

First-principles studies of the influences mechanism of Y, Hf elements on the high temperature oxidation of γ -TiAl alloys

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Abstract. The influences mechanisms of Y, Hf elements on the high temperature oxidation of γ -TiAl alloys were studied by using a first-principle plane wave pseudopotential method within the density functional theory. It is shown that Y, Hf atoms segregate to the γ -TiAl surface by substituting Ti atoms, and Y atom is easier to segregate than Hf. Y, Hf atoms segregated at γ -TiAl surface decrease the adhesion of O and γ -TiAl surface, which decreases the oxidation rate of γ -TiAl alloys and thereby hinders the growth of oxide films. The electron structure calculations suggest that the interaction between O and Ti, Al, Y, Hf atom exists both ionic and covalent binding characteristics, the decrease of the adhesion of O and γ -TiAl surface with the doped Y, Hf is mainly attributed to the weaken covalent interactions. As a result, the results obtained by first principles can make us get a deeper understanding of the mechanism of the segregation of Y, Hf to the γ -TiAl surface and the influence mechanism of surface active elements Y, Hf on the initial oxidation of γ -TiAl alloys.

1. Introduction

The γ -TiAl based alloys exhibit a large number of outstanding properties such as high melting point, low density and high specific strength. Therefore they are being considered as prospective structural materials for applications in aerospace, automobile and energy industries. However, its oxidation resistance can not satisfy the demands for increased operating temperatures, which limits the practical application of TiAl alloys [1]. Similar activities of Ti and Al result in the formation of titania and alumina simultaneously on TiAl alloys. Compared with alumina, titania has high diffusivity and poor protectiveness. This results in the poor oxidation resistance of TiAl alloys at temperatures higher than 1073 K [2]. Therefore the selective oxidation of Al on TiAl alloys surface for improving the oxidation resistance of γ -TiAl was in focus of both experimental and theoretical researches all the time. In 1992, Becker et al. [3] found that the small amounts of addition of Nb to TiAl leads to the formation of a protective Al_2O_3 layer at the metal/scale interface which is very resistant to thermal cycling. The improvement of oxidation resistance by Si is mainly attributed to promoting the formation of continuous and dense Al_2O_3 layer in the oxide scale on TiAl alloys during the initial stages of oxidation [4]. The addition of W element can significantly reduce the oxygen solubility in the TiAl alloys. Owing to this effect, the internal oxidation is inhibited in the alloy [5]. Taniguchi et al [6] found that the addition of Hf is very effective in decreasing the overall oxidation rate at temperature up to 1300K. The excellent oxidation resistance is attributable to the formation of alumina-rich layers



in the scale. Wu et al [7] found that the addition of small amounts of Y was effective in enhancing the oxidation resistance of TiAl-1.4Mn-2Mo-0.3C alloy. They thought that this improvement was due partly to the improved adhesion of the scale and due partly to the formation of a continuous Al_2O_3 layer in the outer scale.

On the theoretical side, Li et al [8] revealed that the abilities of interstitial oxygen and Ti vacancy formation are lowered by Nb addition, thus the diffusion of oxygen and Ti is reduced correspondingly, which enhances the oxidation resistance of TiAl alloy. Wu et al [9] studied the effect of Nb on the bonding characteristics of TiAl alloys. The results suggest that Nb reduces the interactions between Ti and O, and enhances the interactions between Al and O. Meanwhile, with the introduction of Nb, the formation energy barrier of TiO_2 is increased, while the generation of Al_2O_3 is facilitated due to the decrease of the formation energy barrier. Liu et al [10] found that the surface segregation of Si makes the interactions between O and Al atoms stronger whereas those between O and Ti weaker, which is benefit to the nucleation of Al_2O_3 .

However, to the best of our knowledge, there is few theoretical studies reported dealing with the influence of the reactive elements (e.g. Y and Hf) on the high temperature oxidation of TiAl alloys. Thus in this paper, we presents a first principles study on the effect of Hf, Y on O adsorption on the surface of γ -TiAl alloys to reveal the effect mechanism of Hf, Y on the high temperature oxidation of γ -TiAl alloys.

2. Calculation Method and Models

2.1. Calculation Method

In this study, we utilized the CASTEP[11] based on the density function theory (DFT) in MS6.0. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional form was used to describe the exchange-correlation energy [12]. The electron-ion interaction was described with ultra-soft pseudo-potential [13]. The structure models have been relaxed according to the BFGS algorithm [14]. The geometry optimization is completed with a convergence tolerance of energy of 2.0×10^{-5} eV/atom, a maximum force of 0.05 eV/nm, a maximum displacement of 0.02nm and a maximum stress of 0.1GPa. A kinetic energy cut off of 300 eV and a $4 \times 4 \times 1$ K-point mesh for all the electronic structure calculations.

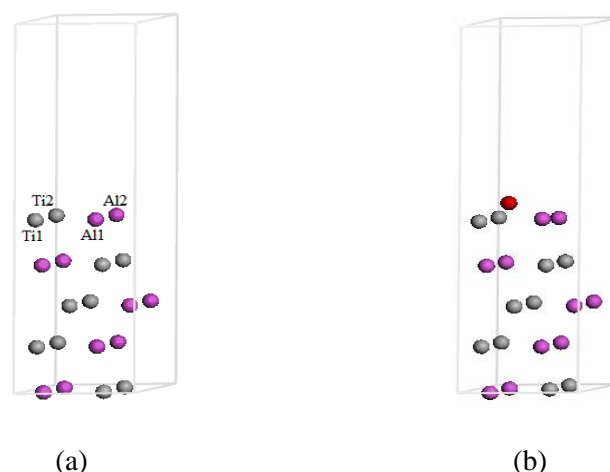


Figure 1. Models of clean (a) and O adsorbed (b) (2×2) γ -TiAl(111) surfaces (Red, pink and gray balls represent O, Ti and Al atoms, respectively).

2.2. Models

The γ -TiAl (111) surface was modeled by a (2×2) supercell of a slab of 5 γ -TiAl (111) layer separated by a 1.1nm-thick vacuum layer. In Ref.15, we found that the most stable sites for O adsorption on γ -TiAl alloy surface are the hcp-Al adsorption sites. In the following, we just discuss the hcp-Al adsorption sites. Figure1(a) shows the clean γ -TiAl (111) (2×2) surface, and figure1(b) represents the γ -TiAl (111) (2×2) surface with O adsorption at hcp-Al sites. When considering the doping of the reactive elements, Y, Hf atom substitutes Ti1 or Al1 atom at the γ -TiAl (111) surface. In our calculations, the three metal layers below the surface were allowed to relax.

3. Results and discussion

3.1. Surface segregation of Hf, Y.

The formation energy of a defect (dopant) is a crucial factor in determining its doping concentration. The lower the formation energy of a defect is, the higher the doping concentration is. One Hf or Y atom substitutes one Ti (or Al) atom in γ -TiAl or at γ -TiAl(111), the impurity formation energy is defined as:

$$E_{imp}^X = E_t^{X-Y \text{ or } Hf} - E_t^X + E_{Ti \text{ or } Al}^{bulk} - E_{Y \text{ or } Hf}^{bulk} \quad (1)$$

Where X represents the γ -TiAl(111) surface or the γ -TiAl bulk; E_t^X and $E_t^{X-Hf \text{ or } Y}$ represent the total energies of X and Hf or Y-doped X; $E_{Ti \text{ or } Al}^{bulk}$ and $E_{Y \text{ or } Hf}^{bulk}$ are the total energies of one Ti or Al and one Hf or Y atom in their bulk states, respectively.

The tendency of an impurity atom to segregate to the surface can be characterized by the surface segregation energy E_{seg} defined as [8]

$$E_{seg}^{sur} = E_{imp}^{sur} - E_{imp}^{bulk} \quad (2)$$

Where E_{imp}^{sur} and E_{imp}^{bulk} donate the impurity formation energy of RE (Hf and Y) at the surface and in the bulk, respectively. A negative E_{seg} indicates that impurity atom is energetically favourable to segregate to the surface. The lower the segregation energy, the stronger the degree of an impurity atom to segregate to the surface is.

The impurity formation energies of Hf and Y in the bulk and at the surface are calculated by equation (1), and the surface segregation energies of Hf and Y are obtained by equation (2). The results are listed in table 1.

Table 1. The calculated impurity formation energies E_{imp} (eV) of Hf, Y at the γ -TiAl(111) surface and bulk γ -TiAl and surface segregation energy

E_{seg} (eV) of Hf, Y at the γ -TiAl(111) surface.					
substituted		Bulk		Surface	
		Ti	Al	Ti	Al
Y	E_{imp}	1.569	2.172	0.146	0.288
	E_{seg}			-1.423	
Hf	E_{imp}	-0.022	4.058	-0.403	0.0225
	E_{seg}			-0.381	

From table 1, it can be seen that the impurity formation energies of Hf or Y substituting for Ti atom, no matter in the bulk or on the surface, are lower than that of Hf or Y substituting for Al atom. This indicates that only Ti atoms in the bulk or on the surface can be substituted by Hf, Y atoms. The

surface segregation energies of Y, Hf calculated with equation (2) are negative, which indicates that Y, Hf atom can segregate to the surface. The surface segregation energy of Y is more negative than that of Hf, which suggests that Y has a stronger segregation tendency to the surface than Hf.

The surface segregation of Y, Hf will influence the composition of the oxide scale and the phase formation. Due to the strong affinity among Y and O atoms, the formation of Y_2O_3 and Y-rich multiphase (Y, Al) O oxides would impede the oxygen transport and the growth rate of the oxide scale.

3.2. The effect of Hf, Y on O adsorption on the γ -TiAl surface

The adsorption energy is an important physical quantity in the surface problem, the higher the adsorption energy, the more stable the surface adsorption is. The adsorption energy of O atom is defined as [8]

$$E_{ads} = -\frac{1}{N}(E_{O/TiAl(111)} - E_{TiAl(111)} - \frac{N}{2}E_{O_2}) \quad (3)$$

Where $E_{O/TiAl(111)}$ is the total energy of a given surface slab containing the pure γ -TiAl surface or the Hf, Y alloyed γ -TiAl surface, $E_{TiAl(111)}$ is the corresponding energy of the bare slab. E_{O_2} is the total energy of an oxygen molecule, which is determined by the optimization of a 1nm cube with O_2 at eight corners. N is the number of adsorbed O atoms on the γ -TiAl(111) surface (here, N=1). According to the definition by equation (3), a positive adsorption energy indicates an exothermic chemisorption of oxygen onto the alloy surfaces. The larger the value of the adsorption energy, the stronger the interaction between O and γ -TiAl(111) surface is, the more possible the adsorption of O will happen, and the more stable the surface adsorption is. The adsorption energies of O atoms adsorbed on clean and Y, Hf segregated surfaces were calculated by equation (3) to be 6.040, 5.237, 5.543 eV respectively, thus it can be seen that the segregation of Y or Hf to γ -TiAl surface lowers the binding energy of O to the γ -TiAl(111) surface. As a result, the initial oxidation rate of γ -TiAl alloy decreases, and the growth the oxide scale is impeded.

3.3. Electronic structure analysis

In order to further analyze the influence mechanism of the surface active elements to the high temperature oxidation of γ -TiAl alloys, the density of states (DOS) of O, Al, Ti, Ti2 (Ti1 is replaced with the doped atom), Y, Hf atoms of the clean and the alloying element segregated O/ γ -TiAl(111) surface systems are calculated and shown in figure 2. For the clean O/ γ -TiAl(111) surface system (see figure 2(a)), the s and p orbitals of Al hybridize with s, p and d of Ti in the nearly whole energy range, indicating a strong covalent bonding combined with the metal-metal valence characteristics. It is clearly that a peak hybridized with O_{2s} orbital and Al_{3p} orbital appear near energy level of -20 eV. The 2p orbital of O hybridize with 3s, 3p of Al in the -10 to -4 eV energy range, while the hybridization of p orbital of O with 4s, 4p, 3d of Ti in the -10 to -4 eV energy range is weak. All these reflect that oxygen adsorption results in the formation of new Ti-O and Al-O bonds, but the Ti-O bond is weaker than and Al-O bond. The existence of Ti-O and Al-O bonds weakens the original Ti-Al bonds.

For the Y segregated O/ γ -TiAl(111) surface systems (Ti1 is replaced with Y) shown in figure 2(b), the interactions between O_{2p} and Al_{3p} electrons are also strong, but the interactions between O_{2p} and Y_{4d} electrons are weak (the peak of Y_{4d} energy level of -5 eV is very small), thus it can be seen that a weaker covalent bonding forms between Y and O. After the substitution of Ti1 with Hf, it is obviously seen from figure 2(c) that the density of states of Hf_{5d} is very different from that of Ti_{3d} (compared with figure 2(a)), the density of states of d orbitals Hf is obviously lower than that of Ti1 and Y, indicating a large change of the bonding behavior. The numerical discussion will be given in next section.

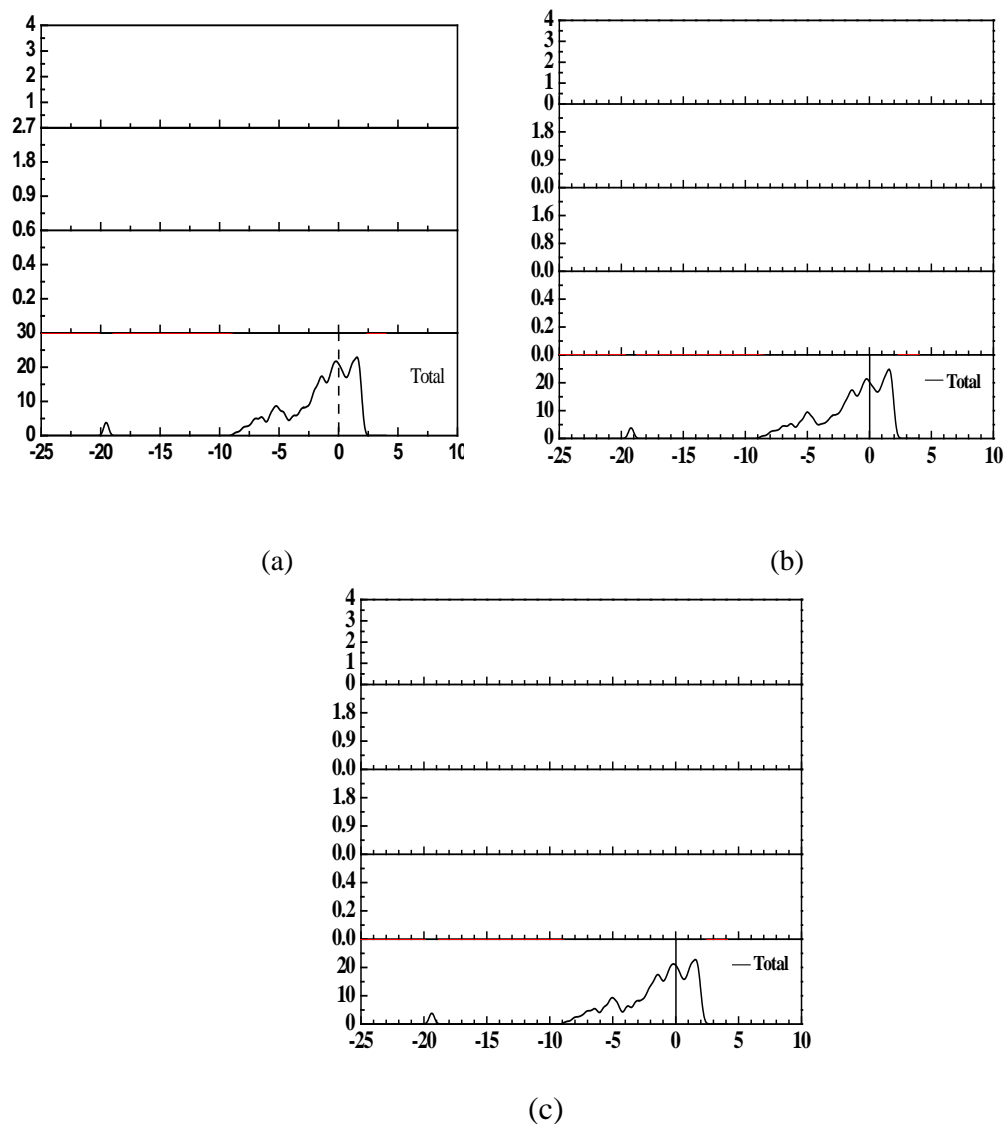


Figure 2. The PDOS of atoms at the clean(a) and the Y(b), Hf (c) segregated O/ γ -TiAl(111) surface systems, and the TDOS of each system.

3.4. Population analysis

The Mulliken overlap populations per unit bond length indicate the overlap degree of electron clouds of two bonding atoms and can be used to quantify the covalent bond strengths [14]. The results of Mulliken population between O and neighbor atoms on the clean and Y, Hf segregated O/ γ -TiAl(111) surface systems are given in table 2. The atomic labeling is shown in figure 1, Y, Hf replaces Ti1.

For the pure O/ γ -TiAl(111) surface system, the overlap population per unit bond length values of O-Ti1, O-Ti2 bonds are smaller than that of O-Al1, indicating stronger covalent interaction between O and Al1. For the Y segregated O/ γ -TiAl(111) surface systems, the population values of O-Y, O-Al1 bonds decrease obviously, while that of O-Ti2 increases. In general, Y substitution for Ti1 reduces the adhesion of O to the γ -TiAl(111). For the Hf segregated O/ γ -TiAl(111) surface systems, the population value of O-Hf bond decreases obviously, the population value of O-Al1 basically does not change, but that of O-Ti2 increases. In general, Hf substitution for Ti1 also reduces the adhesion of O to the γ -TiAl(111) surface. In addition, it can be seen from table 2 that the influence of Y on the

adhesion of O to the γ -TiAl(111) surface is stronger than that of Hf. All these results are consistent with the above discussions of the O adsorption energy and DOS. The surface segregation of Y, Hf reduces the adhesion of O to the surface, thereby reducing the initial oxidation rate of γ -TiAl alloy and improving the oxidation resistance of γ -TiAl alloys.

Table 2. The overlap population per unit bond length of each bond (P_B/L_B) at the pure and segregated O/ γ -TiAl(111) surface systems.

O/ γ -TiAl (111)		Y segregated O/ γ -TiAl (111)		Hf segregated O/ γ -TiAl (111)	
Bond	$P_B/L_B/\text{\AA}^{-1}$	Bond	$P_B/L_B/\text{\AA}^{-1}$	Bond	$P_B/L_B/\text{\AA}^{-1}$
O-Ti 1	0.170	O-Y	0.103	O-Hf	0.131
O-Ti 2	0.170	O-Ti 2	0.216	O-Ti 5	0.178
O-Al1	0.206	O-Al 1	0.173	O-Al 1	0.223

The strength of the ionic bond between atoms is generally determined by the amount of transferred charge. So we performed the calculations of the loss or gain of charge of atoms at the clean and Y, Hf segregated O/ γ -TiAl(111) surface systems. All calculated values are given in table 3. The atom numbering is shown in figure.1.

Table 3. The loss or gain of charge of atoms at the pure and Y, Hf segregated O/ γ -TiAl(111) surface systems (e).

O/ γ -TiAl (111)		Y segregated O/ γ -TiAl (111)		Hf segregated O/ γ -TiAl (111)	
atom	net charge	atom	net charge	atom	net charge
O	-0.78	O	-0.76	O	-0.78
Ti 1	0.40	Y	0.28	Hf	0.08
Ti 2	0.41	Ti 2	0.64	Ti 2	0.63
Al 1	0.28	Al 1	0.15	Al 1	0.27

For the pure O/ γ -TiAl(111) surface system, as seen from table 3, the adsorbed O atom on the surface gains charges, while those metal atoms at the surface lose charges, so the bonding of the adsorbed O to the surface has a partial ionic component. For the Hf segregated O/ γ -TiAl(111) surface systems, the amount of charge obtained O is almost not change. For the Y segregated O/ γ -TiAl(111) surface systems, the amount of charge obtained O is reduce slightly. Thus it can be seen that Y,Hf has little influence on the ionic interaction of the adsorbed O atom with the γ -TiAl(111) surface.

4. Conclusions

We have investigated the influences mechanisms of Y and Hf surface reactive elements on the high temperature oxidation of γ -TiAl alloys by using first-principles calculations. Through the studying, we get the following conclusions:

- The calculations of the impurity formation energies and the surface segregation energies show that Y, Hf atoms segregate to the γ -TiAl surface by substituting Ti atoms, and Y atom is easier to segregate to the γ -TiAl surface than Hf.
- The results of the adsorption energy of O atom on the γ -TiAl surface show that the segregation of Y, Hf atom at γ -TiAl surface decreases the adhesion of O to the γ -TiAl surface, which decreases the oxidation rate of γ -TiAl alloys and thereby hinders the growth of oxide films. The influence of Y on the adhesion of O to the γ -TiAl surface is stronger than that of Hf.
- The calculations of DOS, the overlap population and the loss or gain of charge suggest that the interaction between O and Ti, Al, Y, Hf atom exists both ionic and covalent binding

characteristics, but the decrease of the adhesion of O to γ -TiAl surface with the segregated Y, Hf is mainly attributed to the weakened covalent interactions between O and γ -TiAl surface, and there is no direct relationship between the decrease of the adhesion of O to γ -TiAl surface and the ionic binding of O to γ -TiAl surface.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China under Grant No.51371049

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