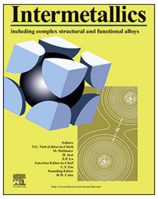
Intermetallics 101 (2018) 72–80

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet



A comparative first-principles study of tetragonal TiAl and $Ti_4Nb_3Al_9$ intermetallic compounds

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ARTICLE INFO

Keywords:
Titanium aluminides
Phase stability
Elastic properties
Elastic anisotropy
First-principles calculations

ABSTRACT

A comparative study on the phase stability and elastic properties of tetragonal TiAl and $Ti_4Nb_3Al_9$ was performed by first-principles calculations based on density functional theory. The results showed that the stability of $Ti_4Nb_3Al_9$ phase is lower than that of TiAl. The polycrystal $Ti_4Nb_3Al_9$ has the better ductility and the lower hardness, sound velocities and Debye temperature than TiAl. Meanwhile, $Ti_4Nb_3Al_9$ has more significant anisotropy of elasticity than TiAl. The above results can provide a valuable reference for designing the novel γ-TiAl-based alloys with γ_1 -$Ti_4Nb_3Al_9$ phase.

1. Introduction

Alloys based on γ-TiAl intermetallic compound have high melting point, low density, high specific strength, good creep and corrosion resistance, making them desirable high temperature structural materials for aerospace and automotive applications [1–7]. However, the practical uses of γ-TiAl-based alloys are severely restricted to their low room temperature ductility, low fracture toughness and insufficient oxidation resistance at temperatures above 800 °C [2]. Alloying is an effective method to improve the properties of γ-TiAl-based alloys. Among various alloying elements, Nb is one of the most important issues. Such alloying element possesses a solubility up to 10 at% in γ-TiAl, leading to the possible synthesis of highly Nb-alloyed TiAl alloys [5]. γ-TiAl-based alloys containing 5–10 at% Nb exhibit superior high temperature properties and are widely recognized as the most perspective high temperature materials [5–8]. The alloying element Nb plays a critical role in improving their strengths and resistances to creep and oxidation at elevated temperature.

The γ-TiAl intermetallic compound has an ordered $L1_0$ crystal structure with face-centered tetragonal (FCT) symmetry. Alternatively, the $L1_0$ structure is considered as a body-centered tetragonal (BCT) lattice. The BCT primitive cell is drawn from the FCT unit cell by a 45° rotation about the [001] axis. It has been proved that Nb atom in γ-TiAl substitute for Ti atom and preferentially occupies the Ti sublattice [9]. With increasing Nb content added to γ-TiAl, a new ternary intermetallic compound designated as γ_1 forms by a continuous ordering process of Nb atoms on the γ-TiAl sublattice [10–12]. The γ_1 phase has the tetragonal structure of lattice parameters *a* in the range of 5.58–5.84 Å and *c* in the range of 8.15–8.45 Å [10]. Its chemical formula has been determined to be $Ti_4Nb_3Al_9$ [13]. The unit cell of γ_1 -$Ti_4Nb_3Al_9$ is made up of eight small γ-TiAl BCT primitive cells. The relationship of lattice parameters between γ_1 -$Ti_4Nb_3Al_9$ and γ-TiAl phases are $a_{\gamma_1} = \sqrt{2}a_\gamma$ and $c_{\gamma_1} = 2c_\gamma$ [13]. The corresponding orientation relationship is $[001]_{\gamma1}$ $//[001]_\gamma$, $(100)_{\gamma1}$ $//(110)_\gamma$ and $(010)_{\gamma1}$ $//(\bar{1}10)_\gamma$.

As one microstructure constituent in high-Nb containing TiAl alloys, γ_1 -$Ti_4Nb_3Al_9$ is of great technological importance as the precipitated strengthening phase [5,14–17]. The strengthening effect is strongly correlated with the lattice misfit and elastic properties of γ-TiAl and $\gamma_1-Ti_4Nb_3Al_9$. Extensive first-principles calculations of the lattice parameter and elastic properties of γ-TiAl, site preference of Nb in γ-TiAl and effect of Nb on the elastic properties of γ-TiAl have been performed in the literature [18–31]. However, the information on the elastic properties of $\gamma_1-Ti_4Nb_3Al_9$ is absent. In the present work, the first-principles calculations have been performed to comparatively study the phase stability and elastic properties of tetragonal TiAl and $Ti_4Nb_3Al_9$ intermetallic compounds. This can provide a valuable reference for the design of novel γ-TiAl-based alloys with $\gamma_1-Ti_4Nb_3Al_9$ phase.

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https://doi.org/10.1016/j.intermet.2018.07.012
Received 23 May 2018; Received in revised form 3 July 2018; Accepted 23 July 2018
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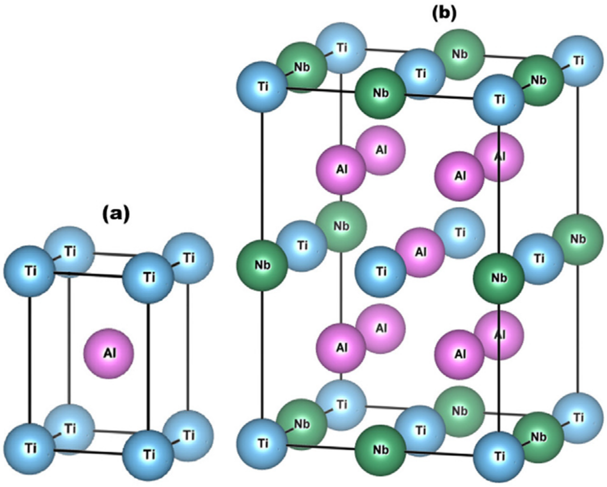

Fig. 1. The computational models of (a) TiAl and (b) $Ti_4Nb_3Al_9$ with tetragonal structure.

2. Methodology

2.1. Calculations of single crystal elastic constants

In view that the unit cell of $Ti_4Nb_3Al_9$ consists of eight small BCT TiAl cells, as seen in Fig. 1, in this study the elastic constants of TiAl are computed by taking the BCT cell as the theoretical model. It is known that the necessary number of independent elastic constants is determined by the crystal symmetry of a material, and increases with the decrease of the crystal symmetry. For tetragonal lattice, six independent elastic constants are usually referred to as C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}. Herein, an efficient strain-energy method is taken to determine the six elastic constants of tetragonal TiAl and $Ti_4Nb_3Al_9$. In the method, the elastic constants are defined as the second derivatives of the strain energy with respect to the applied strain. After applying a small Lagrangian strain $\boldsymbol{\eta}$ in the perfect crystal, the elastic strain energy (ΔE) of the deformed crystal can be expanded in a Taylor series in terms of the strain tensor as

$$\Delta E = \frac{V}{2!}\sum_{i,j=1}^{6} C_{ij}\eta_i\eta_j + O(\eta^3), \tag{1}$$

where V_0 is the volume of the perfect crystal, C_{ij} are the elastic constants in the Voigt notation for $11 \to 1$, $22 \to 2$, $33 \to 3$, $23 \to 4$, $31 \to 5$ and $12 \to 6$, and $O(\eta^3)$ ignores terms of the third and higher order in the magnitude of strain. To calculate all six of elastic constants, six independent strains ($\boldsymbol{\eta}_1$, $\boldsymbol{\eta}_2$, $\boldsymbol{\eta}_3$, $\boldsymbol{\eta}_4$, $\boldsymbol{\eta}_5$, $\boldsymbol{\eta}_6$) are required, as follows [28]:

$$\begin{aligned}
\boldsymbol{\eta}_1 &= \begin{pmatrix} \eta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
\boldsymbol{\eta}_2 &= \begin{pmatrix} \eta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & -\frac{\eta(2+\eta)}{(1+\eta)^2} \end{pmatrix}, \\
\boldsymbol{\eta}_3 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \eta \end{pmatrix}, \\
\boldsymbol{\eta}_4 &= \begin{pmatrix} \sqrt{\frac{1+\eta}{1-\eta}} - 1 & 0 & 0 \\ 0 & \sqrt{\frac{1-\eta}{1+\eta}} - 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
\boldsymbol{\eta}_5 &= \begin{pmatrix} 0 & 0 & \eta \\ 0 & 0 & \eta \\ \eta & \eta & \frac{\eta^2}{4} \end{pmatrix}, \\
\boldsymbol{\eta}_6 &= \begin{pmatrix} \sqrt{1+\frac{\eta^2}{4}} - 1 & \eta & 0 \\ \eta & \sqrt{1+\frac{\eta^2}{4}} - 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\end{aligned} \tag{2}$$

The elastic energies corresponding to the strains $\boldsymbol{\eta}_1$, $\boldsymbol{\eta}_2$, $\boldsymbol{\eta}_3$, $\boldsymbol{\eta}_4$, $\boldsymbol{\eta}_5$ and $\boldsymbol{\eta}_6$ are give by Ref. [28].

$$\begin{aligned}
\Delta E(\boldsymbol{\eta}_1) &= (C_{11} + C_{12})V_0\eta^2 \\
\Delta E(\boldsymbol{\eta}_2) &= (C_{11} + C_{12} + 2C_{33} - 4C_{13})V_0\eta^2 \\
\Delta E(\boldsymbol{\eta}_3) &= \tfrac{C_{33}}{2}V_0\eta^2 \\
\Delta E(\boldsymbol{\eta}_4) &= (C_{11} - C_{12})V_0\eta^2 \\
\Delta E(\boldsymbol{\eta}_5) &= C_{44}V_0\eta^2 \\
\Delta E(\boldsymbol{\eta}_6) &= \tfrac{C_{66}}{2}V_0\eta^2.
\end{aligned} \tag{3}$$

The elastic constants can derive from the resulting changes in the strain energy. To avoid the influence of higher order terms on the estimated elastic constant, the parameter η of each strain varies within ± 0.015 in steps of 0.003. After obtaining the second-order coefficients in the quadratic fitting polynomials of the strain-energy data for each strain mode, the elastic constants are determined based on the equilibrium lattice parameters. Taking $Ti_4Nb_3Al_9$ as an example, the relationship between the strain energy and the strain parameter is illustrated in Fig. 2 for the selected six deformation modes.

2.2. First-principles total-energy and phonon calculations

The present first-principles calculations were carried out on the basis of density functional theory (DFT) as implemented in Vienna Ab initio Simulation Package (VASP) [32–34]. The interaction between ions and electrons was described by the projector augmented wave method [35,36]. The exchange correlation functional was treated within the generalized gradient approximation (GGA) parametrized by Perdew, Burke and Ernzerhof (PBE) [37,38]. The valence electron configurations for Al, Ti and Nb elements correspond to $3s^2 3p^1$, $3s^2 3p^6 3d^2 4s^2$ and $4s^2 4p^6 4d^4 5s^1$. The cut-off energy for plane wave basis set was fixed to be 600 eV. The global break condition for electronic self-consistency loop was specified to be 10^{-6} eV/atom. The irreducible Brillouin zones for BCT TiAl and tetragonal $Ti_4Nb_3Al_9$ were sampled with the meshes of $21 \times 21 \times 14$ and $9 \times 9 \times 7$ k-point generated by the Monkhorst-Pack scheme [39], respectively. Before calculating the elastic constants, the structural optimizations of both intermetallic compounds were conducted by full relaxation with respect to the volume, shape and internal atomic positions until the atomic forces of less than 0.01 eV/Å for cell. To accurately obtain the strain energies for determining the elastic constants, the atomic positions were firstly