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First Principles Study of Bonding Mechanisms at the TiAl/TiO₂ Interface

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Abstract: The adhesion properties of the TiAl/TiO₂ interface are estimated in dependence on interfacial layer composition and contact configuration using the projector augmented wave method. It is shown that a higher value of the work of separation is obtained at the interface between the Ti-terminated TiAl(110) surface and the TiO₂(110)_O one than at that with the Al-terminated alloy. An analysis of structural and electronic factors dominating the chemical bonding at the interfaces is carried out. It is shown that low bond densities are responsible for low adhesion at both considered interfaces, which may affect the spallation of oxide scale from the TiAl matrix.

Keywords: interface; adhesion; titanium aluminides; titanium dioxide; electronic structure; first principles calculations

1. Introduction

Among the big family of intermetallic compounds, Ti–Al alloys attract much attention from both experimental and theoretical researchers. In most studies, γ -TiAl is investigated due to its excellent combination of mechanical properties such as low density, high specific strength, and stiffness, as well as good high-temperature creep resistance [1,2]. However, potential application of the alloy in aeronautical and space technologies is restricted by the poor high-temperature oxidation resistance, which is connected with the growth of non-protective Al₂O₃ + TiO₂ mixed oxide layers on the internal scale [3,4]. To improve the oxidation resistance of the γ -TiAl alloy, numerous treatment techniques, including the addition of alloying elements and surface modification, have been applied [1,2]. There is an option that the oxidation resistance of γ -TiAl might be improved by avoiding the formation of TiO₂ and promoting the formation of an Al₂O₃ protective dense layer. However, the Al chemical activity is reduced in Ti–Al alloys with increasing Ti-content. Therefore, this fact, in combination with the thermodynamic characteristics of the oxides, leads to a larger stability of the interfaces with TiO and TiO₂ rather than with Al₂O₃. Experiments [5–10] have shown that Nb, Mo, W, and Re benefit, whereas V, Mn, and Cu deteriorate the oxidation resistance of γ -TiAl. Since the experimental measurements are very sensitive to many factors, including temperature, partial pressure of oxygen, composition variation, and so forth, the obtained conclusions are often contradictory. It is believed that the alloying with impurities such as Nb, Mo, W, and so forth can increase the activity and diffusivity of aluminum and therefore enhance the formation of the alumina layer [1,11]. It was demonstrated in [12,13] that

some impurities (Nb, Mo, Ta, Hf, etc.) increase the formation energy of an oxygen vacancy in TiO_2 and can suppress the TiO_2 growth.

The oxidation characteristics of γ -TiAl were studied in several studies using methods within density functional theory [14–22]. Li with coworkers [14] established that oxygen prefers to be adsorbed near the Ti atoms regardless of the concentration of oxygen. The authors of [15] emphasized also the oxidation priority of Ti atoms over Al ones. Liu et al. [16] demonstrated that the occurrence of Al self-segregation at the TiAl(111) surface can enhance the interaction between O and Al atoms and promote the growth of a pure alumina layer. It was shown in [17] that alloy doping by Nb increases the diffusion barrier of oxygen and therefore can improve the oxidation resistance. The effect of Nb on the O diffusion was also studied in [18]. Strengthening of the bonding between O and Al and weakening of the Ti–O one due to doping by Si was demonstrated in [19]. The authors conclude that the formation ability of TiO_2 can be reduced. In [20], the mechanisms of the O interaction with low-index TiAl surfaces were studied. The interaction with the Ti-rich surface was found to be much stronger than with the Al-rich one. In our previous work [21], the initial stage of γ -TiAl (001), (100), and (110) surface oxidation was also studied. The preference of the Ti-rich sites for oxygen adsorption was demonstrated, that is in agreement with experiment and earlier theoretical results. Additionally, the O diffusion migration barriers were determined in the bulk TiAl alloy and from surface into bulk [21,22]. Recently, the oxygen temperature dependent diffusion coefficient was studied in γ -TiAl using several models [23–25]. In our paper [25], a comparative study of O diffusion using a statistical approach and the Landman method was performed. We demonstrated that O diffusion along the a axis is faster than along the c axis, whereas the opposite trend was observed in Ti_3Al [26,27]. It is seen that there is much knowledge about the initial stage of TiAl surface oxidation and oxygen diffusion in the alloy.

At the same time, studies of the bonding characteristics at the TiAl–oxide interfaces remain rare. The bonding strength and stability of TiAl/ TiO_2 and TiAl/ Al_2O_3 interfaces were studied in [28–30]. It was shown in [28] that the O–Al bond is stronger than the O–Ti one at the TiAl/ TiO_2 interface. Additionally, authors of [28] concluded that both Ti vacancy and Nb dopant weaken the stability of the $\text{TiAl}(110)_{\text{Al}}/\text{TiO}_2(110)_{\text{O}}$ interface, and Nb makes the oxygen atoms detach from TiO_2 and primarily bond with the Al atomic layer in the TiAl surface. The latter can improve the oxidation resistance of γ -TiAl. In other work [29], the strength of the O–Al and O–Ti bonds were compared at the TiAl/ Al_2O_3 interface. It was also found that the O–Al bond is stronger, rather than the O–Ti one, owing to the O- p and Al- p hybridization, which takes part in a relatively broad energy region in comparison with the overlaps of O- p and Ti- d orbitals. In [30], the influence of alloying elements on the adhesion properties of the $\text{TiAl}(110)_{\text{Ti}}/\text{TiO}_2(110)_{\text{O}}$ interface was studied. It was established that among the considered impurities, Y, Nb, and Pd are suitable to improve the adhesion ability between TiO_2 and TiAl. It is necessary to point out that the surface cells $\text{TiO}_2(110)-(1 \times 1)$ and $\text{TiAl}(110)-(2 \times 1)$ were matched in papers [28] and $\text{TiO}_2(110)-(1 \times 2)$ and $\text{TiAl}(110)-(2 \times 2)$ —in [30], that leads to a misfit along one surface lattice parameter of about 22%. Therefore, a significant distortion of the atomic structure of the oxide film takes place at the interface. Furthermore, the mixed Ti–O layer second from the interface splits substantially, and the distance is comparative with the interplanar one. As a result, the interfacial oxygen atoms incorporate into the Ti interfacial layer of the alloy that leads to large work of separation (4.97 J/m^2), whereas it is only 1.53 J/m^2 if the cleavage plane locates between the shifted O atom and the oxide. Therefore, in order to better understand the bonding characteristics between oxide and alloy, a more reasonable interface with a small mismatch should be studied. In the present work, we focus on the modeling of the TiAl/ TiO_2 interface and its adhesion properties.

2. Computational Details

The atomic and electronic structure of the TiAl(110)/ $\text{TiO}_2(110)$ interface was calculated by the projector-augmented wave (PAW) method in the plane-wave basis [31,32], implemented in the Vienna Ab initio Simulation Package (VASP) code [33–35]. The generalized gradient approximation in the Perdew–Burke–Ernzerhof form (GGA–PBE) was used for the exchange–correlation functional [36].

The energy cut-off for the plane waves was set to 550 eV. For interface calculations, we adopted a k -points mesh of $2 \times 8 \times 1$ obtained by the Monkhorst–Pack method [37]. The total energies were converged up to 10^{-5} eV. The theoretical lattice parameters of the bulk TiO_2 with rutile structure ($a = 4.663 \text{ \AA}$, $c = 2.969 \text{ \AA}$) and the γ -TiAl alloy ($a = 3.977 \text{ \AA}$, $c = 4.081 \text{ \AA}$) are in good agreement with experimental ones [38,39]. More details about structural parameters of both TiAl(110) and TiO_2 (110) surface and interface structures will be discussed in the corresponding section.

The work of separation (W_{sep}) or the ideal adhesion energy at the alloy–oxide interface was calculated as

$$W_{\text{sep}} = [E(\text{TiAl}) + E(\text{TiO}_2) - E(\text{TiAl/TiO}_2)]/S, \quad (1)$$

where $E(\text{TiAl/TiO}_2)$ is the total energy of a supercell containing the multilayered slabs, $E(\text{TiAl})$ and $E(\text{TiO}_2)$ are the total energies of the same supercell containing a single slab of the alloy or the oxide, respectively, and S is the area of the interface.

In order to estimate the surface energy of stoichiometric surfaces the following formula was used:

$$\sigma = (E^{\text{slab}} - N \cdot E^{\text{bulk}})/2S, \quad (2)$$

where E^{slab} is the total energy of the supercell containing a slab and vacuum region, E^{bulk} —the reference energy of the bulk compound per formula unit, N —the number of formula units in the slab, S —the surface area, and factor 2 corresponds to two identical surface on both slab sides.

In the case of nonstoichiometric surfaces of an A_nB_m compound, σ is a function of the chemical potential of any component and can be calculated as follows:

$$\sigma = \frac{1}{2S} \left[E^{\text{slab}} - \frac{N_B}{m} E^{\text{bulk}} - \Gamma_A \mu_A^{\text{bulk}} - \Gamma_A \Delta \mu_A \right], \quad (3)$$

where N_A (N_B) is the number of atoms of element A (B), Γ_A —the excess of element A at the surface with respect to B one:

$$\Gamma_A = N_A - \frac{n}{m} N_B, \quad (4)$$

μ_A^{bulk} —the chemical potential of element A in elementary substance under bulk conditions, $\Delta \mu_A$ —the change of chemical potential of element A in A_nB_m compound with respect to the elementary substance bulk. It may change in the range:

$$-\frac{1}{n} \Delta H_{A_nB_m}^f \leq \Delta \mu_A \leq 0, \quad (5)$$

where $\Delta H_{A_nB_m}^f$ is the formation enthalpy of the compound per formula unit. More details can be found in our earlier paper [22]. Often authors draw σ as function of $\Delta \mu / \Delta H^f$ instead of $\Delta \mu$. This allows us to reach uniformity of the surface stability diagrams for different compounds.

3. Results and Discussion

3.1. Surface Energy

The surface energy of low-index surfaces of the γ -TiAl alloy as a function of the Ti chemical potential is shown in Figure 1a. The atomic structures of the γ -TiAl(001), (100), (110), and (111) surfaces were modeled by 11-layer thin films, whereas slabs of the TiO_2 with rutile structure contained 21–35 atomic layers in dependence on surface orientation. It is seen that the TiAl(100) surface with the stoichiometric composition is the most stable one in the Ti-rich region. At the same time, the TiAl(110) surface with Al termination has the lowest surface energy in the Al-rich and near-stoichiometry regions. In the limit of high aluminum concentrations, the surface energies of both $\text{TiAl}(001)_{\text{Al}}$ and $\text{TiAl}(110)_{\text{Al}}$ surfaces are almost the same. The values of σ for other considered surfaces are higher. One can see from Figure 1b that the stoichiometric TiO_2 (110)_O surface is stable for almost the whole interval of

increase of oxide or alloy slab thickness or vacuum gap results in a change of the work of separation by less than 20 mJ/m². Moreover, doubling the interface cell along the $[1]$ direction of the oxide leads to a difference in W_{sep} of 4 mJ/m².

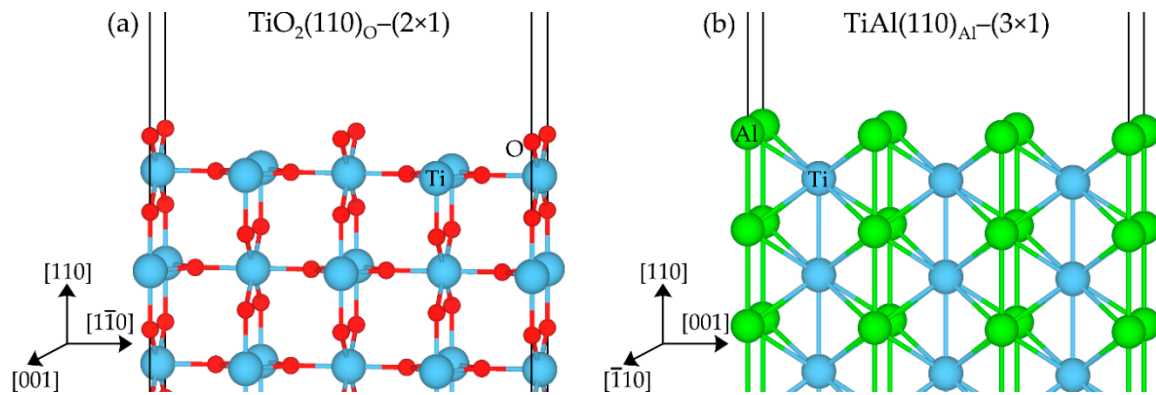


Figure 2. Atomic structure of (a) $\text{TiO}_2(110)_{\text{O}}-(2 \times 1)$ and (b) $\text{TiAl}(110)_{\text{Al}}-(3 \times 1)$ surfaces.

For the modeling of the $\text{TiAl}/\text{TiO}_2(110)$ interface, two configurations (*hollow* and *top*) of contacts with the Al- and Ti-terminated γ - $\text{TiAl}(110)$ surface were considered. Both configurations before relaxation are presented in Figure 3. In case of the *hollow* configuration, one interfacial O atom (O_{2I} in Figure 3a) locates above the Ti_{I-1} atom of the second layer. It is a so-called *H* or *hollow* site for O adsorption on the $\text{TiAl}(110)$ surface (see, e.g., [22]) that was a reason for the configuration denotation. The other interfacial O atom (O_{1I} in Figure 3a) occupies the *short-bridge* position between two Al_{1I} atoms. The *top* configuration can be obtained from the *hollow* one by a shift of the oxide film along the $[1]$ direction by $b_2/2$. As a result, the O_{2I} atom locates now in the *long-bridge* position between two Al_{2I} atoms and O_{1I} —in the *top* one (Figure 3b). The denotation of the *top* configuration is due to this position of the O_{1I} atom. It should be noted that in the case of the Ti-terminated alloy surface, Al and Ti atoms of its film are swapped (Figure S1). The initial interface distance was chosen so that the interatomic distance between the nearest interfacial atoms is slightly greater than the sum of their covalent radii.

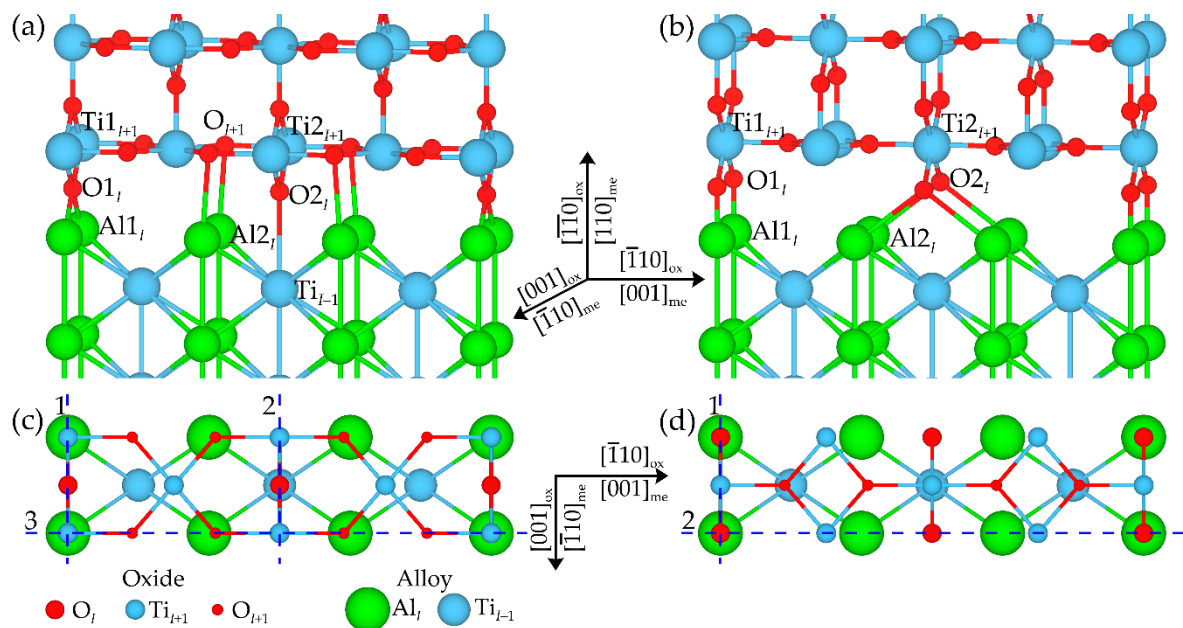


Figure 3. Atomic structures of unrelaxed interfaces with (a,c) *hollow* and (b,d) *top* configuration. Atoms that are important in interfacial bonding are marked. Symbols I and $I \pm 1$ denote atoms of interfacial and subinterfacial layers.

The calculated values of the work of separation and the interfacial distance (d) for all considered structures are given in Table 2. Note that for the d estimation, the averaged values of positions of the interfacial atoms in the oxide and the alloy were used. One can see that for the Al-terminated alloy, the obtained values of W_{sep} are within 0.74–1.27 J/m² that is in line with 0.58–1.64 J/m² [28]. The highest value of the work of separation was calculated for the *hollow* configuration. In work [28], five interface configurations were considered. As the authors of [28] matched TiO₂(110)–(1 × 1) and TiAl(110)–(2 × 1) surface cells (which results in too large misfit), a direct comparison of the present results with earlier ones is impossible. Nevertheless, in the case of the most stable configuration B(Ti–Al) in [28], there are bonds between interfacial O_I and subinterfacial Ti_{I–1} atoms as well as between O_{I+1} and Al_I ones. Our *hollow* configuration demonstrates almost similar chemical bonding. The difference in W_{sep} for these configurations is 0.37 J/m². Some discussion will be given in Section 3.3.

Table 2. Work of separation (in J/m²) and interface distance (d in Å) at the interface TiAl/TiO₂(110)_O.

Alloy Termination	Configuration	W_{sep}	d
Al	<i>hollow</i>	1.27	0.75
	<i>top</i>	0.74	1.38
	[28]	0.58–1.64	
Ti	<i>hollow</i>	2.44	0.62
	<i>top</i>	1.97	0.50
	[30]	4.97	

The values of the work of separation for the interface with the Ti-terminated alloy film increase to almost twice in comparison with the previous case, but they remain substantially lower than the data from [30] (Table 2). It should be noted that the authors of [30] used almost the same surface cells as in [28], they were just doubled along the shortest distance, i.e., TiO₂(110)–(1 × 2) and TiAl(110)–(2 × 2) cells were matched. In the present paper as well as in [30], the formation O_I–Al_{I–1} and O_I–Ti_I bonds is observed. At the same time, in work [30] a huge distortion of the atomic structure of TiO₂ near the interface takes place. The latter allows us to assume that the authors adopted the alloy lattice parameters for interface modeling. As a rule, the parameters of oxide surface cell are used in such calculations [46,47]. It should be noted that enough low values of the work of separation were calculated earlier in several papers, if oxide is terminated by one oxygen layer. For example, W_{sep} equal to 1.37 J/m² was obtained at the Nb(110)/Al₂O₃(1120)_O interface [48] while the value is one order more at the Nb(110)/Al₂O₃(1120)_{2O} one [49]. In the case of the U(110)/Al₂O₃(1120)_O interface, the value of 1.90 J/m² was calculated, but 11.5 J/m² was obtained at the U(110)/Al₂O₃(1120)_{2O} interface [50]. Analysis of both TiAl/TiO₂ interface characteristics will be performed in the next section.

3.3. Atomic and Electronic Factors

Figure 4 demonstrates the distribution of the charge density difference ($\Delta\rho(\mathbf{r})$) for both TiAl(110)_{Al}/TiO₂(110)_O and TiAl(110)_{Ti}/TiO₂(110)_O interfaces in the case of the *hollow* configuration in the planes shown in Figure 3c. We emphasize that $\Delta\rho(\mathbf{r}) = \rho_{\text{ox}} + \rho_{\text{me}} - \rho_{\text{me/ox}}$, where $\rho_{\text{me/ox}}$ is the total charge density of a supercell containing both alloy and oxide slabs; ρ_{ox} and ρ_{me} are the total charge densities of the same supercell containing a single slab of the oxide or the alloy. The section planes were chosen to give a better insight into the charge redistribution near interface bonds.

It is seen in Figure 4a that the formation of O_I–Al_I bonds results in weakening of the bonds between this O_I atom and the nearest Ti_{I+1} ones in the oxide. The latter can be seen by the appearance of pronounced charge depletion regions at the Ti_{I+1}–O_I bonds that leads to charge redistribution around Ti_{I+1} atoms. In accordance with the analysis of charge states performed within DDEC6 method [51–53], Ti_{I+1} atoms lose a smaller charge than those at the clean surface (1.99 el. instead of 2.13 el.), whereas the O_I atom gets additional 0.05 el. In comparison with that on the free oxide surface

(Table 3). Moreover, the overlap population of the $\text{Ti}_{I+1}\text{--O}_I$ bonds decreases significantly at the $\text{TiAl}(110)_{\text{Al}}/\text{TiO}_2(110)_{\text{O}}$ interface. We emphasize that the overlap population is used for the estimation of the bond strength. It should be noted that there is a charge depletion region between Al_{1I} atoms in the alloy. Charge states of these atoms change from -0.24 el. on the clean surface to $+0.69$ el. at the interface.

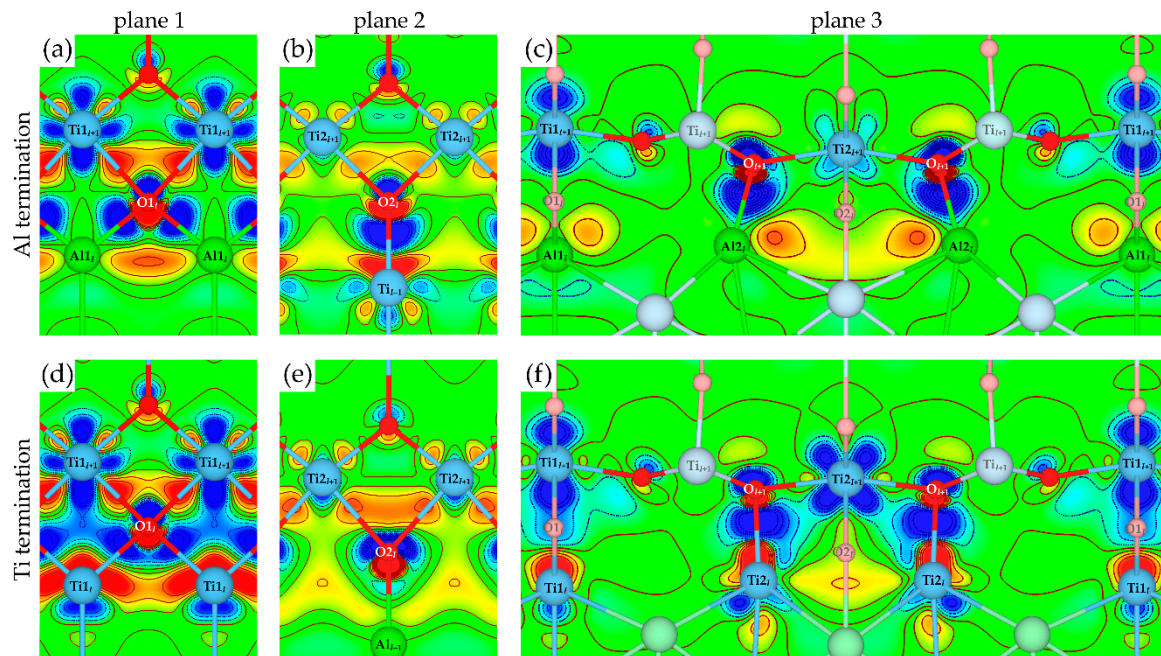


Figure 4. Distribution of the charge density difference ($\Delta\rho$) at the TiAl/TiO_2 interface in the case of the *hollow* configuration in planes shown in Figure 3c: (a–c) Al termination; (d–f) Ti termination. The regions of electron accumulation ($\Delta\rho < 0$) and depletion ($\Delta\rho > 0$) are given in blue and red, respectively. Contours go -0.1 to 0.1 el./ $\text{\AA}^3$ with an isoline spacing of 0.02 el./ $\text{\AA}^3$. Atoms being out of the figure plane are shown in lighter colors.

Figure 4b demonstrates that all Ti atoms surrounding the oxygen at the interface lose the charge: in particular, Ti_{2I+1} atoms have a charge smaller by 0.12 el. than on the free surface; Ti_{I-1} atoms lose 0.13 el., whereas the charge of O_{2I} atoms increases by 0.04 el. It is seen that a large charge accumulation region occurs at $\text{O}_{2I}\text{--Ti}_{I-1}$ bonds, which are responsible for the interface strength. The appearance of both accumulation and depletion regions at these bonds indicates a large covalent contribution in the chemical bonding. Indeed, one can see from Table 3 that the overlap population of the $\text{O}_{2I}\text{--Ti}_{I-1}$ bond is higher than that of the $\text{O}_{1I}\text{--Al}_{1I}$ one by 0.11 el. At the same time, ionicity of the latter bond is higher due to the large positive charge of the Al_{1I} atoms. It is necessary to emphasize that valence p -states of Al are less localized than Ti d -states, which allows them to be more easily involved in the interaction with oxygen. In addition, the in-plane average $\langle\Delta\rho(z)\rangle = \Delta\rho(z)/S$ is given in Figure S2a, where $\Delta\rho(z)$ is a result of in-plane integration of $\Delta\rho(\mathbf{r})$ over the plane and S is the area. It illustrates where the maximum of charge accumulation/depletion is located.

Interfacial $\text{O}_{I+1}\text{--Al}_{2I}$ bonds (Figure 4c) also have an ionic character, and a charge depletion region occurs mainly near Al_{2I} atoms. In spite of that, the $\text{O}_{I+1}\text{--Al}_{2I}$ bond length is almost the same as $\text{O}_{1I}\text{--Al}_{1I}$; the overlap population of the former is larger by 0.078 el. At the same time, Al_{2I} atoms lose a smaller charge in comparison with Al_{1I} (Table 3). All these features indicate that $\text{O}_{I+1}\text{--Al}_{2I}$ has a less ionic but more covalent character and the large charge accumulation region located near O_{I+1} atoms is conditioned primarily by charge redistribution rather than by charge transfer from the alloy atoms.

All mentioned peculiarities of O–Ti and O–Al bonds are still valid in the case of the $\text{TiAl}(110)_{\text{Ti}}/\text{TiO}_2(110)_{\text{O}}$ interface. Formation of the $\text{O}_{1I}\text{--Ti}_{1I}$ interfacial bonds (Figure 4d) leads to a weakening of $\text{Ti}_{I+1}\text{--O}_I$ bonds in the oxide (overlap population is almost one and a half times less (Table 3)), to the appearance of charge redistribution around Ti_{I+1} atoms and localized charge

depletion regions near $Ti1_I$ atoms. The charge state of $Ti1_I$ atoms changes from +0.16 el. on the clean alloy surface to +0.82 el. at the interface (Table 3). Formation of the $O2_I-Al_{I-1}$ bond (Figure 4e) leads to a decrease of charge transfer from $Ti2_{I+1}$ atoms in the oxide to $O2_I$ by 0.24 el. As a result, the charge at Al_{I-1} atoms decreases by 0.28 el. (Table 3). Figure 4f demonstrates $O_{I+1}-Ti2_I$ interfacial bonds, which have also pronounced ionic-covalent character. Although the $O_{I+1}-Ti2_I$ bond length is larger by 0.06 Å than the $O1_I-Ti1_I$ one, the overlap population changes insignificantly (by 0.02 el.). Additionally, $Ti2_I$ atoms have a smaller positive charge in comparison with $Ti1_I$. In general, Figure 4 demonstrates that all formed interfacial bonds have an ionic-covalent character and the formation of the interfacial bonds leads to a decrease of the chemical bonding in both oxide and alloy. The integrated $\Delta\rho(z)$ (Figure S2b) shows that the charge depletion region associated with Al interfacial atoms is more widespread through the slab than that connected with Ti interfacial atoms. This is connected with the nature of valence electrons in Al and Ti. Additionally, it is seen that charge transfer to O interfacial atoms is larger in the case of the $TiAl(110)_{Ti}/TiO_2(110)_O$ interface.

Table 3. Charge states of some interfacial and subinterfacial atoms (Q in el.), bond length between them (d in Å) and averaged overlap population (θ in el.) for pairs of the atoms in the case of the *hollow* interface configuration. The corresponding data for free surfaces of the alloy and the oxide are given also.

Atom	Q	d	θ	Atom	Q	d	θ
TiAl(110) _{Al} /TiO ₂ (110) _O				TiAl(110) _{Ti} /TiO ₂ (110) _O			
Ti1 _{I+1}	+1.99	2.20	0.183	Ti1 _{I+1}	+2.00	2.07	0.253
O1 _I	−0.93			O1 _I	−1.00		
Ti2 _{I+1}	+2.01	2.07	0.255	Ti2 _{I+1}	+1.89	2.23	0.183
O2 _I	−0.92			O2 _I	−0.83		
O1 _I	−0.93	1.89, 1.78 [28]	0.481	O1 _I	−1.00	1.98, 2.22–2.31 [30]	0.483
Al1 _I	+0.69			Ti1 _I	+0.82		
O2 _I	−0.92	1.92, 2.08 [28]	0.594	O2 _I	−0.83	2.07, 1.90 [30]	0.403
Ti _{I−1}	+0.42			Al _{I−1}	−0.02		
O _{I+1}	−1.00	1.90, 1.85 [28]	0.559	O _{I+1}	−1.14	2.04, 1.92 [30]	0.505
Al2 _I	+0.19			Ti2 _I	+0.51		
TiAl(110) _{Al} surface ¹				TiAl(110) _{Ti} surface			
Al _S	−0.24	2.90	0.277	Ti _S	+0.17	2.84	0.302
Ti _{S−1}	+0.29			Al _{S−1}	−0.30		
TiO ₂ (110) _O surface							
O _S	−0.88	1.85	0.406				
Ti _{S+1}	+2.13						
O _{S+1}	−1.13	1.95–2.03	0.279–0.340				
Ti _{S+1}	+2.13						

¹ Symbols S and $S - 1$ ($S + 1$) denote atoms of surface and subsurface layers in alloy (oxide).

Figure 5 demonstrates the local densities of states (DOSs) of the interfacial atoms for both interfaces in the case of the *hollow* configuration. It is seen that sharp peaks of subinterfacial O_{I+1} atoms lying at −7.2, −6.9, and −5.6 eV coincide well with similar peaks of $Al2_I$ (Figure 5a). Similarly, the thin structure of $O1_I$ DOS (position of some peaks) agrees well with that of the $Al1_I$ atom. The difference from the previous case is a wider spread of $O1_I$ and $Al1_I$ states toward negative energies. It should be noted that there is small density of states on both DOS curves for O_{I+1} and $O1_I$ atoms in the band gap, which is typical for metallic oxide due to the presence of the interface states induced by interaction with interfacial alloy atoms. It is known that the valence band of Ti atoms is almost unoccupied. The interaction of Ti_{I-1} with $O2_I$ results in the appearance of low-lying states, which spread in the region from −7.1 eV up to −3.4 eV. Additionally, the shift of the valence band of all O atoms, involved in the formation bonds through interface, toward negative energy is a consequence of charge transfer from nearest metal atoms. The increase of Ti unoccupied states in the region 0.4–0.9 eV is connected with the charge transfer from Ti to oxygen due to their interaction.

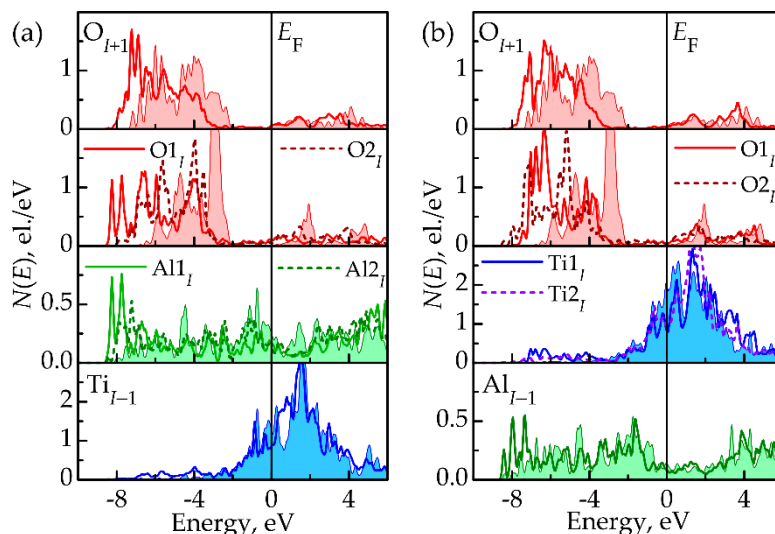


Figure 5. Local DOSs of the interfacial atoms for the *hollow* configuration at the TiAl/TiO₂ interface: (a) Al termination; (b) Ti termination. Shaded areas correspond to DOSs of atoms on the clean surfaces of the oxide and the alloy.

It is necessary to recall that Al *s,p*-states involved much more easily in the interaction with oxygen than Ti *d*-states, which is expressed in a stronger change of Al DOSs than that of Ti. As a result, at the interface with the Ti-terminated alloy surface (Figure 5b), the shift of occupied states of O_{I+1} and O1_I atoms is less pronounced than that in the previous case. However, the states of O2_I atoms interacting with Al_{I-1} atoms spread by 0.7 eV more toward negative energies. In general, DOS curves confirm strong interaction between interfacial atoms. Note that detailed comparison of DOS thin structures can be found in Figure S3.

Now we will discuss the difference in the structural characteristics of the present interfaces with *hollow* configuration and the most stable interfaces from papers [28,30]. The comparison of present interfacial bond lengths with those from paper [28] is given Figure 6a. Within our interface model, there are two O–Al bonds of 1.89 Å (1.78 Å [28]) and two of 1.90 Å (1.85 Å [28]), as well as one O–Ti bond of 1.92 Å (two bonds of 2.08 Å [28]), which are distributed over the area of 39.155 Å² (~22.95 Å² [28]). Thus, the total density of O–Al and O–Ti bonds (the number of bonds per unit area) is 0.102 Å⁻² and 0.026 Å⁻² within the present model and 0.174 Å⁻² and 0.087 Å⁻² according to [28], respectively. It is seen in Figure 6a that our interface model demonstrates about half of the bond density (0.128 Å⁻² in comparison with 0.261 Å⁻² in [28]) and weaker O–Al bonds (larger bond length than in [28]). At the same time, the O–Ti interaction is substantially stronger than that in [28]. The competition of these factors leads to a smaller value of the work of separation than that in [28], but the difference is not large.

In the case of the interface with the Ti-terminated TiAl(110) surface, the bond density is the same (only Al is replaced by Ti and vice-versa): O–Ti—0.102 Å⁻² with bond lengths of 1.98 and 2.04 Å; O–Al—0.026 Å⁻² with bond length of 2.07 Å. At the same time, the situation is quite different in [30]. As the TiO₂ atomic structure is much distorted in [30], formation of additional interfacial bonds is possible. Based on figures of atomic structure and tables with bond lengths from [30], we can conclude that there are four O–Ti bonds with length of 2.22 Å, four O–Ti bonds of 2.31 Å, two O–Ti bonds of 1.92 Å, two O–Ti bonds with unknown length (we can suppose that it is about 1.92 Å), and two O–Al bonds with a length of 1.90 Å per area ~45.9 Å² (Figure 6b). One can see that the bond density within the model from [30] is more than twice as high in comparison with the present model. Moreover, the lengths of some O–Ti and O–Al bonds in [30] are shorter than those in the present paper. As a result, a lower value of W_{sep} than that in [30] was obtained. It is known that compression in the interface plane results in an increase of interlayer distances and weakening of interatomic interaction inside the slab. In turn, that results in strengthening of interatomic interactions at the interface. This can explain the overestimation of the adhesion energy at the interface.

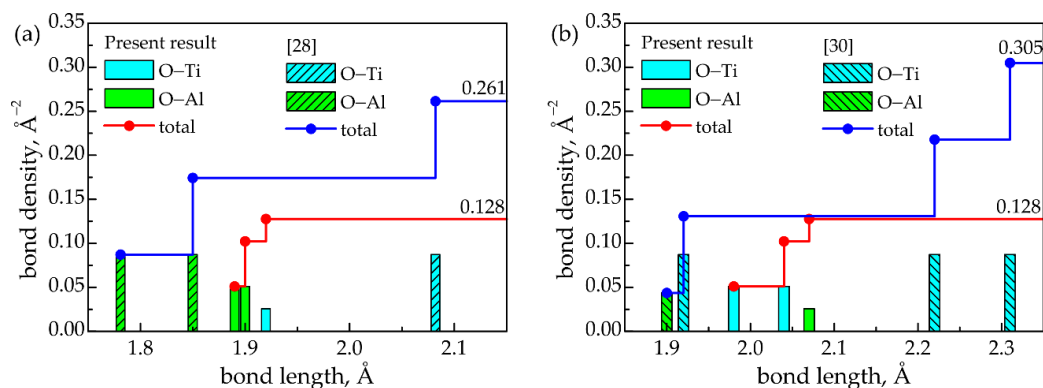


Figure 6. Bond density versus bond length at the TiAl/TiO₂ interface in the case of *hollow* configuration: (a) Al termination; (b) Ti termination.

It should be noted that cleavage between the oxide slab with the TiO-terminated (110) surface and TiAl(110)_{Ti} with O layer (violet plane in Figure S1a) leads to a value of 1.77 J/m², whereas it was equal to 1.53 J/m² in [30]. In accordance with the Griffith fracture theory [54,55], the fracture work (G) of bulk materials along a certain lattice plane can be estimated as double surface energy. If $G < W_{\text{sep}}$, the fracture will occur in the bulk material; otherwise, the fracture will occur at the interface. Our estimation of the surface energy of TiO₂ (Table 1) allows to conclude that the cleavage energy along the (110) plane between two stoichiometric surfaces needs only 0.92 J/m², which is lower than W_{sep} obtained for both considered interfaces with the *hollow* configuration. This means that mechanical failure may be initiated in the oxide.

Finally, we will not discuss the interface with the *top* configuration. The distribution of the charge density difference shown in Figure 7 allows us to understand the peculiarities of the chemical bonding at the interfaces and together with Table S1 the lower values of W_{sep} at them in comparison with the *hollow* configuration.

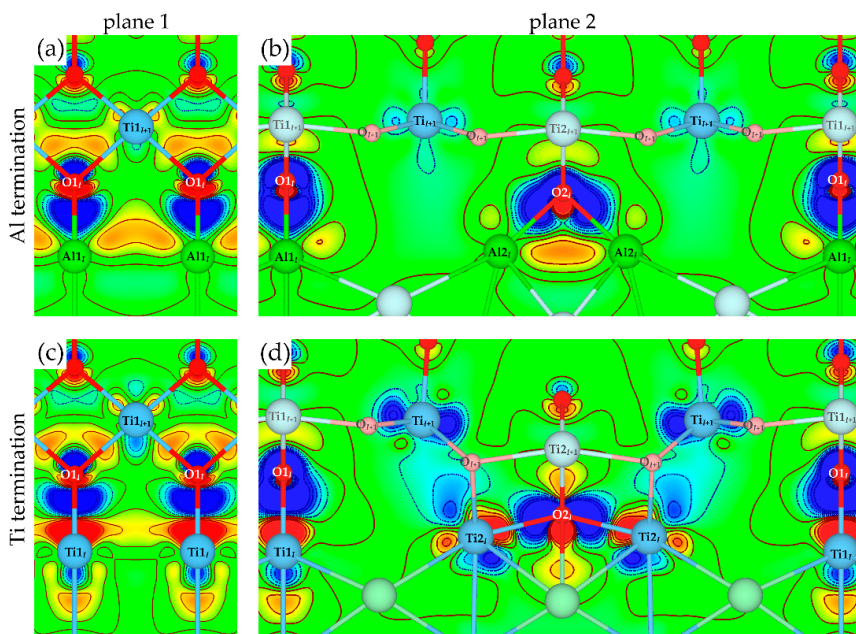


Figure 7. Distribution of the charge density difference ($\Delta\rho$) at the TiAl/TiO₂ interface in the case of the *top* configuration in planes shown in Figure 3d: (a,b) Al termination; (c,d) Ti termination. The regions of electron accumulation ($\Delta\rho < 0$) and depletion ($\Delta\rho > 0$) are given in blue and red, respectively. Contours go -0.1 to 0.1 el./Å³ with an isoline spacing of 0.02 el./Å³. Atoms being out of the figure plane are shown in lighter colors.

4. Conclusions

A comparative study of atomic and electronic structures of the TiAl/TiO₂(110) interface and its adhesion properties in dependence on the alloy surface termination was performed using the projector-augmented wave method. Within a more commensurable interface model than in [28,30], with a smaller misfit between the alloy and the oxide surface cells, the adhesive properties were clarified. The most preferred contact configuration was found to be the *hollow* one, in which one interfacial O atom locates above a Ti(Al) atom of the alloy subinterfacial layer and another interfacial O atom occupies the *short-bridge* position between two Al(Ti) interfacial atoms. The work of separation of 2.44 J/m² was obtained at the TiAl(110)_{Ti}/TiO₂(110)_O interface, whereas a lower value of 1.27 J/m² was calculated at the TiAl(110)_{Al}/TiO₂(110)_O one. The trend in the W_{sep} lowering in dependence on the alloy termination is consistent with that in [28,30]. Although the covalent contribution to chemical bonding is slightly higher at the interface with the Al-terminated TiAl(110) surface, charge transfer from metal to oxygen is higher at the interface with the Ti-terminated one. The overlap population analysis demonstrates that O–Ti bonds are stronger than O–Al ones at both interfaces. The interaction of titanium dioxide with the interfacial atoms of the alloy gives rise to the restoration of bonding in the bulk oxide. In general, the obtained small values of the work of separation at both interfaces are explained by the low bond density. In addition, it should be noted that the predicted adhesion at the TiAl/TiO₂ interface is considerably lower than that based on earlier obtained values of 10.43 J/m² at the TiAl(111)/Al₂O₃(0001)_O [56] and 11.02 J/m² at the Ti₃Al(0001)/Al₂O₃(0001)_O [57] interfaces. We hope that the interfaces with the oxide termination by an oxygen double layer will demonstrate much better adhesive properties as in the case of NiTi/TiO₂(100)_{2O} [58] because of the increase of both ionic–covalent contribution to chemical bonding and bond density. In general, the obtained results allow us to get a better insight into the mechanisms of oxide scale formation on the TiAl surface. Furthermore, it can be useful for the simulation of impurity effects on the adhesion at the interface, which is a subject of our forthcoming work.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/10/10/1298/s1>: Figure S1: Atomic structures of unrelaxed interfaces with *hollow* and *top* configuration in the case of the Ti-terminated alloy surface, Figure S2: In-plane average charge density difference at the interface with the *hollow* configuration; Table S1: Charge states of some interfacial and subinterfacial atoms (Q in el.), bond length between them (d in Å) and averaged overlap population (θ in el.) for pairs of the atoms in the case of the *top* interface configuration.

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