

A FIRST-PRINCIPLE ANALYSIS OF MECHANICAL PROPERTIES OF CARBON DEFICIENT TRANSITIONAL METAL CARBIDE

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Refractory transition metal carbides have intriguing physical and chemical properties, especially when structured down to nanoscale. The lack of study in defected transition metal carbides, is partially due to the synthesis difficulty of refractory materials. The synthesis of defected carbide and their substitutional alloy will be even more difficult than single phase. First principle theory-based simulation can help to conceptualize the effects of substitutional defects on their mechanical properties. In this paper, we performed density functional theory (DFT) simulation of carbon defected $\alpha\text{-MoC}_{(1-x)}$ phases to investigate their formation and mechanical properties for these sub-stoichiometric materials.

Keywords: metal carbide, simulation method, crystal structure, mechanical properties, vacancies

INTRODUCTION

Refractory transition metal carbides (WC, MoC, TaC, HfC, ZrC and etc) exhibit exceptional strong mechanical properties such as high melting temperature [1], high strength, large hardness and wear resistance, and become ideal candidate for structures and devices working in harsh environment such as aerospace engine and waste nozzle [2,3]. Among all the refractory transition metal carbide, molybdenum carbide has also recently been widely studied for their exceptional catalytic activities in their nano/micro architectures [4]. Meanwhile, such family of materials normally exist in non-stoichiometry form with a substantial amount of nonmetal (e.g. carbon) vacancies [5,6]. Although vacancies reduce the number of chemical bonds and potentially decrease the strength of materials, the hardness of transition metal carbide does not follow the coordination counting [7,8]. *Jhi et al.*, addressed an anomaly vacancy hardening and softening mechanical through first principle simulation of TiC_x and NbC_x [9]. Understanding the mechanical properties are essential for potential application of transition metal carbide as structural materials in parts that works at extreme conditions such as high pressure and high temperature [10,11].

In here, it is specifically focused on $\alpha\text{-MoC}_{(1-x)}$ ($0 < x < 0,5$), which is a high energy phase on Mo-C phase diagram. Such metastable phase requires a high metallurgical formation temperature higher than 1 926 °C, the narrow regime on phase diagram and two eutectic points beneath make it difficult to be synthesized in equilibrium metallurgy methods such as laser floating zone furnaces [12] and Tetra Arc Czochralski furnace [13]. The advanc-

es of non-equilibrium metallurgy methods such as ultra-fast laser sintering, high pressure metallurgy methods bring new opportunities to synthesis this high energy phase [6]. Some experimental results demonstrate intriguing mechanical properties on nanostructured $\alpha\text{-MoC}_{(1-x)}$ ($0 < x < 0,5$), and a deeper understanding will be helpful to predict and promote its applications [14,15].

Recent advances in numerical methods have enabled accurate prediction of elastic properties [14]. For example, the molecular dynamics was widely used to study mechanical properties and dynamic behaviors of materials, majorly in relatively simple chemistry Si or some metals like Cu, Au, etc [16]. However, molecular dynamics has significant limitation, not only because the accuracy of force fields is questionable, but also because empirical potentials are unavailable for most materials [17]. There is no specific Mo-C potential in current potential pool, and the ReaxFF based Mo-C is not fully benchmarked [18]. In contrast, first-principle methods can be ideally applied to any materials. The major limitation is that dense k-mesh and q-mesh used for Brillouin zone integration are needed for accuracy, which greatly increase the computational cost. Fully quantum-mechanical calculation of mechanical properties depending critically on dislocation motion are extremely difficult even with the state-of-art computational schemes and facilities [8]. As such, it will here be confined just to the study the lattice constant, elastic modulus, and bulk modulus which is feasible within the ab initio pseudopotential methods [14].

Generation of pseudo random carbon vacancy

$\alpha\text{-MoC}_{(1-x)}$ ($0 < x < 0,5$) is built from $\alpha\text{-MoC}$, which has a unit cell of a face center cubic structure at stoichi-

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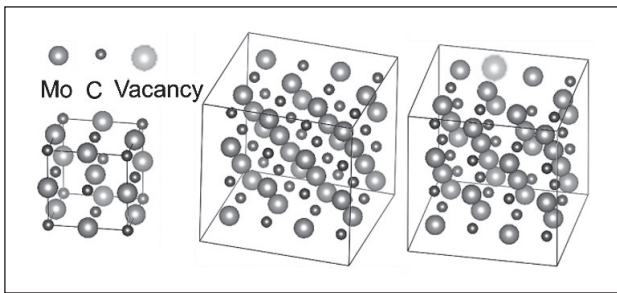


Figure 1 Structure of α -MoC and schematics to generate carbon deficient α -MoC_(1-x) ($0 < x < 0,5$).

ometry (4 : 4). The non-stoichiometry carbide with carbon vacancy is generated by removing x percentage of carbon atoms from a $2 \times 2 \times 2$ supercell of MoC by using pseudo-random number to locate the vacancies, as shown in Figure 1. Generated structures were relaxed using the Vienna Ab Initio Simulation Package to ensure all the forces on the ions were smaller than $0,01 \text{ eV \AA}^{-1}$.

Formation energy and density of states

Relax carbide structures lattice constant (a_0), are presented in Table 1. The displacements calculated result is consistent with experimental results showing a lattice shrinking with increase of carbon vacancies. The vacancy formation energy (E_f) is calculated and presented in Table 1.

$$E_f(x) = E_{coh}(AB_x) - E_{coh}(AB) + \frac{1-x}{2} E_s(B_2)$$

E_{coh} is the cohesive energy per formula unit, A and B denote metal and carbon atoms, respectively, and is the sublimation energy of C. Experimental value of 7,25 at room temperature for carbon [$\frac{1}{2}\text{C} \rightarrow \text{C}_2$] is used. The calculated formation energy is presented in Table 1. It is noticed that the formation energy is positive when $x = 0,44$, which indicates that such phase is thermally dynamically unstable and such phase is not reported in experiments. MoC_{0,66}, MoC_{0,75} are more commonly studied phases for their superconductivity and other properties [6,19].

Table 1 Summary of relax structure of MoC_(1-x) and the vacancy formation energy.

| | $a_0 / \text{\AA}$ | E_f / eV vacancy formation energy |
|---------------------|--------------------|--|
| MoC | 4,319 | NA |
| MoC _{0,95} | 4,225 | -1,36515 |
| MoC _{0,89} | 4,223 | -1,10505 |
| MoC _{0,78} | 4,206 | -0,72683 |
| MoC _{0,66} | 4,188 | -0,17632 |
| MoC _{0,56} | 4,155 | 0,26327 |

Refractory transition metal carbide mechanical properties.

Hardness is one of the most important properties of structure materials. The promise of employing transition metal carbide in high ultra-strong parts in harsh en-

vironment require an understanding of hardness affect by the carbon vacancies, which hence guide the metallurgical stoichiometry. The elastic tensor was calculated using the independent particle approximation, and subsequently the local field effects were included using the random phase approximation. All calculations were performed using Perdew–Burke–Ernzerh (PBE) version of generalized gradient approximation with projected-augmented wave potentials and a wave function energy cutoff of 400 eV; the Brillouin zone was sampled with, respectively, 1 728 and 4 096, k-points, to confirm convergence. Six strain pattern(s) will be used to obtain the elastic constants. For each strain pattern 3 equally spaced strain magnitudes between - 0,005 and 0,005 are employed. This requires a total number of 13 stress calculations. The atoms are relaxed after straining the cell. Vacancies exist at random for normal preparing condition, the shear modulus needs to be average over all possible configurations. Here in Voigt method is used to estimate isotropic elastic moduli by averaging over the anisotropic elastic constant [9]. Density of States, Bulk modulus and Shear Modulus are shown in Figure 2. It is noticed that the bulk modulus and shear modulus of MoC_{0,89} ($x = 0,11$) are 392,2 GPa and 205,4 GPa, respectively, which are both higher than that of α -MoC at 335 GPa and 144 GPa [20]. The bulk and shear modulus drop to 284,8 GPa and 144 GPa when the carbon vacancy increases to 0,22. To understand the behavior of the elastic stiffens at the quantum-mechanical level. Density of states (DOS) of substoichiometric carbide are plotted in Figure 2 to show the electronic structure change due to vacancies. The C 2s orbital lies to the lowest energy, and nonmetal p - metal d bonding states locates above them. The integrated DOS shows that the pd bonding states are reduced in presence of vacancies, which weakens the bond strength. The peak originated near - 2 eV are vacancy-derived states. The metallic

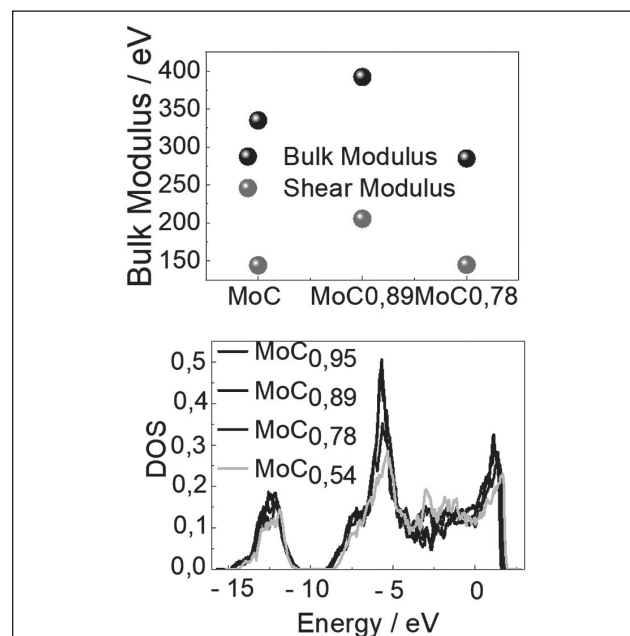


Figure 2 DOS and Elastic Moduli for α -MoC_(1-x)

states near the Fermi level originated from metal d-metal d bonding, which can be a negative contribution to the shear modulus [7]. As such the reduce of dd bonding could compensate the weakening of pd bond strength due the vacancies and gives slight hardening behavior.

CONCLUSION

This paper use simulation method to study the elastic modulus of non-stoichiometric Molybdenum carbide and provide an atomistic understanding of the anomaly vacancy hardening mechanism.

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Note: The responsible translator for language English is associate professor W. Zang - University of Science and Technology LiaoNing, China.