



Mechanical properties of vanadium carbide and a ternary vanadium tungsten carbide

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ABSTRACT

Ab initio total energy calculations are performed on non-stoichiometric vanadium carbide with supercells representing vacancy concentrations of $VC_{0.875}$ and $VC_{0.75}$. The $VC_{0.875}$ supercell retains a cubic symmetry whilst in the case of the $VC_{0.75}$ supercell C vacancies located in close proximity have the lowest energy configuration and the cubic lattice slightly distorts to a monoclinic symmetry. Using a stress–strain calculational procedure, the elastic constants of both the cubic and the monoclinic systems are deduced. In all cases C vacancies decrease the elastic moduli.

A similar analysis is then applied to consider when W is incorporated into VC. In this case it is found that the elastic moduli increase with W content suggesting that a V–W–C alloy could have significant potential as a novel hard material.

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1. Introduction

For some time non-stoichiometric vanadium carbide has been investigated for several potentially useful applications [1,2]. The material displays a unique combination of properties some of which are a high melting temperature, high hardness, good high-temperature strength, and very efficient electrical and thermal conductivities. More recently, there has also been a growing interest in the use of hard transition metal carbides as functional coatings [3] which have similar characteristics as their bulk counterparts and even an urgency to explore other possible materials that can be incorporated into VC. Of such materials WC has been considered to be especially significant.

In stoichiometric VC, the lattice symmetry is simple cubic with a Fm3m space group structure however the material is especially sensitive to the presence of C vacancies. Different structures have been suggested for the non-stoichiometric phases and as such a carbide can contain a substantial concentration of C vacancies that are tentatively located in an ordered octahedral sublattice [4]. A cubic phase seems to be formed over a range from $VC_{0.86}$ to $VC_{0.88}$ and this superstructure has been suggested to have a double lattice spacing with respect to the disordered carbide with a cubic unit cell tentatively assigned in the space group of P4332 or P4132 [5]. Another ordered phase, appropriate to the phase $VC_{0.75}$ appears

in stoichiometries less than $VC_{0.86}$, and this may have trigonal symmetry (space group P31) or a monoclinic (C2, or C2/m) [5] symmetry. The energetics as to how these different ordered phases of vacancies arise has not been considered from the viewpoint of an atomic level investigation and this is one purpose of the present work.

There have also been several investigations on the elastic properties of both stoichiometric and non-stoichiometric vanadium carbide. Extensive Brillouin scattering studies on vanadium carbide have been undertaken in a carbon vacancy concentration ranging from $VC_{0.75}$ to $VC_{0.88}$ [6] and compression measurements have recently been made on $VC_{0.85}$ up to $P = 53$ GPa [7]. As far as the bulk modulus and other elastic constants are concerned, such investigations appear to imply a steady reduction in the magnitude of the elastic constants as the carbon vacancy concentration increases. In addition, with the strong suggestion that at large vacancy concentration the cubic symmetry is reduced to become monoclinic or trigonal, it is also necessary to understand how the large vacancy concentration affects the overall crystal symmetry as well as the related change in elastic constants in order to associate such changes with C vacancies.

The C vacancy content of VC reduces the elastic constants of the material and more recently it has been suggested that incorporation of WC could produce a cubic ternary V–W–C material with a structure similar to VC and possibly with enhanced properties [8–12]. Thus we extend the present work presented here to consider how the presence of W in cubic VC could influence not only the structure of VC but also and especially the trend in the elastic constants of a ternary V–W–C system.

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In this paper we first establish what seems to be the most suitable calculational approach for an analysis of the V-C system and critically examine the elastic constants of non-stoichiometric VC. Thereafter we examine the properties of a ternary material V-W-C.

2. Calculational procedure

The stress-free elastic constants of materials are normally studied at a fundamental level using an energy-distortion approach where the total energy is varied and a variation of the following form applied in the calculation procedure:

$$E(V, \varepsilon) = E(V_0) + \sum_{ij} c_{ij} \varepsilon_i \varepsilon_j$$

where the strain tensor defined as:

$$\varepsilon = \begin{pmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_6/2 \\ \varepsilon_5/2 & \varepsilon_6/2 & \varepsilon_3 \end{pmatrix}$$

takes distortions appropriate to specific lattice elastic constants. In the case of a system with cubic symmetry, there are only three independent elastic constants whereas with a very low symmetry system notably monoclinic or triclinic systems there are far more elastic constants – namely 13 for monoclinic and up to 20 for a triclinic system. The calculation task involving a total energy variation approach in such a case is therefore quite intensive and often prohibitive. In the present case, we have employed a somewhat similar but far less computationally intensive approach to obtain the elastic constants by directly calculating the overall stress matrix, σ , on the system. This is related to the strain tensor according to the well known relation:

$$\sigma = \mathbf{c}\varepsilon$$

where both σ and \mathbf{c} are the very small stress and strain column matrices and ε the 6×6 matrix of elastic constants as before. Therefore, the above equation constitutes six linear equations with six variables ε involving 21 unknown \mathbf{c} . To calculate the elastic constants, \mathbf{c} , very small values (± 0.005 in the present work) of the deformation are employed for a calculation of specific combinations of the stress tensor. The stress tensors are the output of the calculations. The computational intensity is reduced considerably from that used in the more conventional energy-distortion approach. For the cubic structure, only 4 separate calculations were necessary. In the case of the monoclinic system presented here a total of 12 separate calculations were needed to get all the elastic constants.

In the present work the electronic interactions were calculated through the VASP electronic structure code using PAW pseudopotentials [13]. For V we investigated two choices of PAW-potentials appropriate to nominal electronic configurations d^4s^1 and $p^6d^4s^1$ as well as considering both the local density (LDA) and generalized gradient (GGA-PBE) functional. In the case of the perfect stoichiometric cubic system, the results – now shown in Table 1 – indicate that the $p^6d^4s^1$ potential with the GGA-PBE functional was more suited to VC as assessed by agreement of the computed values of interatomic spacing and bulk modulus which was fitted to the Birch Equation of State [14] employing a usual energy–volume approach.

Thus the $p^6d^4s^1$ potential together with the GGA-PBE functional is chosen in subsequent investigations. We point out that using this potential there is good agreement with experiment and also several earlier calculations on aspects of VC [15–21].

Table 1

Calculated cell structure of VC and the bulk modulus as fitted to the Birch Equation of State.

	LDA		GGA	
	a_0 (Å)	B (GPa) (B')	a_0 (Å)	B (GPa) (B')
d^4s^1	4.096	345 (4.17)	4.115	316 (4.26)
$p^6d^4s^1$	4.096	346 (4.12)	4.161	305 (4.19)
Expt. [14]			4.172	303

Table 2

Lattice parameters and cohesive energies of different phases of vanadium carbides.

	VC	VC _{0.875}	VC _{0.75} ^a	VC _{0.75} ^b
Lattice parameter (Å)	4.161	4.145	4.109 ^c , 4.1421 ^d	4.1181 ^c
Cohesive energy (eV/atom)	–9.563	–9.598	–9.6191 ^c	–9.4791 ^d
			–9.6272 ^d	–9.4682 ^d

^a The calculated nonclinically distorted cubic structure when C vacancies are located on adjacent C sites.

^b The simple cubic structure where C vacancies are on next neighbor C sites.

^c A cell of 14 atoms with two C vacancies.

^d A cell of 56 atoms with 8 C vacancies.

2.1. Non-stoichiometric vanadium carbide

In order to introduce carbon vacancies into the system, we must employ a series of supercells with similar starting symmetry as the original cell. A vacancy concentration of VC_{0.85} can be simulated either within a 16-atom supercell with one carbon atom removed whereas for a stoichiometry of VC_{0.75}, again a 16-atom cell is needed but now with two carbon atoms removed. Whereas the former VC_{0.85} 16-atom cell will always have a simple cubic symmetry as there is only one location for the C vacancy; with two C vacancies the 16-atom cell may deform depending on the relative location of the vacancies. In fact, it turns out that only two locations really matter for the C vacancies depending on how close they are located relative to each other. Employing the variable cell approach implemented in the VASP code in all cases, we are therefore able to study both changes occurring in lattice geometry as well as, in the case of the stoichiometry VC_{0.75}, the preferred location of the C vacancies as indicated by the lowest total energy for each of the C vacancy locations.

These results are given in Table 2 where we see that in the case of the VC_{0.75} the energetically most favored structure is when the C vacancies are located on adjacent C sites. To check the cell size effect, we have also used a supercell of 56 atoms with 8 C vacancies and the calculated results are given in Table 2. Again, we see that defect structure with vacancies locating on adjacent C sites is more energetically favorable. From the symmetry of the overall deformed unit cell in this case a monoclinic structure is deduced. When the two C vacancies lie at the more distant locations there was negligible distortion from cubic symmetry.

Now that the symmetry of the supercells is established from the total energy calculations, we use the stress–strain method as described above to evaluate the elastic constants. Values obtained using this method are shown in Table 3.

In order to get some estimate of the overall hardness of the each of the systems we can use the following relations to obtain the bulk and shear moduli of the system [22]. In the case of the monoclinic system, since the four elastic constants c_{15} , c_{35} , c_{16} and c_{46} , are very small:

$$B = \frac{1}{9} (c_{11} + c_{22} + c_{33}) + \frac{2}{9} (c_{12} + c_{13} + c_{23})$$

$$G = \frac{1}{15} (c_{11} + c_{22} + c_{33} - c_{12} - c_{13} - c_{23}) + \frac{1}{5} (c_{44} + c_{55} + c_{66}) .$$

Table 3

Calculated elastic constants (GPa) of stoichiometric and non-stoichiometric VC using the stress/strain approach.

	c_{11}	c_{22}	c_{33}	c_{44}	c_{66}	c_{12}	c_{13}	c_{23}	c_{15}	c_{35}	c_{16}	c_{46}
VC	615			178		154						
VC _{0.875}	619			161		128						
VC _{0.75} ^a	590	591	592	156	141	110	123	124	2.6	2.5	3.4	1.8
VC _{0.75} ^b	515			99		153						

^a The nonclinically distorted cubic structure.^b The cubic structure.**Table 4**

Lattice parameters, cohesive energies, Bulk and Shear moduli (GPa) of different phases of vanadium carbides.

	B (Birch-EOS)	B	G	B (expt)	G (expt)
VC	305	308	210	308 [10]	
VC _{0.875}	272	292	212	237–245 ^c	175–179 ^c
VC _{0.75} ^a	240	272	185	208 ^c	151 ^c
VC _{0.75} ^b	267	274	148		

^a The calculated nonclinically distorted cubic structure.^b The cubic structure.^c The experimental values deduced from Ref. [6] using the relation for cubic systems of $B = (c_{11} + 2c_{12})/3$ and the Voigt shear $G = (c_{11} - c_{12} + 3c_{44})/5$.

While for the cubic structure, we use the following equations:

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

$$G = \frac{1}{5} (c_{11} - c_{12} + 3c_{44})$$

The bulk modulus and shear constants are now given in Table 4 where we also include the value of the bulk modulus as obtained using a least squares fit to the Birch Equation of State and also the experimentally deduced Bulk and Shear modulus.

Overall there is fair agreement between the Equation of State value of the Bulk modulus and that deduced from the stress–strain method. For the exact stoichiometric VC, agreement is very good whereas for the other stoichiometries agreement is about 10% which is acceptable for calculations of this sort. Notably in the case of VC_{0.75} the lowest Bulk as deduced from the Birch Equation of State corresponds to the case where the C vacancies are located at nearest neighbor locations and this is marginally predicted from the stress–strain method. In all cases there is a similar trend as that observed experimentally – namely the elastic moduli of non-stoichiometric VC decrease with C vacancies.

2.2. Ternary vanadium tungsten carbide

In the above section we have established the reliability of the procedure for studies of cubic VC and especially the types of pseudopotentials and appropriate density functional to be employed. Within the limits of an 8-atom cell we now apply the technique to consider the potential properties of a ternary system of the form V_{1-x}W_xC. This ternary alloy has recently been suggested to have superior properties to that of VC. As with V we also use the GGA procedure and with a pseudopotential for W that specifically incorporates d-states. Dimensions of the 8-atom unit cell were allowed to vary – surprisingly there was very little deformation from a cubic symmetry when W was included and thus we have considered the system to have an overall cubic symmetry. This allows us to investigate the elastic constants in a similar way to that we have employed earlier. For a specific stoichiometry in the ternary system we allowed the W atom to replace a V atom in the unit cell and the calculated results are now given in Table 5.

It is noted that the presence of W steadily increases the over lattice constant yet at the same time there is a steady increase in the Bulk modulus. At larger concentrations of V, the presence of

Table 5Unit cell, Birch Equation of State Bulk Modulus and elastic constants of the V-W-C ternary system using the relation for cubic systems of $B = (c_{11} + 2c_{12})/3$ and the Voigt shear $G = (c_{11} - c_{12} + 3c_{44})/5$.

	a (Å)	B (EOS)	B'	c_{11}	c_{12}	c_{44}	B	G
V _{0.25} W _{0.75} C	4.344	351	4.35	856	172	115	400	206
V _{0.5} W _{0.5} C	4.272	335	4.27	815	168	165	384	228
V _{0.75} W _{0.25} C	4.232	321	4.23	715	179	174	358	212
VC	4.161	305	4.19	615	154	178	304	210

W does increases the shear modulus. This result there points to a suggestion that the presence of W in VC will increase the hardness of the material.

3. Conclusion

In conclusion, the present calculations have confirmed that there is a steady reduction in the compressibility and hardness (as indicated by the shear modulus) of VC as the C vacancy concentration is increased. The non-cubic symmetry of VC often observed in the case of high C vacancy concentrations we suggest, from results of the energy calculations presented here, is attributed to C vacancies in very close proximity and gives rise to a monoclinic deformation of the original cubic lattice. A calculation of the elastic constants, gives Bulk and Shear moduli that are in fair agreement with recent experimental work but decrease with C vacancy concentration. On the contrary we have found that incorporation of W into cubic VC increases the Bulk modulus and, at lower concentrations of W, the shear modulus. This suggests that the presence of W in VC may slightly increase the hardness of cubic VC.

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