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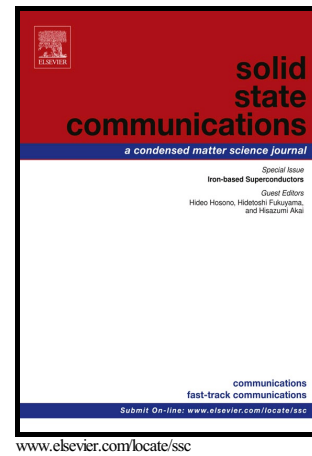
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Defect processes of M_3AlC_2 (M = V, Zr, Ta, Ti) MAX phases

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Abstract

The interest on the $M_{n+1}AX_n$ phases (M = early transition metal; A = group 13-16 element and X = C and/or N) stems from their combination of advantageous metallic and ceramic properties. Aluminium containing 312 MAX phases in particular are deemed to enhance high-temperature oxidation resistance. In the present study, we use density functional theory calculations to study the intrinsic defect processes of M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti). The calculations reveal that Ti_3AlC_2 is the more radiation tolerant 312 MAX phase considered here. In Ti_3AlC_2 the carbon Frenkel reaction is the lowest energy defect process with 3.17 eV. Results are discussed in view of recent experimental and theoretical results of related systems.

Introduction

Nowotny[1] investigated the $M_{n+1}AX_n$ phases (n = integer, M = early transition metal; A = group 13-16 element and X = C or N) phases nearly five decades ago, however, the more recent studies of Barsoum *et al.*[2,3] effectively generated the mainstream interest of the community in this system. The study of Ti_3SiC_2 and the determination of its excellent metallic and ceramic properties (good machinability, high melting temperature high thermal shock resistance, high elastic stiffness, high thermal and electrical conductivity) motivated the synthesis of numerous MAX phases and the consideration of their use in diverse fields such as in-core nuclear, aerospace and automotive applications.[2-5] These metallic and ceramic properties are interlinked to the crystal structure of the MAX phases that consists of the stacking of *n* "ceramic" layer(s) interleaved by an A "metallic" layer (refer to Fig. 1).[2-5]

$M_{n+1}AX_n$ phases have the *P6₃/mmc* space group (no. 194)[1,2] and are characterized by the highly symmetric unit cell. Figure 1 is a schematic representation of the 312 MAX phase, where it can be seen that the atomic layers stacked along the *c*-direction, whereas the M layers in essence enclose an X layer forming an M_2X slab (face-centred-cubic-type stacking sequence).[1,2] These slabs are separated by the A layers, with the stacking around the A layers having an HCP pattern.[1,2]

A key aluminium containing 312 MAX phase that motivated their investigation is Ti_3AlC_2. This is due to its good oxidation resistance in air, which is achieved via the formation of a passivating Al_2O_3 outer layer[6-8]. These properties constitute MAX phases as candidates for passive safety protection of nuclear fuel cladding[9-14] and have triggered a number of irradiation studies which have provided ample evidence of high radiation

tolerance and resistance to amorphization.[15,16] Many studies were performed to examine various MAX phases, often comparing with the important Al-containing and Si-containing phases Ti_3AlC_2 and Ti_3SiC_2 respectively.[17]

The aim of the present investigation is to determine which intrinsic defect processes is energetically favourable in M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti). The results are compared to recent studies in related systems and are assessed in view of the potential applicability of these materials in radiation environments.

Methodology

The plane wave DFT code CASTEP,[18,19] was employed for all the calculations, the exchange and correlation interactions were described by the corrected density functional of Perdew, Burke and Ernzerhof (PBE)[20] in the generalized gradient approximation (GGA) and in conjunction with ultrasoft pseudopotentials.[21] The DFT calculations involved 108-atomic site supercell under constant pressure conditions, with a plane wave basis cut-off of 450 eV and a 3 x 3 x 1 Monkhorst-Pack (MP)[22] k-point grid. To identify the lowest energy interstitial sites we performed a comprehensive search.

Results and discussion

A. Frenkel defect formation

Calculating the energies of Frenkel defects is significant (particularly for nuclear applications) as a low Frenkel pair formation energy is typically associated with a higher concentration of persistent defects. These have the potential to lead to the loss of the

3

crystal structure. The Frenkel reactions in Kröger–Vink notation are given by (in this notation V_X and X_i represent an X vacancy site and an X interstitial defect respectively)[23]

$$M_M \rightarrow V_M + M_i \tag{1}$$

$$A_A \rightarrow V_A + A_i \tag{2}$$

$$X_X \rightarrow V_X + X_i \tag{3}$$

Previous studies have illustrated that in 312 MAX phases there are numerous possible interstitial sites.[9,14] Table 1 reports the energetically favourable interstitial sites for the MAX phases considered here.

B. Antisite defect formation

Antisite defects can form in significant concentrations in a radiation environment as the non-equilibrium point defects formed via radiation can either recombine or occupy alternative lattice site forming antisites.[9,24] From a physical viewpoint low energy antisite formation energies indicate that a significant proportion of residual defects will remain in the host lattice.[9,25] In a MAX phase the antisite formation mechanisms are:

$$M_M + A_A \rightarrow M_A + A_M \tag{4}$$

$$M_M + X_X \rightarrow M_X + X_M \tag{5}$$

$$A_A + X_X \rightarrow A_X + X_A \tag{6}$$
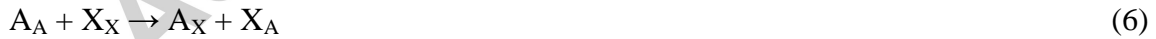
C. Interaction of interstitials with vacancies

For the interstitial defects that form in the M layer the association with V_M is described via:

$$A_i + V_M \rightarrow A_M \tag{7}$$

4

$$X_i + V_M \rightarrow X_M \tag{8}$$
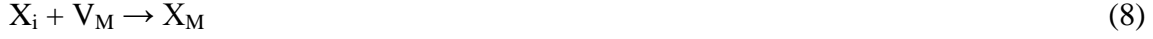
For interstitial defects forming in the A layer:

$$M_i + V_A \rightarrow M_A \tag{9}$$

$$X_i + V_A \rightarrow X_A \tag{10}$$

For interstitial defects forming in the X layer:

$$M_i + V_X \rightarrow M_X \tag{11}$$

$$A_i + V_X \rightarrow A_X \tag{12}$$

Through relations 7-12 it can be assessed whether interstitial defects will recombine with vacancies to produce antisite defects or remain as isolated defects.

D. Displacement of lattice atoms by interstitials

In a radiation environment there is an overstoichiometry of point defects such as interstitials, which can in turn lead to the formation of antisite defects (refer to relations 13-18 below):

$$M_i + A_A \rightarrow M_A + A_i \tag{13}$$

$$M_i + X_X \rightarrow M_X + X_i \tag{14}$$

$$A_i + M_M \rightarrow A_M + M_i \tag{15}$$

$$A_i + X_X \rightarrow A_X + X_i \tag{16}$$

$$X_i + M_M \rightarrow X_M + M_i \tag{17}$$

$$X_i + A_A \rightarrow X_A + A_i \tag{18}$$
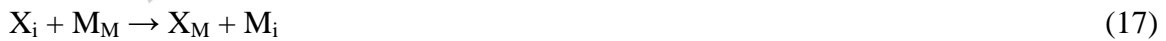
E. Implications of defect processes

The radiation performance of materials is a measure of the difficulty to form and

accommodate point defects under irradiation conditions.[24] The formation and accommodation of defects can be of importance for the material stability as an accumulation of point defects may lead to its destabilization via volume changes and microcracking.[24,26,27] It has been established that displacive radiation can lead to an athermal concentration of Frenkel (and antisite) defects and in this framework the radiation tolerance of a material will depend upon its resistance (i.e. high Frenkel and antisite defect energies) to form persistent populations of Frenkel (and antisite) defects.[24]

On the basis of the defect processes considered here using DFT (refer to Table 1) it can be concluded that Ti_3AlC_2 is the more radiation tolerant 312 MAX phase considered here. The lowest energy intrinsic defect mechanism (relation 3, carbon Frenkel reaction with 3.17 eV) in Ti_3SnC_2 is higher in energy as compared to the lowest energy intrinsic defect mechanisms of V_3AlC_2, Zr_3AlC_2 and Ta_3AlC_2. In essence, under irradiation conditions there will be fewer point defects formed in Ti_3AlC_2 as compared to the other materials considered here.

Considering in more detail the defect reactions it may be concluded that the antisite defect formation reactions 5 & 6 are never of importance. Conversely, the reaction 4 with a range of energies $2.71 - 3.85$ eV may play a role in an irradiated material. This will essentially imply that M_{Al} and Al_M antisites will form.

The interaction of interstitials with vacancies (relations 7-12) reveal that Al_i will readily interact with V_M to form Al_M (reaction 7) and that M_i will interact with V_{Al} to form M_{Al} (reaction 9). This is not the case though for reaction 10 and therefore C_{Al} antisites should not be expected to form via this route. Interestingly, reaction 8 reveals that antisite C_M may form in V_3AlC_2 and Ti_3AlC_2 but not in Zr_3AlC_2 and Ta_3AlC_2.

Regarding M_C antisites they form only in V_3AlC_2 and not in the other 312 MAX considered here (refer to reaction 11). Finally, the displacement of lattice atoms by interstitials is deemed energetically unfavourable apart from the reaction $Zr_i + Al_{Al} \rightarrow Zr_{Al} + Al_i$ in Zr_3AlC_2.

Summary

In the present study we employed DFT calculations to calculate the energetics of the intrinsic defect processes of M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti). For the MAX phases considered here the dominant intrinsic disorder mechanism was calculated to be the Frenkel reaction (C-Frenkel for Ti_3AlC_2 and Ta_3AlC_2; Al-Frenkel for Zr_3AlC_2) and antisite (relation 4 for V_3AlC_2 with C-Frenkel being only 0.02 eV higher). Apart from the antisite mechanism relation 4 which is within 0.1 eV of the dominant C Frenkel reaction for Ti_3AlC_2 other intrinsic defect processes are of lesser importance. The higher intrinsic defect energy for Ti_3AlC_2 implies its superior radiation tolerance as compared to the other 312 MAX phases considered here. Future work needs to consider the impact of point defect concentration on the lattice stability as this may impact the ability of the MAX phase to amorphize under a radiation environment. Finally, diffusion of point defects will play a role as for example the migration energy barriers of self-interstitials and vacancies to diffuse in the lattice and annihilate will need to be determined.

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Table 1. The energetically favourable interstitial sites for the M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti).

	M_i	Al_i	C_i
V_3AlC_2	0.75347, 0.66098, 0.25000	0.66206, 0.33572, 0.25072	0.33761, 0.66659, 0.24999
Zr_3AlC_2	0.75939, 0.84831, 0.25150	0.66870, 0.33984, 0.25077	0.33333, 0.66669, 0.73437
Ta_3AlC_2	-0.11020, 0.66284, 0.25083	0.66398, 0.33254, 0.25078	0.33773, 0.66668, 0.25000
Ti_3AlC_2	0.27651, 0.28686, 0.25068	0.66033, 0.33072, 0.25078	0.33588, 0.66414, 0.25002

Table 2. The calculated defect reaction energies (in eV, for relations 1-9) for the M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti).

Reaction	V_3AlC_2	Zr_3AlC_2	Ta_3AlC_2	Ti_3AlC_2
1) $M_M \rightarrow V_M + M_i$	7.40	6.12	7.43	7.32
2) $Al_{Al} \rightarrow V_{Al} + Al_i$	6.31	1.46	5.84	3.40
3) $C_C \rightarrow V_C + C_i$	2.73	3.47	2.87	3.17
4) $M_M + Al_{Al} \rightarrow M_{Al} + Al_M$	2.71	3.46	3.85	3.27
5) $M_M + C_C \rightarrow M_C + C_M$	9.80	10.60	17.36	10.52
6) $Al_{Al} + C_C \rightarrow Al_C + C_{Al}$	9.36	8.43	10.67	9.26
7) $Al_i + V_M \rightarrow Al_M$	-5.38	-2.39	-4.44	-4.20
8) $C_i + V_M \rightarrow C_M$	-1.15	0.14	1.35	-0.48
9) $M_i + V_{Al} \rightarrow M_{Al}$	-5.63	-1.72	-4.97	-3.25
10) $C_i + V_{Al} \rightarrow C_{Al}$	0.21	0.46	0.58	0.31
11) $M_i + V_C \rightarrow M_C$	-0.63	0.86	5.72	0.51
12) $Al_i + V_C \rightarrow Al_C$	0.12	3.04	1.39	2.39
13) $M_i + Al_{Al} \rightarrow M_{Al} + Al_i$	0.68	-0.27	0.87	0.15
14) $M_i + C_C \rightarrow M_C + C_i$	2.10	4.33	8.58	3.68
15) $Al_i + M_M \rightarrow Al_M + M_i$	2.03	3.73	2.99	3.13
16) $Al_i + C_C \rightarrow Al_C + C_i$	2.85	6.51	4.25	5.55
17) $C_i + M_M \rightarrow C_M + M_i$	7.70	6.26	8.78	6.84
18) $C_i + Al_{Al} \rightarrow C_{Al} + Al_i$	6.51	1.92	6.42	3.71

FIGURE CAPTIONS

M-2 layer
X layer
M-1 layer

Al layer

M-1 layer
X layer
M-2 layer
X layer
M-1 layer

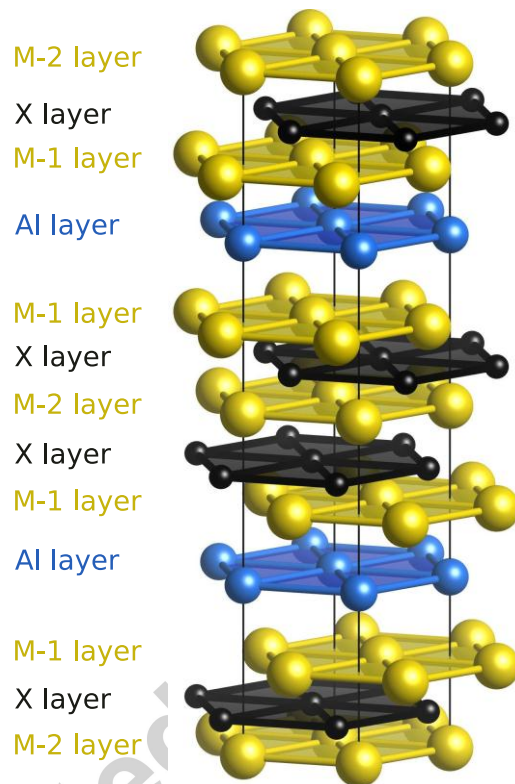Al layer

M-1 layer
X layer
M-2 layer

Figure 1. Crystal structure of the M_3AlC_2 MAX phases (M = V, Zr, Ta, Ti).

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Highlights

a) Al containing 312 MAX phases have enhanced high-T oxidation resistance

b) We use DFT to study the intrinsic defect processes of M_3AlC_2 MAX phases

c) Ti_3AlC_2 is the more radiation tolerant 312 MAX phase considered

d) In Ti_3AlC_2 the C Frenkel reaction is the lowest energy defect process with 3.17 eV