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Vacancy-cluster mechanism of metal-atom diffusion in substoichiometric carbides

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We find, using *ab initio* atomistic simulations of vacancy-mediated diffusion processes in TiC and ZrC, that a multivacancy self-diffusion mechanism is operative for metal-atom diffusion in substoichiometric carbides. It involves a special type of a stable point defect, a metal vacancy "dressed" in a shell of carbon vacancies. We show that this vacancy cluster is strongly bound and can propagate through the lattice without dissociating.

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I. INTRODUCTION

Titanium and zirconium carbides belong to a group of refractory materials characterized by extreme hardness, high wear resistance, and extraordinarily high melting point.[1,2] Phase separation of a mixed carbide (Ti,Zr)C into TiC-rich and ZrC-rich fractions (via spinodal mechanism) can be used in order to achieve even greater mechanical hardness of the material. Phase separation is a diffusion-controlled process and, therefore, detailed knowledge about the diffusion of metal atoms is important for tuning the mechanical properties of carbide materials. Besides, the diffusion in these compounds represents a quite specific case, not fully understood, because of their substoichiometric nature.[3]

The situation with self-diffusion of carbon (C) is rather clear: The mechanism of diffusion and the activation energy seem to be well established in the literature,[4–6] although some discrepancies between the published data remain unresolved.[7] Less is known about self-diffusion of the metal atoms (Me). There are just two experimental studies of Me self-diffusion in TiC[8] and ZrC.[9] Both studies employed the radioactive tracer technique and were performed on slightly off-stoichiometric specimens $TiC_{0.97}$[8] and $Zr(C_{0.966}O_{0.012}N_{0.022})_{0.97}$.[9]

An interpretation of the experimental data on Me self-diffusion is difficult because of unknown grain boundary contribution to the total diffusivity, and also because of rather high temperatures in the experiment.[8] Another complication is the presence of oxygen and nitrogen on the carbon sublattice in Andrievkii's measurements,[9] which could significantly affect the result. Zagryazkin[10] tried to estimate the activation energy for Me self-diffusion in TiC and ZrC as the activation energy for C self-diffusion plus twice the absolute value of formation energy of the carbide. One should be cautious because such an approach gives just a lower-bound estimate of the activation energy for Me self-diffusion, assuming that the diffusion mechanism is the same as that for carbon atoms.

Mechanisms of self-diffusion in nonstoichiometric carbides have been discussed with the main focus on carbon diffusion, for which a single-vacancy and a di-vacancy mechanisms have been considered by different authors.[6,11] For Me self-diffusion, a single-vacancy mechanism (by means of single Me vacancies V_{Me}) is commonly assumed.[6] However, it has been shown by calculations[12] that the single-vacancy mechanism gives almost twice as high activation energy of Me atom diffusion as that found experimentally. Thus, the atomic mechanism of Me diffusion in substoichiometric carbides remains unclear.

The range of nonstoichiometry in carbides of the group IV transition metals is quite high: The concentration of carbon vacancies (V_C) can reach 50%.[3,7] The effects of these vacancies on many physical properties such as, for example, carbon diffusivity[8,9,13] or lattice parameter[13,14] are well known. The tendency towards ordering of carbon vacancies has been observed experimentally[15–22] and studied theoretically;[23–26] at the same time, the effect of constitutional carbon vacancies on the Me diffusion has not been studied.

Here, by means of state-of-the-art *ab initio* atomistic simulations of vacancy-mediated diffusion processes in TiC and ZrC carbides, we show that the assumption of a simple diffusion mechanism is not quite correct. A detailed analysis reveals that the self-diffusion of metal atoms in these carbides involves the formation of a cluster of metal and carbon vacancies, and its subsequent kinetic transformations leading to effective transfer of the metal atoms. This multivacancy mechanism is expected to be relevant to other transition-metal carbide systems as they all have similar kinetic and thermodynamic properties.[6]

II. METHODOLOGY

The present work is based on density functional theory (DFT) calculations of the total energy and employs the generalized gradient approximation (GGA) to the exchange-correlation potential.[27] The calculations are performed using the projector-augmented-wave (PAW)[28,29] method as implemented in the Vienna *ab initio* simulation package (VASP).[30] The VASP-PAW calculations have been performed using a plane-wave cutoff energy of 400 eV. The convergence criteria have been chosen to be 10^{-5} eV for the total energy and 10^{-2} eV/Å for the forces. Ionic relaxations were included in all of the present calculations. The nudged elastic band (NEB) method[31] was used to locate the saddle point and to determine the height of the migration barriers. Between nine and seven images were used in the NEB calculations. The contribution from electronic excitations is included in the usual form of Fermi-function smearing (electronic temperature).[32,33]

A. Supercell calculations of defects

Simulations of various vacancy arrangements and their transformations were performed in this study using a 216-site supercell, built by $(3 \times 3 \times 3)$ repetition of a cubic eight-atom $(\times 8)$ unit cell of the NaCl structure. Brillouin zone integration

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TABLE I. Effects of supercell size N, lattice parameter a (Å), and temperature T on the formation and binding energy of a di-vacancy (2V) in TiC. The total energies U have been obtained from static ion calculations for internally relaxed supercells. Total energies E calculated at $T = 0$ K include the energy of zero-point ionic motion. Free energies F include the contributions due to thermal vibrations and electronic excitations at $T = 2000$ K. Nonconfigurational entropy S_{nc} of the di-vacancy formation and binding is expressed in units of Boltzmann's constant k_B. The phonon contributions have been evaluated using density functional perturbation theory[33–36] in the harmonic approximation.

	Static ions				$T = 0$ K		$T = 2000$ K		
Supercell size N	512	216	128	128	128	128	128	128	128
Lattice parameter a (Å)	4.329	4.329	4.330	4.387	4.330	4.387	4.387	4.387	4.387
Quantity	U	U	U	U	E	E	E	S_{nc}	F
2V formation	5.95	6.06	6.15	6.11	6.11	6.08	6.20	$3.35k_B$	5.62
2V binding		1.48	1.44	1.45	1.45	1.45	1.51	$0.91k_B$	1.35

was done using the 4 × 4 × 4 Monkhorst-Pack **k**-point mesh; the convergence with respect to **k** points was checked up to the 8 × 8 × 8 mesh.

The convergence of the calculations with respect to the supercell size was tested by comparing the formation and binding energies of a di-vacancy in TiC (the nearest-neighbor pair of one titanium and one carbon vacancy) calculated using the 216-site supercell with the formation and binding energies obtained using a larger 512-site supercell (2 × 2 × 2 **k** mesh) and a smaller 128-site supercell (5 × 5 × 5 **k** mesh).

Here we make a distinction between Schottky defect (a dissociated and noninteracting pair of one metal and one carbon vacancy) and di-vacancy in which the two vacancies are bound into a nearest-neighbor (NN) complex. The di-vacancy formation energy may be calculated from the energy $E(N)$ of a supercell containing N atoms and the energy $E(N-2_{\mathrm{NN}})$ of a supercell containing $N-2$ atoms and a bound di-vacancy as

$$E_f(2\mathrm{V}_{\mathrm{MeC}}) = E(N-2_{\mathrm{NN}}) - \frac{N-2}{N}E(N). \tag{1}$$

The binding (dissociation) energy of a di-vacancy in MeC is calculated using the energies $E(N-1_{\mathrm{Me}})$ and $E(N-1_{\mathrm{C}})$ of two supercells containing, respectively, one metal and one carbon vacancy:

$$\begin{aligned} E_b(2\mathrm{V}_{\mathrm{MeC}}) &= E(N-1_{\mathrm{Me}}) + E(N-1_{\mathrm{C}}) \\ &\quad -E(N-2_{\mathrm{NN}}) - E(N). \end{aligned} \tag{2}$$

It follows from Eqs. (1) and (2) that the formation energy of a Schottky defect ($2\mathrm{V_S}$) has been defined as

$$E_f(2\mathrm{V_S}) = E(N-1_{\mathrm{Me}}) + E(N-1_{\mathrm{C}}) - \frac{2N-2}{N}E(N).$$

Alternatively, it can be defined using the energy $E(N-2_{\mathrm{S}})$ of a supercell containing the Me-C vacancy pair in a dissociated configuration:

$$E_f(2\mathrm{V_S}) = E(N-2_{\mathrm{S}}) - \frac{N-2}{N}E(N). \tag{4}$$

For a semiconductor or an insulator the formation energies calculated according to definitions Eqs. (3) and (4) (i.e., using two supercells each containing a monovacancy or using one supercell containing a dissociated vacancy pair) would be different by an energy of the order of the band gap, because of the dependence of the charge state of each vacancy on the presence of other defects in the system. Since the TiC and ZrC compounds are metallic, the charge state of point defects in these materials is controlled by the presence of an overwhelming amount of valence electrons, so the two definitions of the Schottky defect formation energy are equivalent. In the rest of the paper both definitions will be used.

Table I shows that convergence with the number of atoms in the supercell is rather slow. However, quite independently of the supercell size, one gets the formation energy of about 6 eV and the binding energy of about 1.5 eV for a bound di-vacancy in TiC using static-ion calculations.

B. Finite-temperature effects

In order to evaluate the vibrational and electronic contributions to defect energies in the temperature range of our interest (0–2000 K), lattice dynamics of vacancy-free and vacancy-containing TiC supercells have been studied by means of density functional perturbation theory (DFPT)[33–35] as implemented in VASP and PHONOPY[36] packages. The real space force constants were computed for each of the pre-relaxed supercells appearing in Eqs. (2) and (3). The phonon spectra of the supercells were then calculated, and from those the vibrational (free) energy contributions at $T = 0$ K and $T = 2000$ K were evaluated. The phonon spectra and related physical properties of defect-free TiC and ZrC have been investigated previously[37] and will not be discussed here.

As the DFPT calculations are computationally demanding, we had to restrict ourselves to 128-site supecells built by (4 × 4 × 4) repetition of a two-atom (×2) primitive unit cell of the NaCl structure and a 5 × 5 × 5 Monkhorst-Pack **k**-point mesh. The calculations were performed at two supercell volumes of TiC, corresponding to the theoretical equilibrium lattice parameter $a = 4.329$ Å at $T = 0$ K (which virtually coincides with the experimental one extrapolated to 0 K) and $a = 4.387$ Å at $T = 2000$ K.[38] Let us note here, that our goal is to calculate the defect characteristics that are experimentally accessible only at high temperatures, and therefore the calculations should be carried out at the high-temperature lattice parameters. In the present case the difference between calculations done at 0 K and 2000 K lattice parameters is found to be insignificant (the effect of lattice parameter change from the 0-K value to 2000-K value is shown in Table I to be less than 1%), but there are some cases where it can be quite large.[39]

The force constants for the phonon calculations at 2000 K were computed at the same electronic temperature, introduced by using the Fermi function smearing with $\sigma = 0.17234$ eV. The calculated total and free energies of the perfectly occupied and vacancy-containing supercells were combined according to Eqs. (1)–(3) in order to extract the total and free energies of formation and binding of vacancies in TiC presented in Table I.

The data listed in Table I allow one to analyze the relative importance of various temperature-related contributions to the formation and binding energy of a di-vacancy defect in TiC. The zero-point motion and lattice expansion (from the low-temperature to the high-temperature value of the lattice parameter) are found to reduce the di-vacancy formation energy by about 0.03 eV, whereas their effect on the binding energy of the two vacancies is negligible. The temperature effects at 2000 K are more pronounced: The free energy of formation(binding) of a di-vacancy in TiC is lowered by 0.34(0.10) eV in comparison with the values calculated at $a = 4.387$ Å and $T = 0$ K. This lowering is a combined effect of ionic and electronic temperature; if treated separately, the free energy lowering due to ionic temperature is 0.21(−0.03) eV while that due to electronic temperature is 0.20(0.07) eV.

Experimental data on temperature dependence of Arrhenius type are usually analyzed in terms of activation energy (obtained from the exponent) and entropy (obtained from the prefactor). Table I also shows the calculated total energy E and entropy S_{nc} of formation and binding of a di-vacancy in TiC. The calculations yield quite high values of nonconfigurational (vibrational and electronic) entropy changes associated with the di-vacancy formation and binding. The entropy contributions are mainly responsible for the lowering of the free energies of the di-vacancy formation and binding, while the corresponding total energies are found to increase by 0.12(0.06) eV as a result of temperature increase from 0 to 2000 K.

We note that the calculated temperature-induced changes in total energy are small compared with the absolute values of defect formation and binding energies. Therefore, these dynamic contributions can be safely neglected since we are interested in the phenomena on the energy scale of 1–10 eV. Accordingly, the analysis of point defect formation and migration in this paper is entirely based on total energies computed for static (relaxed) ionic configurations in 216-site supercells. As the entropy effects are found to be relatively important, we focus our attention on the activation energies and do not attempt to calculate the prefactors.

III. RESULTS AND DISCUSSION

The temperature-dependent diffusion coefficient in transition-metal carbides is usually expressed in the Arrhenius form,

$$D = D_0 \exp\left(-Q/k_{\mathrm{B}}T\right), \tag{5}$$

where D_0 is the prefactor, $Q = E_m + E_f$ the activation energy for diffusion (which consists of defect formation energy E_f and defect migration energy E_m), k_{B} is the Boltzmann constant, and T the temperature. Let us note that, in the case of carbon diffusion in the nonstoichiometric carbides, only the migration energy contributes to Q[6] since nonthermal (constitutional) carbon vacancies are in abundance. In the case of metal-atom diffusion, both the formation and migration energies should be considered. The formation of Me vacancies is viewed as a thermally activated process during which the composition of the system is conserved.

TABLE II. Formation energy (eV) of single metal vacancy V_{Me}, bound and dissociated di-vacancy $2V_{\mathrm{MeC}}$, and a Frenkel pair (FP) consisting of an interstitial Me-atom and a V_{Me}. The energies are obtained at the calculated equilibrium $T = 0$ K lattice parameters $a_0(\mathrm{TiC}) = 4.329$ Å and $a_0(\mathrm{ZrC}) = 4.701$ Å; data in parentheses are calculated at the experimental lattice parameters $a(\mathrm{TiC}) = 4.387$ Å and $a(\mathrm{ZrC}) = 4.752$ Å corresponding to 2000 K.

Defect	TiC	ZrC
V_{Me}	7.54	7.81
$2V_{\mathrm{MeC}}$ bound	6.06 (5.99)	6.53 (6.49)
$2V_{\mathrm{MeC}}$ dissoc.	7.34	8.02
$\mathrm{FP}_{\mathrm{Me}}$	16.12	18.61

A. Defect formation energies

Ab initio calculations[12] show that V_{Me} in TiC and ZrC can be thermally formed as a Schottky defect, i.e., as a composition-conserving vacancy pair, V_{C} and V_{Me}[41,42] (see Table II). The energy to form a pair of dissociated vacancies has been computed according to Eq. (4) to be 7.34 eV for TiC and 8.02 eV for ZrC. The value for ZrC (calculated in Ref. 12) is in reasonable agreement with the value 8.33 eV obtained in recent VASP calculations using ultrasoft pseudopotentials by Li *et al.*[43] The calculated formation energies of thermal Schottky defects in TiC and ZrC are comparable with the formation energy of single metal vacancies in these carbides via the chemical route:

$$\mathrm{Me}_{\mathrm{MeC}} \rightarrow \mathrm{Me}_{\mathrm{hcp}} + V_{\mathrm{Me}}, \tag{6}$$

where the vacancies are formed by removing Me atoms from the carbide phase and adjoining them to the pure metal (hcp phase). The energy of this chemical process (per one Me vacancy) for TiC and ZrC is given in the first line (V_{Me}) of Table II.

However, as can be seen from Table II, the dissociated configuration of a di-vacancy (or Schottky defect in which the two vacancies are noninteracting) is not energetically favorable. The formation energy of a Schottky defect in TiC[12,40] and ZrC[12] is lowered by 1.3–1.4 eV if the carbon vacancy and the metal vacancy become nearest neighbors to each other, thereby forming a bound di-vacancy ($2V_{\mathrm{MeC}}$).

B. Diffusion mechanisms involving a di-vacancy

Let us consider atomic mechanisms of Me self-diffusion mediated by a thermal di-vacancy. A di-vacancy can perform various diffusive movements as a whole, i.e., without dissociating into the two vacancies. Two such movements, representing simultaneous jumps of two (Me and C) neighboring atoms into the respective vacancies, are schematically shown in Fig. 1(a). One may call these jumps *molecular diffusion*, meaning that the pair of diffusing atoms represents a Me-C molecule.

Such a molecule, aligned in the [100] direction, can make two types of jumps, distinguished by the angle between the jump direction and the vector connecting the Me and C atoms,

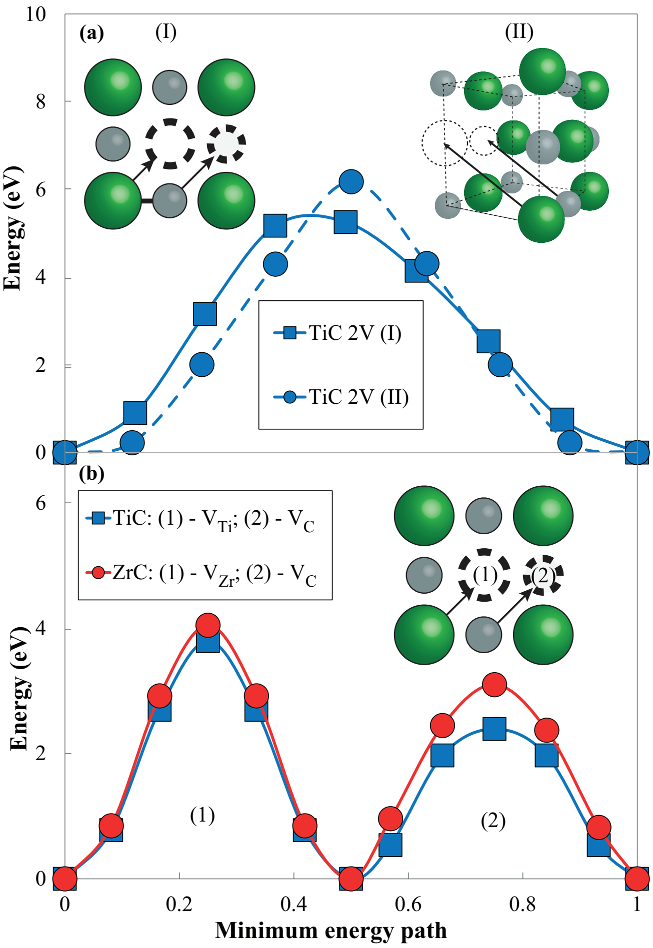

FIG. 1. (Color online) Nudged elastic band method simulations of di-vacancy mediated diffusion. (a) Potential energy profiles for two possible $2V_{MeC}$ "molecular" jumps in the [110] (I) and [101] (II) directions. Dimensionless minimum energy path (MEP) on the *x* axis denotes a distance fraction between the initial to the final positions of a $2V_{MeC}$ (as shown by arrows in the figure). (b) Potential energy profiles for the $2V_{MeC}$ migration process involving consecutive jumps of the two vacancies. Large green circles represent metal atoms; small gray circles, carbon atoms; and empty dashed circles, vacancies (these notations apply to all figures). Here, MEP denotes the overall distance covered by two vacancies during two sequential jumps (as shown by arrows in the figure).

(I) four 45° jumps in the [110], $[1\bar{1}0]$, [101], or $[10\bar{1}]$ direction (and four 135° jumps in the reverse direction) and (II) four 90° jumps in the orthogonal $\langle 011\rangle$ directions. However, according to our calculations presented in Fig. 1, the migration barrier is slightly higher for a simultaneous "molecular" jump [Fig. 1(a)] than for another migration path where the Me and C atoms move separately [one after the other as shown in Fig. 1(b)], in spite of the fact that the strong chemical bond between the jumping atoms is broken in the latter process.

The activation energies for di-vacancy mediated Me diffusion in TiC and ZrC (see Table III), calculated assuming the lowest-energy migration path, are lower than those calculated for the single Me vacancy mechanism (about 13 eV; Ref. 12), but still considerably higher than the experimental values also listed in Table III. Although the effect of V_C is now quite clear, the remaining large disagreement between the theoretical and experimental activation energies suggests that vacancy clusters with more than one carbon vacancy may be involved in the Me diffusion, so let us have a closer look at the role of V_C in the Me diffusion process.

TABLE III. Experimental[8,9] and calculated activation energies Q, migration barriers E_m, and defect formation energies E_f for Me self-diffusion in Ti and Zr carbides. The calculated values are given for the di-vacancy ($2V_{MeC}$) mechanism and for the V_{Me}–$(V_C)_6$ cluster mechanism.

	TiC			ZrC		
Method, mechanism	E_f	E_m	Q	E_f	E_m	Q
Theory, $2V_{MeC}$	5.99	3.79	9.87	6.49	4.05	10.53
Theory, cluster	3.01	3.82	6.83	2.92	4.54	7.46
Experiment			7.64[a]			7.46[b]

[a] Ti in $TiC_{0.97}$; Ref. 8.
[b] Zr in $Zr(C_{0.966}O_{0.012}N_{0.022})_{0.97}$; Ref. 9.

C. Diffusion mechanism involving multivacancy clusters

The effect of carbon vacancies on the Me diffusion in TiC and ZrC comes from the very strong V_{Me}–V_C bonding which lowers the formation energy of a metal vacancy in the presence of carbon vacancies.[12,40] As has been mentioned, the carbon sublattice in TiC and ZrC may incorporate a vast number of vacancies (up to 50%!), so that a metal vacancy has a high probability to surround itself with as many carbon vacancies as it can hold while it forms or migrates through the crystal. It remains to be established how large these V_{Me}–$(V_C)_n$ clusters can grow, and how they can migrate.

1. *Cluster formation*

Assuming that the equilibrium concentration of carbon vacancies in carbon-deficient MeC carbides is very high and almost temperature independent, their effective formation energy is practically zero.[6,42] However, the short-range order of carbon vacancies is different in the initial and the final states: Without the metal vacancy the carbon vacancies V_C tend to avoid each other at the first and second coordination shell (to preferentially become third neighbors) on the carbon sublattice,[24,25] whereas in the V_{Me}–$(V_C)_6$ cluster the six carbon vacancies are situated at the first and second nearest-neighbor positions relative to each other.

Therefore, the growth of a V_{Me}–$(V_C)_n$ cluster will be counteracted by the mutual repulsive interactions of the carbon vacancies at the second coordination shell on the carbon sublattice in both TiC[24,25] and ZrC (see Fig. 2). However, our calculations show that these repulsive interactions of carbon vacancies (Fig. 2) are too weak (in comparison with the attractive V_{Me}-V_C interaction) to prevent another carbon vacancy from joining a V_{Me}-$(V_C)_n$ cluster if the V_C can become another nearest neighbor of the metal vacancy.

One may expect that, when the metal vacancy is fully surrounded by carbon vacancies in the nearest-neighbor shell, the repulsive V_{Me}-V_C interactions will limit further growth of the cluster. Indeed, our total energy calculations presented in Fig. 3 show that the V_{Me}-$(V_C)_6$ cluster is the most stable

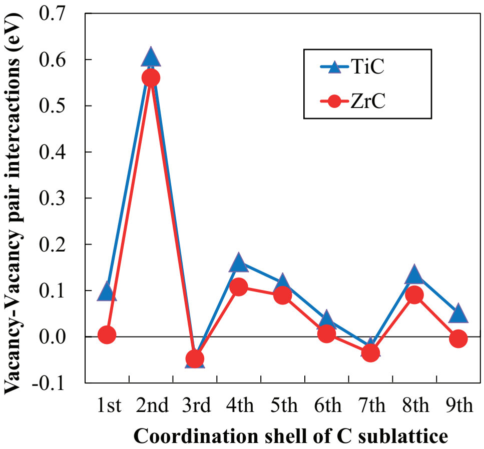

FIG. 2. (Color online) V_C-V_C interactions in TiC and ZrC. Positive sign of interaction corresponds to repulsion, and negative to attraction, between the defects.

configuration of one metal and six carbon vacancies in TiC, and that adjoining the seventh carbon vacancy to the cluster increases the energy of the system.

Let us explain how the formation energy of a multivacancy cluster V_{Me}-$(V_C)_n$ (via the creation of a di-vacancy) has been calculated. First of all, one must take into account the presence of $n-1$ carbon vacancies (distributed as to avoid one another at the first and second coordination shell, to mimic the short-range order of carbon vacancies[24]) in the initial state of the system. Thus, there are only $N = 216 - n$ atoms in the initial state, but Eq. (1) should be re-expressed in the equivalent form that conserves a nonstoichiometric composition:

$$E_f = E(N-2) + E(\mathrm{MeC}) - E(N). \tag{7}$$

Here $E(N-2)$ is the total energy of the supercell containing one V_{Me}-$(V_C)_n$ cluster, $E(N)$ is the energy of the initial configuration of n carbon vacancies, and $E(\mathrm{MeC})$ is the total energy of the stoichiometric carbide per formula unit. Our test calculations of the formation energy of the V_{Me}-$(V_C)_6$ cluster using 216-site and 512-site supercells showed that the result is insensitive to the supercell size.

Various vacancy configurations have been considered in our 216-site supercell calculations for the vacancy clusters. The results are summarized in Table III and Fig. 3(b). The formation energy of the V_{Me}-$(V_C)_6$ cluster is calculated to be about 3 eV and is the lowest among all the considered vacancy clusters containing one metal vacancy. The question to answer now is whether this defect cluster has low enough migration barrier to take part in the diffusion.

2. *Cluster migration*

To search for low-migration-barrier paths for the V_{Me}-$(V_C)_6$ cluster, we first considered discrete configurations of the vacancy cluster, in which all the atoms were resting at relaxed lattice site positions. Thus, we made an exhaustive search and enumerated all 18 irreducible sequences of the seven atom-vacancy exchanges that are necessary for moving such a vacancy cluster by a primitive ⟨110⟩ translation vector in the NaCl structure. The calculated energies for these seven-jump sequences (relative to the energy of the initial configuration) are shown in Fig. 3(c) as open symbols at integer positions along the cluster migration path. Several sequences, possessing the lowest calculated energies for the atoms in the relaxed

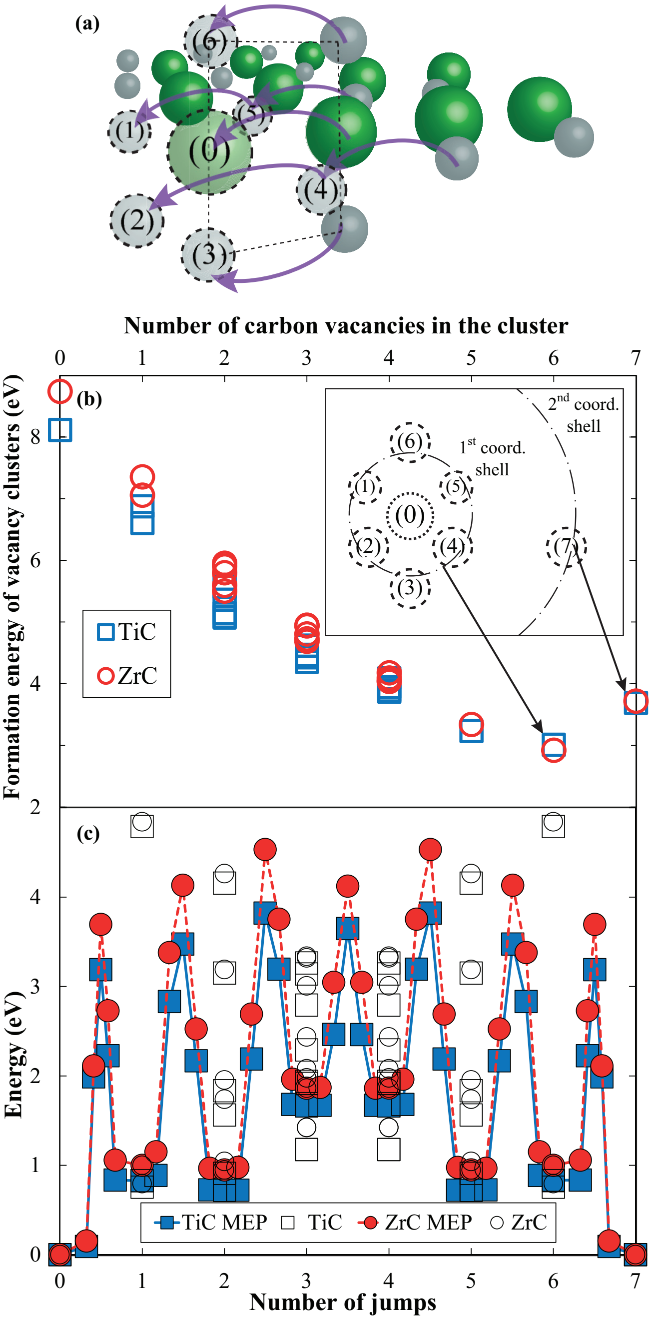

FIG. 3. (Color online) Energetics of formation and migration of a V_{Me}-$(V_C)_6$ vacancy cluster. (a) Schematic representation of the atomic jumps involved in the cluster migration. Number 0 denotes the V_{Me}, whereas numbers 1–6 stand for V_C. The lowest potential energy profile along the migration path is realized for the 5-4-3-0-1-2-6 sequence of vacancy jumps. (b) Formation energy of various V_{Me}-$(V_C)_n$ clusters as a function of the number of carbon vacancies in the cluster n. (c) Potential energy profile (filled symbols connected with lines) along the minimum energy path (MEP) for the V_{Me}-$(V_C)_6$ cluster migration via the seven-jump mechanism. The energies for other possible sequences of vacancy jumps are shown as empty symbols.

lattice site positions, were then selected for nudged elastic band calculations to obtain the barriers for the individual atomic jumps.

In terms of the vacancy numbering introduced in Fig. 3(a), the lowest migration barrier is realized for the 5-4-3-0-1-2-6 type of a seven-jump sequence. The potential energy profile for this sequence of vacancy jumps in TiC and ZrC is shown in Fig. 3(c) by full symbols connected with lines. The migration barrier for this path (the barrier value corresponds to the highest peak of the curve) is thereby found to be about 3.82 eV for TiC and 4.54 eV for ZrC, which gives us the activation energy values that compare much better to the experimental data than the values obtained for the V_{Me} (Ref. 12) or $2V_{MeC}$ (Table III) mechanisms.

Comparison of this result with experimental activation energies suggests that the contribution of multivacancy clusters to the process of Me self-diffusion in TiC and ZrC is overwhelmingly larger than the contributions from single Me vacancies or di-vacancies. Our finding is partly supported by the positron annihilation study[44] of defects in nonstoichiometric TiN and TiC thin films indicating that vacancies should be present on both (metal and nonmetal) sublattices in these compounds. Thermal desorption spectroscopy investigation by Seijbel *et al.*[45] also suggests the presence of vacancy clusters in TiC. However, we could not find any specific experimental investigation of the Me-C vacancy clusters in TiC or ZrC, which could be considered as a direct confirmation of the diffusion mechanism obtained in the present work.

3. Realization of the mechanism

As for the diffusion mechanism suggested here, one can imagine the process where a spontaneously formed thermal di-vacancy diffuses through the crystal lattice, collecting all the carbon vacancies that are met on its way (due to very strong V_{Me}-V_C binding), until a vacancy cluster V_{Me}-$(V_C)_6$ is fully assembled. The activation energy of Me self-diffusion should, in principle, contain the contributions from all possible V_{Me}-$(V_C)_n$ vacancy clusters, with $1 \leqslant n \leqslant 6$. From the analysis of theoretical and experimental data presented in Table III, the contribution of clusters with $n = 6$ appears to be the dominant one, most likely because of the high stability of such a cluster (total binding energy is approximately 4 eV). In our opinion, a comparative statistical-mechanical analysis of the contributions to Me self-diffusion from various multivacancy clusters in carbides could be of great interest, but it is beyond the scopes of the present paper.

IV. SUMMARY

In summary, we have studied the microscopic mechanism of Me diffusion in substoichiometric (C-poor) TiC and ZrC carbides by *ab initio* methods. Studies of thermal defects, namely di-vacancies, have revealed that vacancy clusters should play a significant role in the atomic processes of Me diffusion in the carbides. A symmetric cluster of one V_{Me} surrounded by six V_C in the first coordination shell has been found to be the most energetically stable configuration. The calculated activation energies for the vacancy-cluster mechanism of diffusion are in much better agreement with experimental data than those calculated assuming the single metal vacancy or the di-vacancy mechanisms.

This finding demonstrates that Me diffusion in the substoichiometric carbides is essentially due to the migration of metal vacancies “dressed” in a shell of carbon vacancies. According to the present calculations, such “dressed” Me vacancies are very stable and have almost the same migration barrier as “bare” Me vacancies or di-vacancies. The motion of such a complex defect cluster is a correlated sequence of seven atomic jumps, as described in this paper. The present study may give insights into the atomic mechanisms of diffusion in other complex systems.

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