SCIENTIFIC REPORTS

OPEN

The effects of ordered carbon vacancies on stability and thermo-mechanical properties of V_8C_7 compared with VC

Received: 19 April 2016
Accepted: 04 September 2016
Published: 23 September 2016

XiaoYu Chong, YeHua Jiang, Rong Zhou & Jing Feng

The ordered non-stoichiometric V_8C_7 can form in the VC_γ carbides by the disorder–order phase transformation. The intrusion of ordered carbon vacancies can affect their stability, mechanical, thermal and electronic properties. The relatively thermodynamic stability and mechanical properties at high temperature for the ordered stoichiometric VC and non-stoichiometric V_8C_7 are investigated in this paper by first-principle calculations combined with the quasi-harmonic approximation. The difference between the properties of VC and V_8C_7 can be obtained. We find that the V_8C_7 is thermodynamic more stable than VC, but has weaker elastic heat resistance than VC. Moreover, the minimum thermal conductivity of VC is a little larger than V_8C_7 and a simple way is proposed to characterize the anisotropy of lattice thermal conductivity based on the Cahill's model.

Vanadium carbides display a unique combination of thermal and mechanical properties such as high hardness, high melting point, high-temperature strength, corrosion and wear resistance and very efficient electrical and thermal conductivities. So they are widely used in functional coatings, corrosion protection, high-temperature structural materials, microelectronics and catalysts. Vanadium form the stoichiometric carbides such as VC and the non-stoichiometric cubic monocarbide VC_γ which are all with B1 (NaCl) structure. A feature peculiar to the structure of non-stoichiometric VC_γ is the intrusion of carbon atoms in the octahedral interstices of the metallic sites and the carbon atoms may occupy only a fraction of the interstitial sites, and the rests are filled with structural vacancies. The carbon-atom vacancies arranging randomly on the fcc carbon sublattice is called disordered phases, while the ordered carbon vacancies take on a periodic arrangement. The disordered state of non-stoichiometric carbides is in thermodynamic equilibrium only at a high temperature, whereas the ordered state is in thermodynamic equilibrium at a temperature below 1300 K¹. The disorder–order phase transition in the vanadium carbides and a cubic ordered V_8C_7 phase can arise in the VC_γ carbide over the range $VC_{0.86}$ – $VC_{0.88}$ ^{2,3}. The low-temperature phase V_8C_7 does not have an fcc structure, it crystallizes in the space group $P4_32$ with the vanadium atoms occupying positions slightly off the ideal fcc positions and the carbon atoms having an ordered arrangement on the interstitial sites⁴. The crystal structures of VC and V_8C_7 are presented in Fig. 1. The existence of ordered carbon vacancies can affect the stability, mechanical, thermal and electronic properties of vanadium carbides. The influence of the order-disorder transformation on the electrical resistivity of single crystals of vanadium carbide was studied by Shacklette and Williams⁴. They found that the electrical resistivity of the disordered vanadium carbide is significantly higher than that of ordered phase and the temperature of order–disorder transformation is $1124 \pm 15^\circ\text{C}$ for V_8C_7 . Emmons and Williams studied the thermodynamics of δ - VC_{1-x} order-disorder transformation using powder samples⁵. Lipatnikov's research results show that ordered structure produces much higher hardness and electrical conductivity⁶. They also investigated the disorder–order phase transformations in the region of homogeneity of a non-stoichiometric cubic vanadium carbide, VC_γ ($0.66 < y < 0.88$) and constructed the equilibrium phase diagram of the V–C system which allows for the formation of ordered phases in a non-stoichiometric vanadium carbide¹. Xing *et al.* reported a new type vanadium carbide V_5C_3 and predicted its mechanical properties⁷. In our previous work, we calculated the mechanical and thermal properties of the ordered vanadium carbides system including VC, V_2C , V_4C_3 , V_6C_5 and V_8C_7 ⁸. But the difference for the thermodynamic and mechanical properties of ordered vanadium carbides have not been

Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People's Republic of China. Correspondence and requests for materials should be addressed to J.F. (email: jingfeng@kmust.edu.cn) or Y.J. (email: jiangyehua@kmust.edu.cn)

Figure 1. Crystal structure of VC and V_8C_7 . (a) $2 \times 2 \times 2$ supercell of VC with 32 vanadium atoms and 32 carbon atoms; (b) Unit cell of V_8C_7 with 32 vanadium atoms and 28 carbon atoms.

reported so far. This work contains two aspects. One is the difference for relatively thermodynamic stability and mechanical properties for the ordered stoichiometric VC and non-stoichiometric V_8C_7 at high temperature are obtained and compared with the theoretical and experimental results. The other one is a simple way is proposed to characterize the anisotropy of lattice thermal conductivity based on the Cahill's model.

Results and Discussion

Crystal structure. Figure 2 exhibits the carbon vacancy site in V_8C_7 which is not an fcc structure. Details for the structure of VC and V_8C_7 can be seen in Table S1. By comparing the simulated XRD of VC and V_8C_7 with the experimental results of V_8C_7 and VC_{1-x} , we find our simulated results are in agreement with the experimental results^{9,10}. And from the XRD pattern shown in Fig. 3, it is difficult to distinguish the ordered VC, V_8C_7 and disordered VC_{1-x} . So we investigate the difference of the mechanical and thermal properties of them under different temperature.

Thermodynamic properties. The calculated results of thermal properties from Helmholtz free energy at elevated temperatures are showing in Fig. 4. From Fig. 4(b), we can see that the linear expansion coefficient of V_8C_7 is larger than VC during the temperature from 0 K to 1000 K, which leads to the Lattice constant of V_8C_7 increases more rapidly than the $2 \times 2 \times 2$ supercell of VC with the temperature increasing (Fig. 4(c)).

Moreover, the obtained thermodynamic parameters, such as entropy (S) and Gibbs free energy (G), of VC and ordered V_8C_7 as a function of temperature exhibit in Fig. 5, which are in good agreement with the experimental results¹¹. From Fig. 5(a), the entropy of V_8C_7 is larger than the entropy of VC, indicating that the V_8C_7 is thermodynamic more stable than VC at different temperature. The result can be confirmed by the Gibbs free energy of VC and V_8C_7 as shown in Fig. 5(b). The calculated Gibbs free energy of V_8C_7 is smaller than that of VC, which also suggests that the V_8C_7 is more stable at high temperature and easier to form than VC. What's more, there is a little error between the experimental and theoretical data of entropy and Gibbs energy of VC, which can attribute to the experimental conditions and magnetic contribution to the entropy and Gibbs energy.

The further analysis for the relatively thermodynamic stability of VC and V_8C_7 can be seen in Fig. 6. The Gibbs free energy of $V_{32}C_{32}$ is larger than the system of $V_{32}C_{28}$ and graphite, which shows that the $V_{32}C_{32}$ tends to decompose into $V_{32}C_{28}$ and graphite from the room temperature to 1000 K. And the result supports that the introduction of carbon vacancies in the B1 crystal structure and different symmetry increase the stability of carbides¹². This founding explains the phenomenon that vanadium carbides phases in the high-vanadium iron and steel are not the stoichiometric compounds VC, but always the non-stoichiometric VC_{1-x} such as V_8C_7 and V_4C_3 ¹³.

Elastic properties at finite temperature. The obtained isothermal and isentropic elastic constants of VC and ordered V_8C_7 as a function of temperature from 0 K to 1000 K are displayed in Fig. 7(a,b). Different decreased amplitudes of C_{ij}^T and C_{ij}^S values with the increase of temperature could be found for VC and V_8C_7 . It can be seen clearly that the elastic constants of VC decrease slightly and approach zero slope with the increase of temperature. The reduction in elastic constants values is more pronounced for V_8C_7 than VC, and that such a decrease of C_{11} with temperature is more apparent. The value of C_{11}^S is larger than C_{11}^T for V_8C_7 and the deviation of our calculated results to experimental data for C_{11}^S of V_8C_7 is about 5%.

Using the elastic constants, the aggregate properties of polycrystalline such as the isothermal and isentropic bulk modulus (B^T and B^S), shear modulus (G^T and G^S) and Young's modulus (E^T and E^S) of VC and V_8C_7 are calculated by VRH approach at different temperature. Moreover, the bulk modulus can also be obtained by the thermal equation of states (EOS)¹⁴:

Figure 2. The crystal structure of VC and the ordered carbon vacancy site in V_8C_7 .

Figure 3. The simulated XRD of VC and V_8C_7 . The results are compared with the experimental results of V_8C_7 and VC_{1-x} ^{9,10}.

$$B_T = \left[V \left(\frac{\partial^2 G}{\partial V^2} \right)_{P,T} \right]_V \quad (1)$$

$$B_S = B_T(1 + \alpha\gamma T) \quad (2)$$

where γ is the Grüneisen parameter, α is the thermal expansion coefficient and V is the equilibrium volume. The results are shown in Fig. 7(c–e). It can be found that the modulus values are larger for VC than those for V_8C_7 , which is in accordance with the previous results. Apparently, the mechanical modulus all decrease when temperature increases, and an almost linear decrease could be discerned above 400 K. The response of mechanical properties of polycrystalline to the temperature is quite similar to that of elastic constants of single crystal. The isentropic modulus is larger than the isothermal one for VC and V_8C_7 . And the decrease of mechanical modulus of V_8C_7 is more obvious than VC with the temperature increasing. In addition, the intrinsic hardness (H_V) at different temperature is calculated by Chen's and Tian's models^{15–18} and the results are shown in Fig. 8(f). The intrinsic hardness obtained by Tian's model is higher than that by Chen's model for VC, but this is opposite for V_8C_7 . All the two models describe the hardness with the elastic parameters of materials. But there is an extra intercept term (-3) in Chen's model compared with Tian's model. Indeed, proper hardness model should be selected according to the chemical bonding characteristics of the crystal. The predicted hardness of V_8C_7 is higher than VC but reduce pronouncedly at high temperature. It is known that a material would be less elastic heat resistant if its elastic properties are more sensitive to temperature. So these results indicate that the elastic heat resistant property of VC is superior to those of V_8C_7 . Our theoretical results deviate from other calculated and experimental values of VC and V_8C_7 by less than 3% for B^S and G^S . The slight discrepancy may be attributed to the ignorance of the anharmonic effect and electron and magnetic contribution on the kinetic energy. However, the deviation of our calculated results to experimental data for E^S and H_V of VC is larger than 10%, which may be caused by the relative strong anisotropy of Young's modulus. The anisotropy of Young's modulus for VC and V_8C_7 has been demonstrated and investigated in our previous work⁸. Another important reason is that the single crystal of vanadium carbide in the high vanadium iron and steel grows dependent on the orientations and the morphology of them is always dendritic as reported in ref. 19. So the characterized results of Young's modulus and hardness are related to the location of the vanadium carbide^{20,21}.

The anisotropy of the Young's modulus for VC and V_8C_7 can be evaluated by calculating the Young's modulus as a function of crystallographic orientation. The expressions for Young's modulus in the three principal directions [100], [010] and [001] for cubic crystal is given as²²:

Figure 4. (a) The curve of the volume dependence of total energy; (b) The linear expansion coefficients of VC and V_8C_7 at different temperature; (c) Lattice constant of V_8C_7 and $2 \times 2 \times 2$ supercell of VC as a function of temperature.

Figure 5. (a) The entropy (S) of VC and V_8C_7 as a function of temperature; (b) The Gibbs free energy (G) of VC and V_8C_7 as a function of temperature compared with the experimental data¹¹.

Figure 6. The Gibbs free energy of $V_{32}C_{32}$ and the $V_{32}C_{28} + \text{graphite}$ system as a function of temperature.

$$E_{[100]} = E_{[010]} = E_{[001]} = 1/S_{11} \quad (3)$$

Moreover, in $[1\bar{1}0]$ and $[1\bar{1}1]$ directions, they are calculated by:

$$E_{[1\bar{1}0]} = 4/(S_{11} + S_{12} + S_{22} + S_{66}) \quad (4)$$

$$E_{[111]} = 9/[(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23}) + (S_{44} + S_{55} + S_{66})] \quad (5)$$

Figure 7. Temperature dependent elastic constants, mechanical modulus and intrinsic hardness of VC and V_8C_7 . (a) Elastic constants of VC; (b) Elastic constants of V_8C_7 ; (c) Bulk modulus of VC and V_8C_7 ; (d) Shear modulus of VC and V_8C_7 ; (e) Young's modulus of VC and V_8C_7 ; (f) Intrinsic hardness of VC and V_8C_7 .

Where S_{ij} represents the elastic compliances matrices, which can be calculated directly from $C_{ij}^{-1} = S_{ij}$. The temperature-dependent E^S is plotted in polar coordinates and projected onto the plane as shown in Fig. 8. For VC and V_8C_7 , the curve on (001) plane with maximum values along [100] direction and minimum values along the [110] direction could be observed, while on (110) plane, the maximum values and minimum values could be found along [001] and $[1\bar{1}0]$ directions, respectively. Furthermore, our calculated anisotropy of Young's modulus at 0 K and 1000 K are all a little weaker than other theoretical and experimental results.

Minimum lattice thermal conductivity. This section we will discuss the anisotropy of lattice thermal conductivity for VC and V_8C_7 based on Cahill's model²³:

$$\kappa_{\min} = \frac{k_B}{2.48} n^{2/3} (v_l + v_{t1} + v_{t2}) \quad (6)$$

where n is the density of number of atoms per volume, and v_l , v_{t1} and v_{t2} are the longitudinal and transverse modes, respectively. Cahill's model is suitable for studying the anisotropy of thermal conductivity, because the model already treats the total thermal conductivity as the summation of three acoustic branches. Detailed method for calculating the longitudinal and transverse modes can be found in ref. 24. The results are plotted for VC and V_8C_7 on the (001) and (110) crystallographic planes in Fig. 9. One finds that the anisotropy in the calculated

Figure 8. The planner projections of the anisotropy of Young's modulus of VC and V_8C_7 on (001) and (110) planes at different temperatures.

thermal conductivities k_i due to v_i is stronger than that of v_{i1} and v_{i2} . The shapes of these planar contours are related to the anisotropy in elasticity. At (001) crystallographic plane the most contribution to total thermal conductivities is from k_b , while at (110) crystallographic plane it is k_{t1} . The most intriguing conclusion obtained from these plots is that the total lattice thermal conductivity (k) of VC is almost isotropic. And the thermal conductivity of VC is a little larger than V_8C_7 , which means that the carbon vacancy or defect can decrease the intrinsic lattice thermal conductivity.

It is known that the more strict treatment of the anisotropy in lattice thermal conductivity of single-crystalline involves the computation of phonon dispersions and applying the relaxation time approximation for phonon scattering. And another way to reveal the anisotropy in thermal conductivity is to evaluate the anisotropy in the Grüneisen constant. In this paper, we provide a simpler way to characterize the anisotropy of lattice thermal conductivity.

Conclusions

The intrusion of ordered carbon vacancies in non-stoichiometric vanadium carbides can significantly affect their stability, mechanical, thermal and electronic properties. The relatively thermodynamic stability, mechanical properties at high temperature and minimum lattice thermal conductivity of VC and ordered V_8C_7 are investigated by first-principle calculations combined with the quasi-harmonic approximation. V_8C_7 is more thermodynamically stable at high temperature and easier to form than VC according to the entropy and Gibbs free energy. The isothermal and isentropic elastic constants, mechanical modulus and intrinsic hardness are calculated and we found that the elastic properties of V_8C_7 are more sensitive to temperature than VC, which meaning that the elastic heat resistant properties of VC is superior to those of V_8C_7 . The anisotropic Young's modulus of VC and V_8C_7 are evaluated by calculating the Young's modulus as a function of crystallographic orientation. Finally, the minimum lattice thermal conductivity of VC and V_8C_7 is predicted and a simple way to characterize the anisotropy of lattice thermal conductivity is proposed based on the Cahill's model.

Methods

First-principle calculations details. In this work, all the calculations are performed based on the density functional perturbation theory (DFPT) as implemented in the CASTEP code^{25,26}. A generalized gradient approximation (GGA) approach in the form of Perdew–Burke–Ernzerhof (PBE) was used to calculate the exchange and correlation functional²⁷. The interactions between the ionic cores and the valence electrons were indicated by Ultrasoft pseudo-potentials (UPPs). A plane wave expansion method was applied for the optimization of the crystal structure. A special k-point sampling in the first irreducible Brillouin zone was confirmed by the Monkhorst–Pack scheme, and the k point mesh was selected as $10 \times 10 \times 10$. A kinetic energy cut-off value of 400.0 eV was used for the plane wave expansion in reciprocal space. So the selected values are suitable for the chosen system. The Broyden–Fletcher–Goldfarb–Shannon (BFGS) method was applied to relax the whole structure based on

Figure 9. Anisotropy in thermal conductivity of VC and V₈C₇ at (001) and (110) crystallographic planes.

total energy minimization. The total energy changes during the optimization processes were finally converged to 1×10^{-6} eV and the forces per atom were reduced to $0.05 \text{ eV} \cdot \text{\AA}^{-1}$. The second-order elastic constants (C_{11} , C_{22} and C_{44}) at the equilibrium volumes are calculated using an efficient stress-strain method, which was consisted of applying several different types of Lagrangian strains on crystals and calculated Cauchy stress tensor for each strain after optimizing the internal degrees of freedom²⁸. Then the Voigt–Reuss–Hill approach was used to calculate the bulk (B), shear (G) and Young's modulus (E) for polycrystalline crystals²⁹.

Calculations of the thermodynamic properties. The thermodynamic properties of VC and V₈C₇ can be calculated by means of the quasi-harmonic approximation and thermal electronic excitation. For a system with the given volume (V) and temperature (T), the Helmholtz free energy $F(V, T)$ is obtained through combining vibrational $F_{\text{vib}}(V, T)$ and electronic $F_{\text{el}}(V, T)$ free energy as follows^{30–32}.

$$F(V, T) = E_{\text{stat}}(V) + k_B T \int_0^\infty g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] d\omega + F_{\text{el}}(V, T) \quad (7)$$

where $E_{\text{stat}}(V)$ is the static energy at 0 K and volume V . $g(\omega, V)$ is the phonon density of states at phonon frequency ω and volume V . Moreover, the entropy ($S(V, T)$) is calculated by the vibrational and thermal electronic contribution ($S_{\text{el}}(V, T)$)^{33,34}.

$$S(V, T) = k_B \int_0^\infty \left[\frac{\hbar \omega / k_B T}{e^{\hbar \omega / k_B T} - 1} - \ln(1 - e^{-\hbar \omega / k_B T}) \right] g(\omega, V) d\omega + S_{\text{el}}(V, T) \quad (8)$$

Finally, the temperature dependent equilibrium volume $V(T)$ and Gibbs free energy $G(T)$ are obtained by minimization of the following expression³⁵ using the thermal equation of states (EOS)¹⁴:

$$G(T) = \min_V [F(V, T) + PV] \quad (9)$$

From the results of equilibrium volume $V(T)$, the volume coefficient of thermal expansion (CTE) α_V can be calculated by the following equation^{36,37}:

$$\alpha_V(T) = \frac{dV(T)}{V(T)dT} \quad (10)$$

For the cubic crystal, the linear expansion coefficient (α_l) and volumetric coefficient (α_V) are related by $\alpha_V = 3\alpha_l$.

Calculation of the temperature-dependent mechanical properties. The temperature-dependent isothermal elastic properties can be estimated by a quasistatic approach, which is assumed that the change of elastic properties is mainly caused by volume change and the anharmonic effect as well as the contributions due to the kinetic energy and the fluctuation of microscopic stress tensors are ignored^{38,39}. The procedure for calculating the temperature-dependent isothermal elastic constants (C_{ij}^T) can be summarized in three steps as follows: (i) calculating the static elastic constants at 0 K as a function of volume $C_{ij}(V)$ using the stress-strain energy method; (ii) predicting the volume change as a function of temperature at ambient pressure $V(T, 0)$ using the quasi-harmonic approximation⁴⁰; (iii) then the temperature dependence of isothermal elastic constants can be derived as $C_{ij}(T) = C_{ij}(T(V))$.

Most of the experimental data of elastic stiffness constants are usually reported as isentropic elastic stiffness constants, therefore the calculated isothermal elastic stiffness constants (C_{ij}^T) must be converted to the isentropic ones (C_{ij}^S) with their thermodynamic relationship given by Davies⁴¹. For cubic crystals, the thermodynamic relations can be simplified as⁴²:

$$C_{11}^S/C_{11}^T = C_{12}^S/C_{12}^T = C_P/C_V \text{ and } C_{44}^S = C_{44}^T \quad (11)$$

where C_V and C_P are heat capacities at constant volume and pressure, respectively. Details about the estimations of C_V and C_P from Helmholtz energy and the results can be found in our previous work⁸.

References

- Lipatnikov, V. N. *et al.* Phase transformations in non-stoichiometric vanadium carbide. *J. Phys.: Condens. Matter* **11**, 163 (1999).
- Froidevaux, D. & Rossier, D. NMR investigation of the atomic and electronic structure of vanadium and niobium carbides. *J. Phys. Chem. Solids* **28**, 1197 (1967).
- Henfrey, A. M. & Fender, B. E. F. A neutron diffraction investigation of V_8C_7 . *Acta Crystallogr. B* **26**, 1882 (1970).
- Shacklette, L. W. & Williams, W. S. Influence of order-disorder transformations on the electrical resistivity of vanadium carbide. *Phys. Rev. B* **7**, 5041 (1973).
- Emmons, G. H. & Williams, W. S. Order-disorder phase transformations and specific heat of nonstoichiometric vanadium carbide. *Phys. Solid State* **41**, 474 (1999).
- Lipatnikov, V. N. *et al.* Effects of vacancy ordering on structure and properties of vanadium carbide. *J. Alloys Compd.* **261**, 192 (1997).
- Xing, W., Meng, F. & Yu, R. A new type of vanadium carbide V_5C_3 and its hardening by tuning Fermi energy. *Sci. Rep.* **6**, 21794 (2016).
- Chong, X. Y. *et al.* Electronic structures mechanical and thermal properties of V–C binary compounds. *RSC Adv.* **4**, 44959 (2014).
- Zhao, Z. *et al.* Effects of additives on synthesis of vanadium carbide (V_8C_7) nanopowders by thermal processing of the precursor. *Int. J. Refract. Met. Hard Mater.* **27**, 971 (2009).
- Yan, L. & Wu, E. The preparation of ultrafine V_8C_7 powder and its phase reactions. *Int. J. Refract. Met. Hard Mater.* **25**, 125 (2007).
- Barin, I. & Knacke, O. *Thermochemical Properties of Inorganic Substances (B)*. Berlin: Springer-Verlag, 1973.
- Jang, J. H. *et al.* Stability of (Ti, M)C (M = Nb, V, Mo and W) carbide in steels using first-principles calculations. *Acta Mater.* **60**, 208 (2012).
- Takahashi, J., Kawakami, K. & Tarui, T. Direct observation of hydrogen-trapping sites in vanadium carbide precipitation steel by atom probe tomography. *Scripta Mater.* **67**, 213 (2012).
- Birch, F. Finite elastic strain of cubic crystals. *Phys. Rev.* **71**, 809 (1947).
- Chen, X. Q. *et al.* Modeling hardness of polycrystalline materials and bulk metallic glasses. *Intermetallics* **19**, 1275 (2011).
- Tian, Y. J., Xu, B. & Zhao, Z. S. Microscopic theory of hardness and design of novel superhard crystals. *Int. J. Refract. Met. Hard Mater.* **33**, 93–106 (2012).
- Sun, Z. M., Ahuja, R. & Lowther, J. E. Mechanical properties of vanadium carbide and a ternary vanadium tungsten carbide. *Solid State Commun.* **150**, 697–700 (2010).
- Toth, L. E. *Transition Metal Carbides and Nitrides*, Academic Press, New York (1971).
- Wu, L. *et al.* Understanding the mechanical properties of vanadium carbides: Nano-indentation measurement and first-principles calculations. *J. Alloys Compd.* **548**, 60–64 (2013).
- Pierson, H. O. *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps*, William Andrew, (1996).
- Krzyszowski, J. E. & Leuchtner, R. E. Chemical, Mechanical, and Tribological Properties of Pulsed-Laser-Deposited Titanium Carbide and Vanadium Carbide. *J. Am. Ceram. Soc.* **80**, 1277–1280 (1997).
- Sun, L. *et al.* Anisotropic elastic and thermal properties of titanium borides by first-principles calculations. *J. Alloys Compd.* **579**, 457–467 (2013).
- Cahill, D. G., Watson, S. K. & Pohl, R. O. Lower limit to the thermal conductivity of disordered crystals. *Phys. Rev. B* **46**, 6131 (1992).
- Chong, X. Y. *et al.* Electronic structure, anisotropic elastic and thermal properties of the η phase Fe_6W_6C . *Comp. Mater. Sci.* **108**, 205–211 (2015).
- Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **136**, B864 (1964).
- Segall, M. *et al.* First-principles simulation: ideas, illustrations and the CASTEP code. *J. Phys.: Condens. Matter* **14**, 2717 (2002).
- Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- Wang, S. Q. & Ye, H. Q. Ab initio elastic constants for the lonsdaleite phases of C, Si and Ge. *J. Phys.: Condens. Matter* **15**, 5307 (2003).
- Bai, Y. *et al.* Dependence of elastic and optical properties on surface terminated groups in two-dimensional MXene monolayers: a first-principles study. *RSC Advances* **6**, 35731 (2016).
- Baroni, S. *et al.* Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **73**, 515 (2001).
- Wang, Y., Liu, Z. K. & Chen, L. Q. Thermodynamic properties of Al, Ni, NiAl, and Ni₃Al from first-principles calculations. *Acta Mater.* **52**, 2665–2671 (2004).
- Shang, S. L. *et al.* Phase stability in α - and β -rhombohedral boron. *Phys. Rev. B* **75**, 092101 (2007).
- Xu, W. W. *et al.* First-principles investigation of electronic, mechanical and thermodynamic properties of L12 ordered $Co_3(M, W)$ (M = Al, Ge, Ga) phases. *Acta Mater.* **61**, 5437–5448 (2013).

34. Zhang, Y. *et al.* Polymorphism of M_3AlX phases ($M = Ti, Zr, Hf$; $X = C, N$) and thermomechanical properties of Ti_3AlN polymorphs. *J. Am. Ceram. Soc.* **98**, 2570–2578 (2015).
35. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and $CaCl_2$ -type SiO_2 at high pressures. *Phys. Rev. B* **78**, 134106 (2008).
36. Xiang, H. *et al.* Temperature-dependence of structural and mechanical properties of TiB_2 : A first principle investigation. *J. Appl. Phys.* **117**, 225902 (2015).
37. Dang, D. Y., Fan, J. L. & Gong, H. R. Thermodynamic and mechanical properties of TiC from ab initio calculation. *J. Appl. Phys.* **116**, 033509 (2014).
38. Shang, S. L. *et al.* Temperature-dependent elastic stiffness constants of α - and θ - Al_2O_3 from first-principles calculations. *J. Phys.: Condens. Matter* **22**, 375403 (2010).
39. Wang, Y. *et al.* A first-principles approach to finite temperature elastic constants. *J. Phys.: Condens. Matter* **22**, 225404 (2010).
40. Baroni, S., Giannozzi, P. & Isaev, E. Densityfunctional perturbation theory for quasiharmonic calculations. *Rev. Mineral Geochem.* **71**, 39 (2010).
41. Shang, S. L. *et al.* Effects of alloying elements and temperature on the elastic properties of dilute Ni-base superalloys from first-principles calculations. *J. Appl. Phys.* **112**, 053515 (2012).
42. Davies, G. F. Effective elastic moduli under hydrostatic stress-I. quasi-harmonic theory. *J. Phys. Chem. Solids* **35**, 1513 (1974).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51261013) and Academic Newcomer Award of Doctoral Students in Yunnan Province (2014)

Author Contributions

X.C. performed the calculation and wrote the main part of the paper. Y.J. and R.Z. designed the research and analyzed the data. J.F. provided the idea and participated in the discussion.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Chong, X. Y. *et al.* The effects of ordered carbon vacancies on stability and thermo-mechanical properties of V_8C_7 compared with VC. *Sci. Rep.* **6**, 34007; doi: 10.1038/srep34007 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

© The Author(s) 2016