

Ab initio modeling of the formation and migration of monovacancies in Ti_2AlC

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We performed ab initio calculations for monovacancy formation and migration in Ti_2AlC . Carbon and aluminum vacancies have almost equally low formation energies, respectively, at (Ti- and Al-rich) and (Ti- and C-rich) growth conditions, wherein both defects exhibit a high equilibrium concentration and structural tolerance to large off-stoichiometry in Ti_2AlC . In contrast, V_{Ti} has the highest formation energy at all possible conditions. The intrinsic migration energies of various vacancies are determined to be in the sequence $E_m(V_{Al}) < E_m(V_{Ti}) < E_m(V_C)$.

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High-temperature structural materials for nuclear reactors are currently a hot topic because of the looming energy crisis and the rapid development of nuclear power. Layered ternary carbides or nitrides with the general formula $M_{n+1}AX_n$ (where $n = 1-3$, M is an early transition metal, A is an A-group element, mostly from groups IIIA and IVA, and X is either C and/or N) have also been considered as high-temperature structural materials with potential applications in the nuclear industry, as they possess the following relevant properties: exceptional thermal shock resistance and damage tolerance; excellent oxidation resistance; and elastic stiffness though still readily machinable at room temperature [1]. Although the above attributes ensure MAX phases have a wide range of possible technological applications, there is a common feature underlying all of them, namely the defect-induced microstructural evolution. While damage accumulation as a result of irradiation leads to material degradation, the formation of, and interaction among, point defects can modify the overall physical properties of MAX phases.

At equilibrium, vacancies are usually the dominant intrinsic defects in materials and govern the stoichiometry; this is a key issue in growth behavior and the resulting material properties during crystal growth, thin-film deposition, long-term endurance of MAX ceramics at high temperatures or in corrosive and irradiated environments, etc. Vacancy diffusion, on the other hand, contributes to the kinetics and influences the response to stress in ceramics. According to some unreported preliminary results, vacancy clusters are observed in the electron-irradiated samples of MAX phases by transmission electron microscopy, but its component is unknown and needs to be clarified. To date, despite extensive and successful efforts at characterization of the mechanical properties of MAX phases [2–6], very little evidence is present as to the defect-related properties in these phases.

In the large family of MAX phases, Ti_2AlC is of particular interest since this compound has a comparatively low density (4.11 g cm^{-3}) and excellent high-temperature oxidation resistance due to the formation of a continuous, protective Al_2O_3 scale on the substrate during high-temperature oxidation in air [7,8]. These properties make Ti_2AlC a promising candidate for high-temperature structural application or as a coating material. To optimize the use of MAX ceramics, it is crucially important to understand the proper atomic behavior, and the energetics of formation and migration of point defects in MAX phases.

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All calculations have been performed using the CASTEP [9] code, which performs plane-wave pseudopotential total energy calculations. A vacancy defect is modeled by removing one atom of each species from the supercell composed of 32 atoms, which has proven to be sufficient in our convergence test wherein 48- and 64-atom supercells are employed. In all calculations the plane wave energy cutoff and the Brillouin zone sampling were fixed at 550 eV and $5 \times 5 \times 2$ special k -point meshes, respectively. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudopotential for Ti, Al and C atoms [10]. The electronic exchange-correlation energy was treated under the generalized gradient approximation (GGA-PW91) [11].

The self-diffusion barrier of each species was assumed to be along the (0001) basal plane by neighboring vacancy jump and calculated by searching the transition state linking the two end defective configurations. The scheme we employ to locate the transition state structure via reaction coordinates is called the LST/QST algorithm, and combines the linear (LST) or quadratic synchronous transit (QST) methods with conjugate gradient (CG) refinements [12].

The importance of the defect formation energy as a key quantity describing the behavior of defects has been well clarified by extensive theoretical studies for metals, semiconductors, as well as for ceramics [13–22]. Depending on the relative abundances of the atomic constituents during the crystal growth, the stability of a vacancy defect in Ti_2AlC can be determined by calculating the formation energy defined as:

$$\Delta E_f = E_{\text{def}} - n_{\text{Ti}}\mu_{\text{Ti}} - n_{\text{Al}}\mu_{\text{Al}} - n_{\text{C}}\mu_{\text{C}}, \quad (1)$$

where E_{def} is the total energy for the supercell containing a vacancy, μ_i the chemical potential of each species, and n_i the number of atoms in the supercell. It is clear the chemical potentials μ_i here are not independent but related to the chemical potential of bulk Ti_2AlC , $\mu_{\text{Ti}_2\text{AlC}}$, i.e. $2\mu_{\text{Ti}} + \mu_{\text{Al}} + \mu_{\text{C}} = \mu_{\text{Ti}_2\text{AlC}}$. To maintain a stable Ti_2AlC compound and to prevent pure element formation, the chemical potentials of constituents (μ_{Ti} , μ_{Al} and μ_{C}) must be smaller than the reference energy in standard state. A more detailed description of the computation procedure can be found in Ref. [15]. In addition, precipitation of binary compounds sets further chemical potential restrictions, namely $\mu_{\text{Ti}} + \mu_{\text{C}} \leq \mu_{\text{TiC}}$, $\mu_{\text{Ti}} + \mu_{\text{Al}} \leq \mu_{\text{TiAl}}$ and $4\mu_{\text{Al}} + 3\mu_{\text{C}} \leq \mu_{\text{Al}_4\text{C}_3}$. Based on the calculated vacancy formation energies, the vacancy concentration can be determined according to the Arrhenius formula as follows:

$$C_D = z_D N_S \exp(-\Omega_D/k_B T), \quad (2)$$

where z_D is the number of different possible configurations for a defect per sublattice site, and N_S is the number of the sublattice sites per unit volume. The calculated result of the vacancy defect formation energy dependent on the chemical potential is shown graphically in Figure 1a; Figure 1b is their equilibrium concentration calculated at $T = 1000$ K, which is lower than the decomposition temperature of Ti_2AlC . From Figure 1a, we find the formation of Al and C vacancy defects in Ti_2AlC is most likely to occur, depending on different chemical potential situations. Figure 1a

suggests that V_{Al} is the dominant defect near Ti- and C-rich equilibrium growth conditions, while V_{C} is most favorable in Ti- and Al-rich conditions. On the other hand, V_{Ti} has an extraordinarily high formation energy no matter what growing condition is assumed, and hence it is unlikely to exist in any appreciable amount.

If precipitation of binary compounds, such as Al_4C_3 , TiC and TiAl, is considered, the possible chemical potential for stable Ti_2AlC changes to narrow bounds, as shown by the gray zones in Figure 1. The arrows indicate outer regions where Ti_2AlC and binary bound phases coexist. For example, the left pattern of Figure 1a shows that the energy of formation changes as a function of the chemical potential of Ti; TiAl will appear as the chemical potential of Ti increases away from the right border of the gray zone; and Al_4C_3 will be present if the chemical potential of Ti goes beyond the reverse border. Along the Ti and Al chemical-potential-dependence lines plotted in Figure 1a, the relative stability of each species of intrinsic vacancy follows the same trend irrespective of the binary-bound phase constraints. In addition, along the C chemical-potential-dependence line in Figure 1, a stable Ti_2AlC region is fixed in the zone which favors the formation of C vacancy only. Consideration of binary-bound phases excludes the possible formation of Al vacancies, which have a lower energy of formation in regions where Ti_2AlC and TiC coexist.

As shown in Figure 1b, since the formation energies of Al vacancies are sufficiently low under the Ti- and C-rich limit, these vacancies will come into being spontaneously and their concentration can in extreme conditions reach the order of one mole of Al lattice sites available. In the Ti- and Al-rich limits the relatively immobile C vacancies are overwhelmed and their equilibrium concentration is also extraordinarily high. The strong dependence of concentration on the chemical potential can be due to the fact that Ti- and C(Al)-rich conditions provide a low-energy sink for the removed Al(C) atoms.

Technically, once V_{Al} is created in Ti_2AlC , then due principally to energy or composition fluctuation, high-temperature synthesis or heat treatment will result in the Ti- and C-rich condition being satisfied locally. In this case, according to the order of the energies of formation from Figure 1a, the formation energy of an Al vacancy is the lowest in the Ti- and C-rich environment and the loss of Al atoms from the normal lattice sites of the crystal under this condition is spontaneous. As a result of the loss of a large number of Al atoms, Ti_2AlC might either show structural tolerance to large off-stoichiometry, or when a critical concentration of V_{Al} is reached, the nucleation of binary compound TiC might be initiated in the original place, which is matched to the surrounding Ti_2AlC compound. The latter has been conformed by the intergrowth of TiC and Ti_2AlC frequently identified by high-resolution transmission electron microscopy imaging and X-ray diffraction analysis [23–25]. The situation for V_{C} is quite similar with V_{Al} but occurs in the Ti- and Al-rich limits. However, since a coherent match between Ti_2AlC and TiAl alloy requires a rearrangement of

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