Materials Chemistry and Physics 209 (2018) 200–207

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

The structural, mechanical and thermodynamic properties of Ti-B compounds under the influence of temperature and pressure: First-principles study

Jinzhong Tian, Yuhong Zhao*, Bing Wang, Hua Hou, Yongmei Zhang

College of Materials Science and Engineering, North University of China, Taiyuan, 030051, China

HIGHLIGHTS

- The elastic properties of Ti2B and Ti3B4 under pressure and temperature are studied.
- The thermodynamic properties of Ti-B compounds are systematically studied.
- Ti2B tends to be ductile with pressure, while others exhibit brittle behavior.

ARTICLE INFO

Article history:

Keywords:
Ti-B compounds
First-principles
Mechanical properties

ABSTRACT

The crystal structure and elastic properties of Ti-B compounds were systematically studied by first-principles methods at 0 K. The lattice parameters obtained by generalized gradient approximation (GGA) at 0 GPa match well with those previously reported by other authors and the values of V/V_0 under pressure are arranged in the following order: $Ti_2B < TiB < Ti_3B_4 < TiB_2$. The Ti-B compounds are mechanically stable under pressure and their independent elastic constants increase with pressure. Polycrystalline elastic moduli determined from the elastic constants have a similar trend with the applied pressure. From these results, it is derived that the volume change resistance, shear deformation resistance, stiffness, elastic anisotropy and plasticity of the polycrystalline Ti-B compounds increase with pressure. The volume change resistance, shear deformation resistance and stiffness of Ti—B compounds improve with pressure. Ti_2B tends to be ductile with pressure, while others exhibit brittle behavior where the brittleness of materials is ranked in the following descending order: $TiB_2 > Ti_3B_4 > TiB$. Besides, the elastic moduli predicted for TiB_2 are larger than others compounds of Ti—B, which indicate that TiB_2 has the larger hardness than others. The effects of pressure and temperature on the Debye temperature, heat capacity and bulk modulus of the polycrystalline Ti-B compounds are predicted by using a quasi-harmonic Debye model of the phonon density of states to include the vibrational contribution at the Gibbs energy of the compound. The applied pressure could improve the Debye temperature Θ_D and the bulk modulus B of Ti—B compounds at the given temperatures, and the heat capacities (C_v and C_p) decrease slowly with pressure at a constant temperature.

1. Introduction

The titanium borides (TiB_2, Ti_3B_4, TiB and Ti_2B) as metallic-like compounds have received much attention owing to their high electrical conductivity, excellent wear-resistance and mechanical properties [1]. Moreover, TiB and TiB_2 have been widely applied as reinforcement and grain refiner in metal matrix composites [2,3].

Currently, the studies on the properties of titanium borides have been carried out both by experimental and theoretical methods. The structures of titanium borides were obtained by X-ray diffraction [4–7] and the thermodynamic data of Ti—B system were calculated by Calphad method [8]. The original structure of Ti_2B derived by experiments was regarded as a metastable phase [7]. The structure of Ti_2B was also optimized by Mouffok et al. [9] which has been employed in this paper. Besides, the newer stable structures of Ti_2B have also been predicted by other researchers

* Corresponding author.
E-mail address: zhaoyuhong@nuc.edu.cn (Y. Zhao).

https://doi.org/10.1016/j.matchemphys.2018.01.067
0254-0584/

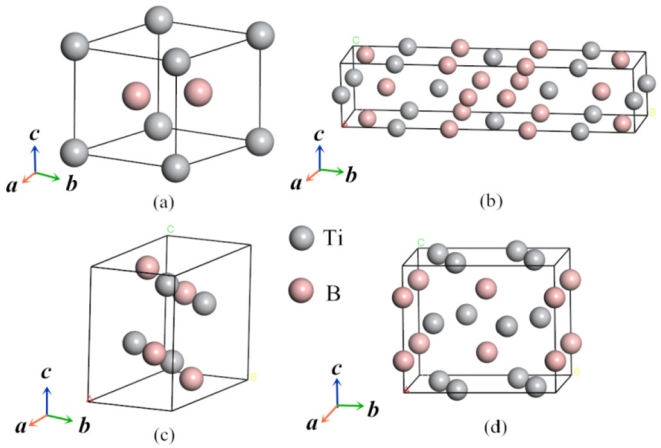

Fig. 1. The crystal structures of Ti–B compounds (a) TiB_2; (b) Ti_3B_4; (c) TiB; (d) Ti_2B.

[10,11]. Panda et al. [12] determined the elastic constants of TiB and proposed the reasoning for its higher modulus and melting point. The density of states, Debye temperature, anisotropy, ground-state and elastic properties of the above titanium borides were systematically studied at 0 GPa [13–15]. Moreover, the influence of pressure on the elastic properties and electronic properties of TiB, TiB_2 and Ti_3B_4 phases were investigated by first-principles [16–18]. We also noted the difference in the reported values of elastic constants of Ti_3B_4 phase at 0 GPa [18,19], which led to Ti_3B_4 phase demonstrating different properties with pressure. Based on the above investigations, it is especially necessary to examine the elastic constants of Ti_3B_4 phase more accurately by first-principles method. Besides, the temperature dependence of thermodynamic properties of Ti–B system has been studied [15,20,21]. However, the mechanical and thermodynamic properties of Ti-B compounds under the conditions of temperature and pressure have not been systematically reported in detail.

In this context, the current paper in detail reports on the work concerning the structural and mechanical properties of Ti–B compounds under different applied pressures. Also, the effects of pressure and temperature on the Debye temperature, heat capacity and bulk modulus of Ti–B compounds have been carefully analyzed.

2. Computational studies

The DFT method has been proven to be one of the most accurate methods for the computation of the electronic structure of solids [22–25]. The crystal structure and physical properties of Ti–B compounds were carried out within ultra-soft pseudopotential [26] as applied in CASTEP [27] code. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [28,29] function was employed as exchange-correlation potential. Ti $3s^23p^63d^24s^2$ and B $2s^22p^1$ were treated as valence electrons in all the calculations. The k-points meshes for TiB_2, Ti_3B_4, TiB and Ti_2B were set to be $\boldsymbol{15 \times 15 \times 12}$, $\boldsymbol{12 \times 3 \times 13}$, $\boldsymbol{6 \times 12 \times 8}$ and $\boldsymbol{9 \times 9 \times 11}$, respectively, while an energy cutoff of 580 eV was set for all the Ti–B compounds. The energy–volume values for each compound were calculated using the full relaxed atomic position in each step, i.e. cell parameters and ionic positions. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [30] was specified for geometry optimization. The convergence threshold of 5.0×10^{-7} eV/atom and 5.0×10^{-6} eV/atom were set for the self-consistent field (SCF) and energy change, respectively.

3. Results and discussion

3.1. Structural properties

The optimized crystal structures and lattice constants for Ti–B compounds are shown in Fig. 1 and Table 1, respectively. The predicted lattice constants match well with the reported results demonstrating the reliability of the present geometric optimization model.

The energy-volume $E(V)$ data can be obtained by first principles calculations at a temperature of 0 K. The $E(V)$ curves are shown in Fig. 2 and are fitted to the Birch-Murnaghan model [31]:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B'_0 + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \quad (1)$$

where V_0 is the equilibrium volume $\left(p = -\frac{dE(V)}{dV}\right)$; B_0 is the bulk modulus given by

$$B_0 = -V\left(\frac{dP}{dV}\right)_{P=0} = V_0\left(\frac{d^2E(V)}{d^2V}\right)_{V_0} \quad (2)$$

and B'_0 is the first pressure derivative of the bulk modulus

$$B'_0 = \left(\frac{dB}{dP}\right)_{P=0} \quad (3)$$

Once the fitting of $E(V)$ data to the Birch-Murnaghan model is obtained, the function pressure-volume $P(V)$ can be calculated by the equilibrium thermodynamic relation [32]:

Table 1
The obtained lattice constants (a, b and c), bulk modulus (B0) and its derivative (B′) at 0 K and 0 GPa.

Phase	Space group	Titanium site	Species	Lattice constants (Å)			B_0	B'
				α	b	c		
TiB_2	P6/mmm	1a(0,0,0)	Present	3.028	3.028	3.222	250.9	3.86
			Exp. [4]	3.030	3.030	3.229	–	–
			Cal. [17]	3.028	3.028	3.222	250.8	3.85
Ti_3B_4	Immm	2c(0.5,0.5,0)	Present	3.259	13.737	3.036	224.0	3.90
		4g(0,0.1851,0)	Exp. [33]	3.259	13.73	3.032	–	–
TiB	Pnma		Present	6.108	3.051	4.567	207.0	3.92
		4c(0.177,0.25,0.122)	Exp. [5]	6.12	3.06	4.56	–	–
			Cal. [16]	6.111	3.05	4.567	209.9	3.79
Ti_2B	I4/mcm	8h(0.166,0.666,0)	Present	5.654	5.654	4.765	160.1	3.46
			Cal. [9]	5.666	5.666	4.754	–	–