Vacancy Hardening and Softening in Transition Metal Carbides and Nitrides

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The effects of vacancies on mechanical properties of the transition metal carbides and nitrides are studied using the *ab initio* pseudopotential approach. Calculated shear elastic stiffness and electronic structures show that the vacancy produces entirely different effects on the mechanical strength of groups IVb nitrides and Vb carbides. It is found that the occupation of shear-unstable metallic *dd* bonding states changes essentially in an opposite way for the carbides and nitrides in the presence of vacancies, resulting in different responses to shear stress. Our study provides an atomistic understanding of the anomaly in hardness for these substoichiometric materials.

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Transition metals in groups IVb and Vb and the first row elements, carbon and nitrogen, together make strong solids in the rocksalt structure [1]. Large hardness, high melting point, and wear resistance are key properties for the technological applications of these materials to cutting tools and hard coatings. These compounds normally exist in substoichiometric phases with a substantial amount of vacancies [1–3]. Nonmetal deficiency is known to be a major source of the nonstoichiometry, and the control of the stoichiometry and the understanding of its effect on mechanical properties are crucial to the design of hard materials based on these compounds. It is expected that vacancies reduce the number of chemical bonds and hence the strength of materials. However, the hardness of transition metal carbides and nitrides does not follow this simple picture of coordination counting. Vacancies can act as pinning centers inhibiting dislocation motion and thus enhancing the mechanical strength. Another intriguing theoretical finding is that the presence of two unsaturated electronic bands near the Fermi level responding oppositely to shear stress makes the hardness of these systems behave in an unusual way as the number of electrons in a unit cell changes [4,5].

Experimentally, the hardness and the elastic moduli of group IVb nitrides such as TiN_x, ZrN_x, and HfN_x decrease as the concentration of the nonmetal vacancy increases [2,6]. In contrast, it is observed that the hardness of the Vb carbides such as NbC_x and TaC_x *increases* consistently and reproducibly as the vacancy concentration increases up to a modest value and reaches a maximum at a vacancy concentration of about 12% [1,2]. It is puzzling that vacancies affect the hardness of these two classes of compounds in such distinctive ways despite similar chemical bonding of these compounds at stoichiometry. In this Letter we report the effects of the vacancy on the mechanical strength of transition metal carbides and nitrides and provide a microscopic origin for the anomalous behavior of hardness of these materials at substoichiometry using the *ab initio* pseudopotential density functional total energy method [7].

An observation that the hardness of the transition metal carbonitrides is intimately connected to their chemical bonding and electronic structures is a key to the unusual behavior of hardness of transition metal carbides and nitrides in the rocksalt structure for substoichiometric phases (i.e., with vacancies) [4]. The electronic structures should, however, be sensitive to the presence of vacancies and differ significantly from those for the stoichiometric phase. The vacancy concentration as well as the alloy composition is shown crucial to the electronic and mechanical properties in these materials [8,9]. Detailed calculations beyond the rigid band model are required to understand the mechanical and electronic properties of the substoichiometric transition metal compounds.

In order to simulate the compounds at substoichiometry, we use the supercell method with up to 15 atoms in a unit cell [10]. For a given vacancy concentration and supercell, we carry out plane-wave total energy calculations based on the pseudopotential density functional theory within the local density approximation. We pay particular attention to the shear stiffness at variable vacancy concentrations because the shear modulus provides a measure of rigidity against the shape deformations involved in the microhardness indentation experiment [4,11,12]. Structural parameters and atomic positions are fully relaxed until the Hellmann-Feynman forces and stresses are less than 0.02 eV/Å and 0.2 GPa, respectively. After obtaining the equilibrium structure, we apply small strains and calculate the quantum mechanical stresses. Elastic constants are then calculated using Hooke's law. Since vacancies are believed to exist at random for normal preparing conditions, the shear modulus averaged over all possible configurations of vacancies is more relevant than individual elastic constants in the present study. There are several ways to make the average but we employ the Voigt method which estimates isotropic elastic moduli by averaging over the

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anisotropic elastic constants [13]. We choose TiN_x and NbC_x with $x = 1$, 0.875, and 0.75 as representative materials of groups IVb nitrides and Vb carbides, respectively, since experimental data on their hardness and other related properties are readily available [14].

Calculated lattice constants and displacements are presented in Table I. Lattice constants decrease as the vacancy concentration increases for both compounds. However, the decrease is less than 1% in all cases considered here. It is found that the metal atoms nearest to the vacancy move outward from the vacancy toward the surrounding nonmetal atoms. The calculated displacements of metal atoms are 0.035 Å for $NbC_{0.875}$ and 0.060 Å for $TiN_{0.875}$, respectively [15]. The larger atomic displacement of TiN indicates that the charge redistribution near the vacancy is more drastic in TiN than NbC. Our calculation is consistent with experiment where a relaxation of the Nb atoms in NbC by 0.03–0.15 Å, depending on the vacancy concentration, is observed [16,17]. It is possible that the vacancy-vacancy interaction in our supercell geometry may affect the calculated displacement. Experimental data for TiN are unavailable.

The control of stoichiometry is an essential step to the design of hard materials based on transition metal carbides and nitrides. Thus here we also examine the energetics of vacancy formation and calculate a formation energy at zero temperature, using the following definition:

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

where E_{coh} is the cohesive energy per formula unit, A and B denote metal and nonmetal atoms, respectively, and E_s is the sublimation energy of the nonmetals. For the sublimation energy we use the experimental values of 7.425 and 4.897 eV at room temperature for carbon [$C \rightarrow \frac{1}{2}C_2$ (graphite)] and nitrogen [$N \rightarrow \frac{1}{2}N_2$ (molecule)], respectively [18]. The calculated formation energy is also presented in Table I. The negative formation energy indicates that the vacancy formation is energetically unfavorable at low temperature for both compounds. At the vacancy concentration of 12.5%, our calculated formation energy in NbC (~0.13 eV in magnitude) is comparable to the thermal energy at typical synthesis temperatures. At a low vacancy concentration, vacancies would form readily and be quenched due to their low mobility in the compounds as temperature decreases.

TABLE I. Calculated lattice constant (a_0), atomic displacement (d), and the vacancy formation energy (E_f) of NbC and TiN as defined in text at variable vacancy concentration. The displacement at $x = 0.75$ cannot be estimated in the present calculation due to the full cubic symmetry of the supercell.

	a_0 (Å)	d (Å)	E_f (eV)
NbC	4.536	···	···
$NbC_{0.875}$	4.518	0.035	−0.13
$NbC_{0.75}$	4.495	···	−0.51
TiN	4.266	···	···
$TiN_{0.875}$	4.258	0.060	−0.47
$TiN_{0.75}$	4.234	···	−1.11

Figure 1 shows the calculated shear modulus after the Voigt average is performed at variable vacancy concentrations. Experimental values estimated from measured elastic constants [19–21] are also plotted for comparison. The calculated shear modulus shown in Fig. 1 exhibits very intriguing features: for TiN_x it decreases monotonically as the vacancy concentration increases. On the other hand, for NbC_x, it remains *almost the same* up to the vacancy concentration of 12.5% and then decreases at higher concentrations. Similar trends are also observed in other materials of groups IVb and Vb such as ZrN_x and VC_x at variable x. Here we focus on TiN and NbC for a direct comparison with experiment. We note that the introduction of vacancies produces entirely different effects on the shear stiffness for the two compounds although their chemical bonding between metal and nonmetal is very similar. The inset of Fig. 1 shows the experimentally measured hardness of the two compounds [1,2]. The hardness of other substoichiometric compounds such as TaC_x (ZrN_x) also exhibits almost the same trend as that of NbC_x (TiN_x). Considering that the hardness of the two compounds changes in the opposite direction as in the case of the shear modulus at small vacancy concentrations (up to ~12%),

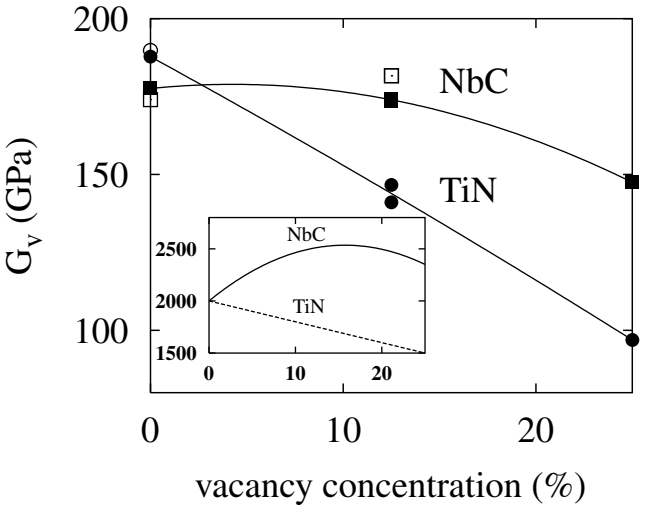

FIG. 1. Calculated Voigt elastic stiffness at variable vacancy concentrations. Filled circles and boxes represent the calculated values for TiC and NbC, respectively. Different data points at the vacancy concentration of 12.5% come from different supercell structures (for NbC, however, the calculated values at different supercells are almost the same and hardly distinguishable). Experimental data at some vacancy concentrations are also plotted for comparison (open circles for TiN and open boxes for NbC, respectively). Solid lines are guides for the eye. Inset shows the measured hardness of NbC (solid line) and TiN (dashed line), respectively, in units of Vickers hardness (Hv).

our results suggest that the behavior of the hardness is closely related to elastic properties.

To understand the behavior of the shear stiffness (and hence the hardness) at the quantum-mechanical level, we investigate the electronic structures of the substoichiometric compounds at equilibrium and sheared conditions. We calculate the density of states (DOS) to see how the electronic states change in the presence of vacancies and how they respond to shear strains. Figure 2 shows the DOS of (a) NbC and (b) TiN with a vacancy concentration of 12.5% [22]. For comparison, the DOS without vacancy is also plotted. It is found that the Fermi level at $x = 0.875$ shifts down by about 0.2 eV from that of the case without vacancies for both compounds. The lowest lying peaks in (a) and (b) of Fig. 2 are derived from the nonmetal (C or N) $2s$ orbitals. Above them, nonmetal p-metal d bonding states are located. The pd bonding states have very strong directional characters and are highly resistive to shear [4,5]. The integrated DOS shows that the pd bonding states are reduced for both compounds in the presence of vacancies, which weakens the bond strength.

The sharp peaks at $E \sim -2$ eV are the vacancy-derived states and their position is in good agreement with the photoemission experiment [23,24]. An integration of the charge density near the vacancy shows that the vacancy is negatively charged with a single electron in the two compounds. The localization of an electron at the vacancy site reflects the partially ionic character of the transition metal carbides and nitrides. The charge density plot (not shown here) shows that the electron at the vacancy site involves in a weak bonding with surrounding metal atoms. However, the vacancy-derived states are found to be insensitive to the applied shear stress and the vacancy state-metal bonding would have a minor effect on the shear stiffness. The charging of the vacancy, on the other hand, leads to a different occupation of some of the electronic states in the two compounds, and the shear stiffness (and correspondingly the hardness) is sensitive to their occupation as discussed below.

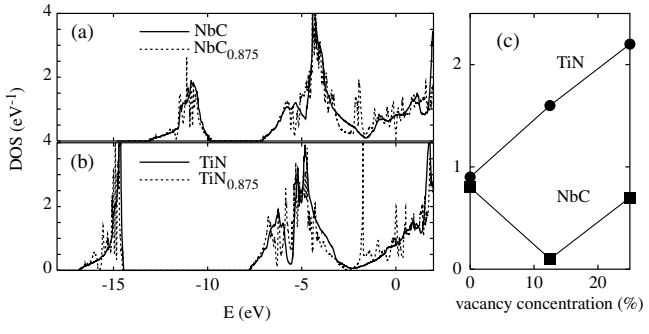

FIG. 2. Density of states per formula unit of substoichiometric compounds for (a) $NbC_{0.875}$ and NbC and for (b) $TiN_{0.875}$ and TiN. The Fermi level of the substoichiometric phase lies at energy zero in both (a) and (b), which is about 0.2 eV below that without vacancy. (c) The DOS at the Fermi level at variable concentrations for TiN_x (filled circles) and NbC_x (filled boxes), respectively.

Of particular interest are the metallic states near the Fermi level that originate from the metal d-metal d bonding between the next nearest neighbor metal atoms. In transition metal carbonitrides (e.g., TiC_yN_{1-y}), it was shown that at a specific alloy composition these dd bonding states begin to be occupied and give a negative contribution to the shear modulus [4]. Here, we observe that the DOS derived from the dd bonding states changes in an essentially different manner in the two compounds as the vacancy concentration increases. Compared to the DOS without vacancies, the DOS from dd bonding states increases substantially in $TiN_{0.875}$ while it is much reduced in $NbC_{0.875}$, especially near the Fermi level. Since the dd bonding states give a negative contribution to the shear modulus as mentioned, the increase in the number of dd bonding states results in a fast decrease of the shear modulus as shown for $TiN_{0.875}$. On the other hand, the reduction of the metallic dd bonding states in $NbC_{0.875}$ compensates for the weakening of the pd bond strength due to the vacancies and gives a slow variation of the shear modulus. It is found that, at higher vacancy concentrations, the DOS from the dd bonding states is *enhanced* for *both* compounds compared to that without vacancies. In short, the contrasting behavior of the shear modulus (and hardness) of the two compounds at substoichiometry is mainly attributed to different trends in the amount of occupied dd bonding states as vacancies are introduced. The change in the occupation of dd bonding states is most significant near the Fermi level. To illustrate this change explicitly, we present the DOS at the Fermi level (N_f), which is mainly derived from the dd bonding states, in Fig. 2(c) at variable vacancy concentrations. Note that N_f of NbC_x reaches a minimum at $x = 0.875$ while it increases monotonically for TiN_x. Similar results were reported by previous studies which used the coherent potential approximation method to incorporate the disordering of vacancies [25]. The calculated N_f also suggests that other anomalies observed in the group Vb carbides, such as the minimum of the magnetic susceptibility at the vacancy concentration of about $\sim$12% and the maximum of the Hall coefficient and the thermopower at a similar concentration, are possibly due to the change in the electronic density of states [26]. The accurate description of these properties, however, should be given within the framework of the transport theory which takes into account the disordering of vacancies and the electronic structure.

We note that the vacancy-derived peaks and their position in the DOS are insensitive to the supercell structures considered here, and that the compounds in the same group (e.g., TiN_x and ZrN_x, or VC_x and NbC_x) exhibit similar features in the DOS. Disordering of vacancies may broaden the vacancy-derived peaks [25], but the essential feature should persist unless there is a strong tendency of clustering of vacancies.

The opposite trends in the DOS can be traced back to the difference in the electronegativity of Ti and N compared with that of Nb and C. It is known that electrons transfer from metal to nonmetal atoms in the transition metal carbides and nitrides. When the nonmetal atoms are removed, the electrons would return to the metal atoms and occupy the metallic states near the Fermi level (*dd* bonding states here). A larger difference of the electronegativity in TiN means a greater charge transfer than in NbC. Accordingly, for TiN, more electrons would return to the *dd* bonding states at the vacancy and give a larger occupation of the *dd* bonding states than for NbC. However, since there is a localized vacancy state which makes the vacancy negatively charged and forms a weak bonding with surrounding metal atoms as described above, the additional electrons occupying the *dd* bonding states are not simply equal to the amount of charge transferred from metal to nonmetal before the vacancy is created. The comparatively less ionic character of $NbC_{0.875}$, in fact, results in a decrease of the occupation of the *dd* bonding states and N_f.

We comment that vacancies at low concentration can enhance the mechanical strength of a solid through dislocation pinning as mentioned previously. Hence hardening by vacancies in NbC_x could be much more drastic than the trend in the shear modulus as observed in the measured hardness (the inset of Fig. 1).

In summary, the effect of vacancies on the mechanical properties of the transition metal carbides and nitrides is studied using a first-principles pseudopotential total energy method. The contrasting behavior of the hardness in groups IVb nitrides and Vb carbides observed in experiment is found to originate from their different behavior in the elastic shear stiffness at variable vacancy concentrations. The occupied metallic *dd* bonding states in TiN, which give a negative contribution to the shear modulus, are enhanced as the vacancy concentration increases and result in a fast decrease of the shear modulus. The reduced *dd* bonding states in NbC result in a much slower decrease of the shear modulus. It is shown that the shear modulus of NbC remains virtually unchanged until the vacancy concentration reaches about 12.5%.

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