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Hardness prediction of the carbides in Fe-based multi-elements alloy by first-principles

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Abstract

The electronic structures of the carbides such as VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 in Fe-based multi-elements alloy were investigated by frst principles. According to the bonding characteristics, the different models were adopted to predict the hardness of these carbides, then, which were compared with experimental. The results show that VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 are all strong covalent solids and a small metallicity, as well as the contribution of d valence electrons to s-p-d hybridization. Their hardness are 25.80 GPa, 24.28 GPa, 11.52 GPa, 17.06 GPa, 15.07 GPa and 12.78 GPa respectively, which are good agreement with experimental.

Introduction

With high hardness and high wear resistance, Fe-based multielement (Cr, Mo, V, W, etc.) alloy has been widely applied for on preparation the workpieces with wear resistance surface coatings by additive manufacturing method.[1,2] In Fe-based multi-element alloy, there are a large number of carbides such as VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6. As the wear resistance phase, the carbides are dispersed on the surface of the workpieces, which significantly improve the wear resistance of the workpieces. The carbides in the Fe-based multi-element alloy not only have different types, but also are not evenly distributed. Especially, the wear resistance of the workpieces is closely related to the hardness of the carbides.[3–5] However, because the sizes of these carbides are very small, it is very difficult to determine the hardness of the carbides by experimental. Therefore, it is necessary to find a simple method to predict the carbide hardness in the Fe-based multi-element alloy. In recent years, it is interesting to explore the hardness in the materials science. Gao[6] proposed a bond resistance model to calculate the hardness of pure covalent and polar covalent crystals. Thereafter, the bond strength model for covalent and ionic crystals by Šimůnek,[7] population model by Gao[8] and electronegativity model by Li[9] were established successively. Later, Guo[10] optimized the bond resistance model, which takes into consideration of metallic component and d valence electrons in crystals. Subsequently, Chen[11] proposed a macroscopic model of the hardness by considering the Pugh's modulus ratio and Teter's empirical correlation. The models mentioned above were all achieved to predict the hardness by first-principles.

In the first-principles calculations, the transition metal carbides display highly covalent characteristics.[12,13] Although the carbides are not the super-hard materials, while existed in

Fe-based multi-elements alloy as the hard phase, which greatly contribute to hardness and wear resistance. Therefore, it is reasonable to predict the carbide hardness by semiempirical theoretical models. In our previous work, a novel Fe-based multi-elements alloy (Cr, Mo, V, W, etc.) was self-designed. Moreover, the type and crystal structure of the carbides existed in this alloy were finally determined.[14] However, it is difficult to accurately determine the hardness of these carbides. In this work, the hardness of the carbides with special structures in this alloy were predicted by different models based on first principles, and then compared with experimental to certify the accuracy and validity of the hardness models.

Materials and methods

The chemistry composition of the Fe-based multi-elements alloy is Fe–11Cr–3Mo–3V–1.5W–1.2C (wt%). The carbides existed in this alloy contain MC, M2C, M7C3 in the grain boundary and M23C6 inside the grain. Different carbides can be distinguished by Murakami etchant[15] (3g K3Fe(CN)6+10g NaOH + 100ml H2O), in which gray MC, black M2C and brown M7C3 were selectively etched. The micro-hardness of the carbides with different colours was measured by HVS-1000 Digital Micro-hardness Tester

Previously, it is known that MC contains VC and WC, and M2C contains V2C and Mo2C, while M23C6 is indexed to cubic Cr23C6. M7C3 exists in the form of hexagonal (Fe,Cr)7C3, while the accurate Fe/Cr ratio and Fe, Cr occupations in the crystal lattice are still unclear.[14] In order to simplify the calculation process, Cr7C3 was chosen to present (Fe,Cr)7C3 instead. First-principles calculations were performed based on density functional theory (DFT) using the Cambridge Serial Total Energy Package (CASTEP). The exchange and correlation functional were described with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The cutof energies were of VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 all set at 310 eV and the numbers of k points were $6 \times 6 \times 6$, $10 \times 10 \times 10$, $5 \times 4 \times 5$, $10 \times 10 \times 10$, $4 \times 2 \times 6$ and $1 \times 1 \times 1$. The convergence criteria for structure optimization and energy calculation were set to high quality with the tolerance for energy of $5 \times 10-6$ eV/atom.

Results and discussions Crystal structures of the carbides The crystal structures of VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 after relaxation are shown in Fig. 1. In Fig. 1(a), (b), (c) and (d), the small gray balls represent C atoms, and the larger pink balls refer to V, W, Mo atoms. In Fig. 1(e), the purple balls represent Cr1 (2b), light blue Cr2 (6c) and pink Cr3 (6c). In Fig. 1(f), the green balls represent Cr1 (4a), pink Cr2 (8c), blue Cr3 (32f) and yellow Cr4 (48h), respectively.

Bond characteristics of the carbides The bond population and length can be obtained from first principles. It is known that only on bond between metal and carbon atoms exists in VC, WC and Mo2C. The Mulliken bond populations are 0.77, 2.12 and 0.92, respectively, which show that they are all strong covalent solids. For V2C, Cr7C3 and Cr23C6, the metal atom bonds with carbon atom and metal atom itself, which reveal the complexity of bonds in these carbides and their covalent characteristics. The total and partial densities of states (DOS) for these carbides are shown in Fig. 2. From Fig. 2, the energy gap near to the Fermi level is absent, which indicates the metallic nature of these carbides. Moreover, the d valence electrons of metal atoms in six carbides contribute to s-p-d hybridization obviously.

Hardness calculations of the carbides The hardness of the carbides such as VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 can be explained by Tian's[10] theory. The hardness of pure covalent crystals can be as follow:

$$H_v(GPa) = AN_a E_h \qquad (1)$$

where A is the proportional constant, for s-p hybridization, A = 14; Na is the covalent bond number per unit area which can be evaluated from $N_a = (N_e/2)2/3$, where Ne is the valence electron density per unit volume; $E_h = 39.74/d2.5$ represents the covalent homopolar gap of corresponding chemistry bond, where d is the bond length in angstroms.

N_e value of X–Y bond per unit volume can be calculated as follow:

$$N_e^{X-Y} = [Z_X/N_X + Z_Y/N_Y]\left[\sum_j N^j(d^j)^3\right] / [V(d^{X-Y})^3] \qquad (2)$$

where ZX and ZY are valence electron numbers of X and Y atoms; NX and NY are coordination numbers of X and Y atoms; d_{X-Y} is bond length of X–Y bond; N_j is the number of j-bond, and d_j is bond length of j-bond in unit cell.

To account for the metallicity effect on hardness, a factor of metallicity $f_m = n_m/n_e$ has been introduced, where nm is the numbers of the electrons that can be excited at ambient temperature, and ne is the total number of the valence electrons in the unit cell. According to Theory of Fermi Liquid,[16] nm can be described by the product of DF and kT, where k is Boltzmann constant; T is room temperature (298K) and DF is the density of electronic states at the Fermi level.

As a result, the metallicity of simple crystals is obtained as follow:

$$f_m = \frac{n_m}{n_e} = \frac{kTD_F}{n_e} = \frac{0.026D_F}{n_e} \qquad (3)$$

The screening effect of the metallic component may be described by introducing correction factor of $e^{-\beta f_m^n}$, in which, β=32.2, n=0.55.[10] Similar with the metallicity contribution to hardness, the screening effect of the ionic component is introduced by $e^{-1.191f_i}$, in which, fi means Phillips ionicity of the chemical bond in a crystal. It can be defined as follow[17] :

$$f_i = [1 - \exp(-|P_C - P|/P)]^{0.735} \qquad (4)$$

where P is the overlap population of a bond in a calculated crystal and Pc is the overlap population of a bond in a pure covalent crystal with an identical structure as the calculated one.

The intrinsic influence of the d valence electrons should result in a proportional coefficient A0 for the s-p-d hybridized crystals different from that for the s-p hybridized crystals in Eq. (1).

Finally, the hardness formula of VC can be expressed by:

$$H_v(GPa) = 1051N_e^{2/3}d^{-2.5}e^{-1.191f_i - 32.2f_m^{0.55}} \qquad (5)$$

In Eq. (5), the definition of f_i, i.e. Pc becomes the biggest obstacle in the calculation. For VC with rock salt structure, Pc = 0.43. Regularly, as long as atomic species of the chemistry bond don't changes, the values of ionicity are comparable even under the condition of the different crystal structures and atom coordination.[7] In general, WC is h-WC[18] investigated in this work. Obviously, there is only one W–C bond in h-WC. Therefore, it is considered that $f_i^{h-WC} = f_i^{c-WC} = 0.644$. Similarly, the value of Phillips ionicity in Mo2C is confirmed to be the same with that of rock salt-structure MoC, i.e. $f_i^{Mo2C} = f_i^{MoC} = 0.301$. Accordingly, the hardness of VC, WC and Mo2C are calculated by Eq. (5) and listed in Table I, which are 25.80 GPa, 24.28 GPa and 17.06 GPa, respectively

Recently, Chen et al.[11] proposed a new macroscopic model of the hardness, which considered that if the material is brittle intrinsically, the relationship between its hardness and shear modulus is linear. However, if plastic deformation should be taken into consideration, the hardness is related to the Pugh's modulus ratio, k = G/B, where G and B are shear modulus and elastic modulus. The brittleness/ductility of materials can be defined by B/G criterion proposed by Pugh.[19] When B/G > 1.75, the material is plastic, in contrast, the material is brittle. Hence, the macroscopic model of hardness can be expressed as follows:

$$H_v = 0.151G \, (G/B < 1.75)$$
$$H_v = 2(k^2 G)^{0.585} - 3 \, (G/B \geq 1.75) \tag{6}$$

Subsequently, the hardness of V2C, Cr7C3 and Cr23C6 calculated by Chen's model listed in Table 1 which are 11.52 GPa, 15.07 GPa and 12.78GPa, respectively. Although both bulk and shear moduli in Chen's model are macroscopic concepts, and the origin of hardness is still not completely understood, so the model is relatively accurate to predict the hardness of the complicated carbides.

Discussion

From the analyses in our previous work, it is known that there are many different kinds of carbides with different morphologies existed in Fe-based multi-elements (Cr, Mo, V, W, C) alloy. The size of the carbides varies from one micron to dozens of microns, which make it very difficult to determine the hardness of all carbides. Therefore, in this work, the hardness of carbides existed in this alloy were predicted by Tian's theory and Chen's model. In order to estimate the accuracy of the calculated hardness, the micro-hardness of MC, M2C and M7C3 with large size were measured, which are shown in Fig. 3.

From Fig. 3, the average values of MC, M2C and M7C3 hardness are 21.2 GPa, 14.4 GPa and 13.4 GPa, respectively. The f_{ve} measured values of M2C are most dispersed, whereas those of M7C3 are most centralized. Additionally, due to the big size (about 50–60 μm) of MC, the indenter is hard to press on the matrix accidentally, which indicates that the calculated MC hardness is accurate. However, this experimental method of the hardness measurement is limited to the carbides which are large size. The hardness of M23C6, which is distributed as tiny particles in the grain with 0.3–0.5 μm, is difficult to be measured experimentally. Moreover, M in MxCy type carbide may represent different alloy elements, which makes it hard to determine the particular kind of carbide by experiment. Therefore, it is of great significance to predict the carbide hardness by first-principles calculation.

The predicted hardness values of the carbides are also illustrated in Fig. 3 and compared with the measured ones. It can be seen that the micro-hardness of MC is slightly smaller than that of calculated one, and five measured values difer a little, which is caused by relatively small hardness difference of MC composed of VC and WC (25.8 and 24.28 GPa). On the contrary, the hardness difference of the composed V2C and Mo2C (11.52 and 17.06 GPa) are a little larger, while the measured values of M2C all foat within the calculated ones between 11.52 and 17.06 GPa. The micro-hardness values of M7C3 are also smaller than those of the calculated ones, and its five measured values difer least. The reason is that M7C3 is only composed by (Fe,Cr)7C3 without other M7C3-types. However, to simplify the calculation process, Cr7C3 is chosen to present (Fe,Cr)7C3 instead, which will certainly result in the deviation to some extent. However, the calculated hardness of MC, M2C and M7C3 by first principles method fairly agrees with measured ones, which indicates that the adopted models are reasonable and accurate.

Conclusion

In summary, the structural and electronic properties of the carbides such as VC, WC, V2C, Mo2C, Cr7C3 and Cr23C6 in a novel Fe-based multi-elements alloy are all strong covalent solids and a small metallicity, as well as the contribution of d valence electrons to s-p-d hybridization. The hardness values of VC, WC, Mo2C are 25.80 GPa, 24.28 GPa and 17.06 GPa by Tian's model, while those of V2C, Cr7C3, Cr23C6 are 11.52 GPa, 15.07 GPa and 12.78 GPa by Chen's model.

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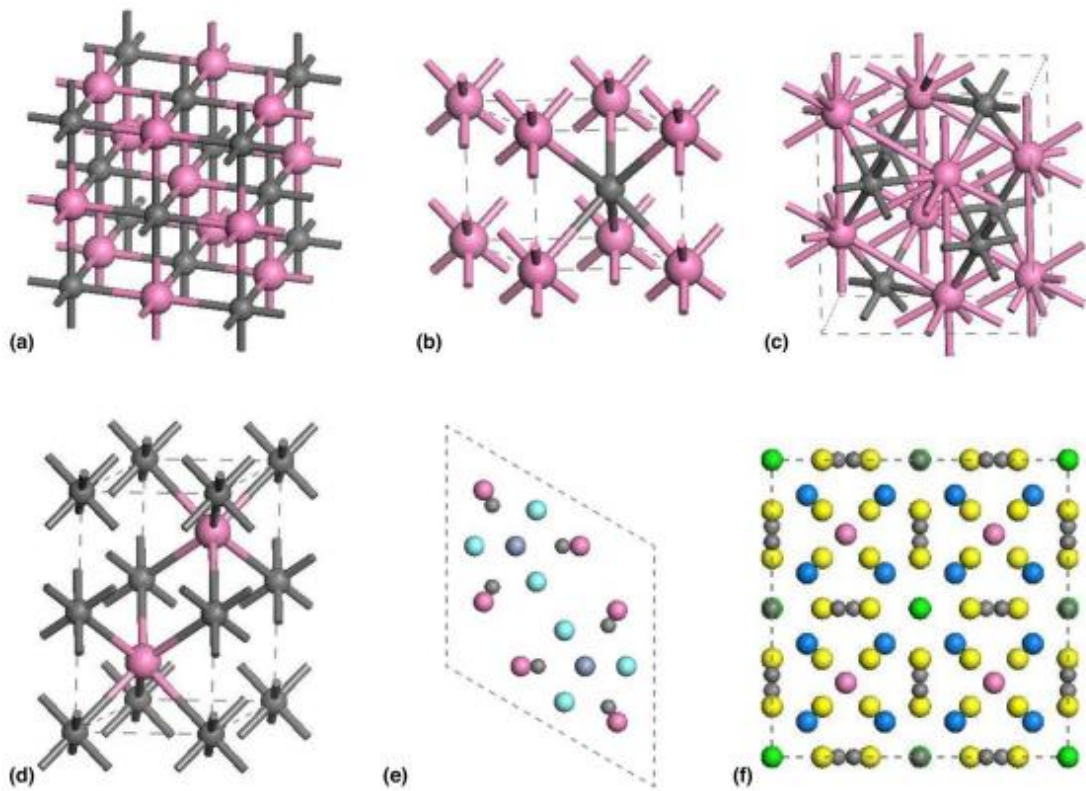
Figure 1. Crystal structures calculated for (a) VC, (b) WC, (c) V_2C, (d) Mo_2C, (e) Cr_7C_3 and (f) $Cr_{23}C_6$, respectively.
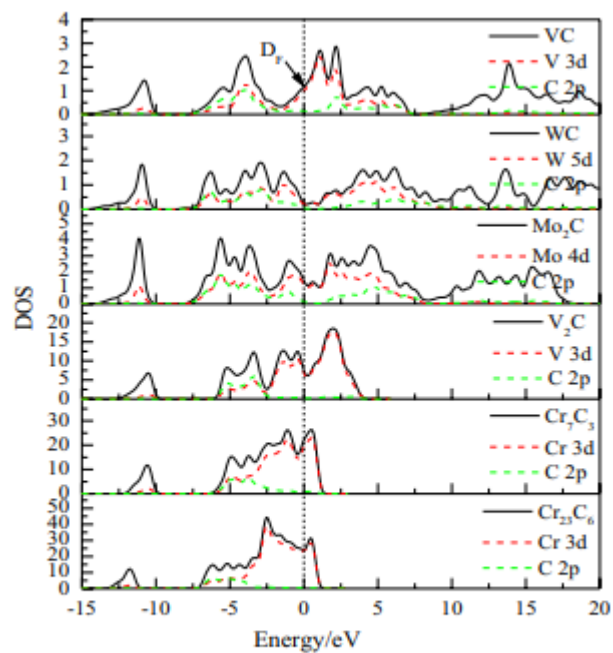
Figure 2. Calculated total and partial DOS of VC, WC, V$_2$C, Mo$_2$C, Cr$_7$C$_3$ and Cr$_{23}$C$_6$ (Dashed lines represent the Fermi level).
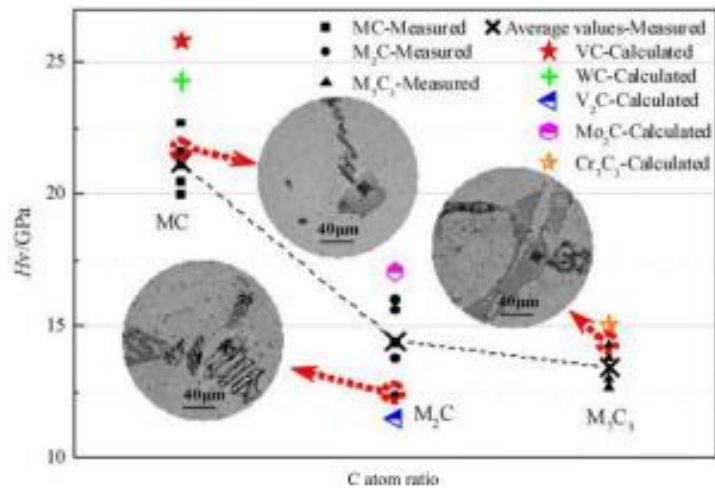
Figure 3. Microhardness of MC, M_2C and M_7C_3.

Table I. Calculated bond parameters, bulk modulus B (GPa), Shear modulus G (GPa), values of B/G and k (G/B) and theoretical Vickers hardness of carbides.

Species	D_F	N_e	f_i	$f_m (\times 10^{-3})$	B	G	B/G	$k (G/B)$	H_{Calc} (GPa)
VC	1.15	1.120	0.469	3.322	293.05	176.90	1.66	0.60	25.80
WC	0.22	0.476	0.644	0.572	380.24	290.15	1.31	0.76	24.28
V_2C	7.56	–	–	14.040	231.53	116.71	1.98	0.50	11.52
Mo_2C	1.34	0.343	0.301	2.178	336.03	181.60	1.85	0.54	17.06
Cr_7C_3	22.4	–	–	10.785	211.46	123.74	1.71	0.59	15.07
$Cr_{23}C_6$	24.2	–	–	3.884	291.55	142.24	2.05	0.49	12.78