

## Ab Initio Modeling of Boron Impurities Influence on the Electronic and Atomic Structure of Titanium Carbide

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The first-principle calculation of boron impurities influence on the electronic and atomic structure of titanium carbide is presented. The density functional theory in the general gradient approximation using the software package ABINIT has been used for numerical calculation. The titanium carbide supercell consisted of 24 atoms. The total energy of titanium carbide supercell and boron impurity atoms with different numbers and locations of impurity atoms was calculated. As a result of this research, it was found that impurity boron atoms showed no tendency to clustering in titanium carbide. The atomic structure changing of titanium carbide in the presence of boron impurities in the substitution and interstitial positions was discussed. The equilibrium distances between adjacent planes of titanium carbide supercell with boron impurities in the substitution and interstitial positions were calculated and analyzed. The boron atoms accumulation on (111) titanium carbide planes leads to an increase in the distance between the adjacent close-packed Ti atoms layers. The electronic structure of titanium carbide, titanium diboride and TiC-supercell with different numbers and locations of boron impurities are discussed. A characteristic feature of titanium carbide supercell spectra with impurity boron atoms is the presence of an impurity subzone, which is located between the local electronic spectra of the 2s and 2p carbon states by about 0.24 Hartree below the Fermi level. There is also a slight increase in the density of electronic states directly below the Fermi level. Different coordinate positions of impurity boron atoms affect only the shape and half-width of the impurity subzone, namely, the half-width of the impurity subzone becomes larger with an increase in the number of impurity atoms in the first coordination sphere of nonmetallic atoms around the impurity.

**Keywords:** Titanium carbide, Boron impurities, Electronic structure, Atomic structure.

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### 1. INTRODUCTION

Ceramic-matrix composites based on TiC-TiB<sub>2</sub> have attracted enormous interest during recent years because, in comparison to single-phase ceramics, they exhibit superior properties including high hardness, good wear resistance, and high fracture toughness. TiC-TiB<sub>2</sub> composites represent promising materials for use as wear-resistant parts like forming dies and cutting tools and exhibit good behavior as high-temperature structural components in heat exchangers and engines. In addition, the use of TiC-TiB<sub>2</sub> in non-structural applications like wall tiles in nuclear fusion reactors, cathodes in Hall-Heroult cells and vaporizing elements in vacuum-metal deposition installations have been under investigation. In comparison to conventional cermets based on WC and TiC, cermets based on TiC-TiB<sub>2</sub> composites exhibit higher hardness and chemical stability at high temperatures and are regarded as a good alternative for wear-resistant applications [1-3].

The doped titanium carbide is interesting as a material with a unique combination of physical properties (ultrahigh hardness, good corrosion resistance, high melting point, relatively high conductivity and thermal conductivity [1, 2]) and as a component for the creation of highly perspective ceramic and metal-ceramic composites (for example, TiC-TiB<sub>2</sub> systems [3]). Therefore, the theoretical study of the peculiarities of the electronic and atomic structure of titanium carbide and titanium carbide with boron impurities as an integral part of modern composite materials is an actual task.

### 2. CALCULATION RESULTS AND DISCUSSION

Ab initio calculation of the boron impurities influence on the TiC electronic and atomic structures was carried out by the density functional theory (DFT) [4] in the general gradient approximation (GGA) [5] using the software package ABINIT [6]. Numerical annealing of the atomic positions was performed according to the algorithm described in [7].

Titanium carbide has a sodium chloride crystal structure, which consists of two fcc lattices of titanium and carbon atoms shifted relative to each other. Accordingly, in planes of type (111) alternating layers are filled exclusively with titanium or carbon atoms with a structure of close-packing of equal spheres. To analyze the boron impurities influence on the titanium carbide structure, we constructed a supercell Ti<sub>12</sub>C<sub>12</sub> containing 24 atoms: three layers of the (111) type of titanium atoms (dense packing of spheres of type A, B and C) and similarly for carbon atoms; in each layer of 4 atoms (Fig. 1). The boron atoms were incorporated into the supercell both as the replacement of carbon atoms and in the interstitial positions corresponding to the positions of boron atoms in TiB<sub>2</sub>.

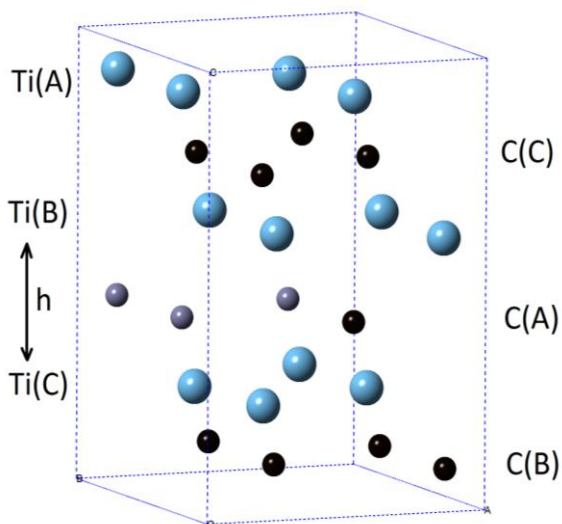
Titanium diboride also consists of titanium atoms layers with a close-packed spheres structure (for example, type A) alternating with graphite-like layers of boron atoms (positions B and C). The distance between the close-packed titanium atoms layers is greater in TiB<sub>2</sub> (6.07 Bohr) than in TiC (4.72 Bohr) by about 28 %. After the impurity boron atoms incorporation into the TiC supercell, for relaxation of internal stresses numer-

ical annealing of the atomic positions was carried out in accordance with the forces calculated from the first principles.

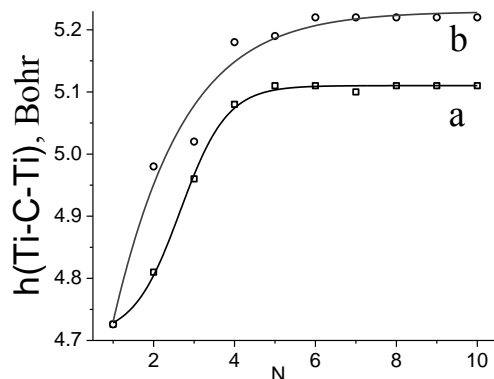
Fig. 2 shows the change in the distance between adjacent layers of close-packed Ti atoms when 3 atoms of boron are placed in the carbon atoms layer between them (a – all three boron atoms replace carbon atoms substitutionally (Fig. 1); b – two boron atoms replace carbon atoms, and the third boron atom is in the interstitial position). It is seen that the ten steps of numerical annealing (N is the number of the annealing step) are sufficient to obtain the equilibrium distance between the corresponding atomic layers. In the case when all the impurity boron atoms are in the substitution state of carbon atoms, the distance between adjacent layers of close-packed Ti atoms increases by 8 % (Fig. 2a). When placing one of the impurity boron atoms in the interstitial position (corresponding to a graphite-like boron atoms layer in  $\text{TiB}_2$ ), the distance between adjacent layers of close-packed Ti atoms increases by 10.5 % (Fig. 2b). The obtained result is quite understandable since the covalent radius of the boron atom is larger than the covalent radius of the carbon atom.

The energy dependence of the electronic density of states of titanium carbide is shown in Fig. 3. We can see the full spectrum of TiC (a) and local spectra of 3d Ti (b) and 2s C, 2p C (c) (local spectra are shifted along the ordinate axis for convenience). A vertical line indicates the Fermi level. As our calculations show, the electronic states near the Fermi level almost completely consist of 3d Ti and 2p C states.

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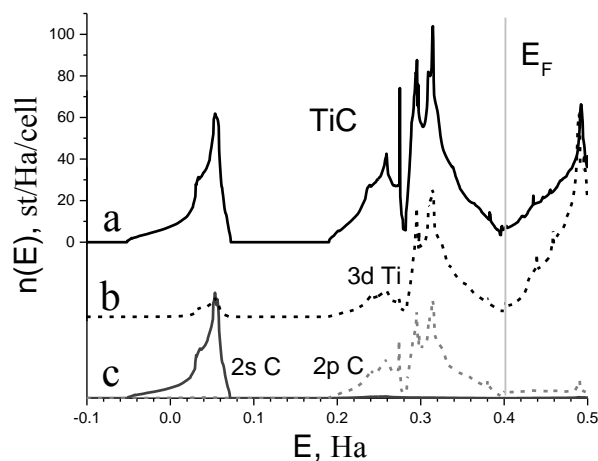
**Fig. 1** –  $\text{Ti}_{12}\text{C}_{12}$  supercell: three boron atoms are in the substitution positions



**Fig. 2** – The change in the distance between adjacent layers of close-packed Ti atoms when 3 atoms of boron are incorporated into the carbon atoms layer between them (a – all three boron atoms replace carbon atoms substitutionally; b – two boron atoms replace carbon atoms, and the third boron atom is in the interstitial position). On the abscissa axis, N is the number of the step of numerical annealing of the atomic positions

It is known that titanium carbide is characterized by metallic, ionic, and covalent bonds [8]. This leads to an interesting combination of physical and chemical characteristics of the material. Our calculations confirm the presence of a metal bond, that is, the presence of a nonzero electronic density of states at the Fermi level, which is formed by roughly the same contributions of the 3d Ti and 2p C states. The ionic nature of the bond is determined by the significant transfer of the electron density (more than 1 electron per atom) from Ti to C. It should be noted that within our calculation method it is impossible to estimate the degree of transfer of charge more accurately.

But the dominant factor determining the nature of electron density near the Fermi level is the covalent bond formation between hybridized  $\text{Ti}3d\text{-C}2p$  orbitals (see Fig. 3). It is the strong covalent bond that determines the high stability, strength, and hardness of titanium carbide.



**Fig. 3** – The electronic density of states: a – TiC, local spectra of 3d Ti (b), and 2s C, 2p C (c)

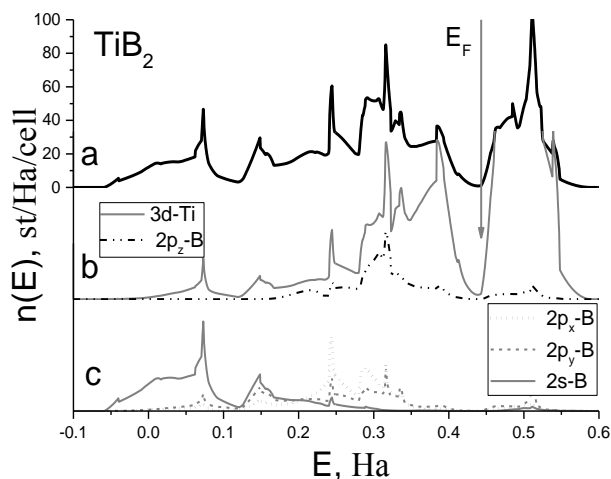


Fig. 4 – The electronic density of states: a –  $\text{TiB}_2$ ; b – local spectra of 3d-Ti and  $2p_z$ -B; c – local spectra of  $2p_x$ -C,  $2p_y$ -C and  $2s$ -C

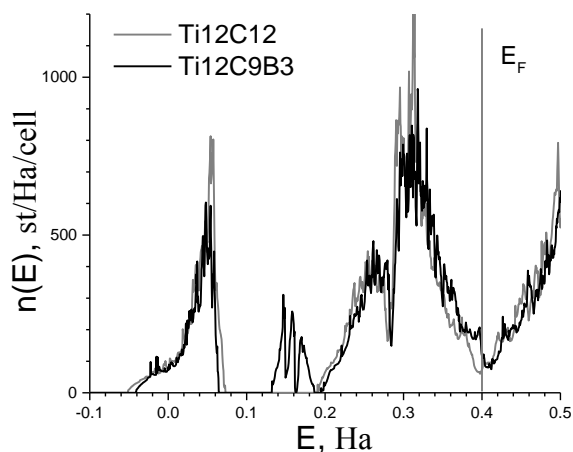


Fig. 5 – The electronic density of states of  $\text{Ti}_{12}\text{C}_{12}$  supercell (gray) and the case of  $\text{Ti}_{12}\text{C}_{10}\text{B}_3$  (black)

The energy dependence of the density of electron states of titanium diboride, which is very similar by physical properties to titanium carbide, is presented in Fig. 4: a – full electronic spectrum of  $\text{TiB}_2$ ; b – local spectra of 3d Ti and  $2p_z$ -B; c – local spectra  $2p_x$ -C,  $2p_y$ -C and  $2s$  C. As in the previous case, mainly 3d Ti and some 2p B electronic orbitals contribute the total density of states near the Fermi level. These electronic orbitals form a strong covalent bond, which leads to a high melting point and hardness in  $\text{TiB}_2$  than the hcp titanium. The Fermi level, indicated by the arrow in Fig. 4, falls exactly into the pseudogap, which leads to the stabilization of the structure. The boron atoms take the  $sp^2$ -hybridization and form  $\sigma$  bonds to link other boron atoms in the graphite-like B layers (Fig. 4c).

Some researchers [9] also reported on the ionic contribution to the nature of the titanium diboride bond: a titanium atom releases two electrons to form  $\text{Ti}^{2+}$  ions, and a boron atom gets one electron to come into  $\text{B}^-$  ion. Within our calculation method, we can only estimate the number of electrons inside the local sphere around a particular atom; the exact number of electrons given or received depends on the choice of the radius of the local sphere, which is ambiguous. In accordance with

our calculations, the titanium atom gives away slightly less than an electron, and the number of electrons around the boron atom remains almost unchanged. The latter, in our opinion, is due to the fact that the structure of titanium diboride is not a structure of densely packed spheres.

The next step was to study the boron impurities influence on the electronic structure of titanium carbide. So, we have calculated the electronic structure of the  $\text{Ti}_{12}\text{C}_{12}$  supercell, in which carbon atoms were replaced by the impurity boron atoms. We have changed the number, location of impurity atoms and the number of neighboring impurities. A detailed description of all cases can be found in [10]. As an example, we present the electronic spectra of the  $\text{Ti}_{12}\text{C}_{10}\text{B}_3$  supercell (Fig. 5), in which 3 carbon atoms are replaced by 3 impurity boron atoms substitutionally (Fig. 1).

Comparing the obtained electron spectra of a supercell with different location of impurity boron atoms with an electron spectrum of titanium carbide, it is possible to note the general features of boron impurities influence on the electronic structure of titanium carbide. The impurity subzone of boron electronic states is located between the local electron spectra of  $2s$  and  $2p$  carbon states by about 0.24 Hartree below the Fermi level. There is also a slight increase in the density of electronic states directly below the Fermi level. Different coordinate locations of boron impurity atoms affect only on the shape and half-width of the impurity subzone. The half-width of the impurity subzone becomes larger with the increasing number of impurity atoms in the first coordination sphere of non-metallic atoms around the impurity.

The total energy of 24 titanium carbide atoms supercell and boron impurity atoms with different numbers and locations of impurity atoms was calculated. There were no regularities in the total energy changing of the supercell when the number and location of neighboring impurity atoms were changed. So, it was found that impurity boron atoms in titanium carbide do not exhibit a propensity to clustering.

### 3. CONCLUSIONS

In this paper, the total energy of 24 titanium carbide atoms supercell and boron impurity atoms with different numbers and locations of impurity atoms was calculated. As a result of this study, it was found that impurity boron atoms in titanium carbide do not exhibit a propensity to clustering.

The electronic structure of the  $\text{Ti}_{12}\text{C}_{12}$  supercell, in which carbon atoms were replaced by the impurity boron atoms, was calculated. The impurity subzone formed due to the presence of boron impurity atoms is located between the local electron spectra of  $2s$  and  $2p$  carbon states by about 0.24 Hartree below the Fermi level. There is also a slight increase in the density of electronic states directly below the Fermi level. Different coordinate locations of boron impurity atoms affect only the shape and half-width of the impurity sub-zone.

The atomic structure changing of titanium carbide in the presence of boron impurities is discussed. The equilibrium distances between adjacent planes of TiC supercell with boron impurities in the substitution and interstitial positions were calculated and analyzed.

One of the most valuable ways to create the TiC-TiB<sub>2</sub> hetero ceramics is the reactive hot pressing of TiC-B<sub>4</sub>C precursors. Hence, the actual problem is to uncover the atomic mechanisms of titanium diboride nucleation mechanisms of TiB<sub>2</sub>. Our ab initio calculations confirm

that the boron atoms being captured by carbon vacancies lead to an increase in the distance between (111) planes in TiC and increase the probability of further boron incorporation into TiC lattice.

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## Першопринципне моделювання впливу домішок бору на електронну та атомну структуру карбїду титану

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Проведено першопринципний розрахунок впливу домішок бору на електронну та атомну структуру карбїду титану. Розрахунок проведено методом функціоналу густини в узагальненому градієнтному наближенні за допомогою пакету програм ABINIT. Надкомірка карбїду титану складалася з 24 атомів. Розраховано повну енергію надкомірки карбїду титану з домішковим бором з різною кількістю та розташуванням домішкових атомів. В результаті проведених досліджень було встановлено, що домішкові атоми бору в карбїді титану не виявляють схильності до кластеризації. Обговорюються зміни атомної структури карбїду титану при наявності домішок бору в міжвузловому положенні та в стані заміщення. Розраховано та проаналізовано рівноважні відстані між сусідніми площинами карбїду титану з домішками бору в положеннях заміщення та занурення. Накопичення атомів бору на площинах (111) карбїду титану призводить до збільшення відстані між сусідніми шарами атомів титану. Представлено електронну структуру карбїду титану, дибориду титану та надкомірки карбїду титану з різним числом та розташуванням домішок бору. Характерною особливістю спектрів надкомірки карбїду титану з домішковими атомами бору є наявність домішкової підзони, яка розташована між локальними електронними спектрами 2s і 2p вуглецевих станів приблизно на 0.24 Хартрі нижче рівня Фермі. Також спостерігається незначне збільшення густини електронних станів безпосередньо під рівнем Фермі. Різне розташування домішкових атомів бору впливає тільки на форму та напівширину домішкової підзони, а саме: напівширина домішкової підзони збільшується при збільшенні кількості домішкових атомів у першій координаційній сфері неметалевих атомів навколо домішки.

**Ключові слова:** Карбід титану, Домішка бору, Електронна структура, Атомна структура.