Journal of the European Ceramic Society 36 (2016) 3593–3599

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Discovering novel VC_{1-x} compounds through hybrid first-principles and evolutionary algorithms

Congwei Xie[a,b], Ning Liu[a,b], Xiang Cheng[a,b], Duan Li[a,b], Qingfeng Zeng[b,a,*]

[a] *International Center for Materials Discovery, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China*

[b] *Science and Technology on Thermostructural Composite Materials Laboratory, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China*

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form 29 March 2016
Accepted 29 March 2016
Available online 16 June 2016

Keywords:
Vanadium carbide
Ultra-high temperature ceramic
Evolutionary algorithm USPEX
Mechanical strength
Atomic rearrangement

ABSTRACT

VC_{1-x} compounds, known as ultra-high temperature ceramics, are able to maintain stability in a range of chemical compositions. Herein, using evolutionary algorithm USPEX, we performed a global search for potentially stable VC_{1-x} compounds. We have discovered two stable compounds ($P3_112$-V_6C_5 and $Pnnm$-V_2C) and a number of near-ground-state compounds ($Fm\bar{3}m$-VC, $P4_332$-V_8C_7, $P\bar{1}$-V_5C_4, $I\bar{4}3m$-V_4C_3, $Cmcm$-V_3C_2, and $Cmcm$-V_3C). The stable $Pnnm$-V_2C is a new structure with lower total energy than experimentally reported α-V_2C. Based on these stable and meta-stable VC_{1-x} compounds, we have systemically investigated their structures, mechanical properties, and chemical bonding. We found that $Cmcm$-V_3C_2 and $Cmcm$-V_3C display different arrangements of vanadium from other VC_{1-x} compounds. We suggest that such rearrangement of vanadium are able to enhance mechanical strength. Most of VC_{1-x} compounds possess very good mechanical properties, indicating that they have potential to be utilized for structural applications.

1. Introduction

Group IVB and VB transition metal carbides have been widely used due to their outstanding properties such as high hardness and melting point, good wear and corrosion resistance, and excellent mechanical strength and chemical stability [1,2]. In particular, these carbides which are also known as ultra-high temperature ceramics (UHTCs) are considered as potential candidates for ultra-high temperature structural applications [3–5]. For instance, they are able to be used in the extreme thermal and chemical environments such as hypersonic flight, atmospheric re-entry, and rocket propulsion [6,7]. However, due to the low fracture toughness of these carbides, these potential ultra-high temperature usage is limited. A possible solution is to incorporate toughening components (e.g. carbon fiber) to form ultra-high temperature ceramic matrix composites (UHTCMCs) [8–10].

Over the past decade, zirconium carbide based UHTCMCs have been widely investigated [11–15], while to our knowledge few work on vanadium carbide based UHTCMC is reported. The most common use of vanadium carbide is to be utilized as an reinforcement to improve mechanical strength of steel and coatings [16–19]. However, we should note that vanadium carbide has potential to be used for the design of UHTCMCs. On the one hand, vanadium carbide possesses very high melting temperature (3100 K [1]) and hardness (26 GPa [20]). On the other hand, vanadium carbide has an advantage in density when used for structural applications, e.g., density of vanadium carbide is lower than that of zirconium carbide.

To gain more information about properties of vanadium carbide it would be helpful to design vanadium carbide based UHTCMCs. Generally, vanadium carbide is able to maintain stability in a range of non-stoichiometric compositions [21–31]. The stoichiometric vanadium carbide is feature by carbon atoms occupying all octahedral interstices in the close-packed lattice formed by vanadium atoms, and its C/V ratio equals to 1. In non-stoichiometric vanadium carbide, due to the deficiency of carbon, C/V ratio is less than 1. Hence, vanadium carbide can be denoted by VC_{1-x}, in which x is the content of missing carbon ($0 \leq x < 1$). It should be noted that non-stoichiometric VC_{1-x}

---

[*] Corresponding author at: Science and Technology on Thermostructural Composite Materials Laboratory, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China.
E-mail address: qfzeng@nwpu.edu.cn (Q. Zeng).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.03.034
0955-2219/

display different properties from their stoichiometric form VC [32–35].

Structures determine properties. In order to understand properties of vanadium carbide more deeply, we need to clarify crystal structures of VC_{1-x}. In the present study, we used the evolutionary algorithm method [36,37] for discovering potentially stable VC_{1-x} compounds. In addition to two thermodynamically stable compounds ($P3_1 12$-V_6C_5 and *Pnnm*-V_2C), we also discovered several near-ground-state compounds ($Fm\bar{3}m$-VC, $P4_3 32$-V_8C_7, $P\bar{1}$-V_5C_4, $I\bar{4}3m$-V_4C_3, *Cmcm*-V_3C_2, and *Cmcm*-V_3C). The stable *Pnnm*-V_2C is a new structure possessing lower enthalpy than previously reported α-V_2C (*Pbcn* [26]). Based on these stable and meta-stable structures, we systematically investigated their properties, especially mechanical properties due to their importance for structural applications. We further revealed how the missing carbon affect properties of VC_{1-x} compounds. Our present study about vanadium carbide may be helpful for the design of vanadium carbide based UHTCMCs.

2. Computational methods

The evolutionary algorithm for structure prediction, as implemented in the USPEX code [36,37], has succeed in predicting many hereto unknown carbides [38–44]. Using the USPEX code, we firstly performed variable-composition structure searches with up to 33 atoms in a unit cell for the V–C system at zero temperature and zero pressure. All structures of the 1st generation are randomly generated, and the succeeding generations are produced by random (20%), heredity (50%), transmutation (10%), and softmutation (20%) operations. For those compositions likely to form stable compounds, we performed fixed-composition predictions (within two to four formula units for each promising composition) to ensure the discovery of the lowest-enthalpy structures. With these structures discovered by fixed-composition calculations, we constructed thermodynamic convex hull to determine stability of VC_{1-x} compounds.

For each candidate structure generated by USPEX, basing on density functional theory [45], we performed first-principles total energy calculation and structural relaxation using the all-electron projector augmented wave (PAW) method [46] as implemented in the VASP code [47]. The Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA [48]) was adopted to describe the exchange-correlation potential. We chosen the electronic configurations of $3d^4 4s^1$ and $2s^2 2p^2$ for V and C, respectively. In these calculations, plane-wave kinetic energy cutoff of 560 eV and uniform *k*-point meshes with reciprocal-space resolution of $2\pi \times 0.03\,\text{Å}^{-1}$ were used. These settings ensure the total energy well converged to <1 meV per atom.

Elastic constants of all the predicted VC_{1-x} compounds were computed by strain–stress method as implemented in the VASP code. Basing on the computed elastic constants, we derived bulk modulus *B* and shear modulus *G* from the Voigt–Reuss–Hill averaging scheme [49,50] for all the predicted VC_{1-x} compounds. With *B* and *G*, their Vickers hardness H_v were obtained by Chen's empirical model [51]:

$$H_v = 2(\kappa^2 G)^{0.585} - 3 \tag{1}$$

where κ (equals to G/B) is the Pugh's ratio [52], noting that H_v calculated by this empirical formula agrees well with experimental data for wide materials.

Elastic constants are also able to be used to verify mechanical stability of a structure. For a mechanically stable structure, its elastic constants C_{ij} should satisfy the Born–Huang criteria [53]. The mechanical stability conditions for the newly predicted orthorhombic *Pnnm*-V_2C is as follows:

$$\begin{gathered} C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \\ [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \\ (C_{11} + C_{22} - 2C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0, \\ (C_{22} + C_{33} - 2C_{23}) > 0. \end{gathered} \tag{2}$$

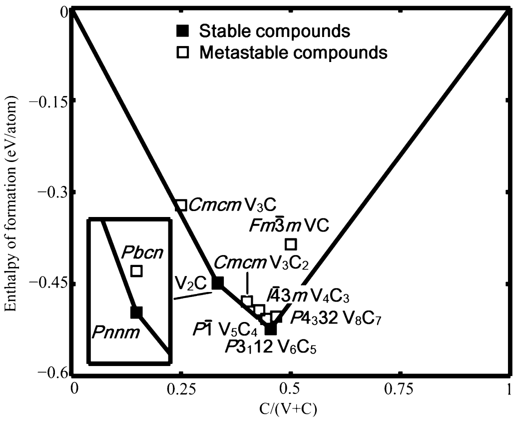

Fig. 1. Thermodynamic convex hull of the V–C system. Solid squares denote stable compounds; open squares metastable compounds.

Phonon dispersion curve, helpful in checking the dynamical stability of the newly discovered *Pnnm*-V_2C structure, was computed by PHONOPY code [54]. Basing on the density functional perturbation theory [55], the present phonon calculation was performed on a 2 × 2 ×2 supercell. To relate mechanical properties with electronic structures, we further computed Bader charges [56] for all the predicted VC_{1-x} compounds.

3. Results and discussion

3.1. Crystal structure prediction and structural properties

The thermodynamic convex hull for V–C system has been constructed. As shown in Fig. 1, only V_6C_5 ($P3_1 12$) and V_2C (*Pnnm*) are thermodynamically stable compounds at zero temperature and zero pressure. We found that the $P3_1 12$-V_6C_5 is same to that reported before [21], while the *Pnnm*-V_2C is a hereto unknown structure. In comparison to the α-V_2C (*Pbcn*) suggested by X-ray diffraction (XRD) experiment [26], the newly discovered *Pnnm*-V_2C has lower formation enthalpy (see inset in Fig. 1), indicating that the *Pnnm*-V_2C is more thermodynamically stable. We have verified the dynamical stability of *Pnnm*-V_2C by computing its phonon dispersion curve. As shown in Fig. 2, no imaginary phonon frequencies are found throughout the Brillouin zone, suggesting the dynamical stability of *Pnnm*-V_2C. We have also found that *Pnnm*-V_2C is mechanically stable due to its elastic constants meeting the Born–Huang criteria [53] (see discussion in Section 3.2).

The verification of thermodynamical, mechanical, and dynamical stability of *Pnnm*-V_2C indicates that the *Pbcn*-V_2C suggested by XRD experiment may be incorrect. To check this possibility, we simulated XRD patterns for *Pnnm*- and *Pbcn*-V_2C using the POWDER CELL code (see Fig. 3). It is shown that XRD patterns of the two structures are almost the same, suggesting the difficulty to determine the correct crystal structure for V_2C compound only by XRD experiment. We have carefully analyzed crystal structures of *Pnnm*- and *Pbcn*-V_2C and figured out the main reasons: (1) both *Pnnm*- and *Pbcn*-V_2C are of orthorhombic symmetry and their structures are