

A first-principles study on elastic properties and stability of $\text{Ti}_x\text{V}_{1-x}\text{C}$ multiple carbide

WANG Xin-hong¹, ZHANG Min², RUAN Li-qun³, ZOU Zeng-da¹

1. Key Laboratory of Liquid Structure and Heredity of Materials of Ministry of Education, Shandong University, Ji'nan 250061, China;
2. School of Mechanical Engineering, Shandong University, Ji'nan 250061, China;
3. Department of Mechanical System Engineering, Kumamoto University, Kumamoto 860-8555, Japan

Received 22 July 2010; accepted 5 November 2010

Abstract: The structure, stability and elastic properties of di-transition-metal carbides $\text{Ti}_x\text{V}_{1-x}\text{C}$ were investigated by using the first-principles with a pseudopotential plane-waves method. The results show that the equilibrium lattice constants of $\text{Ti}_x\text{V}_{1-x}\text{C}$ show a nearly linear reduction with increasing addition of V. The elastic properties of $\text{Ti}_x\text{V}_{1-x}\text{C}$ are varied by doping with V. The bulk modulus of $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ is larger than that of pure TiC, as well as $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has the largest C_{44} among $\text{Ti}_x\text{V}_{1-x}\text{C}$ ($0 \leq x \leq 1$), indicating that $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has higher hardness than pure TiC. However, $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ presents brittleness based on the analysis of ductile/brittle behavior. The $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ carbide has the lowest formation energy, indicating that $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ is more stable than all other alloys.

Key words: elastic properties; $\text{Ti}_x\text{V}_{1-x}\text{C}$ carbide; the first-principles; phase stability

1 Introduction

TiC exhibits excellent properties of high strength, high hardness and good chemical and thermal stabilities, which has been received interest worldwide as reinforcement in metal matrix composites (MMCs) [1–2]. In our previous studies, TiC carbide was in situ synthesized from Fe-Ti30 alloy and graphite to fabricate TiC/Fe composite surface coating [3]. It was found that the wear properties of the composite coatings were improved significantly. However, the volume fraction of TiC is limited because the content of Ti is only 25%–35% (mass fraction) for Fe-Ti30. To increase volume fraction of carbide, vanadium elements were added into raw materials to form TiC and VC type carbide. The results showed that besides TiC and VC carbides, a few of (Ti, V)C were found in the coating [4]. However, a limited investigation of the mechanical properties of this carbide was updated in the literature.

It is well-known that mechanical properties of carbides result from their elastic properties, specifically, the elastic behavior of carbides is controlled primarily by the strength of atomic bonds. Therefore, when other

alloying elements are added into raw materials to form complex carbides, the structure and properties of TiC will be changed, thus it is necessary to clarify the effects of these alloying elements on TiC. ZHOU et al [5] applied the first-principles to investigating the elastic properties and electronic structures of Cr doped Fe_3C carbides. RAMASUBRAMANIAN et al [6] have investigated elastic and thermodynamical properties of $\text{Ti}_{1-x}\text{Zr}_x\text{C}$ using Ab initio method. MAOUCHE et al [7] have analyzed the stability of $\text{Ti}_{1-x}\text{Zr}_x\text{C}$, $\text{Ti}_{1-x}\text{Hf}_x\text{C}$ and $\text{Hf}_{1-x}\text{Zr}_x\text{C}$ by the first-principles method. Those researches showed that the properties and stability of TiC carbides were affected by doping an appropriate amount of element.

In this work, the lattice constants, formation energy and elastic constants of $\text{Ti}_x\text{V}_{1-x}\text{C}$ ($x=0-1$) were calculated by the first principles calculation. The effect of vanadium on the structure stability and elastic properties of TiC was also investigated.

2 Calculation method and crystal structure

In this study, the first-principles calculations based on the pseudopotential plane-wave within the density

functional theory (DFT) were performed by using the Cambridge Serial Total Energy Package (CASTEP). Ultrasoft pseudopotentials were used to represent the electrostatic interaction between valence electrons and ionic cores. The generalized gradient approximation (GGA) [8] is made for electronic exchange-correlation potential energy. After a series tests, the cut-off energies were all set at 380 eV for these compounds. And the Brillouin zone sampling was carried using the $8 \times 8 \times 8$ set of Monkhorst-Pack mesh. Each calculation was converged when the maximum force on the atom was below $0.01 \text{ eV/\AA}$ and the maximum displacement between cycles was below $5.0 \times 10^{-4} \text{ \AA}$. The maximum strain used in the total energy fitting to derive elastic moduli was within 1%. Atomic positions were relaxed and optimized with a density mixing scheme using the conjugate gradient (CG) method.

The calculated energies cannot be directly used to compare the stability. In fact, the stability of one composition with respect to the other depends on its formation energy. A standard method to access the relative stability of the multiple carbides is to calculate the formation energy, which is defined as the energy difference between the alloy and the weighed sum of constituents [9]:

$$\Delta E_{\text{for}}(\text{Ti}_x\text{V}_{1-x}\text{C}) = E_{\text{tot}}(\text{Ti}_x\text{V}_{1-x}\text{C}) - xE_{\text{tot}}(\text{TiC}) - (1-x)E_{\text{tot}}(\text{VC}) \quad (1)$$

where $E_{\text{for}}(\text{Ti}_x\text{V}_{1-x}\text{C})$ is the formation energy of $\text{Ti}_x\text{V}_{1-x}\text{C}$; $E_{\text{tot}}(\text{TiC})$ and $E_{\text{tot}}(\text{VC})$ are the total formation energies of TiC and VC, respectively. All formation energies were calculated relatively to bulk energies and the stabilities of compounds were analyzed using their formation energies.

To access the elastic properties of $\text{Ti}_x\text{V}_{1-x}\text{C}$, the elastic stiffness was calculated. It can be obtained by calculating the stresses when small strains are applied to each relax structure. Elastic strain energy U is calculated as [10]

$$U = \frac{\Delta E}{V_0} = \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} \varepsilon_i \varepsilon_j \quad (2)$$

where ΔE is the energy difference; V_0 is the original volume; C_{ij} is the elastic constant; ε_i and ε_j are strains. Therefore, the energy difference between unformed and deformed sample was firstly calculated to obtain elastic strain energy, then, the elastic constants were obtained. To calculate the elastic constant, the ground state structure is strained according to symmetry-dependent strain patterns with varying amplitudes and a subsequent computing of the stress tensor after a re-optimization of the internal structure parameters. Since any symmetry present in the structure may make some of these components equal and others may be fixed at zero. Thus,

cubic TiC crystal has only three different symmetry elements (C_{11} , C_{12} and C_{44}), each of which represents three equal elastic constants ($C_{11}=C_{22}=C_{33}$; $C_{12}=C_{23}=C_{31}$; $C_{44}=C_{55}=C_{66}$).

The bulk modulus (B) is the ratio of the change in pressure acting on a volume to the fractional change in volume. It describes the response of material to uniform pressure, which is related to the elastic constants by the relation [10]:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (3)$$

The shear modulus (G) is defined as the ratio of shear stress to the shear strain. It is related to the elastic constants by the following equation [11]:

$$G = \frac{1}{2}(G_V + G_R) \quad (4)$$

where

$$G_V = \frac{1}{5}(2C_{44} + C_{11} - C_{12}) \quad (5)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (6)$$

The elastic modulus (E) is a measure of the stiffness of a given materials. The elastic modulus is related to the elastic constants by the following expression [11]:

$$E = \frac{9BG}{3B + G} \quad (7)$$

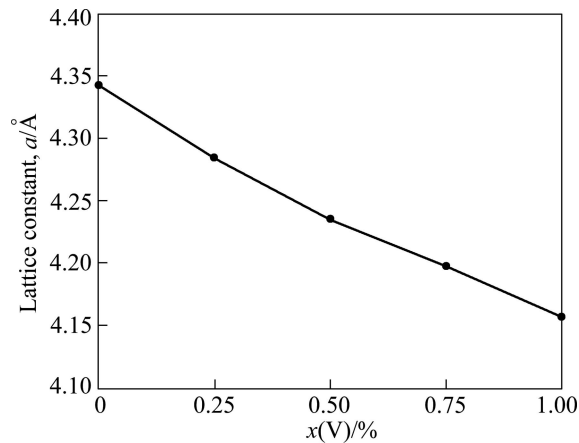
3 Results and discussion

Geometry optimization of lattice constants for $\text{Ti}_x\text{V}_{1-x}\text{C}$ was carried out. The bulk modulus, shear modulus (G) and elastic modulus (E) of $\text{Ti}_x\text{V}_{1-x}\text{C}$ have been calculated using the optimized lattice constants. The calculated results of lattice constants and elastic parameters of TiC are given in Table 1. It can be seen that the present theoretical equilibrium lattice constant of TiC is $4.34303 \text{ \AA}$. This value is close to $4.33 \text{ \AA}$ obtained experimentally by AHUJA et al [12]. The difference between theoretical and experimental equilibrium lattices is about 0.3%. The other theoretical calculation and experimental results of elastic parameters for TiC are also listed in Table 1. It can be found that the present calculations of elastic parameters for TiC show good agreement with the experimental values and other DFT [12–17].

Figure 1 shows the effect of substitutional element of vanadium on the equilibrium lattice constant. It can be found that the lattice constant of TiC shrinks with the addition of V. The main reason is that the atomic radius of vanadium ($r=0.1925 \text{ nm}$) is smaller than that of titanium ($r=0.20 \text{ nm}$) and the lattice parameter of TiC with V dissolution is decreased.

Table 1 Structural equilibrium parameters and elastic stiffness coefficients for TiC

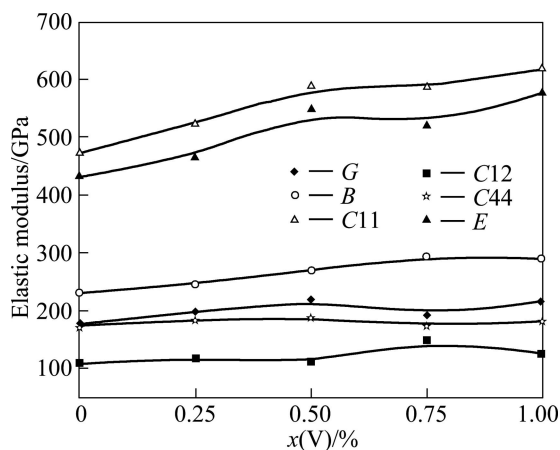
Item	$a/\text{\AA}$	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa	B/GPa	E/GPa	G/GPa
Present	4.3430 31	472.5	108.9	172.4	230.1	431.7	176.1
Experiment	4.33 [12]	513 [13]	106 [13]	178 [13]	233 [16–17]	448 [16]	188 [16]
Calculation	4.3428 [14]	527 [14], 470 [15]	112 [14], 97 [15]	159 [14], 167 [15]	250 [14], 221 [15]	429 [14], 415 [15]	177 [14], 175 [15]

**Fig. 1** Calculated equilibrium lattice constant for $\text{Ti}_x\text{V}_{1-x}\text{C}$

The mechanical stability of the crystal implies that the strain energy must be positive. Thus, for a cubic crystal, the elastic stability criteria at ambient condition are given by the following equation:

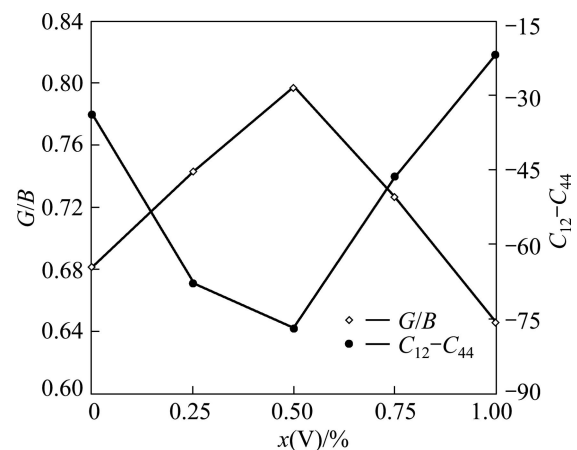
$$C_{11} > 0, C_{44} > 0, C_{11} + 2C_{12} > 0, (C_{11} - C_{12}) > 0 \text{ and } C_{12} < B < C_{11} \quad (8)$$

In the present study, the calculated elastic coefficient C_{11} , C_{12} and C_{44} , B , G and E of $\text{Ti}_x\text{V}_{1-x}\text{C}$ are shown in Fig. 2. It can be observed that C_{11} , C_{44} , $(C_{11} - C_{12})$ and $(C_{11} + 2C_{12})$ are greater than zero; and $C_{12} < B < C_{11}$. This indicates that our results satisfy all the criteria for a cubic crystal. In addition, generally speaking, the larger the moduli are, the higher the hardness of the materials should be. From the calculated

**Fig. 2** Elastic stiffness coefficients and bulk modulus of $\text{Ti}_x\text{V}_{1-x}\text{C}$ as function of vanadium content

G , B and E , it indicates that the G , B and E of $\text{Ti}_x\text{V}_{1-x}\text{C}$ ($0 < x < 1$) are higher than pure TiC, which implies that addition of V has a potential to increase the hardness of TiC. Furthermore, in general, there exists $B > C_{44} > G$ for transition-metal carbides in the rocksalt structure. However, our calculation showed that $B > G > C_{44}$, which indicates that shear modulus C_{44} is the main constraint on stability. It can be found from Fig. 2 that $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has the largest C_{44} among $\text{Ti}_x\text{V}_{1-x}\text{C}$ ($0 \leq x \leq 1$), indicating that $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has higher hardness than pure TiC.

On the other hand, the ductile or brittle behavior of carbide is one of the important mechanical properties for ceramic phase. There existed two empirical criteria available to assess ductile/brittle behavior of materials. One is Pugh's criterion [18]; another is the Cauchy pressure criterion [19]. The former involves the G/B , in which the material is predicated to behave in a ductile manner when G/B is less 0.5; otherwise, it is expected to behave in a brittle manner. The latter involves Cauchy pressure ($C_{12} - C_{44}$), which deems that the more negative the $(C_{12} - C_{44})$ is, the more brittle the material is. Figure 3 shows the calculated G/B and $(C_{12} - C_{44})$ as a function of the titanium content. It can be seen that G/B is slightly increased from 0.765 5 of TiC to 0.809 4 of $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$, but G/B decreases when added V is over 0.5% (mole fraction) in TiC, indicating that V slightly promotes brittleness when V is less 0.5% (mole fraction). This result can also be confirmed via $(C_{11} - C_{44})$ Cauchy pressure criterion. From our calculation, the $(C_{12} - C_{44})$ of TiC and $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ is $-63.470 5$ and $-76.903 8$, respectively.

**Fig. 3** Calculated G/B and Cauchy presser ($C_{12} - C_{44}$) of $\text{Ti}_x\text{V}_{1-x}\text{C}$ as function of vanadium content

This indicates that the hardness of $\text{Ti}_x\text{V}_{1-x}\text{C}$ increases with increasing V content when x is less 0.5% (mole fraction), but the brittleness is increased.

In general, the alloying atom is energetically unfavorable and will not occur when the difference in formation energy between the ternary alloy and the binary systems is positive. However, when the formation energy is negative, the compound is formed more easily and stable. The more negative the formation energy is, the more stable the alloy is. Figure 4 shows the formation energies of compounds calculated from Eq.(1). It can be seen that the formation energies of $\text{Ti}_x\text{V}_{1-x}\text{C}$ ($0 < x < 1$) are negative, which means that all alloys can exist in stable state. Moreover, the $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has the lowest formation energy, which indicates that $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ is more stable than all other alloys. In addition, the formation energies for the entire concentration are negative under ambient conditions, indicating that it is favorable for mixing VC and TiC to form compounds.

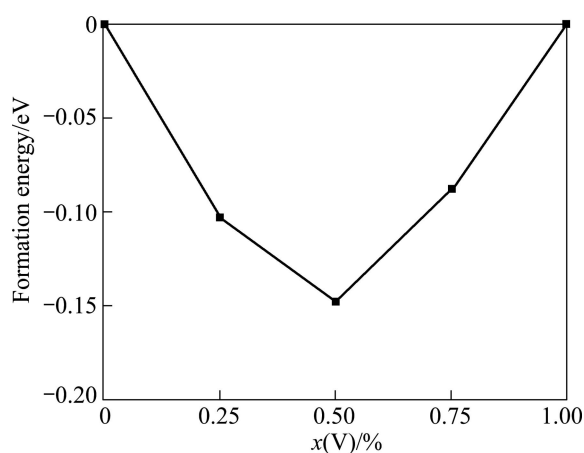


Fig. 4 Calculated formation energy for $\text{Ti}_x\text{V}_{1-x}\text{C}$ alloys

4 Conclusions

1) The calculated results for lattice constants, bulk modulus, elastic modulus and elastic stiffness coefficients of TiC are in reasonable agreement with reported experimental values and previous calculations.

2) The equilibrium lattice constants of $\text{Ti}_x\text{V}_{1-x}\text{C}$ show a nearly linear reduction with the increase of V content. V has a potential to increase the hardness of TiC, but increase the brittleness of TiC.

3) The negative formation energies of $\text{Ti}_x\text{V}_{1-x}\text{C}$ indicate that it is favorable for mixing VC and TiC to form alloys. $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ has the lowest formation energy, meaning that it is more stable than all other componential compounds.

References

[1] WANG Zhen-ting, ZHOU Xiao-hui, ZHAO Guo-gang. Microstructure and formation mechanism of in-situ TiC-TiB₂/Fe

composite coating [J]. Transactions of Nonferrous Metals Society of China, 2008, 18(4): 831–835.

[2] MANSOUR R, MAZIAR S Y, MOHAMMAD R R, SEYED S, RAZAVI T. The effect of production method on properties of Fe-TiC composite [J]. International Journal of Mineral Processing, 2010, 94(3–4): 97–100.

[3] WANG X H, ZHANG M, LIU X M, QU S Y, ZOU Z D. Microstructure and wear properties of TiC/FeCrBSi surface composite coating prepared by laser cladding [J]. Surf Coat Technol, 2008, 202(15): 3600–3606.

[4] WANG X H, CHENG L, ZHANG M, QU S Y, DU B S, ZOU Z D. Reaction synthesis of (Ti, V)C carbide reinforced Fe-based surface composite coating by laser cladding [J]. Surf Eng, 2009, 25(3): 211–217.

[5] ZHOU, C T, XIAO B, FENG J, XING JD, XIE X J, CHEN Y H ETAL. First principles study on the elastic properties and electronic structures of (Fe, Cr)₃C [J]. Computational Materials Science, 2009, 45(4): 986–992.

[6] RAMASUBRAMANIAN S, RAJAGOPLAN M, THANGAVEL R, KUMAR J. Ab initio study on elastic and thermodynamical properties of $\text{Ti}_{1-x}\text{Zr}_x\text{C}$ [J]. Eur Phys J B, 2009, 69: 265–268.

[7] MAOUCHE D, LOUAIL L, RUTERANA P, MAAMACHE M. Formation and stability of di-transition-metal carbides $\text{Ti}_x\text{Zr}_{1-x}\text{C}$, $\text{Ti}_x\text{Hf}_{1-x}\text{C}$ and $\text{Hf}_x\text{Zr}_{1-x}\text{C}$ [J]. Computational Materials Science, 2008, 44: 347–350.

[8] MARLO M, MILMAN V. Density-functional study of bulk and surface properties of titanium nitride using different exchange correlation functionals [J]. Phys Rev B, 2000, 62: 2899–2907.

[9] FERREIRA L G, WEI S H, ZUNGER A. Stability, electronic structure and phase diagrams of novel inter-semiconductor compounds [J]. Int J Supercomput Appl, 1991, 5: 34–56.

[10] CHARLES KITTEL. Introduction to solid state physic [M]. 8th ed. New York: John Wiley and Sons Inc, 2005.

[11] LEVINSHTEIN M, RUMYANTSEV S, SHUR M. Handbook series on semiconductor parameters [M]. Singapore: World Scientific, 1999.

[12] AHUJA R, ERIKSSON O, WILLS J M, JOHNSON B. Structural, elastic, and high-pressure properties of cubic TiC, TiN, and TiO [J]. Phys Rev B, 1996, 53: 3072–3079.

[13] CLERC D G, LEDBETTER H M. Mechanical hardness: A semiempirical theory based on screened electrostatics and elastic shear [J]. J Phs Chem Solid, 1998, 59: 1071–1095.

[14] HAINES J, LEGER J M, BOCQUILLON G. Synthesis and design of superhard materials [J]. Annu Rev Mater Res, 2001, 31: 1–23.

[15] CLERC D G, LEDBETTER H M. Mechanical hardness: A semiempirical theory based on screened electrostatics and elastic shear [J]. J Phs Chem Solid, 1998, 59: 1071–1095.

[16] STAROVEROV V N, SCUSERIA G E, TAO J, PERDEW J P. Tests of a ladder of density functionals for bulk solids and surfaces [J]. Phys Rev B, 2004, 69(7): 075102–075113.

[17] DODD S P, CANKURTARAN M, JAMES B. Ultrasonic determination of the elastic and nonlinear acoustic properties of transition-metal carbide ceramics: TiC and TaC [J]. J Mater Sci, 2003, 38(6): 1107–1115.

[18] PUGH S F. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals [J]. Philo Mag, 1954, 45: 823–843.

[19] FU C L, YOO M H. Electronic structure and mechanical behavior of transition-metal aluminides: A first-principles total-energy investigation [J]. Mater Chem Phys, 1992, 32(1): 25–36.

多组元碳化物 $\text{Ti}_x\text{V}_{1-x}\text{C}$ 弹性性能与稳定性的第一性原理研究

王新洪¹, 张 敏², 阮立群³, 邹增大¹

1. 山东大学 材料液固结构演变与加工教育部重点实验室, 济南 250061;

2. 山东大学 机械工程学院, 济南 250061;

3. 熊本大学 机械系统工程系, 熊本 8608555, 日本

摘 要: 采用基于密度泛函理论的第一性原理赝势平面波方法, 研究过渡族多组元碳化物 $\text{Ti}_x\text{V}_{1-x}\text{C}$ 的结构、稳定性及弹性性能。结果表明: $\text{Ti}_x\text{V}_{1-x}\text{C}$ 的晶格常数随着 V 的增多而线性递减; TiC 晶体中掺杂 V 后导致力学性能发生变化; 与 TiC 相比, $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ 具有较大的体模量和最大的弹性系数 C_{44} , 表明 $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ 具有比 TiC 高的硬度, 但 $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ 的脆性最大; $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ 具有最小的形成能, 表明 $\text{Ti}_{0.5}\text{V}_{0.5}\text{C}$ 最稳定。

关键词: 弹性性能; $\text{Ti}_x\text{V}_{1-x}\text{C}$ 碳化物; 第一性原理; 相稳定性

(Edited by LI Xiang-qun)