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The Impurity Influence on the Formation of Oxide Layers on TiAl Surface

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Abstract. Using *ab initio* approach the segregation of *4d* impurities to low index TiAl surfaces was studied. The site preference for all considered impurities was determined. We demonstrate that Y, Zr, Nb и Mo prefer to occupy the Ti-sublattice whereas other elements are located mainly on the Al-sublattice in case of their low concentration. The influence of impurities on oxygen adsorption on the stoichiometric γ -TiAl(100) surface is investigated. It is shown that the *4d* impurities substituting for Ti result in decrease of oxygen adsorption energy whereas it increases if transition metal impurities occupy the Al-sublattice. The effect of some elements of V and VI groups on the adhesion at interfaces such as TiAl(001)_{Al}/TiO₂(001), TiAl(001)_{Ti}/TiO₂(001), TiAl(100)/TiO₂(001), TiAl(110)_{Al}/TiO₂(100)_O and TiAl(110)_{Ti}/TiO₂(100)_O in dependence on their location in interfacial layers was also studied. Finally, we demonstrate that the *4d* alloying elements with number of electrons from 2 to 5 lead to decrease of the relative stability of Al₂O₃ to TiO₂ and to increase of the formation energy of O vacancy in TiO₂. The latter is beneficial to the oxidation resistance of TiAl alloys.

INTRODUCTION

Titanium aluminides are considered as promising structural materials for the aerospace, aviation, automotive and other industries due to optimal relation of strength and weight. They have good mechanical properties, in particular, high specific strength and melting point, high elastic modulus, elasticity, good creep and heat resistance [1]. The formation of a dense oxide layers with a corundum α -Al₂O₃ structure on surface of Ti-Al alloys with low content of titanium provides high corrosion resistance. However, such alloys are rather brittle materials [1]. At the same time the alloys with larger content of titanium have the insufficient corrosion resistance that limits their use at high temperatures. The latter is related with growth of mixed oxide layers of TiO₂ and Al₂O₃ which were experimentally detected in [2]. The chemical activity of aluminum decreases with increasing titanium content [1, 3] that in combination with the thermodynamic characteristics implies a higher stability of interfaces with TiO₂ than with Al₂O₃. However, Al₂O₃ is found on the surface of Ti–Al alloys even at low temperatures. The outer layers of the oxide films, which are not in contact with the alloy, undergo cracking and partial spallation [1, 4, 5]. Alloying of titanium aluminides with various elements (Al, Sn, Mo, Zr, Ta, Nb, etc.) or even with a combination of elements can improve their functional properties. However, the impurity segregation to alloy surface can affect the mechanisms of alloy oxidation and formation of oxide layers, and also stability and strength of alloy–oxide interfaces. In this connection it is very important to understand the influence of impurities on the processes on external and internal interfaces. Since it is rather difficult at the microscopic level to obtain experimentally information about the initial stage of alloy oxidation, the importance of theoretical approaches within the density functional theory (DFT) increased considerably in last two decades. The DFT methods enable to get the energy characteristics which are useful for understanding surface and interface processes. The goal of this work is theoretical investigation of *4d* impurities segregation to TiAl surfaces and their influence on the O adsorption and also on adhesion at metal–oxide interface.

COMPUTATIONAL DETAILS

The atomic and electronic structures of the TiAl alloy were calculated by the projector augmented wave (PAW) method in a plane wave basis [6] using the generalized gradient approximation for an exchange-correlation functional. The plane-wave cut-off energy was 550 eV. In the electronic structure calculation, the integration over the Brillouin zone was performed using k -points mesh of $7 \times 7 \times 1$ for low-dimensional structures and k -points mesh of $7 \times 7 \times 7$ for bulk alloy. Atomic positions were relaxed using the Newton dynamics until the force at an atom was ~ 0.01 eV/Å. In order to simulate γ -TiAl(001), (110) and (100) surfaces, an eleven layer slab model was used with a vacuum region of ~ 15 Å between slabs. The alloy-TiO₂ interface was modeled by eight atomic layers of alloy and seven-eighteen atomic layers of oxide depending on interface orientation.

The oxygen adsorption energy was calculated by the formula

$$E_{\text{ads}} = -[E(\text{O-TiAlMe}) - E(\text{TiAlMe}) - 1/2 E(\text{O}_2)], \quad (1)$$

where $E(\text{O-TiAlMe})$ and $E(\text{TiAlMe})$ are the total energies of the systems with and without oxygen, and $E(\text{O}_2)$ is total energy of O₂ molecule, Me— $4d$ elements. Adhesion energy at the alloy-oxide interface was calculated as

$$W_{\text{ad}} = [E(\text{TiAl}) + E(\text{TiO}_2) - E(\text{TiAl/TiO}_2)]/S, \quad (2)$$

where S is the area of the interface.

RESULTS AND DISCUSSIONS

Intermetallic γ -TiAl alloy represents the alternated atomic layers containing of Al or Ti atoms in the [001] and [110] direction, therefore, the (001) and (110) surfaces may be terminated by Ti or Al whereas (100) and (011) surfaces have the stoichiometric composition. We remind that the TiAl(100) surface is most stable in a Ti-rich region whereas the Al-terminated TiAl(110) surface is stable in an Al-rich region [7, 8]. In the limit of high aluminum concentrations, the surface energies of TiAl(001)_{Al} and TiAl(110)_{Al} are almost the same. Segregation energies of $4d$ -elements to (001), (110) and (110) surfaces of TiAl alloy are given in Fig. 1.

It is seen that almost all $4d$ elements except Nb and Mo tend to segregate to TiAl(001)_{Ti} and TiAl(110)_{Ti} surfaces which have higher surface energies in comparison with Al-termination of these surfaces. In case of stoichiometric TiAl(100) surface Nb, Mo and Tc prefer to be in subsurface layers if they substitute for Ti. In case of Ru its segregation energy to surface layer is a little bit higher than in subsurface layer. The impurity of the beginning and end of $4d$ period prefer to segregate to (100) surface. At the same time our calculations demonstrate that the impurities of the beginning of the d -periods (Y, Zr, Nb and Mo) prefer to occupy the Ti-sublattice whereas other $4d$ elements prefer the Al or site occupancy preference differs insignificantly and depends on the impurity concentration (Fig. 2a). As was shown in [9] with increase of impurity concentration the probability of impurity atoms to occupy both sublattices is increased. In Fig. 2b the impurity influence on the O adsorption energy on TiAl(100) is shown. There are two hollow H-sites (H_{Al} and H_{Ti}) in the center of rectangle above Al and Ti subsurface atoms with small difference of 0.22 eV in E_{ads} . It is seen from Fig. 2b that almost all considered $4d$ elements substituting for Ti result in decrease of E_{ads} and the change is more pronounced for H_{Ti}-site. However, the O adsorption energy increases if impurities occupy Al-sublattice. It is interesting that Y, Pd, Ag and Cd result in the change of site preference for the O adsorption. The analysis of local densities of states (DOS) and interatomic bond lengths provide explanation of E_{ads} increase/decrease.

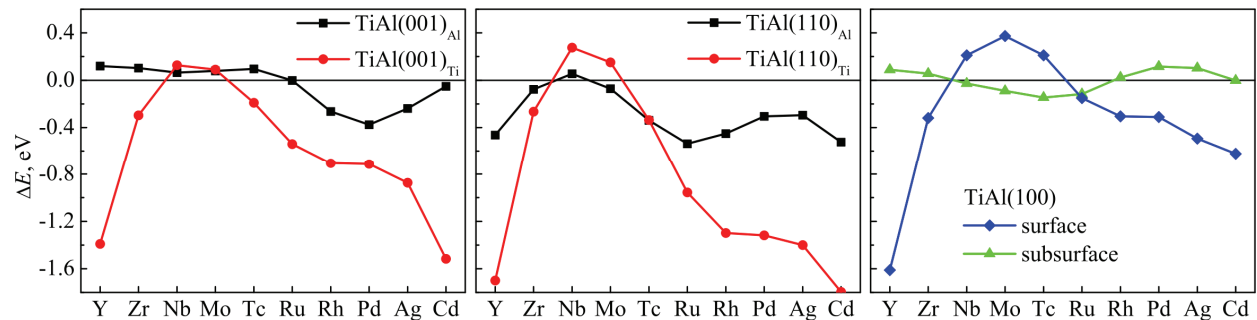


FIGURE 1. Impurity segregation energy to the differently-oriented surfaces of TiAl alloy (the negative values denote the possibility impurity segregation towards surface)

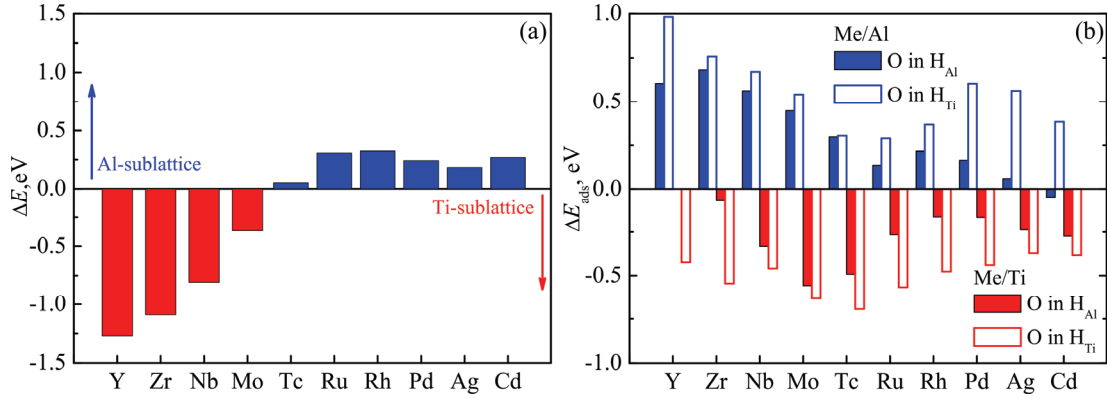


FIGURE 2. The difference in the defect formation energy in case of Ti and Al substitution by impurities (a) and the change in oxygen adsorption energy for doped TiAl(100) versus dopant (b)

To get the better insight into the nature of oxygen adsorption on doped TiAl(100) surface the local DOS were calculated. For example, in case of Al substitution by Zr atom (Fig. 3a) the appearance of additional Zr *d* bonding states in the energy region of -8 to -4 eV results in increase of E_{ads} due to increase of hybridization energy. As can be seen from Fig. 3b, the opposite situation occurs if Pd atom substitutes for Al one: almost fully occupied Pd *d*-states practically don't interact with O *s*-, *p*-states. We remind that O atom prefers to form ionic bond with metal alloy surface and to occupy adsorption sites which provide electrons to fill its *p*-band. In this connection it is much easier for O to get electrons from transition metal atoms with partial occupied band. In case of Pd on Al-sublattice, oxygen adatom shifts away from it and the O–Pd interatomic distance increases by 0.92 \AA in comparison with O–Al one on undoped surface. Significant increase of O interaction with Ti and Al surface atoms partially compensates the breaking of O–Pd bond that leads to small change in the adsorption energy. Substantial drop of E_{ads} in case of Ti substituted by Zr in H_{Ti} -site (Fig. 3c) is conditioned by structural factors: in spite of the O–Zr hybridization is similar to O–Ti one on undoped alloy surface, there is the breaking of two O–Al bonds. It is seen from Fig. 3d that Pd on Ti-sublattice doesn't form bond with oxygen as in case of its location on Al-sublattice and the increase of O–Al and O–Ti hybridizations take place also. The increase/decrease of oxygen–metal interatomic bonds is indicated in Fig. 3. Thus, the competition of structural and electronic factors determines the change in the adsorption energy due to impurity presence in the alloy surface layer. In case of impurity atom in the subsurface layer its influence on O adsorption energy is less pronounced. The impurity influences indirectly but through its hybridization with surface and subsurface Ti and Al atoms

It is seen from Table 1 that the adhesion energy at the interfaces with Ti-termination of alloy is higher than that at the interfaces with Al-termination due to stronger O–Ti hybridization in comparison with O–Al one. On the stoichiometric TiAl(100) surface the adhesion energy is almost equal to average value for both terminations.

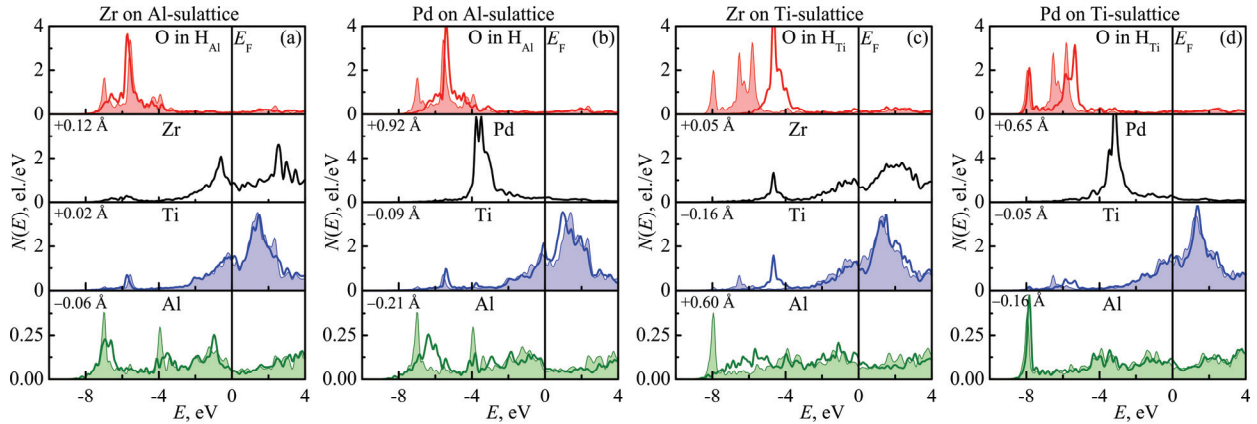


FIGURE 3. Local DOS for the O adsorption on the TiAl(100) doped surface: Zr (a) and Pd (b) on Al-sublattice with O in H_{Al} -site as well as Zr (c) and Pd (d) on Ti-sublattice with O in H_{Ti} -sites. DOS for undoped surface are shown by solid color. The numbers correspond to the changes of interatomic distances on doped surface in comparison with undoped one

TABLE 1. The adhesion energy (W_{ad} in J/m²) at undoped and doped TiAl/TiO₂ interfaces

Contacting surfaces	TiO ₂ (001)		TiO ₂ (100) _O			TiO ₂ (100) _{2O}	
	TiAl(001) _{Al}	TiAl(001) _{Ti}	TiAl(100)	TiAl(110) _{Al}	TiAl(110) _{Ti}	TiAl(110) _{Al}	TiAl(110) _{Ti}
Pure	0.98	2.65	1.74	1.94	2.25	9.92	10.00
Nb	–	2.41	1.42	–	1.65		
Mo	–	1.79	0.77	–	0.82		
Ta	–	2.64	1.64	–	2.06		

It should be noted that in this case there is splitting of the alloy interfacial layer and significant shift of Ti atoms (by 0.81 Å) towards oxide. At the interface with TiO₂(100)_{2O} surface the adhesion energy is significantly higher than that with single layer O-termination due to incorporation of additional O atom into alloy surface. In this case both O atoms have a very strong hybridization with Ti or Al interface atoms. If the cleavage plane passes between two O atoms, the W_{ad} decreases substantially up to 1.53 and 1.20 J/m² for Al- and Ti-termination of alloy surface, accordingly. The alloying of interfacial Ti layers by Nb, Mo and Ta leads to decrease of the adhesion energy (Table 1). The effect of Mo is the most detrimental while in case of Ta impurity it is the smallest one. Finally, the calculations of the oxidation energy of doped Al₂O₃ and TiO₂ [10] allow us to establish that the impurity atoms of Zr, Nb and Mo decrease the stability of Al₂O₃ relative to TiO₂ alongside with increase the formation energy of oxygen vacancy in TiO₂ that is believed to be beneficial for the oxidation resistance of γ -TiAl.

SUMMARY

The segregation behavior of *4d* impurities and their influence on oxygen adsorption properties was investigated within the DFT method. It was established that in case of (001), (110) and (100) surfaces of TiAl alloy the Nb and Mo atoms prefer to be in subsurface layers rather than on the surface. Moreover, these impurities along with Zr, Hf, Ta, W, Re [10] decrease the stability of Al₂O₃ relative to TiO₂ and increase the formation energy of oxygen vacancy in TiO₂. Thus, Nb and Mo can prevent the growth of Al₂O₃ layers during the internal oxidation. It was shown also that the *4d* impurities occupying Ti-sublattice on the TiAl(100) surface result in a decrease of oxygen adsorption energy whereas their influence is opposite in case of substitution of Al atoms. We demonstrate that the segregation of Nb, Mo and Ta to the TiAl/TiO₂ interface decreases the adhesion energy and this negative effect is more pronounced for Mo. In general, the obtained results provide the better understanding of impurity influence on the O adsorption properties and the oxidation of TiAl alloy that is important for improving of its oxidation resistance.

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