



Influence of carbon vacancy formation on the elastic constants and hardening mechanisms in transition metal carbides

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Abstract

For group VB transition metal carbides, as compared to group IVB carbides, an anomalous rise in hardness occurs for substoichiometric carbon concentrations as compared to the stoichiometric monocarbides. Here we report the computationally derived elastic constants, electronic density of states, and activation energies for carbon vacancy migration as a function of carbon content to elucidate their effect on the hardening responses. The changes in elastic properties with respect to carbon vacancy concentration show similar behaviors of elastic softening and decreasing hardness for all of the cubic carbides. The consistent trends of vacancy diffusion energy barriers between all of the group IVB and VB transition metal carbides also suggests that carbon diffusion may not be a significant contributor to the reported hardness differences. Consequently, we propose that the anomalous hardening for substoichiometric behavior is a competition between elastic constant softening and a microstructural-based effect, i.e. domain hardening, that is present in group VB carbides but not in group IVB carbides.

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1. Introduction

The group IVB and VB transition metal carbides are a class of refractory ceramics that are well known for their thermal and structural stability. These materials form compounds that have the highest melting temperatures recorded and exhibit exceptional hardness, which are direct results of the mixed covalent-metallic-ionic bonding present in these compounds. Thus, they are well suited for structural applications at high temperatures where a variety of strengths are required.

At near equal parts transition metal and carbon, these materials typically form the rock salt or B1 structure. This structure is stable for a range of stoichiometry allowing a large amount of carbon loss. For the group VB compounds, the FCC structure of the metal atoms is maintained with the loss up to approximately

25% carbon at elevated temperatures. At lower temperatures, the carbon vacancies can order resulting the precipitation of a Me_6C_5 phase, where Me is the metal atom.¹ Further carbon loss may result in the precipitation of various faulted metal-rich carbide phases such as Me_4C_3 and Me_2C , which do not share the FCC metal sublattice ordering. Of the group VB metal carbides, vanadium carbide is unique. It does not form a stoichiometric B1 structure like TaC or NbC, rather it phase separates to substoichiometric VC_x and graphite, at carbon concentrations equal to or greater than $X \sim 0.88$.² In contrast, the group IVB compounds can sustain much larger losses of carbon concentrations without the loss of the FCC metal sublattice. Thermodynamic and first principle calculations of these compounds have also shown the stability of equivalent vacancy ordered phases retaining the FCC metal lattice,³ but, to the authors' knowledge, these phases have not been experimentally reported. None of the faulted metal-rich carbides are known to form in the group IVB carbides.

It is well known that vacancies can directly affect the thermal and structural stability and exert influence on mechanical properties of materials. Notably, the melting temperature of the group VB carbides has a maximum that is not located at

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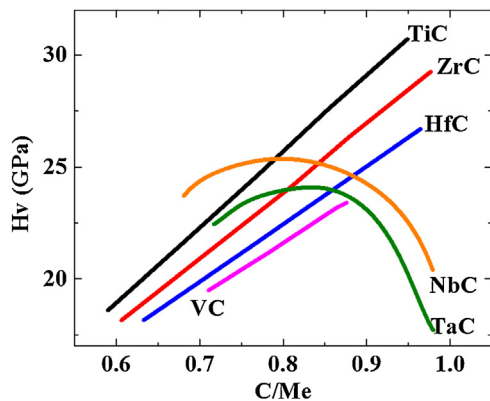


Fig. 1. Representation of hardness as a function of transition metal carbide and carbon content. The image is a rendering of that reported in Ref. ⁴

stoichiometric MeC, but at some measurable carbon loss.¹ Additionally, the hardness measurements have also been reported to similarly trend with the peak hardness being substoichiometric, Fig. 1. For NbC_x and TaC_x this maximum is at C/Me = $x \leq 0.85$.^{4–7} While various studies may not all show the same amount of hardening or the exact same carbon vacancy transitions, it is clear that such a substoichiometric transition occurs. Studies in the group IVB carbides have not shown a similar anomalous hardening and melting temperature behavior; in contrast, in each of these properties, the maximum property is at the stoichiometric C:Me ratio of equal parts.⁷

Numerous theories have been developed to explain this difference in hardness between the group IVB and VB transition metal carbides, including optimal filling of the d-bands,⁴ changes in slip systems,^{8–10} as well as the potential hardening cause by substoichiometric phases.¹¹ The study by Jhi et al.¹² supports, with electronic structure density functional theory (DFT) calculations, the notion that bonding has a direct effect on the hardness through the elastic constants. They showed that the shear modulus of NbC_x does not decrease nearly as much as TiN_x (which shows a comparable loss of hardness similar to TiC_x). Vacancies have also been postulated to control strength and plastic flow in these materials. These theories^{7,13–15} assume that carbon vacancy migration through the dislocation core is necessary for plastic flow at low and moderate temperatures. Collectively, these prior results strongly suggest that the formation and migration of carbon vacancies in these materials is critical in understanding their properties and ultimately how to design these materials.

In this work, we investigate the properties of vacancies in all of the group IVB and VB transition metal carbides using electronic structure density functional pseudo-potential theory. We solely focus on the B1 structure with vacancies and compare our findings with available literatures. Notably, we compute the change in elastic properties with respect to carbon vacancy concentration for all of the cubic carbides. The comparison of these properties enables us to determine its contribution to the hardening/softening in indentation experiments. We also compute the vacancy formation energies as a function of the super-cell size, which allows us to compare the formation energy and stability across the cubic carbides. The computed vacancy migration

energy in all of these materials will be compared against available experiments as well as predict some unmeasured properties. Finally, we examine how the densities of states in these materials change as a function of carbon content in the B1 structure. While numerous papers have computed elastic properties of the pure B1 structures,^{16–20} none have comprehensively computed the properties for a wide range of vacancy concentrations or materials. This self-contained approach will provide unique insight into the similarities and differences between the group IVB and VB cubic monocarbides and help to elucidate the anomalous hardening in group VB carbides that is not observed in group IVB carbides as shown in Fig. 1.

2. Methodology

To compute the energies used in estimating the vacancy formation energies, migration energies and elastic constants, we employed the electronic structure density functional theory as implemented in the Vienna Ab-Initio simulation package (VASP).^{21,22} For all of our calculations, we use the projector augmented wave (PAW) pseudo-potential^{23,24} and evaluate the exchange correlation energy using the Perdew–Burke–Ernzerhoff (PBE) formulation within the generalized gradient approximation (GGA).²⁵ The energy cutoff used in all our calculations was 400 eV and integration in k-space was performed using Monkhorst–Pack with an integration that varied with simulation cell size.²⁶

In order to compute properties as a function of vacancy concentration, many different super-cell sizes were used. The primitive B1 unit cell consists of two atoms, but cannot support any vacancies without forming a pure substance. To resolve this issue, we used two types of super-cells: one that is based on an expanded form of the primitive cell and one that expanded upon the standard FCC unit cell. The primitive unit cell has two atoms and the expanded forms (equal in all directions) have 2, 16, 54, 128, ..., $2^3 N^3$ atoms, where N is the number of atoms in the super-cell. The expanded FCC unit cells have 8, 64, 216, 512, ..., $(2N)^3$ atoms. The 16 and 64 atom unit cells are shown in Fig. 2 for reference. The advantage of using both of these types of super-cells is that removing a single vacancy (either carbon or metal) results in the super-cell retaining its cubic symmetry, even after relaxation, which allows us to simulate the formation of a relatively isolated vacancy as well as determine unambiguously the elastic constants for the sub-stoichiometric monocarbides.

3. Results and discussion

3.1. Elastic constants

Most mechanical properties, i.e. strength and hardness, scale with elastic constants. We have computed both stoichiometric, Table 1, and substoichiometric, Table 2, elastic properties for each of the carbides. In addition, we have provided the lattice constant and cohesive energy for each of the stoichiometric B1 structures in Table 1. To evaluate the enthalpy of formation, the cohesive energies of the pure elements, metal and carbon atoms, were subtracted from the cohesive energy of the compound,

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