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Alloying effects on properties of Al_2O_3 and TiO_2 in connection with oxidation resistance of TiAl

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ABSTRACT

In the present work, a first-principles method is used to calculate the oxidation energies of Al_2O_3 and TiO_2 as well as the formation energy of oxygen vacancy in TiO_2 containing various alloying elements, in order to shed some light on the alloying effects on the oxidation resistance of γ-TiAl. Our calculations demonstrate that almost all alloying elements increase the oxidation energies of Al_2O_3 and TiO_2. The alloying elements with number of d electrons from 2 to 5 in the forth and fifth rows of the periodic table (e.g., Zr, Nb, Mo, Hf, Ta, W) increase significantly the oxidation energy difference between Al_2O_3 and TiO_2, i.e., reduce the relative stability of Al_2O_3 to TiO_2. On the other hand, these alloying elements increase the formation energy of oxygen vacancy in TiO_2. The effects of other alloying elements are less significant or opposite. Observing the experimental mass gains of TiAl alloys and unalloyed TiAl due to oxidation, we find that the elements reducing the relative stability of Al_2O_3 to TiO_2 and increasing the formation energy of oxygen vacancy enhance the oxidation resistance of TiAl whereas others do not. Such correlations are rationalized by analyzing the alloying effects on the internal oxidation of Al in the γ-TiAl matrix and the diffusion of oxygen in TiO_2 surface scale.

1. Introduction

Recent progress makes it feasible and promising for TiAl-based alloys to be used in aero engines and gas turbine components, such as blades, up to 800 °C [1–3]. However, poor oxidation resistance is one of the key obstacles for the practical application of this material at such a high temperature [4–9]. The addition of ternary alloying elements into TiAl may improve efficiently the oxidation resistance [10–14]. Experiments have shown that Nb, Mo, W, and Re benefit [15–19] whereas Mn and Cu deteriorate [18–20] the oxidation resistance of TiAl. However, since the experimental measurement is sensitive to many factors, including temperature, partial pressure of oxygen, and composition variation, etc., different experiments may result in conclusions opposite to each other. Cr, Ag, Hf, Ta, etc., have been reported to be both beneficial and harmful to the oxidation resistance of TiAl by different researchers [13–15,19,21]. Based on the tremendous experimental work, various mechanisms have been proposed to explain the alloying effects on the oxidation resistance of TiAl. The beneficial effects of alloying elements have been ascribed to: (a) slowing down the diffusion of O in TiO_2 (valence control or Wagner-Hauffle rule) [13,22]; (b) inhibiting the internal oxidation (Wagner's scaling model) [13,23]; (c) forming a barrier layer [13,24]; (d) reducing the solubility of Al in TiO_2 [18,25]; and so on. Because of the complexity of the experimental systems, none of the mechanism was found to be universal and it is hard to identify the key factors. Although these mechanisms provide a foundation for the selection of alloying elements, such a foundation is vague due to the lack of sufficient fundamental parameters.

In order to clarify the mechanisms of the alloying effects on the oxidation resistance of TiAl, some first-principles calculations based on density functional theory (DFT) have been performed [26–33]. For example, Song et al. [32,33] found that the oxygen atom prefers the Ti-rich surface that has a high potential of generating TiO_2. Competition between O–Al bonding and O–Ti bonding was observed in the oxygen adsorbed surface regions. However, the O–Ti interaction dominates the adsorption behavior in all considered surfaces with difference indices except for the Al-

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terminated (001) surface. When TiO_2 is formed at the surface, the O–Al bond becomes stronger than the O–Ti bond, which accelerates the formation of Al_2O_3 scale. They suggested that this may be the reason for the formation of TiO_2 scale at the surface but mixed TiO_2/Al_2O_3 scale in the subsurface. The addition of Nb moves the oxygen atoms out of TiO_2 to form O–Al bond such that it improves the oxidation resistance of TiAl. These theoretical work provided valuable fundamental understanding of the oxidation resistance of TiAl. However, most first-principles calculations were focused on the adsorption and absorption of oxygen at the TiAl surface. The adsorption and absorption of oxygen at TiAl surface occur only in the initial stage of the oxidation. Since Ti and Al are both of high oxidation activity, the oxide scale forms easily at the TiAl surface. The oxidation resistance is mainly determined by the morphology, stability, and density of the oxide scale. Therefore, the alloying effects on the properties of the oxide scale are vital to the understanding of the oxidation resistance of TiAl based alloys [34].

Since the affinities of Ti and Al to oxygen are close to each other, TiO_2 and Al_2O_3, with similar stability, grow competitively at TiAl surface during the oxidation process [35,36]. This results in a mixed oxide scale with both TiO_2 and Al_2O_3, instead of a dense and continuous protective layer of Al_2O_3, forming at the TiAl surface. The oxide scale shows obvious layered structure with outer TiO_2 and inner $TiO_2 + Al_2O_3$ layers [13]. The mixed oxide scale cannot prevent the further oxidation of TiAl, which is why TiAl has poor oxidation resistance at high temperature. In principle, tuning the relative stability of TiO_2 and Al_2O_3 by alloying with ternary elements might change the oxide growth mechanism, and, therefore, the morphology of the oxide scale so as to adjust the oxidation resistance. On the other hand, it is the less dense TiO_2 that limits the oxidation resistance. Thus, reducing the formation of TiO_2 layer should improve the oxidation resistance. This might be realized by controlling the transport of oxygen atoms through decreasing the concentration of oxygen vacancies in TiO_2. Based on the above considerations, we investigated the alloying effects on the relative stability of TiO_2 and Al_2O_3 as well as the formation energy of oxygen vacancy in TiO_2 using a first-principles method.

The paper is arranged as follows. The definition of oxidation energy and vacancy formation energy as well as the calculation details are described in Section 2. In Section 3, we report the oxidation energies of TiO_2 and Al_2O_3 and the formation energies of oxygen vacancy in TiO_2 with various ternary alloying elements. Some of these results have been presented before in a Chinese language journal [34], and are included here to facilitate an in-depth discussion. In Section 4, the alloying effects on the oxidation resistance of TiAl are discussed in view of the calculated oxidation energies and vacancy formation energies. Finally, we summarize our work in Section 5.

2. Methodology

2.1. Definitions of oxidation energy and vacancy formation energy

For an oxidation reaction

$$mM+\frac{n}{2}O_2\rightarrow M_mO_n, \tag{1}$$

the reaction energy (i.e., oxidation energy) per O_2 is

$$\Delta H=\left(E_{\mathrm{M_mO_n}}-mE_{\mathrm{M}}-\frac{n}{2}E_{\mathrm{O_2}}\right)\Big/\frac{n}{2}. \tag{2}$$

We adopt a supercell model to calculate the oxidation energy and m and n represent the numbers of sites of the metal and oxygen atoms in the supercell. $E_{\mathrm{M_mO_n}}$, E_{M}, and $E_{\mathrm{O_2}}$ are the energies of the supercell of oxide M_mO_n, the pure metal M, and O_2 molecule, respectively. The oxidation of metals is normally exothermic and ΔH is negative. A larger absolute value of ΔH indicates a more stable oxide. Similarly, if a metal atom in the oxide is replaced by an alloying atom X, the oxidation energy becomes:

$$\Delta H_{\mathrm{X}}=\left(E_{\mathrm{M_{m-1}XO_n}}-mE_{\mathrm{M}}-E_{\mathrm{X}}-\frac{n}{2}E_{\mathrm{O_2}}\right)\Big/\frac{n}{2}, \tag{3}$$

where $E_{\mathrm{M_{m-1}XO_n}}$ and E_{X} are the energies of the alloyed oxide $M_{m-1}XO_n$ and the pure metal X, respectively.

The formation energy of an oxygen vacancy of the unalloyed oxide is defined as:

$$\Delta E=E_{\mathrm{M_mO_{n-1}}}-\left[E_{\mathrm{M_mO_n}}-\frac{1}{2}E_{\mathrm{O_2}}\right]. \tag{4}$$

$E_{\mathrm{M_mO_{n-1}}}$ is the energy of the supercell of the oxide with one oxygen vacancy. For the oxide alloyed with X, the formation energy of an oxygen vacancy is expressed as:

$$\Delta E_{\mathrm{X}}=E_{\mathrm{M_{m-1}XO_{n-1}}}-\left[E_{\mathrm{M_{m-1}XO_n}}-\frac{1}{2}E_{\mathrm{O_2}}\right] \tag{5}$$

where $E_{\mathrm{M_{m-1}XO_{n-1}}}$ is the energy of the supercell of the oxide with one metal atom M nearest to the vacancy being replaced by an alloying atom X.

2.2. Calculation details

All the DFT calculations are carried out by using the Vienna Ab-initio Simulation Package (VASP) [37–39]. The projector augmented wave (PAW) potentials are used to describe the electron–core interaction [40]. The electronic exchange–correlation interaction is described with the generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof [41]. The cutoff energy of 650 eV is adopted after careful tests. For the calculations of the oxidation energies of the alloyed TiO_2 (rutile) and Al_2O_3, the supercell sizes are set as 2 × 2 × 3 and 2 × 2 × 2, respectively, of their primitive cells (see Fig. 1). The k-point meshes are 6 × 6 × 7 for

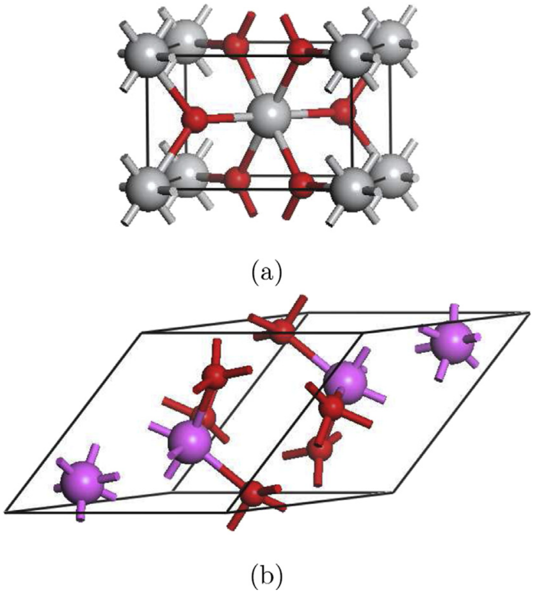

Fig. 1. Primitive cells of rutile TiO_2 (a) and Al_2O_3 (b). The small spheres are for oxygen atoms and the large ones for the metal atoms.