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Structure, Properties and Quantum Chemistry Studies on Non-Stoichiometric Compounds of $(Nb_yTi_{1-y})C_x$

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Abstract: Non-stoichiometric compounds of $(Nb_yTi_{1-y})C_x$, in which the amount of Nb element added is increased from zero to 40% (weight percent), synthesized with self-propagating high temperature synthesis, are studied with SCF-X α-DV, a quantum chemistry calculating method. The chemical bonding is studied to discuss the relation between structures and properties. Several classes of models in which there is no vacancy, one vacancy or two vacancies have been calculated. From the calculated results of bond order, a measure of covalent bond strength, and molecule orbital contour map, an audio-visual method to discuss chemical bonding, we conclude that when Nb element added increases, the vacancies increase correspondingly, the covalent component of the chemical bonds of the samples decreases while the metal-bonding component increases, so the hardness and electrical resistance of the samples decrease.

1 INTRODUCTION

TiC is a typical ceramic material with good properties of high hardness and resistance to high temperature. It takes an important part in science and technology. For example, TiC and TiN are the super-hard materials which are the most commonly studied and used today.[1] On the other hand, TiC, TiN and some other carbides or nitrides of transition metals are a series of non-stoichiometric compounds. Their compositions can be changed over a wide range to improve the properties. So far there is not much explanation for the relationship between their structures and properties. This should be studied in detail, both experimentally and theoretically.

The pattern of the movement of electrons at the outer layers of an atom is studied in quantum chemistry. From this viewpoint, most material properties have something to do with the movement of the valence electrons. The main component of the chemical bond of nonmetal materials, such as ceramics, is covalent or ionic, with the good properties of resistance to high temperature and corrosion but bad properties of mechanics in general. The main component of the chemical bond of metal materials is the metal-bond, which does not have such a high resistance to high temperature and corrosion, but has better mechanical properties. From the viewpoint of the chemical bond, the differences of properties between metal and nonmetal, including the matching or binding property between the compositions of metal and nonmetal in composites, are mainly from the difference of chemical bonds between metal and nonmetal. Therefore, by adjusting the ratio of different bond components, we might be able to synthesize new materials with the good properties of both metal and nonmetal. In this paper, we study the improvement of properties of TiC by adding Nb element to change the composition and the theoretical calculations of quantum chemistry.

2 EXPERIMENT

TiC ceramic is a typical covalent compound with high hardness and electrical resistance. It has a

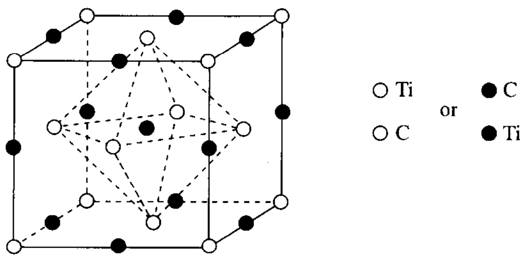

Fig. 1. TiC cell structure.

NaCl-type structure (Fig. 1) in the perfect form. Due to the property of non-stoichiometry, the ratio of mole fractions of Ti:C is usually more than one in the practical samples. In other words, C atoms don't fully occupy the interstitial vacancies of Ti_6 octahedra. It is shown from the phase diagram[2] that if the mole fraction of Ti is 1·0, that of C can be changed from 0·5 to 1·0 to keep the NaCl-type structure.

Nb element has been quantitatively added to TiC crystal with self-propagating high-temperature synthesis (SHS) or special solid–solvent method, forming a series of solid solutions of $(Nb_yTi_{1-y})C_x$. In Table 1 there are experimental results of compositions, crystal cell parameters, hardness and electrical resistances of the samples. Though the amount of Nb element added is increased from zero to 40% (weight percent) and the compositions of samples are changed, the samples still keep their original structure and there is only a slight variation of the crystal cell parameters determined by X-ray analysis. As the summation of mole fractions of Nb and Ti is one, with the increase of the amount of Nb element added, the mole fraction of C element (x) decreases, so the vacancies, formed from being in short supply of C atoms, are increased. Correspondingly, the hardness and electrical resistance of the samples decrease. That is to say that the samples appear less obviously ceramic in character but more metallic with the variation of the compositions. We shall study what the dominant fact is that leads the samples to change their properties.

3 COMPUTATIONAL DETAILS

SCF-Xα-DV was proposed by Ellis and Painter.[3]

The method is based on the Schrödinger equation. With the approximation of one electron orbital, the Schrödinger equation is changed into the Hartree–Fock equation which can be used for the system of atoms, molecules and electrons. Then a statistical approximation is applied to the exchange potential in the Hartree–Fock equation:

$$Vx\ \alpha = -3\ \alpha\ [(3/8\ \pi) \cdot \rho\ (r)]^{1/3} \qquad (1)$$

where $Vx\ \alpha$ is Slater's exchange-correlation operator, α is the exchange potential constant (adjustable from 2/3 to 1 in general) and $\rho(r)$ is the electronic charge density. With the above approximations, the Xα equation is obtained.

The main procedure of the SCF-Xα-DV method is: choose a number of discrete sampling points in a three-dimensional grid. Depending on the quantity of interest, the number can be chosen to give the desired accuracy. Variation is made to the parameter of trial function to obtain all the minimums for the points. The various Coulomb and exchange integrals are approximated numerically by weighted summation of the sampling points. In this way, we can get the matrix elements of secular equations, then obtain the molecular orbital energy levels and wave functions. Though the precision of SCF-Xα-DV is lower than that of an *ab initio* method, it occupies smaller space, computes quickly and is less limited by the capacity of computers. SCF-Xα-DV can be easily used to calculate larger molecules, clusters and solids. Furthermore, its precision is higher than those of the semi-experimental methods of EHMO, CNDO, INDO, etc. SCF-Xα-DV is a good method to use in material science.

The strength of the covalent bond can be measured by Mulliken's overlapping populations,[4] or covalent bond orders. P(A–B) is the overlapping population of electrons between atoms A and B:

$$P\ (A\text{–}B) = \sum_{n} \sum_{i,j} C^{A}_{in}\, C^{B}_{nj} \int \Psi_i\, \Psi_j\, dv \qquad (2)$$

here Ψ_i and Ψ_j are the wave-functions of i and j orbitals of atoms A and B, respectively, C^{A}_{in} and C^{B}_{nj} are coefficients for showing magnitudes of linear combinations of atomic orbitals, the summation of n is extended over all the occupied molecular orbitals.

Table 1. Experimental results of the samples

Numbers	0	1	2	3	4	5	6
Nb (w%)	0	5	10	15	20	30	40
x	0·776	0·754	0·729	0·702	0·675	0·616	0·552
Cell parameters (nm)	0·4324	0·4334	0·4338	0·4343	0·4348	0·4354	0·4354
H (kg/mm2)	2800	2514	2201	2095	1812	1597	1290
R (Ωm)		98·95	27·43	4·30	1·26	1·01	0·97

4 RESULTS AND DISCUSSION

The positions of Ti and C in the TiC cell are equivalent (Fig. 1). The atoms in the cell are divided into the four classes according to their relative positions: (1) The atom at the centre of the cell. (2) The six atoms at the centres of surfaces as the first-nearest neighbours to the first class of atom. (3) The twelve atoms at the centres of edges as the second-nearest neighbours. (4) The eight atoms at the corners as the third-nearest neighbours. The cell can be express as $[\mathrm{CTi_6C_{12}Ti_8}]$ or $[\mathrm{TiC_6Ti_{12}C_8}]$. We have calculated the models of $[\mathrm{Ti^*C_6Ti_{12}C_8}]$ and $[\mathrm{Nb^*C_6Ti_{12}C_8}]$ (the bond orders of the atoms with the asterisk symbol '*' are mainly discussed), as well as $[\mathrm{Ti^*C_6Ti_{12}}]$ and $[\mathrm{Nb^*C_6Ti_{12}}]$ of which the eight C atoms as the third-nearest neighbours to the centre atoms are neglected. Comparing the calculated results, we see that when we select the calculated models and mainly study the results of some classes of atoms, only the first and second-nearest neighbours to the classes of atoms are present in the models, from which reliable results may be obtained in general.[5]

To study the effects on chemical bonds and properties of the samples of both Nb addition and the vacancies from losing C atoms at the same time, based on the model of $[\mathrm{CTi_6C_{12}Ti_8}]$, firstly, a vacancy is formed in the cell centre by removing a C atom. Considering that the amount of Nb added is smaller than that of Ti, the model should maintain its best symmetry reasonably well. To calculate and study this symmetry conveniently, we divided the six atoms, as the first-nearest neighbours to the cell centre (C atom or vacancy), into the two sub-classes of atoms. The first sub-class of atoms is two atoms (Ti or substituted by Nb) at the top and bottom, which is indicated by an asterisk. The second sub-class of atoms is four Ti atoms in the horizontal plane. To let the model consist of the first and second-nearest neighbour atoms to the first sub-class of atoms, we add the two C atoms in the directions of centres of the planes and the eight Ti atoms in the directions of the centres of the edges at the top and bottom. The vacancy is expressed as '□'. The first class of models (Fig. 2, it also includes the second class of models which will be discussed later) and the results of bond order are:

$[\mathrm{C^*(Ti_2^*Ti_4)C_{12}Ti_8C_2Ti_8}]$, P(Ti*–C)=0·4517
P(Ti*–Ti)=0·0679(class 1–1)
$[\mathrm{C^*(Nb_2^*Ti_4)C_{12}Ti_8C_2Ti_8}]$, P(Nb*–C)=0·5958
P(Nb*–Ti)=0·0537(class 1–2)
$[\square^*\mathrm{(Ti_2^*Ti_4)C_{12}Ti_8C_2Ti_8}]$, P(Ti*–C)=0·3046
P(Ti*–Ti)=0·1359(class 1–3)
$[\square^*\mathrm{(Nb_2^*Ti_4)C_{12}Ti_8C_2Ti_8}]$, P(Nb*–C)0=0·3837
P(Nb*–Ti)=0·0990(class 1–4)

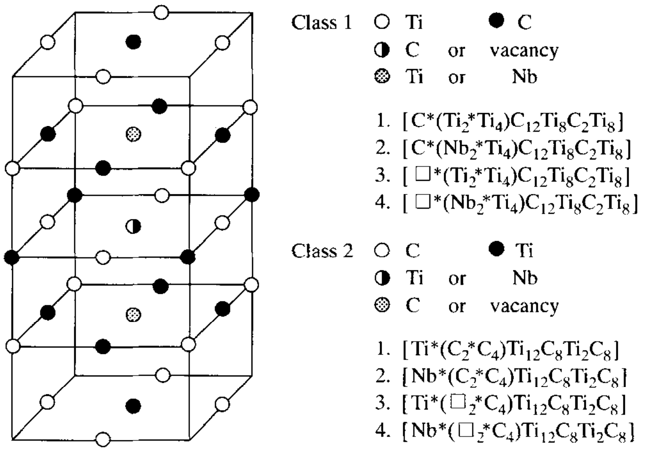

Fig. 2. The calculated models.

P(Ti*–C) and P(Nb*–C) are the measures of the covalent bonding between metal and nonmetal atoms. As the metal-bonding is a special delocalized covalent bonding without directivity and saturability, in the limited models here, the overlapping populations of P(Ti*–Ti) and P(Nb*–Ti) can be considered as measures of the metal-bonding between the metal atoms in the models. This overlap or characteristic of the metal-bonding can be seen in the contour maps (in each map there are 7–8 metal atoms and 6–8 C atoms) of the orbitals of the models. Comparing the models of (1–1) and (1–2), or (1–3) and (1–4), we see that when Nb is substituted for Ti, P(Nb*–C) is slightly larger than P(Ti*–C), but P(Nb*–Ti) is somewhat smaller than P(Ti*–Ti). It means that there is a small increase of ceramic-character and decrease of metal-character, which is opposite to the variational tendency of hardness and electrical resistance of the samples shown in Table 1. As the above differences of bond order are small, there is not a large effect on the chemical bonding and the properties of the samples due to Nb substitution for Ti. Nb element itself doesn't play an important role in affecting the properties of the models.

Comparing the models of (1–1) and (1–3), or (1–2) and (1–4), when the vacancy from losing a C atom is formed, there are the obvious changes of a decrease of P(Ti*–C) and P(Nb*–C) and an increase of P(Ti*–Ti) and P(Nb*–Ti). The covalent component of chemical bonds of the samples decreases but the metal component increases, so there is some decrease of ceramic-character and increase of metal-character, which is consistent with the variational tendency of hardness and electrical resistance of the samples due to the variation of compositions that the vacancies increase with the increase of amount of Nb element added, as shown in Table 1. The vacancy from losing a C atom plays a dominant role in affecting properties of the models.

We further calculated the second class of the models (Fig. 2). Compared with the first class of models, the positions of vacancies and Nb atoms are exchanged, the positions of Ti and C atoms are also exchanged. The second class of models and the results are:

$$[\mathrm{Ti}^*(\mathrm{C}_2^*\mathrm{C}_4)\mathrm{Ti}_{12}\mathrm{C}_8\mathrm{Ti}_2\mathrm{C}_8],\ P(\mathrm{Ti}^*\text{–}\mathrm{C})=0{\cdot}3039$$
$$P(\mathrm{Ti}^*\text{–}\mathrm{Ti})=0{\cdot}0145(\text{class } 2\text{–}1)$$
$$[\mathrm{Nb}^*(\mathrm{C}_2^*\mathrm{C}_4)\mathrm{Ti}_{12}\mathrm{C}_8\mathrm{Ti}_2\mathrm{C}_8],\ P(\mathrm{Nb}^*\text{–}\mathrm{C})=0{\cdot}4107$$
$$P(\mathrm{Nb}^*\text{–}\mathrm{Ti})=0{\cdot}0127(\text{class } 2\text{–}2)$$
$$[\mathrm{Ti}^*(\square_2^*\mathrm{C}_4)\mathrm{Ti}_{12}\mathrm{C}_8\mathrm{Ti}_2\mathrm{C}_8],\ P(\mathrm{Ti}^*\text{–}\mathrm{C})=0{\cdot}1617$$
$$P(\mathrm{Ti}^*\text{–}\mathrm{Ti})=0{\cdot}0793(\text{class } 2\text{–}3)$$
$$[\mathrm{Nb}^*(\square_2^*\mathrm{C}_4)\mathrm{Ti}_{12}\mathrm{C}_8\mathrm{Ti}_2\mathrm{C}_8],\ P(\mathrm{Nb}^*\text{–}\mathrm{C})=0{\cdot}2115$$
$$P(\mathrm{Nb}^*\text{–}\mathrm{Ti})=0{\cdot}0779(\text{class } 2\text{–}4)$$

Notice there are two vacancies in the model (2–3) or (2–4). The variational tendency of bond order of the second class of models is consistent with that of the first class of models and gives support to the above discussions. Lastly, we draw the contour maps (the figures are omitted) of the valence orbitals of the first and second classes of models. From the maps we can directly see the characteristic or strength of the covalent or metal-bonding between atoms in the models. It is an audio–visual method to discuss chemical bonding. With the maps we see that there is less difference between the models (1–1) and (1–2), (1–3) and (1–4), (2–1) and (2–2) or (2–3) and (2–4), which also gives support to the above discussion that Nb element itself doesn't play an important role in affecting the properties of the models. On the other hand, the strongest covalent bonding is between a C atom and its neighbouring metal atoms but hardly any metal-bonding among the metal atoms in the models (1–1), (1–2), (2–1) or (2–2) in which there is no vacancy from losing a C atom. There is weaker covalent bonding and some stronger metal-bonding in the models (1–3) or (1–4) in which there is one vacancy. The least strong covalent bonding and the strongest metal-bonding are in the models (2–3) or (2–4) in which there are two vacancies. This also gives support to the above discussion that the vacancy from losing a C atom plays a dominant role in affecting the properties of the models.

5 CONCLUSIONS

When Nb is substituted for Ti, P(Nb*–C) is slightly larger than P(Ti*–C), but P(Nb*–Ti) is somewhat smaller than P(Ti*–Ti). It means that there is a small increase of ceramic-character and decrease of metal-character. As the effect on the chemical bonding and the properties of the samples due to Nb substitution for Ti is not great, Nb element itself doesn't play an important role in affecting the properties of the models.

When vacancies from losing C atoms are formed, the obvious changes are a decrease of P(Ti*–C) and P(Nb*–C) and an increase of P(Ti*–Ti) and P(Nb*–Ti). In other words, the covalent component of the chemical bonds of the samples decreases but the metal component increases, so there is some decrease of ceramic-character and increase of metal-character, which is consistent with the variational tendency of hardness and electrical resistance of the samples due to the variation of compositions that the vacancies increase with the increase of amount of Nb element added. The vacancy from losing a C atom plays a dominant role in affecting the properties of the models.

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