechanical properties and oxidation resistance might be affected by such defects. First principles calculation methods can explore the interface structure evolution, stability, and mechanical properties.

To shed light on the adhesion and mechanical properties of the interfaces, here are some of the available methods based on DFT calculations. Due to the different thermal expansion coefficient and thermo-mechanical properties between the oxide and matrix, the interfaces will produce tensile and shear stress. Firstly, for the simulations of the tensile tests, the interfacial fracture under tension by applying the strain between atomic layers has been studied. When the local stress concentration occurs and the strain exceeds 80%, the fracture of an interface can be identified. It provides a good reference for the analysis of oxide spalling from the alloy matrix [45,46]. Secondly, to explore the sliding friction and shear behaviors of the atomic layers of the interface system, the effect on the sliding barrier can be calculated. When the relative position of the interface changes, the bond length and bond energy vary accordingly. As the periodic change of the atomic arrangement, the energy correspondingly has the highest and lowest points thus forming a potential barrier. In order to overcome the potential barrier and maintain the sliding within the atomic layers, it is necessary to calculate the force of horizontal friction. The lower initial energy indicates that the interface is easier to slide, and the sliding barriers reflect the stability and shear resistance of the interfaces [47,48]. Similar to the surface system, alloying elements can also segregate in the interface. The segregation behavior can not only affect the chemical properties and mechanical properties of the interface but also the diffusion properties of metal ions at the interface, which has significant influence on the oxidation process of Ti-Al alloys [49,50].

For the Ti-Al alloys, we have studied the stability and adhesion property of the γ-TiAl/Al$_2$O$_3$ and γ-TiAl/TiO$_2$ interfaces [51–54]. The influence of different stacking forms and relative positions on the stability was investigated. It was found that Al$_2$O$_3$ and TiO$_2$ tend to bond with Al and Ti atoms respectively on the surfaces of the γ-TiAl alloy. The results also indicate that the alloying elements and defects can affect the strength of the interfaces. The Y, Nb, and Pd have the largest strength effect on the TiO$_2$/TiAl interface, they will help to prevent the oxide from peeling off and may improve the oxidation resistance in cyclic oxidation conditions [53]. For the Al$_2$O$_3$/TiAl interface system, to evaluate the strength, the work of adhesion is defined as follows:

$$W_{ad} = (E_{a-i} - E_{a-s-i} - E_{s-i}) / A \tag{2}$$

where E_{a-i} is the total energy of the interface, E_{a-s-i} and E_{s-i} stand for the energy of the Ti-Al and Al$_2$O$_3$ slabs, respectively, A stands for the interface area. The fitting curves are obtained using the universal binding energy relation (UBER) curve [55,56]:

$$E_{a-i} = E_{a-s-i} + E_{s-i} - 2AW_{ad}\left(1 + \frac{x - x_0}{\lambda}\right)exp\left[-\frac{x - x_0}{\lambda}\right] \tag{3}$$

where x is the distance between the slabs, x_0 is the equilibrium distance, λ is a Thomas-Femi screening length specific to the materials of the two sides of the interface. The plane-averaged charge (PAC) describes the charge distributions along with the c directions of the two kinds of interfaces, where the positive and negative values stand for the gaining

and losing of charges for forming the interfaces. As shown in Figure 3, the influence of alloying elements on the interactions of γ-TiAl/Al$_2$O$_3$ is limited, while they greatly enhance the adhesion strength of α_2-Ti$_3$Al/Al$_2$O$_3$ interface. The enhancement of strength may result from the strong interactions between the alloying elements and the Al$_2$O$_3$. Other investigations also proved that alloying elements like Mo can decrease the adhesion energy of the TiO$_2$/γ-TiAl interface and cause negative effects [57]. The segregation of B and Nb elements at the interfaces of α-Al$_2$O$_3$(0001)/γ-TiAl(111) and TiO$_2$(110)/γ-TiAl(111) has been founded. The B addition can significantly enhance the adhesion of the Al$_2$O$_3$/γ-TiAl interface, while the effect of the Nb on the adhesive strength of the TiO$_2$/γ-TiAl interface is insignificant [58,59].
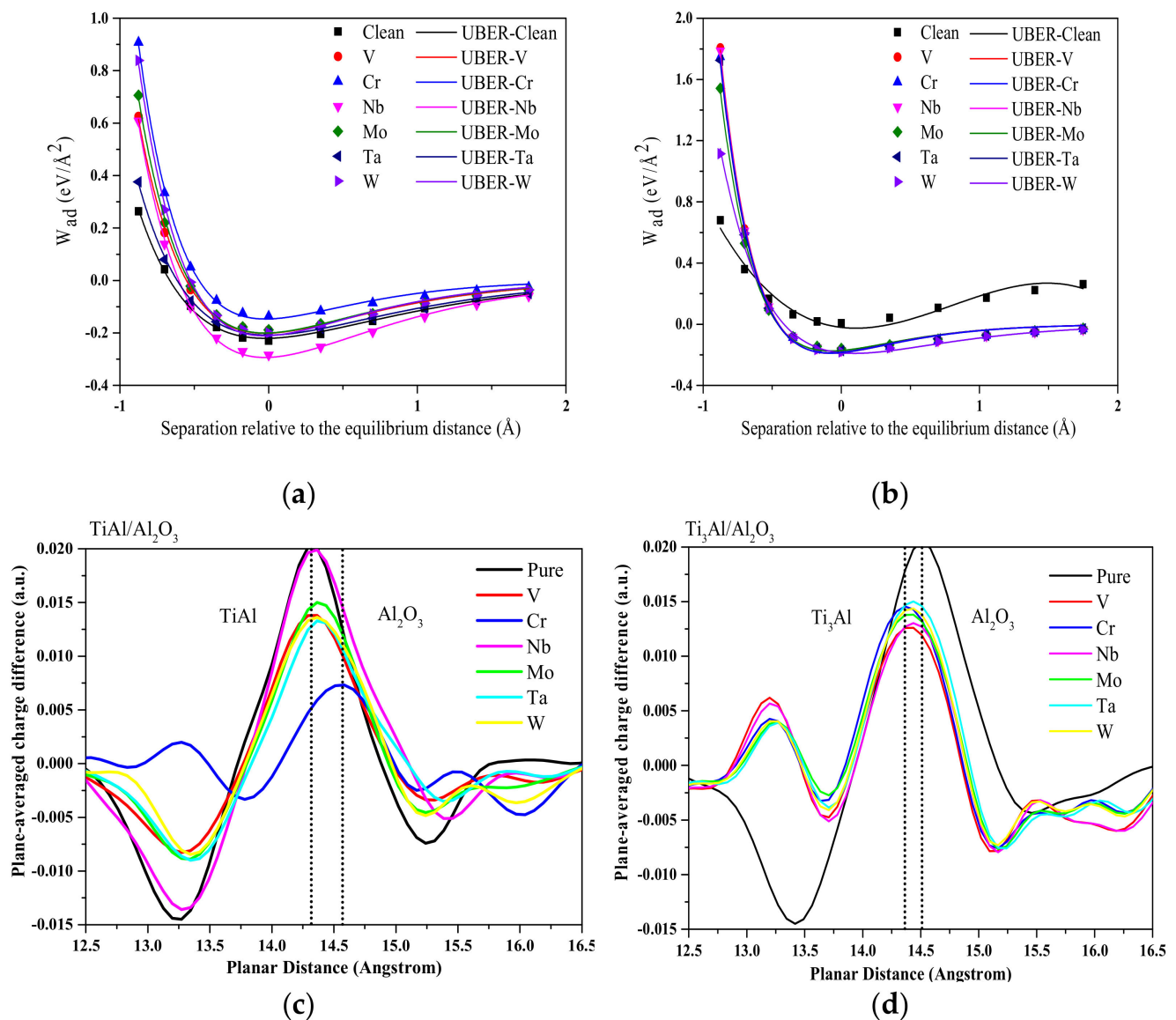
Figure 3. Variation of work of adhesion via the separation of (**a**) γ-TiAl/Al$_2$O$_3$ and (**b**) α_2-Ti$_3$Al/Al$_2$O$_3$. Differences of PACs between interface and separated slabs displayed along the direction perpendicular to the interface (**c**) γ-TiAl/Al$_2$O$_3$ and (**d**) α_2-Ti$_3$Al/Al$_2$O$_3$.

As stated before, Ti-Al alloys may contain a large number of interfaces between different phases, some researches also revealed their effects on the oxidation progress. For the Ti$_2$AlNb alloy [60], the calculation results about the binding force, stability and electronic structure of O(001)/B2(110) interface indicate that the thick atomic layers of the two phases have similar properties to the bulk structure. The Ti-Nb and Ti-Al bonds

maintain the adhesion of the interface. Similar conclusions were also obtained in our calculations, in which the stability and oxygen adsorption properties of the $O(1\bar{1}0)/B2(21\bar{1})$ interface were studied. As shown in Figure 4, the influence of relative positions on the stability has been systematically calculated. For turning the relative position between the O and B2 phases, in the a–b plane, eight steps complete a period in each direction. The HCP stacked interfaces (in which the frontal atoms of the O phase are located at the top of the atoms in the second layer of the B2 phase) display the lowest formation energy values. The oxygen adsorption in the interface is thermodynamically stable, but the adsorption energies are higher than that of oxygen on the O(010) surface. Therefore the O/B2 coherent interface without defects has limited influence on the oxidation resistant properties of the Ti_2AlNb alloys.

For the $TiAl/Ti_3Al$ interface, the adsorption behavior will lead to the deterioration of mechanical properties. The oxygen adsorption can affect the shear strength of the $TiAl/Ti_3Al$ interface, the oxygen atoms tend to combine with Ti atoms at the interface. In the four interface models with different stacking, although the formation energy of the oxygen-containing system is lower, the addition of oxygen will lead to the decrease of shear strength. If the oxidation occurs at the interface, the mechanical properties of the alloy will deteriorate [61,62]. The existence of P element can decrease the bonding strength of $TiAl/Ti_3Al$ interface, since the P is more likely to bond with Ti, causing the weakness of Ti-Al bonding. This indicates that the addition of P has a negative effect on the plasticity of $TiAl/Ti_3Al$ interface [63].

3.3. Bulk Properties

Due to the adsorption and diffusion of oxygen atoms on the alloy surface, mixed oxides form under the competition of each component in the alloys. The thermodynamic stability properties of the oxides are important due to the great influence on the formation and growth of the oxides.

Al_2O_3 is slightly easier to form compared to TiO_2 according to the calculated formation energy. The influence of 26 elements including the second to the fifth period on the stability of Al_2O_3 and TiO_2 was investigated. Almost all these elements can decrease the stability of the oxides. The Nb, Mo, W, Re, and other elements can significantly reduce the stability of Al_2O_3 relative to TiO_2. Therefore, they can reduce the internal oxidation of aluminum, promoting the formation of dense oxide film structure and improving the oxidation resistance of the alloy [57,64,65]. The theoretical calculations have revealed the nuclear and growth of oxides, for example, through phonon calculations, the bond length and bond energy in the oxide can be quantified to analyze the growth trend of the oxide. The parameters like melting point, bulk modulus and enthalpy of formation can be analyzed as well [66,67]. By performing such investigations, the alloying elements Cr, Ti, Zr, Hf, Y, and Nb are found to increase the Al-O bonding. Therefore, elements like Nb can promote the formation of Al_2O_3 and inhibit the formation of TiO_2, thus forming a compact and stable Al_2O_3 oxide film on the surface of the TiAl alloys and improving the oxidation resistance [68].

Diffusion of elements is another key problem during the oxidation of alloys. The diffusion of elements is a very complex process, which is affected by the external environment, micro-structure, defects, and so on. With the progress of the oxidation behavior, the oxygen adsorption on the surface gradually approaches saturation. At high temperature, the activity of both the oxygen and the metal ions are greatly improved. The interfaces, oxides, and even the grain boundaries will become the channels for the diffusion of elements. The continuous diffusion behavior is the main control factor of oxide growth.

(**a**) (**b**)

(**c**)
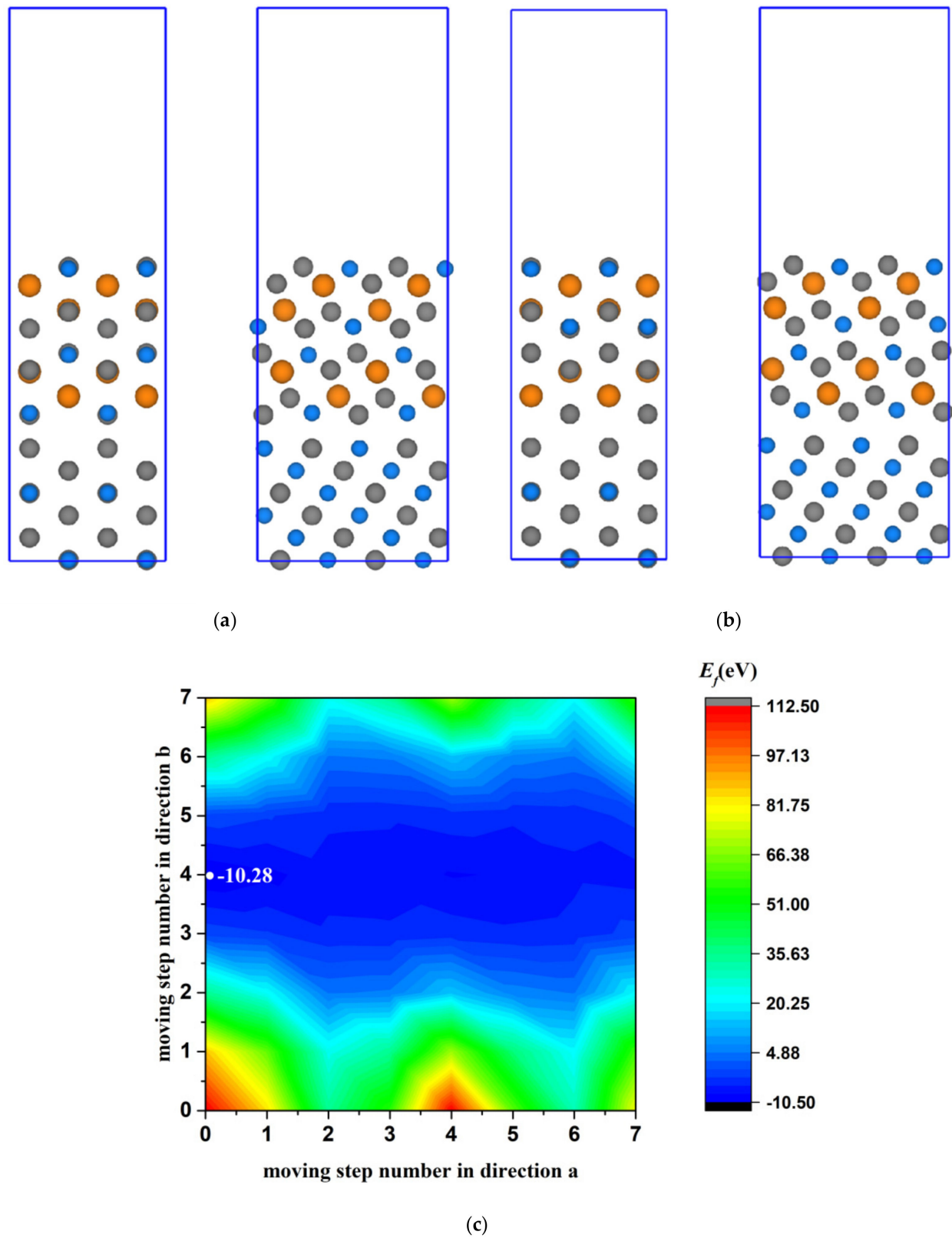
Figure 4. (**a**) Schematics of "OT" stack of the O/B2 interface (**b**) schematics of "HCP" stacks of the O/B2 interface (side views), (**c**) formation energy surface against the relative positions between O and B2 phases. Gray, orange, and blue balls denote Ti, Nb, and Al atoms, respectively.

First principles calculations have been applied to systematically explore the dissolution and diffusion behavior of oxygen atoms in TiAl. Compared with the tetrahedral interstitial sites, oxygen tends to be adsorbed in octahedral sites, especially in the Ti-rich environment. After relaxations, some oxygen atoms migrate to the adjacent "α" and "β" positions, and phonon calculations show that these adsorption sites can be used as ideal starting and ending points in the diffusion simulations. Through the Nudged Elastic Band (NEB) calculations, the minimum barrier that oxygen atoms need to cross when it diffuse from the β to α position is about 0.2 eV. The relationship between temperature and diffusion rate is also considered, and the calculation conclusions are consistent with the relevant experiments [69]. Combining first principles calculation results with other theoretical models, the diffusion behavior can be analyzed more deeply. For instance, the mathematical statistics and Landman model can be applied to fit the curve of temperature and diffusion rate, which is difficult to be obtained from the experiments since the impurity of the sample and the oxygen concentrations are hard to be controlled accurately [70].

The diffusion behaviors of elements in the Ti-Al alloys are more complex than that of the original system. Generally, only the chemical environment around the diffusion path of solute atoms should be considered, and the structure far away from the path is regarded as the original component without alloying. The effects of alloying elements can be divided into three categories: local short-range-trapping effect, local long-range-trapping effect, and non-trapping effect. According to the studies of the effect of Nb doping on the diffusion properties of oxygen atoms in γ-TiAl bulk, Nb can inhibit the activity of oxygen atoms. The closer the distance between Nb and O is, the more obvious the inhibition effect is. This finding is consistent with the experimental results showing that doping an appropriate amount of Nb in TiAl can reduce the formation of TiO_2 [71]. The addition of Nb has a significant effect on increasing the diffusion barrier of oxygen atoms in TiAl alloy, and with the increase of Nb contents, the ability to hinder the diffusion also increases, indicated by the drop of the diffusion coefficient of O [68]. At the same time as the diffusion of oxygen, the metal ions also continue to diffuse in both the matrix and the oxides. The Si and Y can be double doped in the Ti-Al alloys. When both of them replace the Ti atoms, the diffusion of Ti vacancies becomes more difficult. Therefore, the formation of TiO_2 is inhibited, and Al vacancies are easy to diffuse. That is to say, Al atoms are easier to move and diffuse to the surface and bonding with oxygen atoms, thus promoting the formation of a dense Al_2O_3 oxide layer [72]. In order to explore the influence of alloying elements on the growth rate of TiO_2, the stability of TiO_2 after alloying with Si, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Pd, Ag, Sn, La, Ce, Hf, Ta, and Pt and the diffusion properties of these alloying elements in TiO_2 were investigated [73]. Si, Nb, Hf, Ce, La, and Ta can stably replace Ti atoms in TiO_2. The formation energies of Ce, Hf, and Ta doped systems are negative. In contrast, the formation energy of interstitial doping is generally lower than that of displacement doping. The bonding between the alloying elements and the oxide is strong. Four kinds of diffusion paths of alloying elements in TiO_2 are considered, in which the Sub-VAC-short defect has lower formation energy than the Sub-VAC-long defect. According to NEB calculation results, when alloying elements diffuse along the inter-inter path, the barrier is the smallest, less than 1 eV (Figure 5), which may cause the diffusion of elements during the oxidation of Ti-Al alloys. Incidentally, when applying DFT-based calculations on the oxides like TiO_2, there are matters needing attention, such as the use of the DFT+U method. Though the electronic structure features can be described by using the local density approximation (LDA) and the generalized gradient approximation (GGA), the bandgap of semiconductors is usually underestimated since the existence of strongly correlated d-electrons. To avoid the unacceptable increase of cost carried by using hybrid DFT, the Hubbard U correction method (DFT+U) can offer a more efficient way to treat the problem in describing partially filled electronic states, though such an approximate method can not totally eliminate the band gap underestimation [74,75]. The DFT+U method has been widely used in the first principles calculations related to transition metals, such as applying correction on the Ti $3d$ orbital in the TiO_2 system.
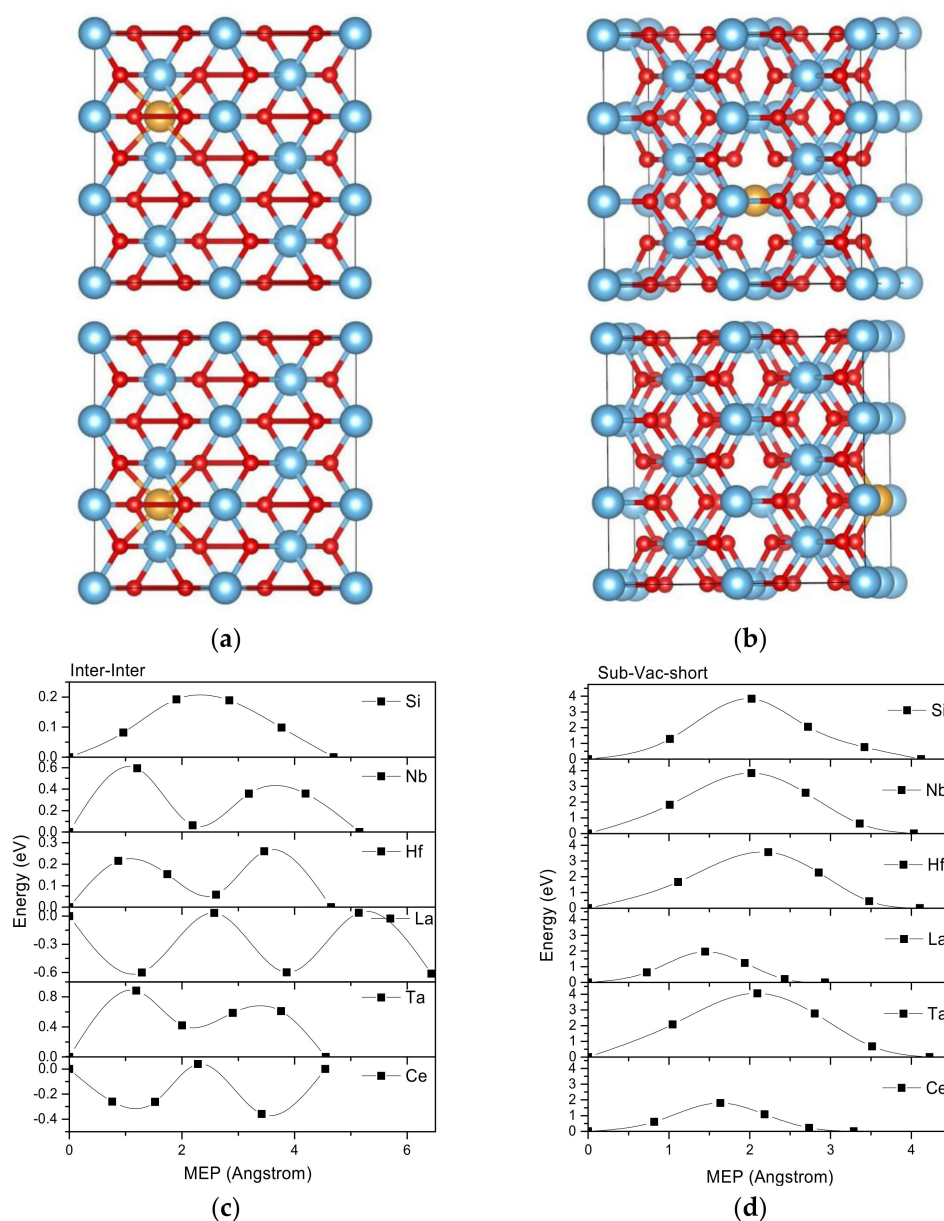
Figure 5. The diffusion paths of alloying element in TiO_2 system (side views). (**a**) Inter-Inter, (**b**) Sub-Vac-long, and the minimum energy path (MEP) of (**c**) Inter-Inter, (**d**) Sub-Vac-short.

4. Summary

Oxidation behaviors of Ti-Al-based alloys have been widely studied, and a clear understanding of their oxidation products, microstructure, and oxidation kinetics has been established. In the absence of anti-oxidation protection films, the elemental competition leads to the inevitable formation of mixed oxides, and it is difficult to guarantee the oxidation-resistant performance of materials at high temperatures. Among the anti-oxidation modifications of Ti-Al alloys, alloying has been widely studied because of its simplicity and effectiveness. In order to explore the reaction mechanism and the effects of alloying elements during the oxidation process of Ti-Al alloys, theoretical studies based on first principles calculations have been greatly employed. The specific research contents can be divided into three parts:

(1) The surface oxidation properties of Ti-Al alloys such as the surface stability, oxygen adsorption properties, and doping effects have received the most attention. Although there is a strong tendency to form TiO_2 on the original alloy surfaces, the interactions

between oxygen and titanium can be inhibited to a certain extent by alloying. The alloying elements like B, Si, Cl show an obvious segregation tendency on the surfaces of the alloys and weaken the binding between oxygens and metal atoms. The high cation valence elements like Ta and W are effective in hinder the reaction between Ti and O, agreeing with the valence control mechanism.

(2) In order to explore the bonding properties between the oxides and the alloy matrix, the interface systems are greatly studied, mainly focusing on the representative oxides (TiO_2 and Al_2O_3) and Ti-Al matrix. Not surprisingly, the alloy elements have different influences on the stability and adhesion properties of the interfaces, such as Nb can enhance the strength of the TiO_2/γ-TiAl interface while Mo may play a negative role in this system, generally, the elements that own obvious segregation tendency may have more effects on the adhesion strength.

(3) The diffusion properties and the stability of the oxides have also been studied. Some typical alloying elements such as Nb can not only segregate in the oxides and optimize the structure of the oxides. They also reduce the diffusion rate of oxygen atoms, and thus inhibit the rapid growth of the oxide.

Theoretical studies have provided valuable suggestions on the atomic and electronic scales and can help to optimize and promote the oxidation resistant properties of Ti-Al alloys. However, the oxidation process of Ti-Al alloys are complex due to the competition between various oxides, e.g., TiO_2 and Al_2O_3. Further studies can be expected by combining theoretical and experimental methods on the kinetic and phase transformation properties during the oxidation process of Ti-Al alloys.

References

1. Bewlay, B.P.; Nag, S.; Suzuki, A.; Weimer, M.J. TiAl alloys in commercial aircraft engines. *Mater. High Temp.* **2016**, *33*, 549–559. [CrossRef]
2. Pollock, T.M. Alloy design for aircraft engines. *Nat. Mater.* **2016**, *15*, 809–815. [CrossRef] [PubMed]
3. Liu, G.L.; Li, Y. The Electronic Theory Study on High-temperature Oxidation Mechanism of TiAl alloy. *Acta Phys. Sin.* **2012**, *61*, 177101.
4. Swadzba, R.; Marugi, K.; Pyclik, L. STEM Investigations of γ-TiAl Produced by Additive Manufacturing after Isothermal Oxidation. *Corros. Sci.* **2020**, *169*, 108617. [CrossRef]
5. Mogale, N.F.; Matizamhuka, W.R. Spark Plasma Sintering of Titanium Aluminides: A Progress Review on Processing, Structure-Property Relations, Alloy Development and Challenges. *Metals* **2020**, *10*, 1080. [CrossRef]
6. Garip, Y. Investigation of isothermal oxidation performance of TiAl alloys sintered by different processing methods. *Intermetallics* **2020**, *127*, 106985. [CrossRef]
7. Tian, S.; Jiang, H.; Zhang, G.; Zhang, Y.; Lin, H.; Yang, Y. Investigation on the initial oxidation behavior of TiAl alloy. *Mater. Res. Express* **2019**, *6*, 106595. [CrossRef]
8. Dai, J.; Zhu, J.; Chen, C.; Weng, F. High temperature oxidation behavior and research status of modifications on improving high temperature oxidation resistance of titanium alloys and titanium aluminides: A review. *J. Alloys Compd.* **2016**, *685*, 784–798. [CrossRef]
9. Lim, H.; Liew, W.; Melvin, G.; Jiang, Z.-T. A Short Review on the Phase Structures, Oxidation Kinetics, and Mechanical Properties of Complex Ti-Al Alloys. *Materials* **2021**, *14*, 1677. [CrossRef]

10. Cobbinah, P.V.; Matizamhuka, W.; Machaka, R.; Shongwe, M.B.; Yamabe-Mitarai, Y. The effect of Ta additions on the oxidation resistance of SPS-produced TiAl alloys. *Int. J. Adv. Manuf. Technol.* **2020**, *106*, 3203–3215. [CrossRef]

11. Bacos, M.P.; Ceccacci, S.; Monchoux, J.P.; Davoine, C.; Gheno, T.; Rio, C.; Morel, A.; Merot, J.-S.; Fossard, F.; Thomas, M. Oxidation Behavior of a Spark Plasma Sintered Ti–48Al–2W–0.1B Alloy at 800 °C. *Oxid. Met.* **2020**, *93*, 587–600. [CrossRef]

12. Galetz, M.C.; Ulrich, A.S.; Oskay, C.; Fahsing, D.; Laska, N.; Schulz, U.; Schutze, M. Oxidation-induced Microstructural Changes of the TiAl TNM-B1 Alloy after Expo-sure at 900 °C in Air. *Intermetallics* **2020**, *123*, 106830. [CrossRef]

13. Knaislová, A.; Novák, P.; Cabibbo, M.; Jaworska, L.; Vojtěch, D. Development of TiAl–Si Alloys—A Review. *Materials* **2021**, *14*, 1030. [CrossRef] [PubMed]

14. Ralison, A.; Dettenwanger, F.; Schutze, M. Oxidation of Orthorhombic Ti$_2$AlNb Alloys in the Temperature Range 550–1000 Degrees C in Air. *Mater. High Temp.* **2003**, *20*, 607–629. [CrossRef]

15. Chou, K.; Chu, P.-W.; Marquis, E.A. Early oxidation behavior of Si-coated titanium. *Corros. Sci.* **2018**, *140*, 297–306. [CrossRef]

16. Garip, Y.; Ozdemir, O. Investigation of Cyclic Oxidation Behavior of (Cr, Mo, Si)-Containing (α2 + γ) TiAl-Based Alloys Synthesized by ECAS Sintering. *Phys. Met. Metallogr.* **2020**, *121*, 322–329. [CrossRef]

17. Mengis, L.; Ulrich, A.S.; Watermeyer, P.; Liebscher, C.H.; Galetz, M.C. Oxidation Behaviour and Related Microstructural Changes of two β0–phase containing TiAl Alloys between 600 °C and 900 °C. *Corros. Sci.* **2021**, *178*, 109085. [CrossRef]

18. Neelam, N.S.; Banumathy, S.; Bhattacharjee, A.; Rao, N.; Zafir, A. Comparison of the Isothermal and Cyclic Oxidation Behavior of Cr and Mo Containing γ-TiAlNb alloys. *Corros. Sci.* **2019**, *163*, 108300. [CrossRef]

19. Garip, Y.; Ozdemir, O. A study of the cycle oxidation behavior of the Cr/Mn/Mo alloyed Ti–48Al–based intermetallics prepared by ECAS. *J. Alloys Compd.* **2020**, *818*, 152818. [CrossRef]

20. Pan, Y.; Lu, X.; Hayat, M.D.; Yang, F.; Liu, C.; Li, Y.; Li, X.; Xu, W.; Qu, X.; Cao, P. Effect of Sn addition on the high-temperature oxidation behavior of high Nb-containing TiAl alloys. *Corros. Sci.* **2020**, *166*, 108449. [CrossRef]

21. Dadé, M.; Esin, V.; Nazé, L.; Sallot, P. Short- and long-term oxidation behaviour of an advanced Ti2AlNb alloy. *Corros. Sci.* **2019**, *148*, 379–387. [CrossRef]

22. Liu, C.C. Investigation of Properties and Metal Injection Moulding of Sn Micro-alloyed High Nb Containing TiAl Alloy. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2018.

23. Zeng, S.W. Research on Hot Deformation and Oxidation Behavior of TiAl Containing Nb, Mo. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2015.

24. Zhao, P.; Li, X.; Tang, H.; Ma, Y.; Chen, B.; Xing, W.; Liu, K.; Yu, J. Improved High-Temperature Oxidation Properties for Mn-Containing Beta-Gamma TiAl with W Addition. *Oxid. Met.* **2020**, *93*, 433–448. [CrossRef]

25. Liu, J. Research on the Effect of Microstructure on the Oxidation Behavior of γ-TiAl Alloys. Ph.D. Thesis, Northwestern Polytechnical University, Xi'an, China, 2017.

26. Li, D.; Zhang, G.; Lu, G.; Wang, J.; Liu, C. Optimizing high-temperature oxidation behaviors of high-Nb-containing TiAl alloys by addition of boron. *Corros. Sci.* **2020**, *177*, 108971. [CrossRef]

27. Pan, Y.; Lu, X.; Hui, T.; Liu, C.; Liu, B.; Xu, W.; Zhang, C.; Sun, J.; Qu, X.; Zhang, J. High-temperature oxidation behaviour of TiAl alloys with Co addition. *J. Mater. Sci.* **2020**, *56*, 815–827. [CrossRef]

28. Song, Y.; Dai, J.H.; Yang, R. Mechanism of Oxygen Adsorption on Surfaces of Gamma-TiAl. *Surf. Sci.* **2012**, *606*, 852–857. [CrossRef]

29. Li, H.; Liu, L.M.; Wang, S.Q.; Ye, H. First-Principles Study of Oxygen Atom Adsorption on γ-TiAl(111) Surface. *Acta Metall. Sin.* **2006**, *42*, 897–902.

30. Wang, L.; Shang, J.X.; Wang, F.H.; Chen, Y.; Zhang, Y. Oxygen Adsorption on Gamma-TiAl Surfaces and the Related Surface Phase Diagrams: A Density-functional Theory Study. *Acta. Mater.* **2013**, *61*, 1726–1738. [CrossRef]

31. Bakulin, A.V.; Kulkova, S.E.; Hu, Q.-M.; Yang, R. Initial oxidation of TiAl: An ab-initio investigation. *AIP Conf. Proc.* **2014**, *1623*, 39–42. [CrossRef]

32. Li, H.; Wang, S.Q.; Ye, H.Q. Initial Oxidation of γ-TiAl(111) Surface: Density-functional Theory Study. *J. Mater. Sci. Technol.* **2009**, *25*, 569–576.

33. Zhou, Y.; Xiong, H.; Yin, Y.; Zhong, S. First principles study of surface properties and oxygen adsorption on the surface of Al3Ti intermetallic alloys. *RSC Adv.* **2019**, *9*, 1752–1758. [CrossRef]

34. Li, Y.; Dai, J.H.; Song, Y. Adsorption Properties of Oxygen Atom on the Surface of Ti$_2$AlNb by First Principles Calculations. *Comput. Mater. Sci.* **2017**, *139*, 412–418. [CrossRef]

35. Duan, X.; Warschkow, O.; Soon, A.; Delley, B.; Stampfl, C. Density functional study of oxygen on Cu(100) and Cu(110) surfaces. *Phys. Rev. B* **2010**, *81*, 075430. [CrossRef]

36. Das, N.K.; Shoji, T. Early Stage Oxidation of Ni-Cr Binary Alloy (111), (110) and (100) Surfaces: A Combined Density Func-tional and Quantum Chemical Molecular Dynamics Study. *Corros. Sci.* **2013**, *73*, 18–31. [CrossRef]

37. Liu, S.Y.; Shang, J.X.; Wang, F.H.; Liu, S.Y.; Zhang, Y.; Xu, H.B. Ab Initio Atomistic Thermodynamics Study on the Selective Oxidation Mechanism of the Surfaces of Intermetallic Compounds. *Phys. Rev. B* **2009**, *80*, 5. [CrossRef]

38. Liu, S.Y.; Shang, J.X.; Wang, F.H.; Zhang, Y. Surface Segregation of Si and Its Effect on Oxygen Adsorption on a Gamma-TiAl(111) Surface from First Principles. *J. Phys. Condes. Matter.* **2009**, *21*, 7. [CrossRef]

39. Zhang, G.Y.; Liu, G.L.; Bao, J.S.; Liu, C.M.; Zhang, H. Energetic Studies on the B Effect on the Oxidation of γ-TiAl Alloys. *Adv. Mater. Res.* **2014**, *1052*, 28–33. [CrossRef]

40. Wu, X.X.; Wang, Q.E.; Wang, F.H.; Zhou, Y.S. First-principles Study on Chemisorption of Cl on γ-TiAl(111) Surface. *Acta Phys. Sin. Chin. Ed.* **2010**, *59*, 7278–7284.

41. Kulkova, S.E.; Bakulin, A.V.; Kulkov, S.S. Oxygen adsorption on the doped TiAl(1 0 0) surface. *Comput. Mater. Sci.* **2019**, *170*, 109136. [CrossRef]

42. Wei, D.B.; Li, F.K.; Li, S.Q.; Wang, S.; Ding, F.; Liang, H.; Yan, Y.; Zhang, P. A Combined Experimental and First-principle Study on the Effect of Plasma Surface Ta–W Co-alloying on the Oxidation Behavior of γ-TiAl at 900 °C. *J. Mater. Res.* **2020**, *35*, 516–526. [CrossRef]

43. Pan, Y.; Pu, D.L.; Li, Y.Q.; Zheng, Q.H. Origin of the Antioxidation Mechanism of RuAl(1 1 0) Surface from First Principles Calculations. *Meter. Sci. Eng. B Adv.* **2020**, *259*, 114580. [CrossRef]

44. Tian, X.F.; Wang, Y.; Li, L.S.; Wu, M.; Yu, Y. First Principles Studies of Oxygen Adsorption on the g-U (1 1 0) Surface and Influences of Mo Doping. *Comp. Mater. Sci.* **2020**, *179*, 109633. [CrossRef]

45. Yang, J.; Wang, Y.; Huang, J.; Wang, W.; Ye, Z.; Chen, S.; Zhao, Y. First-principles calculations on interface structure and fracture characteristic of TiC/TiZrC nano-multilayer film based on virtual crystal approximation. *J. Alloys Compd.* **2018**, *755*, 211–223. [CrossRef]

46. Yang, J.; Wang, Y.; Huang, J.; Ye, Z.; Sun, X.; Chen, S.; Zhao, Y. First-principles calculations on Ni/W interfaces in Steel/Ni/W hot isostatic pressure diffusion bonding layer. *Appl. Surf. Sci.* **2019**, *475*, 906–916. [CrossRef]

47. Shi, Z.; Liu, S.; Zhou, Y.; Xing, X.; Ren, J.; Yang, Q. Structure and properties of YAlO₃/NbC heterogeneous nucleation interface: First principles calculation and experimental research. *J. Alloys Compd.* **2019**, *773*, 264–276. [CrossRef]

48. Shi, J.Z.; Shao, W.; Hu, T.S.; Zhao, C.; Xing, X.; Zhou, Y.; Yang, Q. Adhesive Sliding and Interfacial Property of YAlO₃/TiC Interface: A First Principles Investigation. *J. Alloys Compd.* **2019**, *805*, 1052–1059. [CrossRef]

49. Wang, J.; Enomoto, M.; Shang, C. First-principles study on the interfacial segregation at coherent Cu precipitate/Fe matrix interface. *Scr. Mater.* **2020**, *185*, 42–46. [CrossRef]

50. Ren, Z.; Qin, J.; Liu, R.; Zhang, X. Vacancy mediated alloying strengthening effects on Al/Al3Zr interface and stabilization of L1₂-Al₃Zr: A first-principles study. *J. Alloys Compd.* **2020**, *825*, 153825. [CrossRef]

51. Wang, B.; Dai, J.; Wu, X.; Song, Y.; Yang, R. First-principles study of the bonding characteristics of TiAl(111)/Al₂O₃(0001) interface. *Intermetallics* **2015**, *60*, 58–65. [CrossRef]

52. Song, Y.; Xing, F.; Dai, J.; Yang, R. First-principles study of influence of Ti vacancy and Nb dopant on the bonding of TiAl/TiO₂ interface. *Intermetallics* **2014**, *49*, 1–6. [CrossRef]

53. Dai, J.; Song, Y.; Yang, R. Influence of alloying elements on stability and adhesion ability of TiAl/TiO₂ interface by first-principles calculations. *Intermetallics* **2017**, *85*, 80–89. [CrossRef]

54. Li, Y.; Dai, J.; Song, Y. Enhancing adhesion of Al₂O₃ scale on Ti-Al intermetallics by alloying: A first principles study. *Comput. Mater. Sci.* **2020**, *181*, 109756. [CrossRef]

55. Rose, J.H.; Smith, J.R.; Ferrante, J. Universal features of bonding in metals. *Phys. Rev. B* **1983**, *28*, 1835–1845. [CrossRef]

56. Rose, J.H.; Smith, J.R.; Guinea, F.; Ferrante, J. Universal features of the equation of state of metals. *Phys. Rev. B* **1984**, *29*, 2963–2969. [CrossRef]

57. Bakulin, A.V.; Kulkov, S.S.; Fuks, A.A.; Kulkova, S.E. The impurity influence on the formation of oxide layers on TiAL surface. *AIP Conf. Proc.* **2018**, *2051*, 020023. [CrossRef]

58. Hao, H.N.; Wang, X.; Wang, F.H. First-principles Study on the Clean and Nb Doped TiO₂(110)/γ-TiAl(111) Interfaces. *Adv. Mater. Res.* **2013**, *602–604*, 555–558.

59. Wang, A.; Liu, P.; Xie, J.; Ma, D.; Mao, Z. First-principles investigation on the atomic structure, stability and electronic property of O(001)/B2(110) interface in Ti₂AlNb alloys. *J. Alloys Compd.* **2020**, *817*, 152734. [CrossRef]

60. Li, Y.; Dai, J.; Song, Y. First-principles investigation on stability and oxygen adsorption behavior of a O/B2 interface in Ti₂AlNb alloys. *J. Alloys Compd.* **2020**, *818*, 152926. [CrossRef]

61. Wei, Y.; Zhang, Y.; Zhou, H.-B.; Lu, G.-H.; Xu, H. First-principles investigation on shear deformation of a TiAl/Ti₃Al interface and effects of oxygen. *Intermetallics* **2012**, *22*, 41–46. [CrossRef]

62. Wei, Y.; Zhou, H.B.; Zhang, Y.; Lu, G.H.; Xu, H. Effects of O in a Binary-phase TiAl-Ti₃Al Alloy: From Site Occupancy to Interfacial Energetics. *J. Phys. Condensed Matter.* **2011**, *23*, 7. [CrossRef]

63. Li, Z.Z.; Wei, Y.; Zhou, H.B.; Lu, G.H. Investigating the Effects of Phosphorus in a Binary-phase TiAl-Ti₃Al Alloy by First-principles: From Site Preference, Interfacial Energetics to Mechanical Properties. *Eur. Phys. J. B* **2016**, *89*, 280. [CrossRef]

64. Ping, F.P.; Hu, Q.M.; Bakulin, A.V.; Kulkova, S.E.; Yang, R. Alloying Effects on Properties of Al₂O₃ and TiO₂ in Connection with Oxidation Resistance of TiAl. *Intermetallics* **2016**, *68*, 57–62. [CrossRef]

65. Ping, F.P.; Hu, Q.M.; Yang, R. Investigation on Effects of Alloying on Oxidation Resistance of γ-TiAl by Using First Principle. *Acta Metall. Sin.* **2013**, *49*, 385–390. [CrossRef]

66. Shang, S.L.; Wang, Y.; Brian, G.; Liu, Z. Understanding Slow-growing Alumina Scale Mediated by Reactive Elements: Perspec-tive via Local Metal-oxygen Bonding Strength. *Scr. Mater.* **2018**, *150*, 139–142. [CrossRef]

67. Wu, G.; Cui, G.; Qu, S.; Feng, A.; Cao, G.; Ge, B.; Xiang, H.; Shen, J.; Chen, D. High-temperature oxidation mechanisms of nano-/submicro-scale lamellar structures in an intermetallic alloy. *Scr. Mater.* **2019**, *171*, 102–107. [CrossRef]

68. Cheng, F. First-Principles Calculations of the Effect of Nb on Oxidation Resistance and Friction and Wear of TiAl Alloys. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2019.

69. Epifano, E.; Hug, G. First-principle Study of the Solubility and Diffusion of Oxygen and Boron in γ-TiAl. *Comp. Mater. Sci.* **2020**, *174*, 109475. [CrossRef]

70. Bakulin, A.V.; Kulkov, S.S.; Kulkova, S.E. Diffusion Properties of Oxygen in the γ-TiAl Alloy. *J. Exp. Theor. Phys.* **2020**, *130*, 579–590. [CrossRef]

71. Zhao, C.Y.; Wang, X.; Wang, F.H. First-principles Study of Nb Doping Effect on the Diffusion of Oxygen Atom in γ-TiAl. *Adv. Mater. Res.* **2011**, *304*, 148–153. [CrossRef]

72. Song, Q.G.; Wang, L.G.; Zhu, Y.X.; Kang, J.H.; Gu, W.F.; Wang, M.C.; Liu, Z.F. Effects of Si and Y Co-doping on Stability and Oxidation Resistance of γ-TiAl Based Alloys. *Acta Phys. Sin.* **2019**, *68*, 196101.

73. Dai, J.; Wang, L.; Wu, X.; Song, Y.; Yang, R. Effects of alloying elements on the stability of TiO_2 and their diffusion properties studied by first principles calculations. *Mater. Today Commun.* **2018**, *17*, 40–45. [CrossRef]

74. Anisimov, V.I.; Zaanen, J.; Andersen, K.O. Band Theory and Mott Insulators: Hubbard U Instead of Stoner I. *Phys. Rev. B* **1991**, *44*, 943. [CrossRef]

75. Dudarev, S.L.; Botton, G.A.; Savrasov, S.Y.; Humphreys, C.J.; Sutton, A.P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **1998**, *57*, 1505–1509. [CrossRef]