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First-principles investigation of effects of alloying elements on Ti/TiO_2 interface

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Abstract

The properties of the interface between titanium alloys and the rutile TiO_2 are crucial for improving oxidation resistance of titanium alloys. In this work, the first-principles method is used to predict the adhesion strength of the doped Ti/TiO_2 interface. The stability of the Ti/TiO_2 interface is enhanced by element Cr whereas reduced by element V. We also investigated the alloying elements segregation behavior near the Ti/TiO_2 interface. It is found that some elements, like V and Cr, tend to stay on the metal side of the interface. Hence, the oxidation resistance of titanium alloys has been increased by these alloying elements. This work not only helps us have a better understanding of the alloying atoms distribution in the Ti/TiO_2 interface but also find some clues of increasing the stability and oxidation resistance of titanium alloys.

Key words: first-principles method, Ti/TiO_2 interface, alloying effects, oxidation resistance

1. Introduction

Because of their low density, high strength and excellent corrosion resistance, titanium alloys are excellent candidates for application in aero engines and gas turbine components. In such applications, titanium alloys suffer from high working temperature. Poor oxidation resistance is one of the key obstacles to the practical application of this type of material at a temperature higher than 600 ℃. Improving the oxidation resistance is one of the key issues for the design of high-temperature titanium alloys.

At relatively low temperature, the thin layer of an oxide film (primarily rutile TiO_2 [1–4]) formed at the surface is protective. This is why titanium alloys possess excellent corrosion resistance at low temperature. At high temperature, the fast diffusion of oxygen through the oxide layer into the bulk results in excessive growth of oxide and embrittlement of the oxygen-enriched, near-surface alloy [5]. When the thickness increases to some extent, the oxide layer flakes from the alloy matrix due to the accumulation of stress at the interface between the oxide layer and the alloy matrix induced by their crystal lattice mismatch, which results in the loss of mass of the alloys. Alloying is believed to be an efficient method of solving the problem [6]. Alloying elements may increase the adhesive energy of the metal-oxide interface, which eventually enhances the oxidation resistance of the investigated system.

The growth of rutile on pure titanium exhibits a preferred direction in the experiment, with the Ti($10\bar{1}0$)/TiO_2(100) interface having the smallest mismatch [2]. In our previous work, the structure and cohesive property of the Ti($10\bar{1}0$)/TiO_2(100) interface have been investigated by using the first-principles method [7]. In the present work, we consider the alloying effects on the doped low-misfit Ti($10\bar{1}0$)/TiO_2(100) interface. First-principles calculation with density functional theory (DFT) is a powerful method to provide fundamental information on interfaces between two solids at the atomic level as well as at the electronic structure level [8, 9]. The purpose of this work is to determine the optimal atomic structure and energy of the alloying Ti($10\bar{1}0$)/TiO_2(100) interface. We attempt to investigate the alloying effects on the interface properties, including the interfacial bind-

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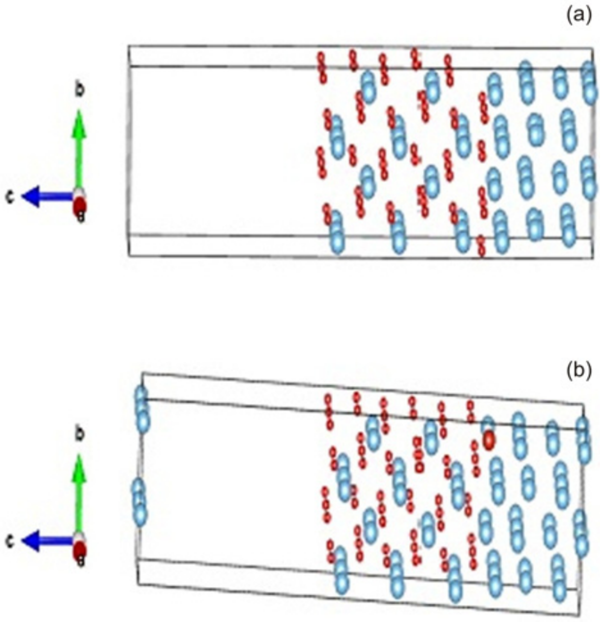

Fig. 1. A 2 × 2 supercell model of $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface (a) and a V-doped alloying $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface (b) with the V atom in red color.

ing energy as well as the alloying atoms distribution.

2. Calculation methodology

Previous work shows that the O-O-Ti terminated $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface is the most stable and has the largest interface adhesion energy [9]. Therefore, this interface configuration was chosen for constructing the supercell models of alloying interfaces in this work. It is also found that the $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface with the interface distance of 0.1 nm has the lowest system energy after comparing some interface energies with different distances between $\mathrm{Ti}(10\bar{1}0)$ and $\mathrm{TiO}_2(100)$ surface. We describe this phenomenon in the next part of the paper. As is shown in Fig. 1a, a 2 × 2 supercell model of $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface, which consists of 96 atoms, is devised for the present study. To accomplish the goal of alloying, one of the Ti atoms in the first layer of $\mathrm{Ti}(10\bar{1}0)$ surface was substituted by another alloying atom, for example, the V atom, which is presented in Fig. 1b. Both the interface and the surface models have the vacuum thickness of 1.5 nm.

The first-principle software Vienna Ab initio Simulation Package (VASP) [10], in which the valence electronic states are described using periodic plane waves, is used for the density functional theory (DFT) studies. The Kohn-Sham equation was solved iteratively using a plane wave basis set with a cutoff energy of 450 eV to represent the valence electrons. To describe the core–valence interaction, we used projector augmented wave (PAW) approach [11]. The electron exchange and correlation were treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functionals [12, 13]. The Brillouin-zone integrations were performed using Monkhorst-Pack (MP) grids [14] and a Gaussian smearing [15] of SIGMA = 0.2 eV. The ionic positions were relaxed using the conjugate gradient method for the interface model. A 4 × 3 × 1 Γ-centered k-point grid was used in the relaxation of the interfaces, while 4 × 4 × 1 grid was adopted for final energy calculation. The interface structure is visualized by the VESTA software program [16].

3. Results and discussion

It should be noted that the oxidation of titanium and its subsequent burning processes should be avoided. The theoretical modeling of the dynamics of titanium oxidation had been investigated recently by our group [17]. It is the $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface that has appropriately described oxidation processes in the titanium alloys. In this work, we present a DFT study of the doped alloying $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface, to determine the alloying effects on the stability and segregation properties across the interface.

3.1. Alloying effect on interface cohesion

The work of adhesion is used for measuring the binding strength at the interface. The larger absolute value of work of adhesion indicates the stronger binding strength of the interface. In this paper, the work of adhesion between the $\mathrm{Ti}(10\bar{1}0)$ surface and the $\mathrm{TiO}_2(100)$ surface was calculated by using the following definition:

$$W_{\mathrm{ad}} = (E^{\mathrm{interface}}_{\mathrm{Ti/TiO_2}} - E^{\mathrm{slab}}_{\mathrm{Ti}} - E^{\mathrm{slab}}_{\mathrm{TiO_2}})/S, \tag{1}$$

where the $E^{\mathrm{interface}}_{\mathrm{Ti/TiO_2}}$ is the total energy of $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface at a given distance between the surfaces of $\mathrm{Ti}(10\bar{1}0)$ and $\mathrm{TiO}_2(100)$, $E^{\mathrm{slab}}_{\mathrm{Ti}}$ and $E^{\mathrm{slab}}_{\mathrm{TiO_2}}$ are the total energies of free $\mathrm{Ti}(10\bar{1}0)$ and $\mathrm{TiO}_2(100)$ surfaces, respectively, and S represents the interface area.

At first, we attempt to find the most stable $\mathrm{Ti}(10\bar{1}0)/\mathrm{TiO}_2(100)$ interface by varying the distance between the surfaces of $\mathrm{Ti}(10\bar{1}0)$ and $\mathrm{TiO}_2(100)$. The work of adhesion calculated by Eq. (1) versus the distance between two surfaces is plotted in Fig. 2. It can be seen from the figure that the value of obtained W_{ad} is more negative with the decreasing inter-slab separations and is increasing again when the separation is

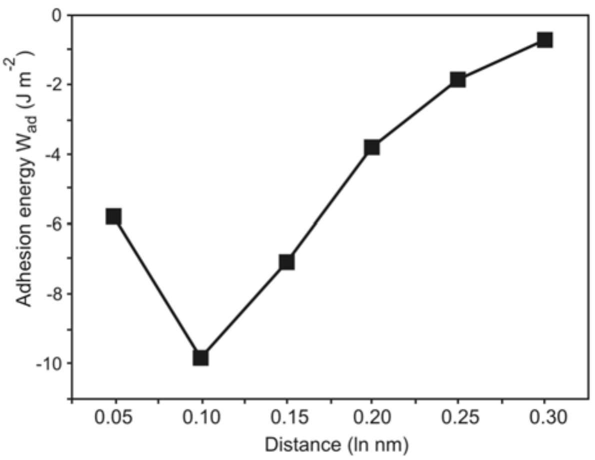

Fig. 2. The variation of the interface adhesion energy with the distance between surfaces of Ti(10$\bar{1}$0) and TiO$_2$(100).

Table 1. The calculated work of adhesion (adhesion energy) W_{ad} of the V and Cr doped alloying Ti(10$\bar{1}$0)/TiO$_2$(100) interfaces (pure Ti stands for the interface with no alloying element)

Alloying element	Adhesion energy (J m^{-2})
Pure Ti	–10.34 [9]
V	–9.01
Cr	–14.40
Sn	–9.95
Pb	–9.76

less than 0.1 nm for all the considered supercells. The Ti(10$\bar{1}$0)/TiO$_2$(100) interface with 0.1 nm inter-slab separation has the lowest interface system energy and the largest absolute value of interface adhesion energy, which represents the most stable interface configuration.

After the preparations mentioned above, we constructed the alloyed interface of 2 × 2 interface supercell and investigated the alloying effects on the stability and segregation properties of the Ti(10$\bar{1}$0)/TiO$_2$(100) interface. Table 1 presents the calculated work of adhesion W_{ad} of some doped alloying Ti(10$\bar{1}$0)/TiO$_2$(100) interfaces. Let us take the alloying elements of V and Cr as an example. As is shown in Table 1, the adhesion energy of V and Cr doped alloying interfaces is –9.01 and –14.40 eV, respectively. The element Cr has the potential of stabilizing the Ti(10$\bar{1}$0)/TiO$_2$(100) interface because this alloying interface adhesion energy is much higher than the pure Ti(10$\bar{1}$0)/TiO$_2$(100) work of adhesion of the interface. On the contrary, the V-doped alloying interface does not have strong affinity compared with the simple interface. Thus, this element can not be regarded as the proper candidate for alloying Ti(10$\bar{1}$0)/TiO$_2$(100) interface. The adhesion energies of the Sn and Pb-doped alloying Ti(10$\bar{1}$0)/TiO$_2$(100) interfaces are calculated and listed in Table 1. The adhesion energies of these doped alloying interfaces are comparable to the adhesion energy of pure Ti(10$\bar{1}$0)/TiO$_2$(100) interface. It could be concluded that both Sn and Pb have no obvious effects on the stability of the Ti(10$\bar{1}$0)/TiO$_2$(100) interface and the adhesion energy of the Ti(10$\bar{1}$0)/TiO$_2$(100) interface has been influenced only a little bit by these elements.

It is well known that the instability of the interface could result in the slide or dislocation of the interface. Indeed, the work of adhesion has a close relationship with the cleavage energy at the interface. The more work of adhesion, the more cleavage energy is needed to dissociate the interface. Hence, the work of adhesion is the determining factor for describing the stability of the interface.

3.2. Segregation of alloying atoms

In this work, we have determined where the alloying atoms locate (in bulk Ti, bulk TiO$_2$, Ti side of the interface layer, or TiO$_2$ side of the interface layer), i.e., the segregation behavior of the alloying atoms [18]. To this end, we calculated the total energies of the supercells with an alloying atom X in the center of Ti layers ($E_{\text{Ti-B}}$ for bulk-like Ti), in the center of TiO$_2$ layers ($E_{\text{TiO}_2\text{-B}}$ for bulk-like TiO$_2$), at the Ti side of

Table 2. The segregation energies of alloying atoms around the Ti(10$\bar{1}$0)/TiO$_2$(100) interface. $E_{\text{Ti-B}}$, $E_{\text{Ti-S}}$, $E_{\text{TiO}_2\text{-B}}$, and $E_{\text{TiO}_2\text{-S}}$ are the total energies with alloying atoms replacing a Ti atom in the center of bulk Ti layers, the interface layer at the Ti side of the interface, in the center of bulk TiO$_2$ layers, and the interface layer at the TiO$_2$ side, respectively, taking the $E_{\text{Ti-B}}$ as reference (the unit of energy is in eV)

Alloying element	$E_{\text{Ti-B}}$	$E_{\text{Ti-S}}$	$E_{\text{TiO}_2\text{-B}}$	$E_{\text{TiO}_2\text{-S}}$
V	0	9.15	4.68	1.58
Cr	0	–4.21	8.65	8.36
Sn	0	–21.15	–24.09	–20.28
Pb	0	–11.80	–12.84	–20.24

the interface layer ($E_{\text{Ti-S}}$), and at the TiO_2 side of the interface layer ($E_{\text{TiO}_2\text{-S}}$), respectively. The segregation energies are listed in Table 2, taking the total energy $E_{\text{Ti-S}}$ as reference.

Table 2 displays the segregation energy for some alloying elements in the Ti($10\bar{1}0$)/TiO_2(100) interface. As is seen in the table, different alloying atoms exhibit different segregation behavior. The system with V in the center of Ti layer has the lowest energy among the four considered configurations, i.e., V tends to stay in the bulk of Ti side. The favorite locations for Cr, Sn, and Pb are the interface layer at Ti side, in bulk TiO_2, and the interface layer at the TiO_2 side, respectively. The Cr atom prefers to be in the neighborhood of the interface, which means that Cr is the most suitable alloying element used for oxidation resistance in coating technology. When the alloying atom prefers to be in the metal matrix rather than in the oxide side, it means that the alloying atom tends to stabilize the titanium metal and increase its oxidation resistance. Alternatively, the metal is oxidized to form the corresponding oxide.

4. Conclusions

As a basic approach for improving the properties of the metal material, alloying of the Ti/TiO_2 interface has a large impact on the adhesion ability of the interface. In this work, the effects of alloying elements (V, Cr, Sn, and Pb) on the adhesion and segregation of Ti($10\bar{1}0$)/TiO_2(100) interface were theoretically investigated using the first-principles method. The main results are summarized as follows:

1. The alloying element Cr can enhance the stability of the Ti/TiO_2 interface.
2. V tends to stay in the bulk of Ti side. The favorite locations for Sn and Pb are in bulk TiO_2 and the interface layer at the TiO_2 side, respectively.
3. The alloying element Cr is found to stay at the interface layer at Ti side, and, therefore, may increase the oxidation resistance.

Overall, this work helps us find some clues of improving the interface adhesion strength and oxidation resistance of the titanium alloys.

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