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Phase stability, mechanical properties and electronic structures of Ti—Al binary compounds by first principles calculations

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HIGHLIGHTS

- The phase stability, electronic structures and mechanical properties were systematically investigated by contrast.
- Mechanical properties were illustrated associating with chemical bonding characters.
- The anisotropy of Young's modulus was discussed by 3D curve contours.

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ABSTRACT

The stability, mechanical properties and electronic structures of Ti_3Al, TiAl, $TiAl_2$ and $TiAl_3$ have been systematically investigated by the first-principles calculation. The four Ti—Al binary compounds are thermodynamically stable intermetallics depending on their negative formation enthalpy and cohesive energy. The bulk modulus (B), shear modulus (G), Young's modulus (E), Vicker's hardness (H_V) and Poisson's ratio (ν) are calculated. With the increment of Al content, the bulk modulus and Poisson's ratio decrease while the shear modulus, Young's modulus and hardness gradually increase. The ratio of B/G decreases with Al increment, implying the weakening of ductility. In addition, the mechanical anisotropy of Ti—Al compound has been revealed by the analysis of the anisotropy index, three-dimensional surface contours of the Young's modulus and the planar projections on the low index planes (including (100), (010), (100) and (110)). TiAl shows the most anisotropic structure while Ti_3Al has the least anisotropy. The density of states (DOS) and electron density distribution map are discussed to analyze the electronic structures and chemical bonding characters. The Ti—Al binary compounds are composed of both metallic and covalent bonds, and the covalent bonding character can be strengthened with the increase of Al content.

1. Introduction

In recent years, Ti—Al alloys have attracted the attention of intensive researchers for the potential for applications in automobile and aerospace industries, due to its low density, high specific elastic modulus and strength [1–8]. TiAl based alloys have been the most attractive in current researches due to the considerable properties for application in blades. The mechanical and thermal properties of TiAl based alloy are mainly attributed to the features of τ-TiAl intermetallic. As we know, intermetallics usually show the advantages of both metals and ceramics benefiting from the distinct bonding characters (both metallic and covalent bondings). So, intermetallics are believed to have great potential for industrial applications involving high specific yield strength, high stiffness, high hardness, good thermostability and corrosion-resistance. However, as a common drawback for intermetallics, poor ductility impedes their applications for engineering components. In this context, single TiAl phase can't be regularly used as a structural component and it's difficult to process the TiAl based alloy owing to its low ductility at room temperature.

To overcome this barrier, enormous efforts have been devoted to preparing TiAl alloys with refined and homogeneous microstructure, including heat treatment, thermal mechanical processing and alloying

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technique [3–5,7–19]. Traditionally, the addition of boron was regarded as an effective technique to refine the grain size [20]. Unfortunately, boride particles resulting from boron addition can act as potential crack initiation and propagation sites in turn. In this case, it's essential to explore some new designing techniques to prepare TiAl alloys with both good strength and fracture toughness. Sun et al. [21] have fabricated a new multilayered Ti−Al intermetallics by spark plasma sintering, which provides a new possibility to improve the fracture toughness. Herein, four Ti−Al intermetallics with different Al contents play important roles in controlling the microstructure and mechanical properties.

In fact, other Ti−Al intermetallics except TiAl also have great potentials for good mechanical and thermostable properties. According to Ti−Al binary diagram [22,23], mainly four binary compounds can be obtained for low temperatures including Ti_3Al, TiAl, $TiAl_2$ and $TiAl_3$ [24,25]. By far, intensive studies including experimental and theoretical studies have been done as for TiAl intermetallic, to explore the effective toughening ways. A few previous works involved the crystal structure, phase stability and mechanical properties of Ti_3Al and $TiAl_3$ [26–30]. Nevertheless, there were scarcely some relevant reports with regard to $TiAl_2$ before. In this case, a systematic research is essential to compare the mechanical properties and electronic structures of the Ti−Al alloys. Therefore, the phase stability, electronic structures, mechanical properties as well as some thermodynamic properties of Ti−Al binary compounds have been systematically investigated by the first-principles calculation in this paper. The calculated results was summarized and analyzed by contrast and relationship. This work is envisaged to provide predicted information for designing new Ti−Al alloys with better comprehensive properties.

2. Methods and details

In this paper, the first-principle calculations were implemented based on density functional theory (DFT) performed in CASTEP code [31]. Ultrasoft pseudopotentials were used to describe the interactions of ionic core and valence electrons. Generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) scheme was employed to evaluate the exchange correlation energy [32]. A special k-point method proposed by Monkhorst-Pack was used for the energy integration in the first irreducible Brillouin zone [33]. In this work, k-point mesh was selected as $12 \times 12 \times 12$ for all calculated Ti−Al compounds. The kinetic energy cut-off of 500 eV was used for plane wave expansions in reciprocal space. The Broyden–-Fletcher–Goldfarb–Shannon (BFGS) optimization method was used to obtain the equilibrium crystal structure of each compound. During the optimization process, the total energy changes were finally reduced to 2×10^{-6} eV and the Hellman-Feynman forces acting on per atom were converged to less than 0.01 eV/Å. The elastic constants of Ti−Al compounds were calculated based on the generalized Hooker's law by stress-strain method. Several different strain patterns were used to calculate the crystal structure and Cauchy stress tensor for each strain mode was evaluated.

From Ti−Al binary equilibrium phase diagram [22,23], six kinds of phases can be found depending on Al content, namely α-Ti, Ti_3Al, TiAl, $TiAl_2$, $TiAl_3$ and Al [21,34]. As we know, there are usually several different crystal structures for these Ti−Al binary compounds. To simplify the work, the most thermostable structure for each compound has been selected to conduct the calculation in this work. According to Tan's report [35], the most thermostable structures of Ti_3Al, TiAl, $TiAl_2$ and $TiAl_3$ belong to space groups of $P6_3/mmc$ (Ti_3Al), P4/mmm (TiAl), Cmmm ($TiAl_2$) and I4/mmm ($TiAl_3$), respectively. Accordingly, the lattice structures for all investigated crystals have been established, as shown in Fig. 1. The six phases in Ti−Al system exhibit hexagonal (Ti and Ti_3Al), tetragonal (TiAl and $TiAl_3$), orthorhombic ($TiAl_2$) and face-centered cubic (Al) lattice, respectively. The atom coordinates of all four intermetallics are shown in Table 1.

3. Results and discussion

3.1. Crystal parameters and phase stability

The calculated lattice parameters of the four Ti−Al binary compounds as well as Ti and Al crystals have been listed in Table 1. By contrast, we can find that the crystal parameters calculated in this work show good agreement with other calculated and experimental results. The tiny deviation may result from the different calculation methods or experimental conditions; generally, the lattice parameters obtained by experimental way are measured at ambient temperature while the calculation using GGA-PBE method is conducted at 0 K. On the other hand, the thermodynamic stability of crystals and compounds can be evaluated by the cohesive energy and formation enthalpy. In this work, the cohesive energy and formation enthalpy of the four Ti−Al binary compounds were calculated by Eqs. (1) and (2) [36,37], respectively:

$$E_{coh}(Ti_xAl_y) = \frac{E_{tol}(Ti_xAl_y) - xE_{iso}(Ti) - yE_{iso}(Al)}{x + y} \quad (1)$$

$$\Delta H_r(Ti_xAl_y) = \frac{E_{tol}(Ti_xAl_y) - xE_{coh}(Ti) - yE_{coh}(Al)}{x + y} \quad (2)$$

where $E_{coh}(Ti_xAl_y)$ is the cohesive energy of Ti_xAl_y per atom; $\Delta H_r(Ti_xAl_y)$ is the formation enthalpy of Ti_xAl_y per atom; $E_{tol}(Ti_xAl_y)$ is the total energy of Ti_xAl_y. $E_{iso}(Ti)$ and $E_{iso}(Al)$ are the energy of a single Ti and Al atom respectively; $E_{coh}(Ti)$ and $E_{coh}(Al)$ represent the cohesive energy of Ti and Al crystal.

As shown in Table 1, the cohesive energy and formation enthalpy of Ti, Al and the Ti−Al binary compounds have also been listed. First of all, it can be visibly found that the values of cohesive energy and formation enthalpy are negative for all the Ti−Al compounds, implying the crystal structures of these compounds in this work are thermodynamically stable. Generally, formation enthalpy acts as the criteria to decide the thermodynamical stability of the compound. The lower the formation enthalpy, the more thermodynamically stable the compound. From Table 1, the formation enthalpies are −0.279, −0.404, −0.426 and −0.396 eV/atom for Ti_3Al, TiAl, $TiAl_2$ and $TiAl_3$, respectively. The varying trend of formation enthalpy as a function of Al percent is presented in Fig. 2. The formation enthalpy of the Ti−Al binary compound decreases firstly and then increases with the increment of Al percent. $TiAl_2$ shows the lowest formation enthalpy of −0.426 eV/atom, indicating the best thermodynamical stability. Except that, TiAl and $TiAl_3$ also shows relatively good thermodynamical stability. The calculated results in this work agree well with the previous experimental and some other calculated values [1,27,35,38–42].

3.2. Mechanical properties

In this work, the elastic constants of Ti−Al binary compounds were calculated by the stress-strain approach based on the generalized Hooker's law. Generally, elastic stiffness can provide a relationship between the mechanical and dynamical behavior of crystals [37]. The elastic stiffness constants (C_{ij}) of Ti_3Al, TiAl, $TiAl_2$ and $TiAl_3$ are listed in Table 2. On the other hand, according to Boron-Huang's lattice dynamic theory, the elastic stiffness constants of Ti−Al compounds have to meet the corresponding requirements for various crystal structures to reach mechanical stability. The mechanical criterions can be expressed as Eqs. (3)–(5) [43–45]:

Hexagonal system (for Ti_3Al):

$$C_{11} > 0,\ C_{44} > 0,\ (C_{11} - C_{12}) > 0,\ (C_{11} + C_{12})C_{33} > 2C_{13}^2 \quad (3)$$

Tetragonal system (for TiAl and $TiAl_3$):

$$C_{44} > 0,\ C_{66} > 0,\ C_{11} > |C_{12}|,\ (C_{11} + C_{12})C_{33} > 2C_{13}^2 \quad (4)$$

Orthorhombic system (for $TiAl_2$):