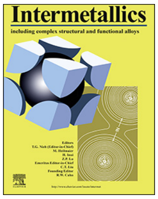
Intermetallics 101 (2018) 1–7

Contents lists available at ScienceDirect

Intermetallics

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



The elastic behaviors and theoretical tensile strength of γ-TiAl alloy from the first principles calculations

Jia-Hua Wang, Yong Lu*, Xiao-Lin Zhang, Xiao-hong Shao**

Beijing University of Chemical Technology, College of Science, Beijing 100029, China

ARTICLE INFO

Keywords:
Elastic modulus
Tensile strength
First-principles calculation

ABSTRACT

The temperature dependent elastic modulus and theoretical tensile strength have been investigated by the first-principles calculations to get insight into the mechanical performance of γ-TiAl in the case of high temperature and impurity. The phase stability of γ-TiAl at elevated temperature has been proved by calculating the phonon dispersion relations and elastic constants. The elastic modulus B, G and E decrease linearly by 8%, 22%, and 20% respectively with the temperature increasing from 0 K to 850 K. The reduction of B is small, indicating that the resistance to external pressure for γ-TiAl is still superior at high temperature. The reduced G/B ratio of 0.488 endows γ-TiAl fairly good ductility at elevated temperature. The tensile test shows that the ideal tensile strength is somewhat reduced due to the presence of impurity (C, O, P, and S) in comparison with pure γ-TiAl. Compared to C, P, and S, the O impurities are more easily trapped in γ-TiAl matrix with largely negative formation energy. For the γ-TiAl compound, the values of theoretical tensile strength corresponding to the first phonon instability are 16.1 GPa, 5.3 GPa, 6.3 GPa, and 14.6 GPa along [100], [001], [110], and [111] directions, respectively. For TiAl-O system, we obtained the values of 15.1 GPa, 10.8 GPa, 6.4 GPa, and 13.3 GPa, respectively.

1. Introduction

Titanium-aluminium alloys have attracted much attentions from the aerospace community and turbine power generation markets during the last decade. The attractive high temperature strength retention and improved elastic modulus make them potentially superior high-temperature materials [1–4]. For more widespread application of these alloys as high-temperature structures [5,6], detailed studies of fundamental properties such as the phase stability, elastic behaviors, and tensile strength are warranted. Especially, intermetallic titanium aluminides based on the ordered γ-TiAl phase provide many of the qualities required in innovative structural high-temperature applications. In order to gain more insight into the mechanical and thermal stability of these alloys under high temperature and mechanical loads, extensive studies, both experimental and theoretical, have been performed. For example, Tanaka et al. [7,8] have described the experimental procedure and measured the elastic constants of single-crystal γ-TiAl from 4 K to room temperature; Zou et al. [9] have studied the phase stability of ordered TiAl alloys in various structures by first-principles calculations; Liu et al. [10] and Tang et al. [11] have investigated the shear deformation behaviors in γ-TiAl using the density functional theory (DFT) calculations; Fu et al. [12] studied the structural and elastic properties of γ-TiAl under high pressures, and so on.

As known, elastic constants are closely related to many fundamental solid-state properties, such as bulk modulus, specific heat, phonon group velocity, Debye temperature, and melting point [13,14]. Also, from the elastic constants, one can gain insight into the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding. Experimentally, elastic constants have been directly used in the evaluation of elastic strains under external or thermal stresses to test the structural stability of a crystal. For most pure metals, elastic constants can be accurately measured over a wide range of temperature and pressure. However, the data for alloys and intermetallic compounds are relatively scarce because of the polycrystal and defects. Especially at elevated temperature, due to the increased defects concentration, the sample preparation and maintenance are difficult, which may lead to large error. Since the elastic constants for singe crystal are required in basic studies, in contrast, many efforts have been paid theoretically. For γ-TiAl, most of the theoretical calculations are limited to values at 0 K [10,12,15], which could not reflect the performance of such alloy at high temperature. Currently, by combining the density functional perturbation theory (DFPT) and quasi-harmonic approximation (QHA) method, the temperature dependent elastic constants (TDEC) of materials can be obtained theoretically [16–19].

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* Corresponding author.
** Corresponding author.
E-mail addresses: luy@mail.buct.edu.cn (Y. Lu), shaoxh@mail.buct.edu.cn (X.-h. Shao).

https://doi.org/10.1016/j.intermet.2018.07.001
Received 15 January 2018; Received in revised form 26 June 2018; Accepted 2 July 2018
0966-9795/

Thus, in this study, we focus on the TDEC of γ-TiAl based on the QHA method and continuum elasticity theory [16,19]. Meanwhile the thermodynamic stability has also been concerned by calculating phonon dispersion curves to help to understand the evolution of elastic properties upon temperature.

Under mechanical loads, it is of great importance to investigate the ideal strength of materials in order to understand the mechanical performance. The theoretical strength sets an upper bound on the attainable stress, which is an intrinsic property of materials determined by the electronic and ionic behaviors. Many studies have been performed to focus on the ideal strength from single crystals to intermetallic compound systems [20–23]. Impurity is one of the uncontrollable factors which can strongly affect the mechanical properties of materials. The ideal strength has also been extended to the systems containing defects [24–27]. Thus, in this study, we employ the first-principles computational tensile test (FPCTT) [28] to calculate the stress-strain relationship and obtain the ideal tensile strength of pure γ-TiAl and impurity containing systems. The anisotropy of the tensile strength is considered by pulling these systems along four different crystal orientations, i.e., [100], [001], [110], and [111]. These data can help to provide a basic understanding of the mechanical performance of γ-TiAl in the high-temperature and impurity conditions.

2. Theoretical methods

At ambient pressure, the Helmholtz free energy $F[X(\delta);\, T]$ can be expressed as [19].

$$F[X(\delta);\, T] = E[X(\delta)] + A_{vib}[X(\delta);\, T] + F_{ele}[X(\delta);\, T] \tag{1}$$

where $X(\delta)$ represents a deformed configuration tensor which is a function of deformation δ, and T is the temperature, respectively. $E[X(\delta)]$ is the total energy of the specific deforming configuration, $A_{vib}[X(\delta);\, T]$ is the vibrational Helmholtz free energy which can be calculated by QHA [29,30], and $F_{ele}[X(\delta);\, T]$ is the thermal electronic contribution to the free energy. Under QHA, the $A_{vib}[X(\delta);\, T]$ can be evaluated from phonon density of states (DOS) $g(\omega)$ by Ref. [31].

$$A_{vib}[X(\delta);\, T] = k_B T \int_0^{\infty} g(\omega) ln\left[2sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right] d\omega \tag{2}$$

where $\omega = \omega(V)$ depends on volume and thus Eq. (2) contains anharmonic effects by thermal expansion. $F_{ele}[X(\delta);\, T]$ in Eq. (1) can be obtained from the energy and entropy contributions, i.e., $E_{ele} - TS_{ele}$ [32]. The electronic entropy S_{ele} is of the form, $S_{ele}[X(\delta);\, T] = -k_B \int n(\varepsilon, X(\delta))[flnf + (1-f)ln(1-f)]d\varepsilon$, where $n(\varepsilon)$ is electronic DOS, and f is the Fermi-Dirac distribution. The energy E_{ele} due to the electron excitations takes the following form: $E_{ele}[X(\delta);\, T] = \int n(\varepsilon, X(\delta)) f\varepsilon d\varepsilon - \int^{\varepsilon_F} n(\varepsilon, X(\delta))\varepsilon d\varepsilon$, where ε_F is the Fermi energy.

γ-TiAl belongs to the tetragonal crystal, thus it has six independent elastic constants, i.e., C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}. The elastic constants can be defined by means of a Taylor expansion of the total energy, $F(V, \delta)$, for the system with respect to a small strain δ on the equilibrium cell according to the following law [33]:

$$F(V, \delta) = F(V_0, 0) + V_0\left[\sum_i \tau_i \xi_i \delta_i + \frac{1}{2}\sum_{ij} C_{ij}\delta_i \xi_j \delta_j\right] \tag{3}$$

where $F(V_0, 0)$ and V_0 are the total energy and volume of the equilibrium cell without strains, respectively, τ_i is an element in the stress tensor, $\xi_{i/j}$ is a factor of the Voigt index [34], and $\delta_{i/j}$ is the small strain applied on the equilibrium cell. In order to calculate these elastic constants, we select the sets of distortions: (δ, δ, 0,0,0,0), (δ, $-\delta$, 0,0,0,0), (0,0, δ, 0,0,0), (0,0,0, δ, 0,0), (δ, δ, δ, 0,0,0), (0,0,0,0,0, δ) as six deformation modes on the equilibrium cell with δ varying from -0.03 to 0.03 in steps of 0.006. Then at different temperatures, these elastic constants can be obtained by the solving the following equation set,

$$\begin{cases} 2C_{11}^T + 2C_{12}^T = D_1^T \\ 2C_{11}^T - 2C_{12}^T = D_2^T \\ C_{33}^T = D_3^T \\ 4C_{44}^T = D_4^T \\ 2C_{11}^T + 2C_{12}^T + 4C_{13}^T + C_{33}^T = D_5^T \\ 4C_{66}^T = D_6^T, \end{cases} \tag{4}$$

where D_1^T, D_2^T, D_3^T, D_4^T, D_5^T and D_6^T represent the second-order strain derivatives of the Helmholtz free energy under the above six kinds of deformation forms, respectively.

In this study the first principles calculations were performed based on DFT [35,36] using the projector augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) [37]. The exchange correlation energy function are described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [38] form and the plane-wave basis set is limited by the cutoff energy of 600 eV. In the Brillouinzone (BZ) integration, we use a 13×13×13 grid with the Monkhorst-Pack scheme [39]. The 3×3×3 supercell (128 atoms) is constructed to model the impurity containing system. The DFPT method is used to calculate the phonon dispersions in the BZ using the supercell and PHONOPY package [40]. The QHA method is used to calculate the volumetric expansion and thermodynamic properties associated with the lattice vibrations.

3. Results and discussion

3.1. Thermodynamic properties

The γ-TiAl phase shares the tetragonal crystal and crystallizes in the $L1_0$ structure. The primitive unitcell contains two Ti atoms occupying $2e$ sites and two Al atoms occupying $1a$ and $1c$ sites, respectively. After structure relaxation, the equilibrium lattice parameters a and c are predicted to be 3.98 Åand 4.08 Å, respectively, in excellent agreement with the experiment values of 4.01 Åand 4.07 Å^{41}. In order to introduce the two individual structural parameters, a and c, into the QHA scheme, for a given parameter a, the total energy $E(c/a)$ of the system is calculated with c/a varying by a set of value around the equilibrium one at ground state. The optimal c/a can be determined by polynomial fitting of the $E(c/a)$ curve, and the corresponding volume can be obtained. Then the unit cell volume is varied to a set of value around the equilibrium one to obtain the volumetric expansion upon temperature based on the QHA method. At the given temperature T, the equilibrium volume follows from a minimization of $F(V, T)$ with respect to V. For each volume, the phonon dispersion relations were calculated. The calculated free energy versus volume curves for a number of selected temperatures are plotted in Fig. 1(a). As a result, the equilibrium volume $V(T)$ can be derived by fitting the data to the Vinet equation of states for each temperature. As depicted in Fig. 1(b), the equilibrium volume increases along with the increase of temperature. The constant volume thermal expansion α_V is defined by $\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, which is also shown in the inset of Fig. 1(b). There is an obvious inflexion between 200 K and 400 K, over which the increase rate of α_V decreases. At 850 K, the thermal expansion coefficient for γ-TiAl is about 3.55×10^{-5} K^{-1}.

According to the volumetric expansion upon temperature based on QHA, we plotted in Fig. 2 the phonon dispersion curves at several typical temperatures, i.e., 0 K, 300 K, and 850 K. For all these phonon dispersion relations, there are no unstable branches with negative vibrational frequencies, indicating the thermodynamical stability of γ-TiAl and the validity of QHA method at temperatures up to at least 850 K. As shown in Fig. 2, the phonon frequencies are shifted towards the low-frequency domain along with volumetric expansion.