First-Principles Study of Alloying Effects on the Oxidation Resistance of -TiAl (Postprint)

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Abstract

Using the first-principles plane-wave pseudopotential method, we calculated the oxidation energies of Al2O3 and TiO2 containing different transition-group alloying atoms and analyzed the influence of alloying on the relative stability of Al2O3 and TiO2. The computational results indicate that almost all alloying elements increase the oxidation energies of Al2O3 and TiO2, thereby decreasing their stability. The difference in oxidation energies between Al2O3 and TiO2 demonstrates that Nb, Mo, W, Re, etc., significantly reduce the stability of Al2O3 relative to TiO2; therefore, they can suppress the internal oxidation of the Al constituent in -TiAl and improve the high-temperature oxidation resistance of -TiAl.

Full Text

Investigation on Effects of Alloying on Oxidation Resistance of -TiAl by Using First Principles

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Abstract

The oxidation energies of Al O and TiO containing different transition metal alloying elements were calculated using a first-principles plane-wave pseudopotential method, and the effect of alloying on the relative stabilities of Al O and TiO was also analyzed. The results showed that almost all the alloying elements increased the oxidation energies of Al O and TiO , i.e., destabilized both Al O and TiO . Comparing the oxidation energies of Al O and TiO , it was found that W, Mo, Re, Nb, etc., decreased significantly the stabilities of Al O relative to that of TiO , indicating that these alloying elements may hamper efficiently the inner oxidation of Al in the -TiAl matrix so as to increase the high-temperature oxidation resistance of -TiAl.

KEY WORDS first principle, -TiAl, alloying, oxidation energy, relative stability, internal oxidation

-TiAl alloys have attracted extensive attention as lightweight high-temperature structural materials due to their excellent specific strength and creep resistance at elevated temperatures (*cid* : 24). However, poor oxidation resistance at high temperatures limits their practical applications. The oxidation behavior of TiAl alloys is complex, involving the competitive formation of Al O and TiO scales. While a continuous Al O layer provides effective oxidation protection, the simultaneous growth of TiO compromises this protective effect.

Previous experimental studies have shown that alloying additions can significantly influence the oxidation resistance of -TiAl. Elements such as Nb, W, Mo, and Re have been reported to improve oxidation resistance, while others like Cr may have detrimental effects. The mechanisms behind these alloying effects remain incompletely understood, particularly regarding how different elements affect the relative stability of Al O versus TiO during the oxidation process.

In this work, we employ first-principles calculations to systematically investigate the effects of various transition metal alloying elements on the oxidation energies of Al O and TiO . By comparing the relative stabilities of these oxides in the presence of different alloying elements, we aim to provide theoretical guidance for designing -TiAl alloys with improved oxidation resistance.

[Figure 1: see original paper] Overview of the effects of the alloy elements on the oxidation resistance of -TiAl [7—11,13,15]

The oxidation process in -TiAl involves the reaction of Al and Ti with oxygen to form Al O and TiO . The relative stability of these oxides determines the protective nature of the oxide scale. According to thermodynamic principles, the formation of a continuous external Al O layer (external oxidation) is preferred over internal oxidation of Al, which leads to mixed oxide formation and poor protection. The competition between Al O and TiO formation can be described by the reaction:

$ $

The relative stability is governed by the Gibbs free energy change (ΔG) of this reaction. A negative ΔG favors Al O formation, while a positive value indicates preferential TiO formation.

Computational Methodology

First-principles calculations were performed using the plane-wave pseudopotential method based on density functional theory (DFT). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed for exchange-correlation effects. Ultrasoft pseudopotentials were used to describe electron-ion interactions, with a plane-wave cutoff energy of 400 eV. The k-point mesh was set to ensure energy convergence within 10 eV per atom, and forces on all relaxed atoms were converged to less than 0.1 eV/nm.

Supercell models were constructed for both Al O and TiO with substitutional alloying elements. For Al O , a 2×2×1 supercell containing 24 Al and 36 O atoms was used, while for TiO a 3×3×1 supercell with 36 Ti and 72 O atoms was employed. Transition metal elements (Nb, Mo, W, Re, etc.) were substituted at cation sites to simulate alloying effects.

Results and Discussion

Structural Properties The calculated equilibrium lattice parameters for TiO and Al O are summarized in Tables 1 and 2, respectively. The results show good agreement with experimental data and previous theoretical calculations, validating our computational approach.

Calculated equilibrium lattice parameters of TiO in comparison with experimental and other theoretical data

Calculated equilibrium lattice parameters of Al O in comparison with experimental and other theoretical data

Oxidation Energies The oxidation energy (ΔH) for each oxide system was calculated as the energy difference between the oxidized state and the reference states of the constituent elements. The effect of alloying elements on the oxidation energies of Al O and TiO is shown in Figure 2.

[Figure 2: see original paper] Effect of alloying on the oxidation energies of Al O (a) and TiO (b)

The results demonstrate that almost all alloying elements increase the oxidation energies of both Al O and TiO , indicating a destabilizing effect on both oxides. However, the degree of destabilization differs between the two oxides, which critically affects their relative stability.

Relative Stability The relative stability between Al O and TiO in the presence of alloying elements was evaluated by comparing their oxidation energies.

Figure 3 illustrates the change in relative stability (ΔΔH) induced by different alloying elements.

[Figure 3: see original paper] Effect of alloying on the relative stability of Al O and TiO

Elements such as W, Mo, Re, and Nb significantly decrease the relative stability of Al O compared to TiO . This destabilization of Al O relative to TiO suggests that these elements may suppress the internal oxidation of Al in the -TiAl matrix. The mechanism involves the preferential interaction of these alloying elements with the oxide structure, altering the electronic states and bonding characteristics.

Electronic Structure Analysis To understand the underlying electronic mechanisms, we analyzed the density of states (DOS) for pure and doped oxide systems. Figure 4 shows the total and projected DOS for Al O and TiO .

[Figure 4: see original paper] Total and atomic projected densities of states for Al O (a) and TiO (b)

The valence band of Al O is dominated by O 2p states, while the conduction band consists primarily of Al 3s and 3p states. For TiO , the valence band comprises O 2p states hybridized with Ti 3d states, and the conduction band is mainly Ti 3d character. The band gap of Al O is approximately 6.0 eV (GGA value, underestimated compared to the experimental ~8.7 eV), while TiO shows a gap of about 1.7 eV.

Charge Transfer Analysis Bader charge analysis was performed to investigate the charge redistribution induced by alloying elements. Table 3 presents the charge transfer effects of W and Cu doping in Al O and TiO .

Effects of W and Cu on the charge transfer in Al O and TiO

In pure Al O , Al loses electrons (+2.481 e) and O gains electrons (-1.654 e). In pure TiO , Ti transfers +2.280 e to O (-1.136 e). When W is doped into Al O , the charge on Al changes slightly to +2.478/+2.480 e, while O becomes less negative (-1.545/-1.549 e). The W dopant itself carries a positive charge of +1.825 e, indicating electron transfer to neighboring O atoms.

In TiO , W doping reduces the positive charge on Ti from +2.280 to +2.195 e, while the O charge becomes more negative (-1.395 e). The W dopant carries a significant positive charge of +2.785 e, suggesting strong interaction with oxygen. This enhanced charge transfer correlates with the observed destabilization of TiO relative to Al O .

The difference in charge transfer behavior between W and Cu is notable. Cu doping results in less pronounced charge redistribution, with Cu carrying only +1.301 e in TiO , which correlates with its weaker effect on oxidation resistance compared to W.

Mechanism of Alloying Effects The enhanced oxidation resistance by elements like W, Mo, Re, and Nb can be explained by their influence on the competitive oxidation process. These elements destabilize Al O more significantly than TiO , which may seem counterintuitive since Al O is the desired protective scale. However, this relative destabilization actually suppresses the internal oxidation of Al, promoting the formation of a continuous external Al O layer rather than dispersed internal oxide precipitates.

The schematic in Figure 6 illustrates the difference between internal and external oxidation morphologies. Internal oxidation occurs when oxygen dissolves in the alloy and reacts with Al internally, forming discrete Al O particles. External oxidation forms a continuous surface layer that provides better protection.

[Figure 6: see original paper] Schematic morphology of Al O in different growth models: (a) internal oxidation, (b) external oxidation

The key to improving oxidation resistance is promoting external oxidation at the expense of internal oxidation. Elements that destabilize Al O relative to TiO reduce the driving force for internal Al O formation, thereby favoring external scale growth when the overall Al activity is sufficient.

Conclusion

First-principles calculations reveal that transition metal alloying elements W, Mo, Re, and Nb significantly decrease the relative stability of Al O compared to TiO . This selective destabilization suppresses internal oxidation of Al in -TiAl alloys, thereby promoting the formation of protective external Al O scales and improving high-temperature oxidation resistance. The electronic mechanism involves modified charge transfer and bonding characteristics in the oxide structures. These theoretical findings provide guidance for designing oxidation-resistant -TiAl alloys through strategic alloying additions.

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