First principles study the stability and mechanical properties of MC (M = Ti, V, Zr, Nb, Hf and Ta) compounds

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ABSTRACT

The first principles calculations based on density functional theory (DFT) were adopted to investigate the stability, elastic constants, chemical bonding, Debye temperature and hardness of MC (M = Ti, V, Zr, Nb, Hf and Ta) compounds. The cohesive energy and formation enthalpy of these carbides indicate that they are thermodynamically stable structures. The population analysis was used to discuss the chemical bonding of these carbides. The elastic constants and moduli of these compounds were calculated. The results show that the bulk moduli of the carbides of transition metals from the fourth group (TiC, ZrC, HfC) are lower than the fifth group (VC, NbC, TaC). However, the Young's moduli of the carbides from fourth group are higher than the fifth group. The hardness of compounds was estimated using a semi empirical hardness theory.

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1. Introduction

Carbides of transition metals are very important technological materials due to their outstanding physical and chemical properties such as extreme stiffness, wear resistance, corrosion resistance, high melting point and thermal conductivity. Such outstanding characteristics allow for their wide use in cutting tools and wear-resistant parts of various mechanisms operating at high temperatures and pressures. Therefore, carbides of transition metals are extensively investigated both by theoretically and by experimentally [1–6]. Elliott and Kempter [7] studied the thermal expansion of binary transition metal carbides Ti, V, Zr and so on. Storms and Krikorian [8] discussed the variation of lattice parameter of transition metal carbides. Zhang et al. [9] studied the mechanical properties of $Fe_{7-x}Cr_xC_3$ carbides. They concluded that these carbides are all thermodynamic stability, and $Fe_4Cr_3C_3$ is potentially a high-strength and hard material among all $Fe_{7-x}Cr_xC_3$ carbides. Xiao et al. [10] investigated the mechanical properties and chemical bonding characteristics of Cr_7C_3 type multicomponent carbides. They pointed out that W or Mo substituted Cr_7C_3 type carbides have larger bulk and shear moduli than B doped carbides, and the chemical stability of $(Fe, Cr)_7C_3$ carbides is improved due to chemical bonding modifications through doping with B. However, the mechanical properties of early transition metal mono-carbides have not yet been discussed systematically in current literatures. In this work, the stability, mechanical properties, chemical bonding, Debye temperature and hardness of MC will be investigated from first principles calculations as performed in the CASTEP code to ensure meaningfulness of the performed comparison and reliability of the established trends in the considered group of compounds. All calculated results were compared to the corresponding experimental or theoretical findings, which show in good agreement. In the chosen group, TiC, ZrC and HfC are the carbides of the transition metals from the fourth group of the periodic table and VC, NbC and TaC are formed by the metals from fifth group. Therefore, by virtue of such selection of the studied compounds, it will be possible to see how the stability, Debye temperature and hardness vary with changing transition metals across the groups and periods in the periodic table. The crystal structures of MC (M = Ti, V, Zr, Nb, Hf and Ta) are shown in Fig. 1.

2. Methods and details

The first principles calculations based on density functional theory (DFT) were carried out to investigate the stability, mechanical properties, chemical bonding, Debye temperature and hardness of MC compounds. The interactions between valence electrons and ionic cores were represented by ultrasoft pseudopotential. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerh (PBE) scheme [11] was used to calculate the exchange–correlation energy. Valence electron configurations included in this research were $2s^2p^2$ for C, $3s^23p^63d^24s^2$ for Ti, $3s^23p^63d^34s^2$ for V, $4s^24p^64d^25s^2$ for Zr, $4s^24p^64d^45s^2$ for Nb, $5s^25p^65d^26s^2$ for Hf and $5s^25p^65d^36s^2$ for Ta, respectively. The max cut-off value of kinetic energy was selected as 450 eV for the plane waves. Monkhorst–Pack scheme [12] was used for k-point sampling in the first irreducible Brillouin zone (BZ), as $10 \times 10 \times 10$ for all of compounds. The total energy changes during the optimization process were
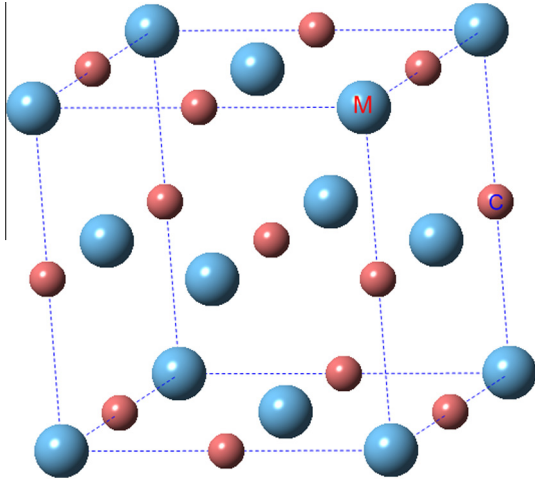
Fig. 1. The crystal structure of NaCl-type MC (M = Ti, V, Zr, Nb, Hf and Ta) compounds.

Table 1
The optimized parameters and the calculated cohesive energy and formation enthalpy of the MC (M = Ti, V, Zr, Nb, Hf and Ta) compounds.

Species	Lattice constants (Å) $a = b = c$	Cohesive energy (eV/atom)	Formation enthalpy (kJ/mol)
TiC	4.33 (4.33[a])	−8.6	−180.9 (−184[b])
VC	4.16 (4.16[a])	−8.1	−116.6 (−117[b])
ZrC	4.71 (4.69[c])	−9.0	−182.9 (−185[b])
NbC	4.48 (4.47[a])	−9.5	−140.9 (−141[b])
HfC	4.71 (4.70[a])	−8.9	−146.8
TaC	4.58 (4.48[d])	−9.5	−142.8

[a] Ref. [13].
[b] Ref. [14].
[c] Ref. [15].
[d] Ref. [16].

finally converged to 1×10^{-6} eV and the force per atom was reduced to 0.01 eV/Å. In order to investigate the relative stability of MC compounds, the cohesive energy and formation enthalpy were calculated using the following equations:

$$E_{coh}(MC) = E_{total}(MC) - E_{iso}(M) - E_{iso}(C) \tag{1}$$

$$\Delta_r H_m(MC) = E_{coh}(MC) - E_{coh}(M) - E_{coh}(C) \tag{2}$$

Where, $E_{coh}(MC)$ and $\Delta_r H_m(MC)$ are the cohesive energy and formation enthalpy of binary transition metal carbides, respectively; $E_{tot}(MC)$ is the total energy of binary transition metal carbides; $E_{coh}(M)$ is the cohesive energy of M element (M = Ti, V, Zr, Nb, Hf and Ta); $E_{coh}(C)$ is the cohesive energy of graphite; $E_{iso}(M)$ is the total energy of M atom (M = Ti, V, Zr, Nb, Hf and Ta) and $E_{iso}(C)$ is the total energy of C atom.

3. Results and discussion

3.1. Stability

In this section, the stability of transition metal carbides was mainly discussed. Since the GGA approach was used for geometry optimizations, the results of lattice constants could be overestimated. The optimized parameters, cohesive energy and formation enthalpy are listed in Table 1. From Table 1, we can know that the values of this work are in good agreement with the literatures previously [13–16]. Moreover, the lattice parameters of TiC, ZrC and HfC (group IV) are higher than the lattice parameters of VC, NbC and TaC (group V), which are consistent with the variation of formation enthalpy. The relative stability of these carbides can be described by cohesive energy and formation enthalpy. The

calculated cohesive energy values of TiC, VC, ZrC, NbC, HfC and TaC are −8.6 eV/atom, −8.1 eV/atom, −9.0 eV/atom, −9.5 eV/atom, −8.9 eV/atom and −9.5 eV/atom, respectively. Therefore, the NbC is more stable than other carbides from the point view of cohesive energy. However, the stability of compound is determined by the formation enthalpy, so the negative value of formation enthalpy is indicated for the stable crystal structure. The lower the formation enthalpy, the more stable the compound. We can also find that the formation enthalpy values of TiC, VC, ZrC, NbC, HfC and TaC are −180.9 kJ/mol, −116.6 kJ/mol, −182.9 kJ/mol, −140.9 kJ/mol, −146.8 kJ/mol and −142.8 kJ/mol, respectively, which are consistent with the corresponding experimental values. Thus, the compound of ZrC may be the most stable among them.

3.2. Elastic constants and moduli

The elastic constants C_{ij} (i, j = 1,2,4) determine the response of the crystal to external forces, as characterized by bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio σ. So the elastic constants C_{ij} of the studied MC compounds play important role for application as abrasive resistance phases. A stress–strain approach based on the generalized Hooke's law was used to calculate elastic constants, and the results are illustrated in Table 2. It can be seen that the calculated values in this work are consistent with other experimental and theoretical results [13,17–19]. For cubic crystal, the mechanical stability conditions are [20].

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0 \tag{3}$$

We verified that all of the studied MC compounds satisfy these conditions, implying that they are mechanically stable. The bulk modulus, shear modulus, Young's modulus can be estimated using Voigt–Reuss–Hill (VRH) approximation. The Voigt–Reuss–Hill approximation is an average of the two bounds, namely the lower bound of Voigt and upper bound of Reuss, which provides the best estimation for the mechanical properties of polycrystalline materials from the known elastic constants [21].

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{4}$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \tag{5}$$

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

$$G_{VRH} = \frac{1}{2}(G_V + G_R) \tag{7}$$

$$E = \frac{9B_{VRH}G_{VRH}}{(3B_{VRH} + G_{VRH})} \tag{8}$$

$$\sigma = \frac{(3B_{VRH} - 2G_{VRH})}{[2(3B_{VRH} + G_{VRH})]} \tag{9}$$

where B_V, B_R and B_{VRH} are the bulk modulus calculated by Voigt, Reuss and Voigt–Reuss–Hill approximation, respectively. G_V, G_R and G_{VRH} are the shear modulus calculated by Voigt, Reuss and Voigt–Reuss–Hill approximation, respectively. E is the Young's modulus and σ is the Poisson's ratio, which is both calculated by Voigt–Reuss–Hill approximation. The results of these moduli are presented in Table 3, which are in good agreement with previous reports [22–25]. In many cases, the larger bulk modulus of the compound, the higher hardness [26–28]. Therefore, we may conclude that ZrC is less hard than others. Moreover, the bulk moduli of the carbides of transition metals from fourth group (TiC, ZrC, HfC) are lower than