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Ab Initio Study of Phase Equilibria in TiC$_x$

P. A. Korzhavyi,[1] L. V. Pourovskii,[2] H. W. Hugosson,[2] A. V. Ruban,[3] and B. Johansson[1,2]

[1]*Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology,
SE-100 44 Stockholm, Sweden*
[2]*Condensed Matter Theory Group, Department of Physics, Uppsala University, SE-751 21 Uppsala, Sweden*
[3]*Center for Atomic-Scale Materials Physics and Department of Physics, Technical University of Denmark,
DK-2800 Lyngby, Denmark*

The phase diagram for the vacancy-ordered structures in the substoichiometric TiC$_x$ ($x = 0.5-1.0$) has been established from Monte Carlo simulations with the long-range pair and multisite effective interactions obtained from *ab initio* calculations. Three ordered superstructures of vacancies (Ti$_2$C, Ti$_3$C$_2$, and Ti$_6$C$_5$) are found to be ground state configurations. Their stability has been verified by full-potential total energy calculations of the fully relaxed structures.

Transition metal carbides have a unique combination of properties (chemical stability, great hardness, high melting point, excellent electrical and thermal conductivity) making them highly suitable for many technological applications [1]. These properties are very sensitive to the concentration and ordering of structural vacancies on the carbon sublattice. As much as one-half of the carbon lattice sites can be vacant in the group IV and V transition metal carbides having the NaCl (*B*1) prototype crystal structure. Ordering of vacancies in some carbide systems, e.g., VC$_x$, has been well established experimentally [2,3] and also studied theoretically [4].

Vacancy ordering in TiC$_x$ remains a difficult scientific problem which at the same time is of high technological importance. The existence of at least two vacancy-ordered structures, the cubic [5,6] and trigonal [6,7] forms of hemicarbide Ti$_2$C, is now well established experimentally; see Ref. [8] for a review. However, quite different ordering temperatures have been reported for Ti$_2$C: As low as ~1000 K, Refs. [6–10], or as high as ~2000 K, Refs. [5,11]. This large experimental uncertainty is the main reason why vacancy-ordered TiC$_x$ phases are not included in the Ti-C phase diagrams [12].

A thorough theoretical investigation of the phase equilibria in TiC$_x$ is still lacking, although many details of bonding and ordering in this system are now well understood. In particular, the high strength of the Ti-C bonds is mainly due to the strong hybridization of the titanium *d* states with the *p* states of carbon [13]. Formation of a carbon vacancy involves breaking six such bonds and would cost a high energy. However, the remaining Ti-C bonds around the defect become strengthened due to the redistribution of the electron charge on the vacancy neighbors [14]. This effect stabilizes the carbon vacancies and gives rise to both vacancy ordering and lattice relaxation.

Indeed, the vacancies in TiC are experimentally found to prefer the third nearest-neighbor separation distance, $\langle 1\frac{1}{2}\frac{1}{2}\rangle$, and tend to avoid each other at the nearest-neighbor (NN) and, especially, at the next-nearest-neighbor (NNN) distances on the fcc sublattice of carbon [15], in order not to interfere with the bond strengthening around each of the vacancies. The lattice relaxation around vacancies in TiC consists in a shortening of the strengthened Ti-C bonds [14,16,17], which stabilizes the vacancies even further, especially at small concentrations.

Previous theoretical considerations [8,18] of vacancy ordering in TiC$_x$ have been based on semiempirical methods and restricted to a few pair interactions. At the same time, long-range pair as well as multisite interactions should be important in the phase equilibria of this system due to a highly degenerate ground state given by positive NN and NNN pair interactions [19]. For instance, the cubic ($Fd3m$) and trigonal ($R\bar{3}m$) forms of Ti$_2$C cannot be distinguished if their total energy is expressed in terms of pair interactions only.

In the present work we assess the problem of the phase equilibria in titanium carbide using a combination of electronic structure and statistical mechanical methods. First, we obtain the effective long-range pair and multisite carbon-vacancy interaction energies from first-principles calculations. Next, we perform Monte Carlo (MC) simulations and obtain vacancy-ordered structures at different vacancy concentration and temperatures. Finally, we investigate the stability of the obtained ground state structures using total energy full-potential linear muffin-tin orbital (LMTO) method calculations [20] where we also fully relax all the structures.

The energy of the system in some configurational state σ may be expressed in the cluster expansion form [21]:

$$E(\sigma) = \sum_f D_f J_f \bar{\Pi}_f(\sigma), \qquad (1)$$

where the summation runs over different clusters (figures), f, consisting of several lattice sites (pairs, triplets, quartets, etc.), D_f is the number of f-type clusters per formula unit of TiC$_x$, J_f is the effective interaction energy for cluster f, and $\bar{\Pi}_f$ is the product of spinlike variables S_i of cluster f averaged over all symmetry-equivalent clusters in the configuration σ of vacancies on the carbon sublattice.

The spinlike variable, S_i, is equal to $+1$ (-1) if site i is occupied by a carbon atom (vacancy).

We adopt the following notations for the interaction energies: J_{2n} is the pair interaction for the nth coordination shell of the fcc carbon sublattice; J_{31} and J_{32} are the three-body interactions for the NN triangle and the triangle with two NN sides and one NNN side, respectively; J_{41} is the four-body interaction for the NN tetrahedron.

The effective interaction energies were calculated using two complementary methods, the Connolly-Williams method (CWM) [21,22] and the generalized perturbation method [23] with screened Coulomb interactions (SGPM) [24] in the framework of the LMTO Green's function technique [25,26] in the multipole-corrected atomic sphere approximation [27,28]. The CWM calculations were based on the total energies of 19 vacancy-ordered TiC$_x$ (unrelaxed) structures with $0.5 \leq x \leq 1.0$. As has been established in Ref. [17] the lattice relaxation contribution to the ordering energy, which is neglected in these calculations, is small. The effective SGPM interactions were calculated for the random 50% carbon-vacancy alloy on the carbon sublattice.

The calculated interaction energies are listed in Table I. The tendency of vacancies to be separated by the third nearest-neighbor distance is consistent with a positive sign of J_{21} and J_{22} and a negative sign of J_{23}. The SGPM and CWM interactions agree reasonably well with each other [29] and yield similar results for the structures and temperatures of vacancy ordering in the MC calculations. In the following we report on our results obtained using the SGPM interaction energies.

In Fig. 1 we compare the short-range order (SRO) parameters calculated using the MC method with those obtained by diffuse neutron scattering measurements [8,15] for two fcc TiC$_x$ alloys. The agreement between theory and experiment is very good, and therefore we conclude that the effective interactions adequately describe the configurational energy of the carbon-vacancy alloy.

The phase equilibria for TiC$_{0.5}$-TiC have been obtained from Monte Carlo simulations (canonical ensemble, Metropolis algorithm) in the temperature interval 200–2000 K. An fcc $32 \times 32 \times 32$ simulation box (32 768 carbon sublattice sites) with periodic boundary conditions and a temperature step of 50 K were used. The phase transitions were located using the calculated configurational

contribution to the heat capacity and also by structural analysis, in real as well as in reciprocal space.

The calculated phase diagram is presented in Fig. 2. At temperatures of about 1000 K, a nearly second-order transition is observed from a disordered fcc TiC$_x$ into either a cubic or a trigonal form of the hemicarbide Ti$_2$C$_{1+y}$, depending on the composition. Although the many-body interactions enabled us to resolve the two forms of Ti$_2$C$_{1+y}$ as separate phases we were, however, unable to locate the boundaries of the corresponding two-phase region by the Monte Carlo method. Instead, in the region indicated in Fig. 2 as a cross-hatched area, we observed a hysteresis behavior: The Ti$_2$C$_{1+y}$ phase was obtained in its cubic form upon cooling and in the trigonal form upon heating. This behavior did not change when the simulation box was enlarged up to $48 \times 48 \times 48$ (110 592 sites). A coexistence of the cubic and trigonal forms of Ti$_2$C$_{1+y}$ has been reported experimentally [8] for TiC$_{0.63}$.

At temperatures below 500 K, an additional ordering into phases Ti$_3$C$_2$ and Ti$_6$C$_5$ takes place. These two vacancy-ordered structures are closely related to the trigonal form of Ti$_2$C$_{1+y}$: All these three structures can be described as a sequence of alternating, completely filled and partially filled $(111)_{B1}$ carbon layers. There is only a short-range order of vacancies and carbon atoms within the partially filled layers in the $R\bar{3}m$ structure of Ti$_2$C$_{1+y}$, whereas in the Ti$_3$C$_2$ and Ti$_6$C$_5$ phases these layers become long-range ordered as shown in Fig. 3. Note that the carbon atoms (vacancies) in the partially filled layers of Ti$_3$C$_2$ (Ti$_6$C$_5$) are third nearest neighbors.

Stacking of the $(111)_{B1}$ partially filled layers occurs along the following three vectors: $\mathbf{v}_1 = a_0[1\frac{1}{2}\frac{1}{2}]_{B1}$,
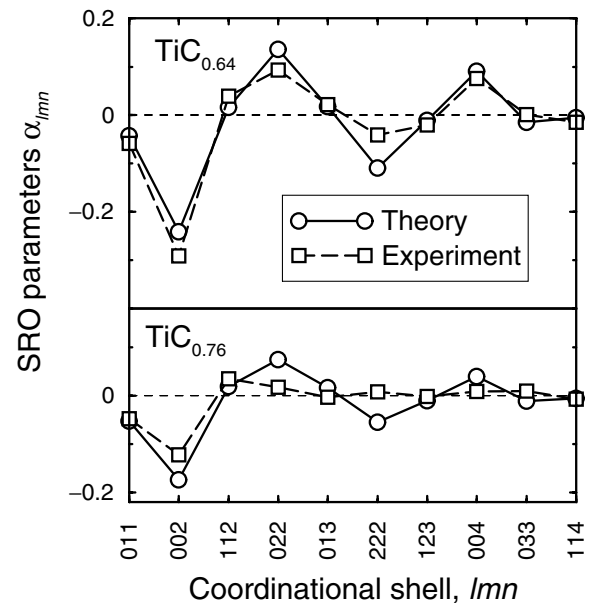
TABLE I. Effective carbon-vacancy interactions in TiC$_x$ (degrees Kelvin). See text for the definitions.

	J_{21}	J_{22}	J_{23}	J_{24}	J_{25}	J_{26}
SGPM	54	181	−10	−1	−12	24
CWM	113	246	−13	−5		
	J_{27}	J_{28}	J_{31}	J_{32}	J_{41}	
SGPM	1	−5	−10	53	−6	
CWM			−33	64	−6	

FIG. 1. Calculated and experimental SRO parameters, α_{lmn}, for ten coordination shells $(a_0/2)[lmn]$ in TiC$_{0.64}$ and TiC$_{0.76}$ fcc alloys at 900 °C.
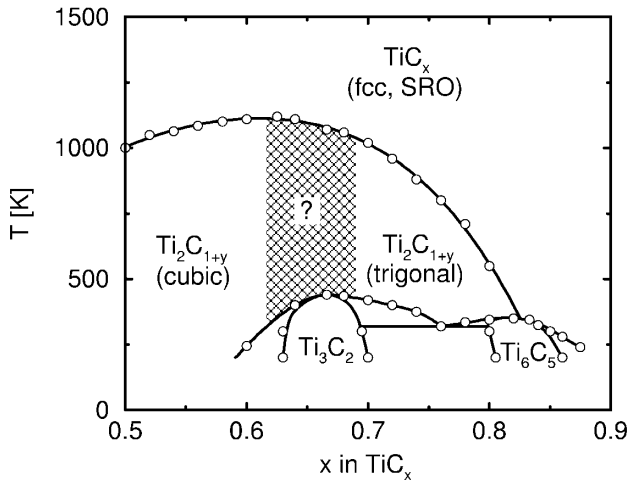
FIG. 2.   Calculated phase diagram of the order-disorder transitions in TiC_x. Open circles indicate the phase boundaries as obtained in our Monte Carlo simulations. The cross-hatched area shows the domain where the Ti_2C_{1+y} forms as a cubic phase from the fcc TiC_x upon cooling, but as a trigonal phase by disordering the Ti_3C_2 phase upon heating.

$v_2 = a_0[\frac{1}{2}1\frac{1}{2}]_{B1}$, or $v_3 = a_0[\frac{1}{2}\frac{1}{2}1]_{B1}$, where a_0 is the lattice parameter of the underlying NaCl ($B1$) structure. Different kinds of stacking produce structures of different symmetries, similar to the case of V_6C_5 [4]. The stacking sequence $v_1v_2v_3, v_1v_2v_3, \ldots$ produces a trigonal structure [2]; another stacking sequence $v_1v_2, v_1v_2, \ldots$ produces a monoclinic structure [3]. Yet another monoclinic structure may be obtained by a linear stacking along only one of the three vectors. All possible structures of this kind are nearly degenerate in energy. Their relative stability depends on the very weak pair interactions beyond the eleventh coordination shell, so the stacking of layers in the real material may be uncorrelated (a trigonal structure) or dependent on external factors (a lower-symmetry structure). To determine the energy of the ground state for Ti_3C_2 and Ti_6C_5, it is therefore sufficient to consider the simplest, linear stacking sequence. In the following, we treat them as monoclinic structures with
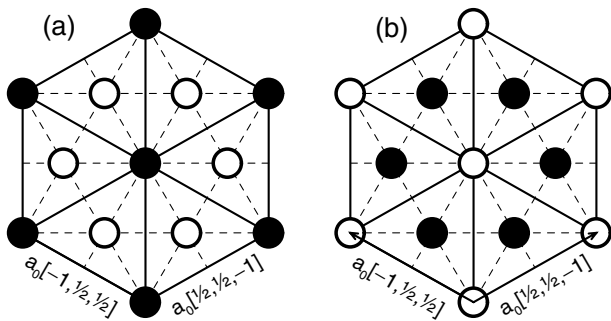

FIG. 3.   Ordered structures within the partially filled $(111)_{B1}$ carbon layers of Ti_3C_2 (a) and Ti_6C_5 (b). Carbon atoms are shown by full circles, vacancies by open circles.

the space group $C2/m$, which was first suggested for the ground state of substitutional A_2B and A_5B alloys [19].

It is also noteworthy that the orthorhombic $C222_1$ structure suggested for Ti_3C_2 in Ref. [8] and the monoclinic $C2/m$ Ti_3C_2 structure have identical pair correlation functions up to third nearest-neighbor distance. Also the three- and four-body correlation functions considered in this work are the same for these two structures. Both structures give superstructure reflections of the $(\frac{2}{3}, \frac{2}{3}, 0)$ type, which are consistent with the diffuse neutron diffraction maxima observed in $TiC_{0.61}$ at $600\,°C$ [8]. An important difference is that in the $C2/m$ structure (as well as in all the other trigonal-related structures discussed above), the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$-type superstructure reflections are inherited from the $R\bar{3}m$ structure, whereas the diffraction spectrum of the orthorhombic Ti_3C_2 does not have such reflections.

The thermodynamic stability of the Ti_2C, Ti_3C_2, and Ti_6C_5 phases has been verified using full-potential calculations; see Ref. [17] for the details. For the stoichiometric TiC we obtain a lattice parameter $a_{TiC} = 4.273\,Å$ which compares well with the experimental value $4.330\,Å$; see Ref. [16].

The calculated lattice spacing in the Ti_2C $Fd3m$ structure, $a_0 = 0.994a_{TiC}$, as well as the crystallographic parameter for position Ti(32e), $x = 0.2445$, is in perfect agreement with experimental data [5] (the lattice parameter of Ti_2C is $2a_0$). The calculated lattice parameters and atomic positions in the Ti_3C_2 and Ti_6C_5 structures are given in Table II.

In Fig. 4 we show the full-potential calculated heat of formation for the ordered TiC_x alloys. At the Ti_2C composition, the cubic $Fd3m$ structure is slightly lower in energy than the trigonal $R\bar{3}m$ structure of the same composition. However, at higher carbon concentrations, the structures obtained by stacking of partially filled $(111)_{B1}$ carbon layers, Ti_3C_2 and Ti_6C_5, become more stable than the structures derived from the cubic $Fd3m$ structure by a gradual

TABLE II.   Atomic positions in the Ti_3C_2 and Ti_6C_5 crystal structures (space group $C2/m$) calculated at lattice parameters $a = c = a_0\sqrt{3/2}$, $b = 3a_0/\sqrt{2}$, $\beta = 109.47°$, where $a_0 = 0.9969a_{TiC}$ for Ti_3C_2 and $a_0 = 1.0001a_{TiC}$ for Ti_6C_5.

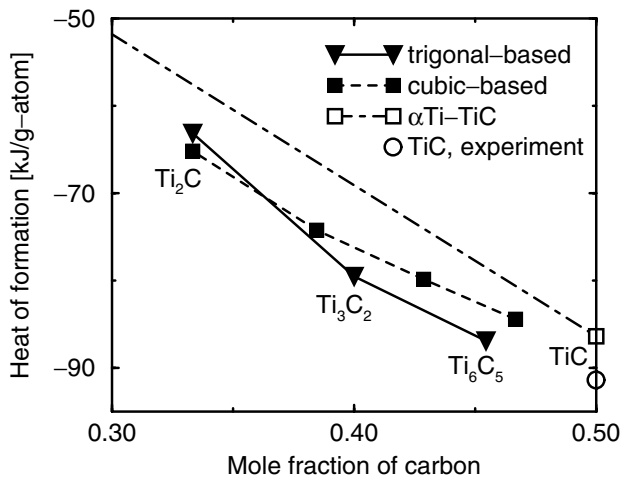| Atom	Wyckoff notation	x	y	z
		Ti_3C_2		
C_1	$2a$	0	0	0
C_2	$4g$	0	0.3327	0
C_3	$2d$	0	0.5	0.5
Ti_1	$4i$	0.7379	0	0.2439
Ti_2	$8j$	0.2513	0.1614	0.2373
		Ti_6C_5		
C_1	$2a$	0	0	0
C_2	$4g$	0	0.3332	0
C_3	$4h$	0	0.1665	0.5
Ti_1	$4i$	0.7603	0	0.2390
Ti_2	$8j$	0.2410	0.1736	0.2462

FIG. 4.   The calculated heat of formation for vacancy-ordered structures in TiC$_x$. The experimental value for TiC is taken from Ref. [30].

filling of vacancies [17]. This finding is fully consistent with the cubic-to-trigonal transition observed in our Monte Carlo simulations.

In conclusion, we find that the TiC$_x$ alloys, depending on the carbon content, may undergo two ordering processes: one at T $\approx$ 1000 K (into cubic or trigonal Ti$_2$C$_{1+y}$ structure) and the other at T $\approx$ 500 K (into Ti$_3$C$_2$ or Ti$_6$C$_5$ structures). The full-potential calculations confirm the stability of the cubic Ti$_2$C, and monoclinic Ti$_3$C$_2$ and Ti$_6$C$_5$ at 0 K. The calculated ordering temperatures are in close agreement with those experiments in which special measures have been taken to prevent contamination of the samples [6–10]. Much higher ordering temperatures obtained in some experimental studies [5,11] can be attributed to the presence of either hydrogen or oxygen impurities. In view of its importance the effect of impurities may deserve further investigations.

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