Communication

A first-principles study of hypothetical Ti_4AlB_3 and V_4AlB_3 phases

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ABSTRACT

In this paper, we employed the pseudopotential plane-waves method to investigate the structural, elastic properties, bond stiffness and thermal properties for hypothetical layered ternary ceramic Ti_4AlB_3 and V_4AlB_3 phases. By calculating the formation energy and elastic constants, the stability of these two hypothetical structures was discussed from the energetic and mechanical point of view. The B/G ratio and Poisson ratio were calculated to discuss the bond composition of Ti_4AlB_3 and V_4AlB_3 compounds. In addition, we calculated the bond stiffness for different bonds in Ti_4AlB_3 and V_4AlB_3. The ratio of the weakest bond stiffness to the strongest bond stiffness was presented to explore their mechanical properties. What's more, by calculating longitudinal, transverse sound, mean sound velocities, and the Debye temperatures, we discussed the thermal conductivity of hypothetical Ti_4AlB_3 and V_4AlB_3 phases.

1. Introduction

$M_{n+1}AX_n$ (MAX) compounds, as a new type of ceramic materials, possess a layered-hexagonal structure alternately stacked by M-X octahedron slabs and weakly bonded A slabs. M is an early transition metal, A is a group 13–16 element, and X is mainly C or N. The unique structure makes their excellent characteristics. They possess both metallic and ceramic excellent properties [1], such as high damage tolerance, high-temperature oxidation resistance, thermal and electrical conductivity [2]. Due to their excellent features, it leads to MAX having an important application in many fields. And a lot of investigations have been done on this type of materials in theory and experiment. But studies are focus on MAX (X = C and N) compounds [3–5].

Searching promising MAX phase materials is the growing demand of industry and technology. Ramzan et al. [6] presented a modified type of MAX phases, Ti_4AlH_3 and Ti_3AlH_2, by replacing carbon with hydrogen in the existing structure Ti_4AlC_3 and Ti_3AlC_2 by DFT calculations. Khazaei1 et al. [7] investigated the electronic structures, formation energies, and mechanical properties of hypothetical MoAlB phases. Bai et al. [8] calculated the crystal structure, electronic structure, lattice dynamics and elastic properties of a hypothetical MAX phase compound MoAlB.

In our present study, we introduce two hypothetical MAB phases, Ti_4AlB_3 and V_4AlB_3, by having hydrogen as a X instead of nitrogen or carbon in their corresponding existing MAX (X = C or N) phases. Then, we focus on the stability, mechanical, elastic and thermal properties of

hypothetical Ti_4AlB_3 and V_4AlB_3, and predict the bulk, shear and Young's moduli, Poisson's ratio, longitudinal, transverse sound, mean sound velocities, and Debye temperature of these two materials based on DFT calculations. These results are comparable with the properties of their corresponding existing MAX (X = C or N) phases.

2. Computational methods and details

In this work, first-principles study of hypothetical Ti_4AlB_3 and V_4AlB_3 phases are carried out by standard Kohn-Sham self-consistent density functional theory [9,10] in the *ab initio* plane-wave code ABINIT. Using the conjugate gradient (CG) algorithm, the structures of hypothetical Ti_4AlB_3 and V_4AlB_3 phases are optimized. The self-consistency tolerance is set to 5×10^{-7} eV for the total energy per atom and 0.002 eV/Å for atomic force in the structural optimization. The generalized gradient approximation designed by Perdew, Burke, and Ernzerhof (PBE) [11,12] is considered as the exchange-correlation energy in these calculations. Pseudopotentials plane-wave method is employed to describe the valence electron interaction with the atomic core. The valence electronic configurations for Ti, V, Al and B are set as $3s^23p^63d^24s^2$, $3s^23p^63d^34s^2$, $3s^23p^1$ and $2s^22p^1$, respectively. A plane-wave basis set with an energy cutoff of 550 eV is closed to ensure a stable state of the system energy. The Brillouin zone sampling is performed using Monkhorst-pack grid [13].

3. Results and discussions

3.1. Structural and mechanical stability

To confirm the structure of Ti_4AlB_3 and V_4AlB_3, we have taken the Ti_4AlN_3 and V_4AlC_3 structural parameters as an initial guess by replacing the nitrogen and carbon with boron in the both structures, respectively [14,15]. And both of them have hexagonal structures and crystallized in the P63/mmc space group No. 194. The ground state structures of Ti_4AlB_3 and $V4AlB_3$ were determined by the DFT calculations.

To analyze the stability Ti_4AlB_3 and V_4AlB_3, we calculated the formation energy of them. The formation energies are define by

$$\triangle E = E(M_4AlB_3) - 4E(M) - E(Al) - 3E(B) \quad (1)$$

where $E(M_4AlB_3)$ is the total energy of bulk M_4AlB_3 per unit cell; $E(M)$, $E(Al)$, and $E(B)$ represent the total energy of M (M = Ti, V), Al, and B per atom, respectively. The total energies of the M and Al elements were estimated from their most stable bulk structures. $E(B)$ was estimated from the total energies of α-boron. Our computed values of formation energy for Ti_4AlB_3 and V_4AlB_3 are -0.30 and -0.55 eV/atom, respectively. This shows the stability of Ti_4AlB_3 and V_4AlB_3 with respect to decomposition ($\triangle E < 0$) from an energy point of view.

Ti_4AlB_3 and V_4AlB_3 are hexagonal phases, the mechanical stability criteria for hexagonal phase are as follows,

$$C_{12} > 0, \ C_{11} - C_{12} > 0, \ C_{33} > 0, \ C_{44} > 0,$$

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

Combined with the calculated elastic constants $C_{ij}(GPa)$ presented in Table 1, we can see that the stability of Ti_4AlB_3 and V_4AlB_3 from the mechanical point of view.

In addition, for the hexagonal phase, the elastic modulus, Young's modulus E and Poisson's ratio ν can be obtained based on elastic constants by following formula,

$$B = (2/9)(C_{11} + C_{12} + C_{13} + C_{33}/2] \quad (3)$$

$$G = (1/15)(2C_{11} + C_{33} - C_{12} - 2C_{13}) + (1/5)[2C_{44} + (1/2)(C_{11} - C_{12})] \quad (4)$$

$$E = 9BG/(3B + G) \quad (5)$$

$$\nu = (3B - 2G)/2(3B + G) \quad (6)$$

From Table 1, we can see that the bulk modulus of Ti_4AlB_3 and V_4AlB_3 are much larger than that of shear modulus. It is similar to those of the corresponding M_2AC and M_2AN phases. It is due to the bulk modulus are mainly related to the M-X (X = C, N or B) covalent bonding in the M-X slabs while the shear modulus are mainly related to the weak M-A bonding in the M-A slabs. The M-X covalent bonds are much stronger than M-A bonds.

Pugh [21] used the B/G ratio to evaluate the brittleness of materials. If the B/G ratio is less than 1.75, the material is considered to be brittle, otherwise, it is considered to be ductile [22]. According to the value of B and G listed in Table 1, we can concluded that Ti_4AlN_3 and V_4AlB_3 are ductile, while other compounds are brittle.

The Poisson ratio value can be used to measure the degree of the covalent bonding. For covalent materials, Poisson ratio is small ($\nu = 0.1$), whereas for ionic materials this value is about 0.25 [23]. For Ti_4AlB_3 and V_4AlN_3, their Poisson ratios are 0.288 and 0.261, respectively, i.e. a higher ionic or weaker covalent contribution in intraatomic bonding for these two compounds. For other compounds, their Poisson ratios are between 0.1 and 0.25, so they possess partial ionic and covalent components.

3.2. Compressibility and bond stiffness

To investigate the compressibility of MAX compounds, He at al proposed a simple model to characterize the bond stiffness [5,24,25]. According to this model, the bond stiffness k can be obtained by fitting a quadratic curve to the relative bond lengths d/d_0 (d_0 is the bond length at 0 GPa) as a function of P. The pressure dependence of relative bond lengths can be expressed as a form of polynomial function ($d/d_0 = C_0 + C_1P + C_2P^2$) (where P is the hydrostatic pressure, C_i (i = 0, 1, 2) are the quadratic fitting coefficients). And the bond stiffness k can be calculated by following formula,

$$k = \left| \frac{d(d/d_0)}{dP} \right|^{-1} = |C_1 + 2C_2P|^{-1} \quad (7)$$

Using the above method, we presented the relationship of the normalized bond length changed as pressure for Ti_4AlB_3 and V_4AlB_3 phases in Figs. 1(a) and 2(a). By fitting the pressure dependence of relative bond lengths to polynomial function, we obtained the quadratic fitting coefficients for different bonds. And then the bond stiffness can be calculated formula (7). In Figs. 1(b) and 2(b), we plotted the bond stiffness as a function of P for Ti_4AlB_3 and V_4AlB_3 phases.

From above Figs. 1 and 2, we can see that the Ti1-Al1 and V1-Al1 bonds are the most compressible for Ti_4AlB_3 and V_4AlB_3, respectively. While the Ti1-B2 and V1-B2 bonds are the least compressible for Ti_4AlB_3 and V_4AlB_3, respectively. Using formula (7), the calculated bond stiffness at 0 GPa can be obtained. We can classified all the bonds in Ti_4AlB_3 into three groups: Ti1-B2 bonds have the highest stiffness (775 GPa); Ti2-B1 and Ti2-B2 bonds have relatively low bond stiffness (562–641 GPa); and the stiffness of Ti1-Al1 are weakest (331 GPa). Similarly, V1-B2 bonds have the highest stiffness (917 GPa); V2-B1 and V2-B2 bonds have relatively low bond stiffness (730–833 GPa); and the stiffness of Ti1-Al1 are weakest (441 GPa) for V_4AlB_3.

Previous studies [8,25–27] show that the ratio of the weakest bond stiffness to the strongest bond stiffness for MAX compounds can be considered as an indicator of mechanical properties. If this ratio is greater than 1/2, the compounds usually possess a low damage tolerance and fracture toughness; while when this ratio is approximately 1/3 to 1/2, the compounds usually have low hardness, high thermal shock resistance, high fracture toughness, high damage tolerance. Due to their ratio less than 1/2, Ti_4AlB_3 and V_4AlB_3 may be possess such unusual mechanical properties.

As a contrast, we presented the normalized bond length and bond stiffness as a function of P for Ti_4AlN_3 and V_4AlC_3 in Figs. 3 and 4.

In Table 2, we presented the coefficients of second order polynomial fit of relative bond length as a function of pressure for M_4AlB_3(M = Ti, V). It can seen that the coefficient C_1 is minus while the C_2 is positive. It

Table 1

Elastic constants $C_{ij}(GPa)$ and elastic moduli B, G for V_4AlC_3, V_4AlN_3 and V_4AlH_3 we calculated in this work.

	$C_{11}(GPa)$	$C_{12}(GPa)$	$C_{13}(GPa)$	$C_{33}(GPa)$	$C_{44}(GPa)$	B(GPa)	G(GPa)	ν
Ti_4AlC_3	400.3 [16]	76.3 [16]	70.4 [16]	312.0 [16]	155.4 [16]	170.6 [16]	153.7 [16]	0.154 [16]
Ti_4AlN_3	407.3 [17]	94.6 [17]	100.5 [17]	363.5 [17]	162.0 [17]	196.4 [17]	154.6 [17]	0.188 [17]
Ti_4AlB_3	202.9	99.4	74.0	200.4	66.1	122.1	60.2	0.288
V_4AlC_3	458 [18]	107 [18]	110 [18]	396 [18]	175 [18]	218 [18]; 55 [19]	170 [18]	0.191 [18]
V_4AlN_3	382 [20]	143 [20]	122 [20]	381 [20]	116 [20]	213 [20]	121 [20]	0.261 [20]
V_4AlB_3	328.7	76.2	119.0	312.6	144.5	177.5	125.1	0.215