Virtual crystal approximation study of the complex refractory carbides based on Ti-Nb-Mo-V-C system with CASTEP computer code

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Abstract

In the present study virtual crystal approximation with first principles CASTEP computer code was performed for investigation of multicomponent carbides in Ti-Nb-Mo-V-C system. The analysis of a computed properties data for fifteen carbides with equimolar metals components ratios showed, that elastic constants have significant positive deviation from rule of mixtures. Systematization of computed quantitative (elastic and lattice constants, hardness and fracture toughness) together with qualitative (charge density) data allowed us to distinguish ternary (Nb,Ti,Mo)C carbide as the most suitable compound for development wear-resistant materials and coatings.

Keywords 1

Computing from first-principles, CASTEP code, multicomponent carbides, elastic constants, wear-resistance

1. Introduction

Progress in engineering material science, structure-based materials and drug design highly depends on efficiency of implementation well revised theories and models into high-throughput computer codes. In the recent decades first-principles calculations based on density functional theory [1] has been the dominant technique for the quantum mechanical modelling of 3D periodic solids due to its high robustness, predictive power and reproducibility of results, when validating against experimental data. Computing properties of disordered solid solutions using so-called virtual crystal approximation (VCA) technique [2] within DFT framework is an effective approach to reach sufficient accuracy at relatively low computational cost, when compared to supercell [3], special quasirandom structure (SQS) [4] and effective cluster interaction (ECI) [5] methods. Similar approaches based on rectangular and hexagonal cells [6, 7] for modelling complex cyber-physical systems are used in analysis of medical and biological processes [8]. The general limitation of the VCA is the low accuracy in calculation of excess properties such as mixing enthalpy or volume for the interstitial solid solutions [9], which are characterized by significant deviation from Vegard's law. However, mechanical properties, such as elastic constants, in many cases can be determined with high precision

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even for multicomponent systems like high entropy alloys (HEAs) and ceramics (HECs). S. Wang at el. [10] calculated the lattice constants (LC) using VCA implemented in Cambridge Serial Total Energy Package (CASTEP) [11] for the and SQS method for the FeCoNiCr – based HEAs and showed that the accuracy of both methods is very close to each other and to available experimental data, when calculated systems of elements with similar atomic radius and electronic configuration. Results of successful VCA computations using CASTEP code for HECs of Ti-Zr-Hf-V-Nb-Ta-C system, based on data analysis of computed properties, including heats of formations, elastic constants and melting points reported in [12]. It was found that TiHfVTaC quaternary carbide has the best combination of properties among fifteen investigated compounds.

Experimental investigations of complex refractory compounds require special high temperature equipment, pure fine or ultrafine powders of initial components, which makes such type of experiments very expensive. Using first-principal computing codes for prediction properties of complex compounds allows to decrease number of experiments and determine most significant trends in composition – properties relationship, using data analysis information technologies.

2. Computational details and models

The general concept underlying the VCA for a $(A_{1-x}B_x)C$-type compounds is the compositionally averaging of AC and BC parent phases pseudopotentials and obtaining resulting external potential ($V_{VCA}(r)$) according to the formula :

$$V_{VCA}(r) = (1-x)V_{AC}(r) + xV_{BC}(r), \quad (1)$$

where x – composition. Within the DFT approach for a system with N_v valence electrons total energy (E_{tot}) of a can be written as

$$E_{tot}[\{\phi_i\},\{R_I\}] = U(\{R_I\}) + \sum_i \phi_i \left|-\frac{1}{2}\nabla^2 + V_{ext}\right| + \frac{1}{2}\iint dr dr' \frac{n(r)n(r')}{|r-r'|} + E_{XC}[n], \quad (2)$$

where R_I shows location of the lattice site I and V_{ps}^I is the corresponding pseudopotentials, $n(r)$ is the electron density, E_{XC} is the exchange-correlation energy, $U(\{R_I\})$ is the energy of ions interaction and V_{ext} is the external pseudopotential, which in terms of VCA for a MC-type multicomponent carbides can be represented as

$$V_{ext}(r,r') = \sum_I \sum_M w_M^I V_{ps}^M (r - R_{IM}, r' - R_{IM}), \quad (3)$$

where V_{ps}^M is a pseudopotential for a given metal component M, which located on a lattice site I (fig. 1) and w_M^I represents its relative amount, so the total value on each site is equal to 1. Lattice models were constructed for MC-type carbides with FCC structures (spacegroup - Fm3m), where M was pure Ti, Nb, V, Mo and their combinations in equiatomic ratios, while other sites were filled with carbon.

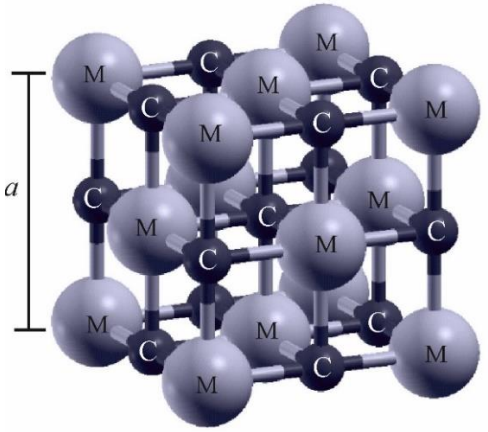

Figure 1: Crystal structure of the MC-type carbide with FCC lattice

In the present study calculations were performed by VCA method, implemented CASTEP 19.11 code based on DFT. The equilibrium lattice geometry was computed by BFGS [13] algorithm within general gradient approximation (GGA) for the Perdew-Burke-Ernzerhof exchange-correlation functional [14]. The electron-ion interactions were treated by ultrasoft Vanderbilt pseudopotentials (C19 version) generated on the fly. The integration over Brillouin zone was performed using 8×8×8 Monkhorst-Pack [15] ***k***-points mesh at the 520 eV plane wave energy cutoff. Convergence tolerance of self-consistent field (SCF) was set to 10^{-5} eV/atom, 3×10^{-2} eV/Å and 5×10^{-2} GPa for total energy, max ionic force and max stress, respectively. After the reaching of equilibrium geometry, "stress-strain" method at strain amplitude of 0.03 Å was used to obtain components of elastic tensor for further prediction of mechanical properties.

3. Results and discussion

To cover all MC-type carbides of the Ti-Nb-Mo-V-C system with equimolar ratio of metal components 15 structures (four unary, six binary, four ternary and one quaternary carbide) were optimized (relaxed). Their lattice parameters are listed in table 1. The comparison calculated results against available experimental data reported in [16, 17, 18] for some unary stochiometric carbides shows that calculation error in all cases does not exceed 10 % (typical error of DFT calculations). This indicates good accuracy of structure relaxation with chosen parameters and allows to extend calculations for the mechanical properties determination using "stress-strain" method.

Table 1
Lattice constants of the calculated structures

Structure/a, Å	Structure/a, Å	Structure/a, Å
NbC/4.4826	(Nb,V)C/4.2411	(Nb,Ti,V)C/4.2598
TiC/4.3291	(Nb,Mo)C/4.4111	(Nb,Ti,Mo)C/4.1647
VC/ 4.1363	(Ti,V)C/4.2038	(Nb,V,Mo)C/4.2727
MoC/4.3641	(Ti,Mo)C/4.1907	(Ti,V,Mo)C/4.2336
(Nb,Ti)C/4.2463	(V,Mo)C/4.2179	(Nb,Ti,V,Mo)C/4.2491

At the next stage, components C_{ij} of a 6×6 stress tensor were computed for all structures in order to calculate elasticity characteristics: bulk modulus (B), shear modulus (G) and Young's modulus (E) by Voight-Reuss-Hill (VRH) averaging scheme using following equations:

$$B = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23}), \quad (4)$$

$$G = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5}(C_{11} + C_{22} + C_{33}), \quad (5)$$

$$E = \frac{9GB}{G + 3B}\ . \quad (6)$$

The calculated elastic properties are shown in fig. 2. As can be seen, elastic properties demonstrate significant deviations from rule of mixtures. For example, complex carbides (Nb,Ti)C and (Nb,Ti,Mo)C show extremely high values of all elastic moduli, which is much more higher than for pure unary carbide components as well as for calculated according to the rule of mixtures or statistical prediction [19], while their lattice parameters well agree with the Vegard's law. In the general case, it can be seen that increasing of the alloying system complexity leads to the increasing of all elastic moduli.

According to the Oganov and Mazhnick [20] there is a strong correlation between Young's modulus, Poisson's ratio (ν) and hardness, measured by Vickers method (HV), which is described by following formula:

$$HV = 2\left(\frac{9E(1-2\nu)^2}{8(1+\nu)^3}\right)^{0,585} - 3\,, \quad (7)$$

where Poisson's ratio can be calculated for known B and G using (6) and following equations:

$$B = \frac{E}{3(1-2\nu)}, \quad G = \frac{E}{2(1+\nu)}. \tag{8}$$

Another important materials characteristic, which can be derived using computed components of a stress tensor, is a fracture toughness represented through the critical tension stress intensity coefficient (K_{Ic}) as

$$K_{Ic} = f_{EN}\alpha_0^{-\frac{1}{2}}V_0^{\frac{1}{6}}[\zeta(\nu)E]^{\frac{3}{2}} \tag{9}$$

where f_{EN} is the electronegativity factor, α_0 is the constant depending on the chemical bonding characteristics in material (α_0 is equal to 8840 GPa for covalent and ionic crystals), V_0 is the volume per 1 atom and $\zeta(\nu)$ is the empirical fitting function of Poisson's ratio.

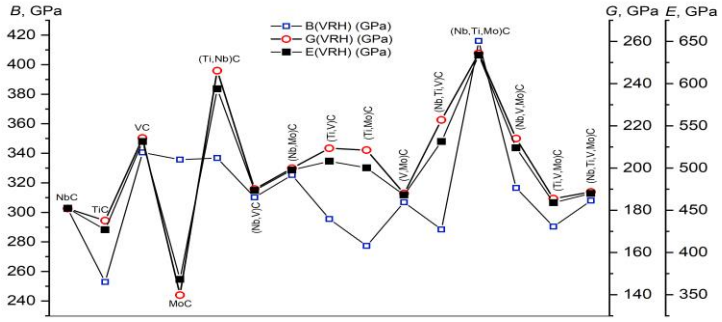

Figure 2: Computed elastic properties for MC-type carbides with different metal components ratio

The Vickers hardness as well as fracture toughness, calculated by Eqs. (7) and (9), respectively, using utilities, which include machine learning approach, developed by USPEX laboratory [21] are shown in Fig. 3. As can be seen from figure, increasing overall trends for *HV* and K_{Ic}, when alloying system becomes more complex are very similar to the elastic moduli changes in the same systems. (Ti,Nb)C and (Nb,Ti,Mo)C also show the most favorable combination of properties in terms of hardness-toughness relationship, which is most desirable for many practical applications [22]. Moreover, despite high hardness of the (Nb,Ti,Mo)C its fracture toughness is highest among all investigated structures, which is unusual for carbide-like materials with high amount of covalent bonds. Such combination of properties makes this compound very good candidate for using as a component of impact wear resistant materials and coatings [23] for exploitation in extreme operating conditions, caused by high specific loads.

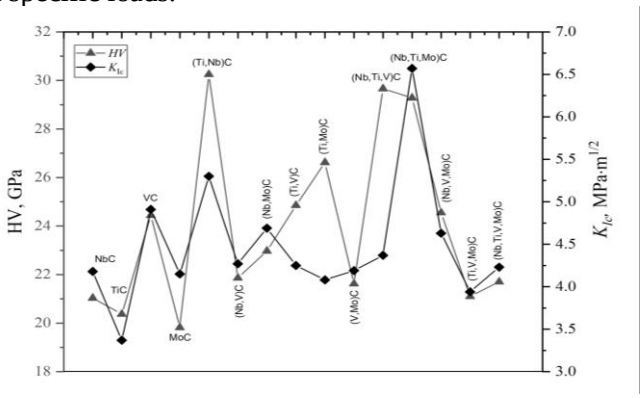

Figure 3: Computed Vickers hardness and fracture toughness for MC-type carbides with different metal components combinations in equiatomic ratios

Analysis of electron density data maps (EDM) (fig. 4) shows that areas with low electron density (highlighted in orange) become smaller, when number of mixed metal core atoms increasing. For the (Nb,Ti,Mo)C carbide isocharge lines indicating strength of interatomic bonding show that electron density between in metal-carbon (M-C) as well as in metal – metal (M-M) pairs is relatively low. This can be described as a formation covalent bonds provided by M-C couples and metallic bonding provided through M-M interactions. Other calculated structures are also characterized by mixture covalent-metal bonding, but its manifestation is relatively weaker. Weak interatomic bonding was detected for (Nb,Ti)C carbide, despite its mechanical properties is rather high. This discrepancy needs additional investigations, so it does not allow to classify this structure as an optimal. However, computed differences in electron density distributions gives only qualitative proof of the nonlinearity composition – properties relationships in given systems.

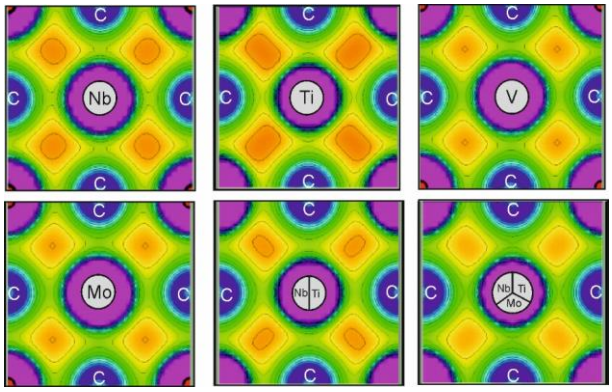

Figure 4: Computed charge density maps of unary and complex carbides with high elastic modulus

4. Conclusions

The effect of alloying of MC-type (FCC structure) refractory carbides with Nb, Ti, Mo and V in equimolar rations and all possible combinations on the elastic moduli, Vickers hardness and fracture toughness has been studied via first principles computing. CASTEP computer code with implemented virtual crystal approximation approach. The calculated values of lattice constants and elastic moduli, checked against literature experimental data for a known carbide structures of a given system are in good agreement, because the maximum error does not exceed 10 %. It was found, that ternary carbide of (Nb,Ti,Mo)C has the best combination of predicted mechanical characteristics, such as Young modulus (~ 650 GPa), Vickers hardness (~ 29 GPa) and fracture toughness (~ 6.5 $MPa \cdot m^{1/2}$), besides electron density map for this compound indicates presence strong covalent-metallic interatomic bonding, which corresponds to the high mechanical properties. The general limitation of the proposed approach is the rather low accuracy of the thermodynamic stability regions prediction. This requires additional calculation or experimental investigation of formation energies for selected compounds with promising mechanical properties. So, it can be expected that using complex (Nb,Ti,Mo)C carbides in pure state or as a reinforcing phases in composites and composite coatings can be useful for increasing their abrasion wear resistance.

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