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Journal of the European Ceramic Society 29 (2009) 773–777

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Energetics of point defects in TiC

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Received 9 May 2008; received in revised form 26 June 2008; accepted 27 June 2008

Abstract

Density functional theory was used to evaluate the energetics of point defects in TiC_x ($x < 1$): C vacancies and Al substitution at a C site. Our ambition is to contribute towards understanding the underlying atomic mechanisms enabling the Al intercalation into TiC_x and the subsequent formation of Ti_3AlC_2. The difference between the energy of formation for an Al substitution at a C site and a bulk C vacancy is 0.224 eV. Furthermore, only 49 meV/vacancy is required to order the existing bulk C vacancies. Surface effects were also considered: the energy of formation for Al on TiC(1 0 0) at a vacant surface C site is smaller by 2.779 eV than in the case of the C surface vacancy, indicating that Al is likely to be incorporated. Based on these energy differences, it is reasonable to assume that Ti_3AlC_2 is formed by Al surface ingress into TiC_x and that vacancy ordering takes place.

Keywords: Carbides; Defects; Density functional theory

1. Introduction

Intercalation may be defined as the reversible inclusion of an atom or a molecule between two crystalline planes or two other molecules.[1–6] Intercalation is of relevance in solid-state physics and chemistry as well as molecular biology. For instance, many compounds, such as graphite,[1,2] some oxides and sulphides (e.g. V_2O_5 and MoS_2)[3] as well as various clays,[5] possess an enhanced stability and electrical conductivity upon intercalation and can be used in rechargeable lithium batteries, for oil logging, in paper manufacturing and catalysis, to name but a few applications. Magnetic properties can also be altered. For instance, in Ni_3Al the Curie temperature can be tailored by intercalating with carbon.[4] Intercalation of, e.g. daunomycin, ethidium bromide, novantrone and proflavine[6] in DNA is used for chemotherapeutic treatments in medicine. Recently, it has been suggested that bulk synthesis time and temperature of Ti_3AlC_2 can significantly be reduced if a rapid intercalation process route is followed.[7] However, the energetics of underlying atomic mechanisms is not understood.

Ti_3AlC_2 is a so-called $M_{n+1}AX_n$ phase (space group $P6_3/mmc$). These phases are interleaved compounds comprising of $M_{n+1}X_n$ and A layers, where M is an early transition metal, A is mainly IIIA or IVA group element, X is C or N and n is an integer value.[8–10] Due to this nanolaminated structure, these phases exhibit a combination of properties, usually associated with metals and ceramics; they are machinable, possess high stiffness, good thermal shock resistance, good corrosion resistance and they are good conductors of heat and electricity.[8] $M_{n+1}AX_n$ phases are used as formers for healthcare products, hot pressing tools and resistance heating elements.[11,12] Ti_3SiC_2-based composites with Ag or Cu show a potential for electrical contact applications.[13–16] A major challenge in processing these nanolaminates is a reduced synthesis temperature. For instance, Ti_3AlC_2 can be grown at 1400–1600 °C by hot isostatic pressing[17] or by solid–liquid reaction synthesis and simultaneous *in situ* hot pressing process.[18] Riley and Kisi have demonstrated that Ti_3AlC_2 can be synthesised by the rapid intercalation of Al in $TiC_{0.67}$ (space group $Fm\bar{3}m$) at 400–600 °C below the conventional processing temperature.[7] The authors have suggested that, after the ingress of molten Al into $TiC_{0.67}$, vacancy ordering facilitates the formation of Ti_3AlC_2.[7]

In this work, we study the energetics of point defects at a C site in TiC_x ($x < 1$): C vacancies and Al substitution at a C site. Our ambition is to contribute towards the understanding of

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doi:10.1016/j.jeurceramsoc.2008.06.027

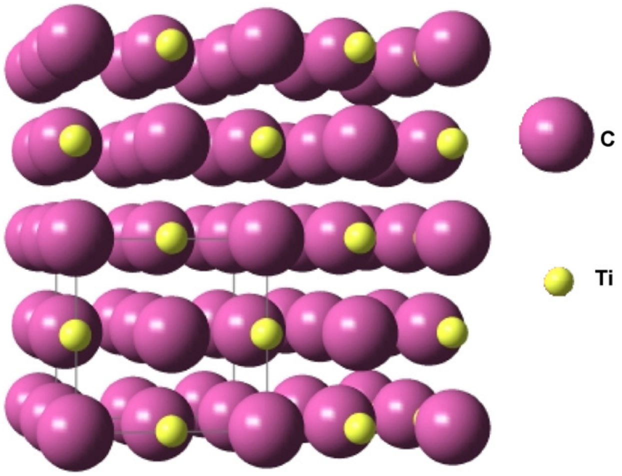

Fig. 1. $2 \times 2 \times 2$ TiC supercell (64 atoms) used in this work. The TiC unit cell (space group $Fm\bar{3}m$) is depicted with solid lines.

atomic mechanisms enabling the rapid intercalation of Al into TiC_x and the subsequent formation of Ti_3AlC_2[7] and $M_{n+1}AX_n$ phases in general. The difference between the energy of formation for an Al substitution at a C site and a bulk C vacancy is 0.224 eV. Surface effects were also considered and we found that the energy of formation for Al on TiC(1 0 0) at a vacant surface C site is smaller by 2.779 eV than in the case of the C surface vacancy, indicating that Al is likely to be incorporated. Based on these energy differences, it is reasonable to assume that the formation of Ti_3AlC_2 is formed by Al surface ingress into TiC_x and C vacancy ordering.

2. Theoretical methods

The theoretical study was carried out using density functional theory,[19] as implemented in the Vienna *ab initio* simulation package (VASP), where the projector augmented wave potentials with the generalized-gradient approximation are employed.[20] The following parameters were applied: convergence criterion for the total energy of 0.01 meV, Blöchl corrections for the total energy,[21] a cut-off of 500 eV, integration in the Brillouin zone according to Monkhorst–Pack[22] with 262,144 grid points in the FFT-mesh and no spin polarization. TiC supercells containing 64 atoms, as shown in Fig. 1, were relaxed with respect to atomic positions and cell volumes. This supercell size was chosen based on the test trials having the requirement of fully containing all local relaxation effects of a vacancy or a substitution. Bulk moduli were obtained by fitting the energy–volume curves using the Birch–Murnaghan equation of states.[23] Energy of formation (E_V or E_S) for the vacancy or Al substitution at a C site, respectively, was calculated as follows:

$$E_V = \frac{E_{TiC,V(C)} + nE_C - E_{TiC}}{n},$$
$$E_S = \frac{E_{TiC,S(Al)} + nE_C - E_{Al} - E_{TiC}}{n} \qquad (1)$$

where $E_{TiC,V(C)}$, E_C, E_{TiC}, $E_{TiC,S(Al)}$ and E_{Al} are the total energy of TiC with n C vacancies, the total energy of isolated C (broken periodic boundary conditions), the total energy of the defect-free TiC, the total energy of TiC with an Al substitution at a C site and the total energy of isolated Al (broken periodic boundary conditions), respectively. This procedure was used for describing the energetics of both bulk and surface point defects. Local lattice relaxations relative to the defect site in TiC were obtained using:

$$R_n = \frac{\Delta d_{ij}}{d_{ij}^0} \qquad (2)$$

where Δd_{ij} and d_{ij}^0 are the bond length difference and the original bond length, respectively. In order to shed some light on mobility of Al in bulk TiC, its migration energy was calculated. There are several possible pathways for Al to move to a neighbouring vacant site. Hence, we identified a saddle point in the plane perpendicular to the shortest path. The migration energy for Al in [1 1 0] direction was calculated by evaluating the energy difference between the stepwise displaced Al and the supercell with Al at its ideal site. In this procedure, Al was always quenched at its displaced position while all other atoms were fully relaxed.

3. Results and discussion

Table 1 contains the calculated data of the lattice parameters, the bulk moduli and the energy of formation for the point defects in TiC. The following bulk configurations were investigated: (i) one C vacancy, (ii) three C vacancies dispersed in the TiC lattice [(0,0,0), (1/4,3/4,0), (1/4,1/4,1/2)], (iii) three C vacancies ordered along the [1 1 0] direction [(0,0,0), (1/4,1/4,0), (1/2,1/2,0)] as well as (iv) one Al substitution at a C site. The calculated lattice parameter for TiC is 0.2% larger than the experimental value[24] and hence is in good agreement. As C vacancies are introduced, there is no significant change in the lattice parameter. On the other hand, introducing an Al substitution in the TiC_x lattice ($x < 1$) at the C site causes an increase of the lattice parameter by 0.6%, which may be explained by the larger size of Al as compared to C. The calculated bulk modulus for pure TiC is 12.1% larger than the experimentally obtained value,[25] which is within the expected deviation for the exchange-correlation approximation used here. Minor changes in the bulk moduli are observed when C vacancies or an Al substitution

Table 1
Calculated lattice parameters (a), bulk moduli (B), and energy of formation (E_V or E_S) for the C vacancy or Al substitution at a C site in bulk and surface TiC

	a (Å)	B (GPa)	E_V or E_S (eV/defect)
TiC	4.338	265	–
TiC–vacancy (single), bulk	4.338	260	9.916
TiC–vacancy (single), (1 0 0) surface	–	–	9.763
TiC–vacancy (triple)			
Bulk			
Ordered	4.339	251	10.072
Dispersed	4.339	251	10.023
TiC–Al substitution, bulk	4.366	254	10.140
TiC–Al substitution, (1 0 0) surface	–	–	6.984