Brief Communications

Electronic structure and stability of polymorphous modifications of titanium monocarbide

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The electronic structures and stabilities of five polymorphous modifications (PM) of titanium monocarbide, TiC, with the NaCl (B1), CsCl (B2), zinc blende (B3), würtzite (B4), and NiAs (B8) structural types, were studied by the non-empirical, self-consistent linear "muffin-tin" orbital—tight-binding (LMTO-TB) method. The equilibrium unit cell volumes, lattice parameters, and the densities of electronic states were calculated. Depending on the structural type (coordination number, CN), the PM of TiC possess essentially different conducting properties (semimetallic for CN 6 (B1, B8), metallic for CN 8 (B2), and semiconducting for CN 4 (B3, B4)). Based on the results of calculations of the total band energies, it was found that the stabilities of these PM of TiC decrease in the order B1 > B8 > B3 > ~ B4 > B2. The nature of chemical bonding in the five PM of TiC was analyzed in the tight-binding approximation with EHT parametrization.

Key words: titanium monocarbide, polymorphous modifications, electronic structure, quantum-chemical calculations, tight-binding approximation, non-empirical quantum-chemical calculations, LMTO-TB method, stability, chemical bonding.

Titanium carbide is a typical representative of a large community of high-melting interstitial phases based on transition d-metals of Groups III—VI, which possess an unusual combination of thermomechanical properties (an increased mechanical strength and a high melting temperature) with intriguing electromagnetic and thermal emission characteristics and are of great scientific and technological value.[1,2]

The Ti—C system is characterized by a broad homogeneity region ($TiC_{1.0-0.5}$). It is well known[1,2] that only one compound, titanium monocarbide TiC_x, with a cubic structure of the NaCl type, is formed under equilibrium conditions in this system. Until recently, this cubic phase with octahedral coordination of the atoms (the coordination number, CN, equals 6) and a Ti/C ratio ≥ 1 has been considered as unique.

Recent advances in the field of nanoscale technology[3] provided the possibility of synthesizing a number of novel carbon-titanium compounds such as molecular clusters (the so-called met-cars,[4,5] *e.g.*, Ti_8C_{12}, and

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other cage structures of the Ti_nC_m type[6—10]), endofullerenes (of the $Ti@C_{28}$ type[8,11,12]), and Ti-doped carbon nanotubulenes.[13,14] A distinctive feature of all these compounds is that both the CN of the atoms and the metal/non-metal ratio can vary over a wide range, the latter parameter being sometimes much less than unity. These nanoscale objects are fairy stable and can serve as a basis for the preparation of new crystalline carbon-titanium materials with unusual properties. Recently, theoretical predictions of the properties of some of the new high-carbon condensed phases in the Ti—C system, *e.g.*, titanium dicarbide TiC_2, with structure of the CaC_2, ThC_2, CsCl, and CaF_2 types,[15] and higher nanocrystalline titanium carbide Ti_8C_{12}, with met-cars as structural units,[16,17] have been reported.

In this work, we considered a particular aspect of the problem of the search for new phases in the carbon—titanium system. This is associated with the possibility for polymorphic transformations accompanied by changes in the coordination numbers of the atoms to occur provided that the carbide composition, $TiC_{1.0}$, remains unchanged. To this end, we calculated a set of characteristic parameters for five structural modifications of titanium monocarbide with three main types of coordination of the atoms in binary crystals. These are the polymorphous modifications (PM) with the NaCl (B1, CN 6), CsCl (B2, CN 8), zinc blende (B3, CN 4), würtzite (B4, CN 4), and NiAs (B8, CN 6) structural types.

The energy band structures (EBS) of these PM were calculated by the non-empirical, self-consistent linear "muffin-tin" orbital—tight-binding (LMTO-TB) method based on the density functional theory.[18,19]

Parameters of local interatomic interactions (the crystal orbital overlap populations, COOPs) were calculated in the tight-binding approximation[20] with EHT parametrization[21] and used then in discussing the nature of chemical bonding and stability of the above-mentioned PM of TiC.

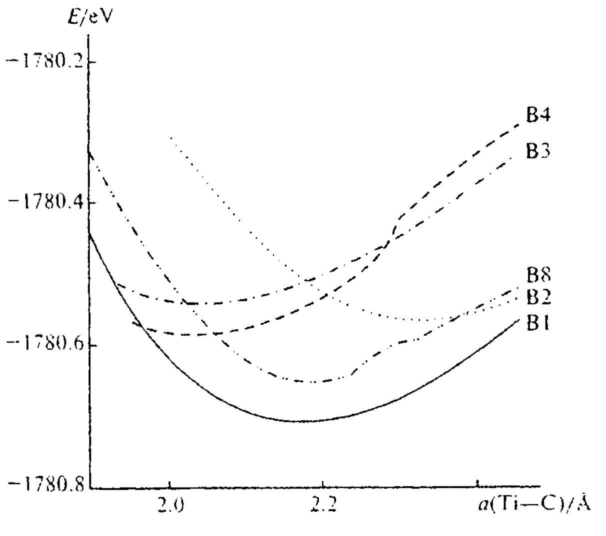

Fig. 1. Dependence of the total band energy (E_{tot}) on the Ti—C interatomic distance for different polymorphous modifications of TiC. Obtained from the LMTO-TB calculations.

Table 1. The equilibrium unit cell volumes (V_0) and lattice parameters (*a*, *c*), total band energies (E_{tot}), and total crystal orbital overlap populations of the Ti—C bonds (COOP) for different polymorphous modifications of titanium monocarbide

Structure	CN	V_0 /Å^3*	a*	c*	$-E_{tot}$ /eV*	Total COOP** Ti—C/e
			Å			
B1	6	20.326	4.332	—	1780.71	2.57
B2	8	19.426	2.688	—	1780.54	2.12
B3	4	26.046	4.705	—	1780.56	2.55
B4	4	25.568	3.307	5.40	1780.59	2.53
B8	6	21.451	3.048	5.33	1780.65	2.56

* Obtained from the LMTO-TB calculations.

** Obtained from semiempirical tight-binding calculations with the EHT parametrization.

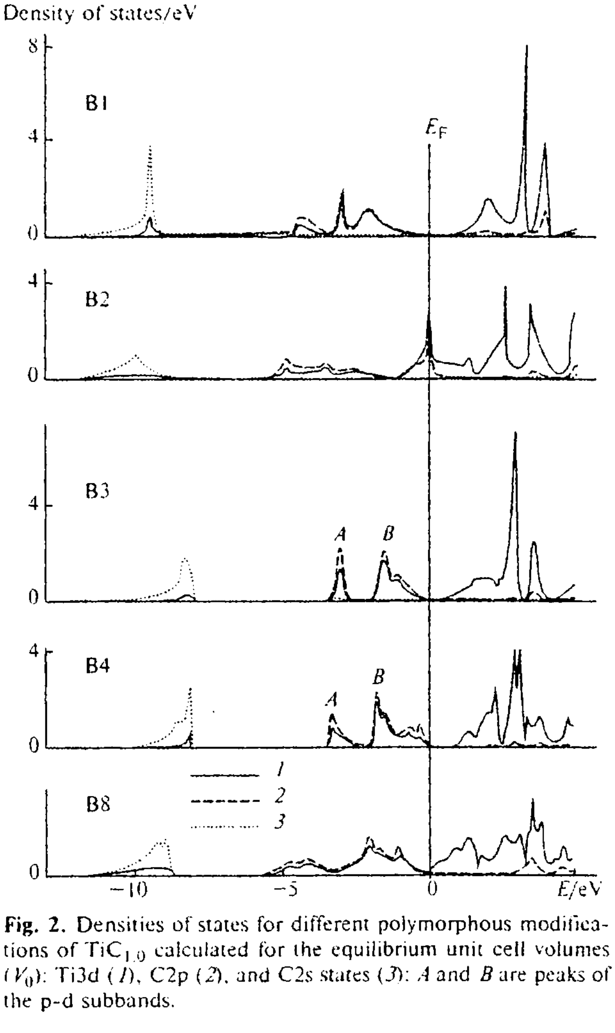

Fig. 2. Densities of states for different polymorphous modifications of $TiC_{1.0}$ calculated for the equilibrium unit cell volumes (V_0): Ti3d (*1*), C2p (*2*), and C2s states (*3*); *A* and *B* are peaks of the p-d subbands.

First, parameters of the equilibrium states were determined for each PM from the dependences of the total band energies (E_{tot}) on the unit cell volume (V) (Fig. 1). The equilibrium unit cell volumes (V_0) and interatomic distances (a_0) corresponding to the minimum E_{tot} values are listed in Table 1.

The simplest formal analysis of the E_{tot} values shows that the cubic TiC structure (B1) with CN 6 is the most stable. The calculated and experimental lattice constant values are close (4.332 and 4.3281 Å,[1] respectively). Stabilities of the five PM of TiC decrease in the order B1 > B8 > B4 ~ B3 > B2. Among hypothetical structures, the B8 structure with octahedral coordination of the atoms, which is typical of real TiC (B1), is the most stable. Less stable are the B3 and B4 structures with CN 4 and the B2 structure with CN 8 was found to have the lowest stability. Hence, the search for new metastable TiC phases should be continued among the structures with CN 6 (*e.g.*, various derivatives or analogs of the B1 structure[22]).

Consider the problem of relative stability of different TiC PM in the context of the EBS and chemical bonding in the corresponding structures. The densities of states (DOS) calculated for the V_0 values of the five TiC modifications are plotted in Fig. 2. The EBS of the cubic $TiC_{1.0}$ (B1) has been studied in detail.[23,24] We found that the TiC (B1) valence band consists of (i) a band of quasi-core C2s states and (ii) the main valence subband of the hybrid Ti3d-C2p states (the p-d band) responsible for the effects of interatomic interactions in TiC, which are separated by a band gap (see Fig. 2). This is in good agreement with previous calculations. Judging from the position of the Fermi level (E_F) in the region of the DOS minimum (a pseudogap[24]) between the bands of filled bonding p-d states and antibonding vacant Ti3d,4s states, this PM of TiC is expected to possess semimetallic conducting properties.[1,2,23,24]

The patterns of the energy band spectra of the B8 and B1 modifications of TiC are similar. Mutual arrangement and the compositions of the main spectral subbands (of the C2s, p-d, and Ti3d,4s states), as well as their widths, are retained. The Fermi level is near the DOS minimum, between the filled p-d band and the band of free delocalized metallic states.

Another spectral pattern was found for two TiC modifications with CN 4 (B3 and B4). As the CN changes from 6 to 4, the valence band becomes narrower, the energy gap between the C2s and p-d bands changes, the p-d band is divided into two subbands (peaks *A* and *B*, Fig. 2), and a band gap between the bonding p-d and antibonding Ti3d subbands appears. One should expect that the B3 and B4 metastable PM of TiC will possess semiconducting properties.

The pattern of the energy band spectrum of the last TiC structural modification (B2) with CN 8 again changes essentially. The most important distinctive feature of this spectrum is the appearance of an intense peak of nonbonding states near E_F (see Fig. 2). Because of this and unlike other PM, B2-TiC is expected to possess metallic properties.

Consider the nature of stability of different TiC polymorphous modifications using the COOPs of the two-center Ti—C, Ti—Ti, and C—C bonds, obtained in the tight-binding approximation with EHT parametrization, for the equilibrium lattice constants found from the non-empirical LMTO-TB calculations.

According to our calculations, the COOPs of the Ti—Ti bonds are an order of magnitude lower than those of the Ti—C covalent bonds, while the COOPs of the C—C bonds are negligible. Therefore, the estimates of the total effects of chemical bonding for different TiC modifications were obtained by comparing the total COOPs (TCOOPs) of the bonds the metal atom forms with all carbon atoms in the nearest environment. As follows from the data listed in Table 1, the TCOOPs of the $Ti-(C)_n$ bonds (n = 6 (B1, B8), 4 (B3, B4), and 8 (B2)) change in the same order as the E_{tot} values of the corresponding TiC modifications. The most stable B1 and B8 phases with CN 6 are characterized by the highest TCOOPs associated with the strongest chemical bonds, the less stable B3 and B4 PM with CN 4 also have somewhat lower TCOOPs, and the lowest TCOOP value was found for the B2 modification with CN 8.

Thus, as in the case of stable cubic (B1) carbides of transition d-metals of Groups III—VI,[23,24] the chemical bonding in polymorphous modifications of titanium monocarbide is in essence due to directed covalent Ti—C bonds formed as a result of Ti3d-C2p valence orbital overlaps. Changes in the type of the crystal structure (CN) control the hybridization type of the valence p-d orbitals (the strength of the Ti—C covalent bonds), which are responsible for the order in which the stabilities of the TiC polymorphous modifications studied in this work are changed.

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