

# AB INITIO CALCULATION OF CHARACTERISTICS OF A HCP-Ti-C SYSTEM IN $\alpha$ -TITANIUM

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*The relative energies of possible phases in a Ti-C system in the hcp-lattice of titanium are calculated. A probability of formation of a more energetically favorable structure is shown than that of NaCl, which is well-known from the phase diagram of Ti-C. The results of calculations of lattice parameters, elasticity moduli, and charge density distribution in the predicted phase are presented. The relationship between the atomic structure peculiarities and the chemical bonding type in this phase is discussed.*

**Key words:** titanium, carbon, simulation.

Titanium and its alloys have been extensively applied in numerous areas of engineering and medicine; they are major structural materials for aerospace and ship-building industries, on the one hand, and traumatology, orthopedics, dentistry, etc., on the other. Within recent years, focus has been made on the use of nanostructured titanium exhibiting much better strength and plasticity characteristics compared to conventional alloys. While the grain size of ordinary titanium is of the order of tens of microns, in nanostructured titanium it is as low as 100 nm and even smaller. Grain size reduction results in a considerable increase in the grain-boundary relative area and energy per unit volume of material. Hence, there is a significant increase in the thermodynamic driving force resulting in grain growth and decrease in nanostructured state stability. The grain growth is accompanied by grain-boundary motion, which could be considerably slowed down, given secondary-phase inclusions. There is a number of experimental data supporting that nanostructured state of technical-grade titanium (Russian designation: hcp-alloy BT1-0) can be stabilized by incorporating Ti-C into its structure [1]. It is well known from the phase diagram of Ti-C that carbide phases of a NaCl-type structure can be formed in this system. However, some studies show that the structure of nanosized inclusions in the BT-01 alloy is different from that of NaCl. For instance, L.S. Bushnev, et al. [2] reports the presence of a (0001) reflection in the diffraction pattern of submicrocrystalline titanium alloy BT1-0, which is structurally forbidden in pure  $\alpha$ -Ti. Note that there were no reflections corresponding to carbides. The authors of that paper, therefore, suggested that there might be a certain coherent Ti<sub>2</sub>C phase in submicrocrystalline  $\alpha$ -Ti, which is responsible for the (0001) reflection. In this study, using an ab-initio approach, we revealed the presence of an hcp-phase of Ti<sub>2</sub>C, which is energetically more favorable than titanium carbide of the NaCl structure in  $\alpha$ -Ti, and calculated its lattice characteristics, including elasticity moduli.

The calculations were performed using the ABINIT software [3] within the framework of the charge-density functional theory with representation of the electron wave functions in the plane-wave basis. As the valence electrons, we used 3s-, 3p-, 3d-, 4s-orbitals for Ti and 2s, 2p – for the C atom. The effective action of the skeletal electrons was described using the RAW-potential. In order to prescribe an exchange-correlation potential, we used a generalized gradient approximation. The energy cutoff for the plane-wave basis was found to be 680 eV, which ensured an accuracy of about 2 meV/at in calculating the total energy of the systems under study. The equilibrium lattice parameters were derived via optimization of the calculation grid shape and ion positions so that the force acting upon each ion was as low as 3 meV/Å.

The quality of reconstructing the characteristics of titanium using our PAW-potential is evident from Table 1, which lists the calculated lattice constants and elasticity moduli of several phases of titanium:  $\alpha$ -hcp,  $\beta$ -bcc, fcc- and

TABLE 1. Characteristics of Phases Present in Ti and Ti<sub>2</sub>C(sl2x1)

Phase	$a$ , Å	$c$ , Å	$d_1$ , Å	$d_2$ , Å	$B$ , GPa	$C_{11}$ , GPa	$C_{12}$ , GPa	$C_{13}$ , GPa	$C_{33}$ , GPa	$C_{44}$ , GPa
$\alpha$ -Ti	2.94	4.64	2.32	2.32	113	179.5	82.5	75.5	191	44.5
$\alpha$ -Ti (experiment)[6]	2.95	4.68	2.34	2.34	110	176	87	68	191	51
$\beta$ -Ti	3.25	–	–	–	107	87	116	–	–	41
$\omega$ -Ti	4.58	2.83	–	–	113.5	200.5	81.5	52	251	56
Ti(fcc)	4.11	–	–	–	108	134	95.5	–	–	61
Ti <sub>2</sub> C(sl2x1)	3.06	4.92	2.32	2.6	133.5	328	57.5	44	253	27

$\omega$ -phases. It is clear from Table 1 that the calculated lattice constants of hcp-titanium are different from those found experimentally by no more than 1%, with the respective differences in the calculated and experimental elasticity moduli being below 10%. Note that the calculated values of the elasticity moduli testify that the stability criteria are valid for the hcp-phase, which implies its formation under certain conditions in agreement with the recent work [4]. The calculated elasticity moduli of the bcc-lattice of titanium are indicative of instability of the  $\beta$ -phase of titanium at 0 K in accordance with the phase diagram of Ti and the decrease in the shear moduli of the  $\beta$ -phase of titanium to zero with a decrease in the temperature. As shown by the ab-initio investigations [5], at the temperature of absolute zero the  $\omega$ -phase, in terms of its energy, lies 5 meV/at lower than that of  $\alpha$ -Ti. The calculated values of elasticity moduli in the  $\omega$ -phase agree well with those obtained in [5]. Table 1 also lists the characteristics of energetically more favorable Ti<sub>2</sub>C with an hcp-lattice, which was observed by the authors of this work in  $\alpha$ -titanium. Description of this lattice and the method used to compare it with other model lattices of the Ti–C system is given further in the text.

Commercially obtained titanium BT1-0 generally contains up to 0.3 at.% carbon located in octahedral interstitial positions. Given the decrease in the total energy per carbon atom, an ordered structure can possibly be formed in  $\alpha$ -Ti. Then, if a Ti <sub>$m$</sub> C <sub>$n$</sub>  structure is formed, variation in the total energy per carbon atom would be given by

$$\Delta E = (E_{\text{Ti}_m\text{C}_n} - 0.5mE_{\text{Ti}_2}) / n - (E_{\text{Ti}_{48}\text{C}} - E_{\text{Ti}_{48}}), \quad (1)$$

where  $E_{\text{Ti}_m\text{C}_n}$  is the energy of a calculation grid consisting of  $m$  titanium atoms and  $n$  carbon atoms,  $E_{\text{Ti}_2}$  is the energy of two titanium atoms in the lattice of  $\alpha$ -Ti,  $E_{\text{Ti}_{48}\text{C}}$  the energy of the superlattice of  $\alpha$ -Ti containing 48 titanium atoms and one carbon atom in the octahedral interstitial position, and  $E_{\text{Ti}_{48}}$  is the energy of the superlattice of  $\alpha$ -Ti containing 48 titanium atoms. The superlattice is chosen sufficiently large in order to rule out the effect of the superlattice size calculated per the value of  $\Delta E$  within the calculation accuracy used. The value of  $\Delta E$  provides for comparison of the energy efficiency of different lattices of carbides in  $\alpha$ -Ti.

In order to find the structure of Ti–C inclusions in  $\alpha$ -Ti, which possesses the minimum value of  $\Delta E$ , we made a list of possible Ti–C lattices, relying on the well-known lattices of metal carbides and model lattices, which agree with the results of x-ray diffraction analysis of BT1-0 [1]. Seven phases of titanium carbide have been considered. All the phases, except for TiC(NaCl), represent the structures with carbon atoms embedded in octahedral and tetrahedral interstitial positions of the hcp-lattice of titanium. The structure TiC(SHP) is an hcp-lattice with alternating atomic layers of  $A$  and  $B$ . Here, layer  $A$  is made up by titanium atoms, and layer  $B$  – by carbon atoms. The structures Ti<sub>2</sub>C<sub>2</sub> (tetraone) and Ti<sub>6</sub>C<sub>4</sub> (tetratwo): in the former case, a half of tetrahedral interstitial positions are filled, and in the latter, filling of the tetrahedral positions occurs with a number of vacancies along the  $z$  axis. In Ti<sub>2</sub>C<sub>2</sub> (octa), octahedral interstices are completely filled, and in Ti<sub>2</sub>C<sub>4</sub> (tetra) it is the tetrahedral interstices that are completely filled. In Ti<sub>2</sub>C, a half of the octahedral interstices along the  $z$ -axis are filled. To prescribe an hcp-lattice, we selected the following translation vectors:  $(\sqrt{3}/2a, -1/2a, 0)$ ,  $(0, a, 0)$ ,  $(0, 0, c)$ . Table 2 summarizes the values of the total energies  $E$  and

TABLE 2. Energy Characteristics of Ti–C Phases (See Eq. (1))

Phase	$E$ , Hartree	$\Delta E$ , eV/at. C
$\alpha$ -Ti <sub>2</sub>	-117.31	-
TiC(NaCl)	-64.463	-0.06
TiC(SHP)	-64.412	1.3
Ti <sub>2</sub> C <sub>4</sub> (tetra)	-140.23	2.02
Ti <sub>2</sub> C <sub>2</sub> (octa)	-128.9	0.22
Ti <sub>2</sub> C(sl2x1)	-123.12	-0.23
Ti <sub>2</sub> C <sub>2</sub> (tetraone)	-128.89	0.44
Ti <sub>6</sub> C <sub>4</sub> (tetratwo)	-375.03	0.82
Ti <sub>48</sub> C	-2821.2	0
Ti <sub>48</sub>	-2815.4	-

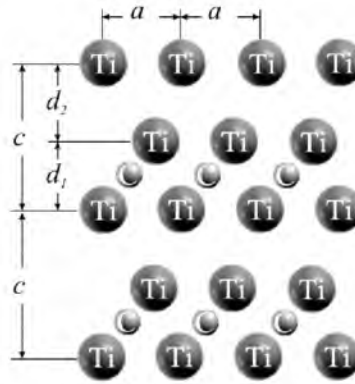


Fig. 1. Plane (010) in the structure of Ti<sub>2</sub>C(sl2x1).

$\Delta E$  calculated using Eq. (1). It is clear that the structure Ti<sub>2</sub>C(sl2x1) has the least corresponding value of the energy  $\Delta E$ , and the energy  $\Delta E$  per carbon atom in this structure is 0.17 eV/at. lower than that in rock salt, TiC(NaCl).

Figure 1 illustrates an hcp-lattice of Ti<sub>2</sub>C. From Table 1 it is evident that the spacing  $d_1$  between the (0001) planes of titanium separated by the respective planes of carbon (Fig. 1) is equal to 2.32 Å, and the spacing  $d_2$  between the same planes of titanium atoms without any carbon atoms in between is found to be 2.6 Å – which is by far larger than the one in the former case, despite the presence of embedded carbon atoms in the former case. For comparison, in the NaCl-type structure the shortest spacing between titanium and carbon atoms is 2.17 Å, while in the structure of Ti<sub>2</sub>C(sl2x1) it is equal to 2.11 Å, i.e., closer to the equilibrium atomic spacing calculated in this work for a two-atomic molecule of TiC, 1.60 Å. In pure hcp-titanium, the spacing between the (0001)-planes is 2.32 Å, which coincides with the value of  $d_1$  in Ti<sub>2</sub>C(sl2x1) between titanium planes separated by a plane of carbon atoms (Fig. 1). Note that  $d_2$  exceeds the respective interplanar spacing in pure titanium. Therefore, a characteristic feature of the hcp-lattice in Ti<sub>2</sub>C(sl2x1) is a strong interaction between titanium and carbon atoms, which results in closer packing of their planes (attraction of the planes) and serves as a compensation for the tensile effect of interstitial impurities and, hence, weaker interaction between titanium atoms in the planes without any carbon atoms in between. On the whole, incorporation of carbon to form Ti<sub>2</sub>C(sl2x1) results in dilatation of the hcp-lattice of titanium (see Table 1); the presence of interstitial atoms as such is, however, insufficient for us to get an insight into the physical causes of dilatation, it is necessary to address the effect of carbon on formation of chemical bonding in Ti<sub>2</sub>C(sl2x1).

Shown in Fig. 1 is the charge density distribution that we obtained in the (010) plane of Ti<sub>2</sub>C; for comparison the figure depicts this distribution for an hcp-lattice of Ti. The plane selected for analysis contains titanium and carbon atoms from different planes of the (0001) type, which allows one to follow variation in the character of bonding

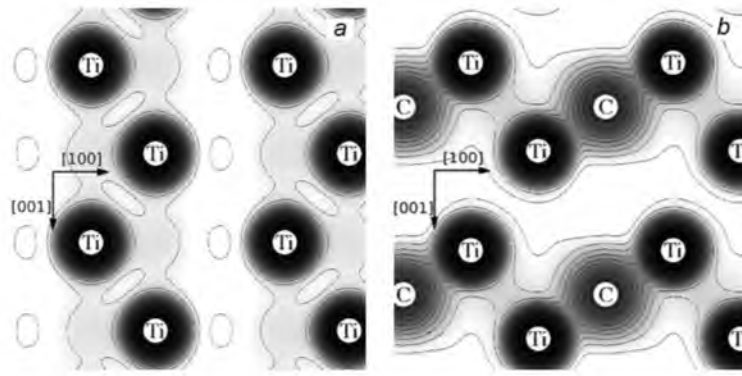


Fig. 2. Electron charge density distribution in plane (010):  $\alpha$ -Ti (a) and  $\text{Ti}_2\text{C}(\text{sl}2 \times 1)$  (b).

between titanium atoms as a result of intrusion of an interstitial carbon atom in every second space between close-packed planes. It is clear from Fig. 2 that two main characteristics of this change are: 1) the minimum between the nearest atoms in the hcp-lattice of Ti is replaced by a local maximum in  $\text{Ti}_2\text{C}$  for the case of Ti atoms separated by a plane of carbon atoms and 2) the density in the space between planes of Ti atoms where no interstitial carbon atoms intrude is decreased. Figure 2b also shows a directional character of density distribution between the nearest titanium and carbon atoms. These features of density distribution are indicative not only of the covalence of the resulting Ti–C bonding, but also of its strengthening or weakening between two groups of atomic pairs of titanium, which results in smaller  $d_1$  and larger  $d_2$ , as compared to those in pure hcp-titanium, respectively.

The phase diagram of Ti–C, which has been by now determined [7, 8], contains only one stoichiometric titanium carbide, TiC, with the structure of rock salt, wherein titanium atoms form an hcp-lattice and carbon atoms fill all octahedral interstices in this lattice. This finding agrees well with the results of ab initio calculation of the energy characteristics of bonding in model lattices of Ti–C [9], which, among other things, report the maximum bonding energy in TiC which is higher than the one in the lattice of  $\text{Ti}_2\text{C}$  discussed in this study. Note that the authors of [9] calculated bonding energy in Ti–C systems in comparison with the energy of atomic carbon in vacuum. Due to the energy reference chosen in [9], the authors in fact succeeded in finding a more energetically favorable titanium carbide formed in an ideal-gas atmosphere of carbon atoms. In that case, it is the number of carbon atoms per one titanium atom in the carbide, which greatly affects the bonding energy due to high bonding energy of an individual carbon atom with titanium, which eventually accounts for the more favorable energy of titanium carbide TiC with the structure of NaCl, wherein one carbon atom corresponds to one titanium atom [9].

If carbon is found in hcp-titanium as a solution (e.g., the above-mentioned Alloy BT1-0 with a low concentration of carbon), then when it forms carbide inclusions in the lattice of hcp-titanium, stoichiometry does not play the main role in contrast to the case discussed in the previous paragraph, since the main energy gain due to formation of the Ti–C bonding was already achieved during solution of carbon. The observed preference of carbon atom to combine from solution and form an hcp-lattice of  $\text{Ti}_2\text{C}$  rather than that of TiC(NaCl) (Table 2) is accounted for by the energy loss required for transformation of an fcc-lattice of Ti into an hcp-lattice of Ti, which makes the basis of titanium carbide with the rock salt structure. Apart from the possibility of phase formation according to the energy criterion, mechanical stability of the phase lattice is required for this phase to be formed. As follows from the calculated elasticity moduli presented in Table 1, the hcp-phase of  $\text{Ti}_2\text{C}$  satisfies the stability criteria of the hcp-lattice:  $C_{11}, C_{12}, C_{13} > 0$ ,  $(C_{11} - C_{12})/2 > 0$ , and  $(C_{11} + C_{12} - C_{13}^2/C_{33}) > 0$ .

The description of the hcp-phase of  $\text{Ti}_2\text{C}$  presented in this work can serve a basis for its experimental investigation, including the method of high-resolution electron microscopy. Proximity of the values of lattice constants of  $\text{Ti}_2\text{C}$  and hcp-titanium testifies to a possibility of formation of this phase in the alloys based on hcp-titanium in the form of coherent inclusions. Formation of this phase can stabilize the grain structure by pinning grain boundaries and can give rise to formation of stoppers to dislocation motion. It is therefore promising to use the  $\text{Ti}_2\text{C}$ -phase to improve strength properties of alloys based on hcp-titanium by subjecting them to thermomechanical treatment. This would

require the knowledge of the phase diagram of the Ti–C system in the region of low concentration of carbon, taking into account the Ti<sub>2</sub>C phase and the size of its inclusions, as well as the description of mechanical properties of the lattice of Ti<sub>2</sub>C. These investigations are currently under way.

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