Heavy ion irradiation damage in Zr₂AlC MAX phase

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Abstract

Zr₂AlC MAX phase-based ceramic material with 33 wt.% ZrC has been irradiated with 22 MeV Au⁷⁺ ions between room temperature and 600°C, achieving a maximum nominal midrange dose of 3.5 displacements per atom. The response of the material to irradiation has been studied using scanning electron microscopy, transmission electron microscopy and X-ray diffraction. Under room temperature irradiation, the ions caused a partial amorphisation of the MAX phase. At high temperatures, irradiated Zr₂AlC remained crystalline, but developed an increased density of dislocations and stacking faults in the (0001) basal planes. The irradiated material also exhibited a temperature-dependent microcracking phenomenon similar to that previously reported in other MAX phase materials.

1. Introduction

MAX phases are a relatively new family of ceramic materials which are also referred to as nano-lamellar ceramics. Their name comes from their crystal structure, in which planes of strong metallic bonds and planes of weaker non-metallic bonds are structured in succession. As a consequence of the distinct covalent and metallic bonds within these phases, they have unique properties reflecting aspects of both metals and ceramics [1]. They generally have good electrical and thermal conductivity, good thermal diffusivity, and are oxidation resistant [2]. Their properties have made them attractive to material scientists seeking to replace existing materials used for high temperature applications [3]. For example, MAX phases are being studied as fuel cladding materials in nuclear reactors in both bulk form and as coatings [4]. Various members of the MAX phase family have been nominated as candidates for materials in the nuclear industry. These are mainly Ti-based MAX phases [5–8] but there are also variations incorporating Cr and V [9]. Zr-based MAX phases are of particular interest for use in nuclear reactors because of the superior neutronic properties exhibited by Zr. Zr has a relatively low thermal neutron absorption cross-section, meaning that it is relatively neutron transparent and can therefore be advantageous in maintaining a high neutron economy in nuclear reactors [10]. For this reason, it is systematically exploited in current generation nuclear reactors. One particular Zr-based MAX phase that is thought to be potentially

useful in nuclear environments is Zr_2AlC [11,12]. The high neutron transparency of Zr in this phase will offer highly desirable reactor neutronics and fuel economics. In addition, the presence of the Al component is thought to help form a protective oxide layer for high temperature steam oxidation resistance [12,13], although this is yet to be established.

MAX phases are layered carbides or nitrides described by the general formula $\text{M}_{n+1}\text{AX}_n$, (MAX) where M corresponds to an early transition metal, A to the A-group elements, X is either carbon or nitrogen and n is an integer, commonly equal to 1, 2 or 3 [14,15]. They all have a hexagonal crystal structure and belong to the space group $P6_3/mmc$. One X atom is bonded to 6 M atoms forming an M_6X octahedron. The octahedra alternate in between layers of pure A elements located at the centres of the trigonal prisms. The structure of Zr_2AlC , a M_2AX (211) type, is illustrated in Fig. 1 where the M, A and X elements are Zr, Al and C respectively.

The irradiation resistance of a candidate material is an important factor during the screening of materials for nuclear applications, particularly those that are situated in the reactor core. Hence, numerous MAX phases have been tested for their irradiation resistance. Reported studies from irradiated Ti_3SiC_2 show a variety of responses to high energy heavy ion irradiation. For instance, upon irradiation with Xe^{2+} ions to 10 displacements per atom (dpa) at room temperature and -223°C , Ti_3SiC_2 demonstrated good irradiation tolerance, i.e. it showed little amorphisation and radiation-induced defects [5]. In contrast to this, Zhang et al. [16] reported the irradiation-induced transformation of Ti_3SiC_2 into TiC upon irradiating with I^{2+} ions to 10.3 dpa up to 250°C . However, this MAX phase did not completely decompose. Song et al. [6] also reported the phase transformation of Ti_3AlC_2 into TiC upon irradiating with He^{2+} ions to 52 dpa at room temperature, 300°C and 500°C . Le Flem et al. [17] showed that irradiation of $\text{Ti}_3(\text{Si,Al})\text{C}_2$ with 93 MeV Xe ions to 6.67 dpa highly disrupted the layered structure of $\text{Ti}_3(\text{Si,Al})\text{C}_2$, but that it did not completely induce amorphisation. Liu et al. [18] revealed an irradiation-induced phase transformation of $\text{Ti}_3(\text{Si,Al})\text{C}_2$ into $\beta\text{-Ti}_3(\text{Si,Al})\text{C}_2$, a phase with a rearranged stacking sequence. Other experiments have shown MAX phases to be unsuitable in irradiation environments. For example, Clark et al. [19] reported high damage in Ti_3AlC_2 and concluded that the material was not fit for structural applications in irradiation environments near 400°C because of the formation of surface cracks and crystal amorphisation. Tallman et al. [20] showed that Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC and Ti_2AlN remained fully crystalline under neutron irradiation up to 0.1 dpa at 360 and 695°C . All the phases except Ti_2AlC were reported to dissociate into their respective MX compounds, while Ti_2AlC showed greater stability in neutron environments. Overall, it is evident that the present studies on irradiated MAX phases show that their irradiation tolerances are highly sensitive to the elements and exact stoichiometry of the respective phases.

Table 1Structural Parameters of Zr_2AlC and ZrC .

Formula	Zr_2AlC	ZrC
Lattice parameters (Å)	a : 3.3237(2) Å c : 14.5705(4) Å	a : 4.6796(3) Å
Space group	$P6_3/mmc$ (194)	$Fm\bar{3}m$ (225)
Atomic positions		
Zr	4f	4a
C	2c	4b
Al	2a

Fig. 1. (a) the unit cell of Zr_2AlC , (b) projection in real space along $[11\bar{2}0]$ and (c) projection in real space along $[1\bar{1}00]$. In each figure the $[0001]$ direction is vertical.

2. Experimental

2.1. Material

The Zr_2AlC MAX phase material used in these experiments was synthesised at KU Leuven, Belgium; a comprehensive description of the synthesis method is reported by Lapauw et al. [21]. In brief, powders of stoichiometric mixtures of ZrH_2 , Al, and graphite were mixed in a Zr:Al:C ratios of 2:08:1.2 and milled by ZrO_2 balls in isopropanol for 12 hours, after which the powder was hot pressed at 1200°C for one hour. Rietveld analysis of XRD data showed that the

synthesised material contained 67 wt.% Zr₂AlC, 33 wt.% ZrC and traces of intermetallic phases [20]. The bulk material was sectioned into cubes of 5 mm sides and polished on one side to a 0.2 µm finish with an ordinary diamond suspension. The samples were then cleaned using acetone, followed by methanol, in an ultrasonic bath for 10 minutes.

2.2. Irradiation experiments

The ion irradiation experiments were performed at the Ion Beam Centre (IBC) at Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Germany. The irradiation was performed using a 3 MV Tandetron accelerator under high vacuum (3×10^{-6} mbar) [22]. The accelerator supplied a scanning beam of Au⁷⁺ ions at 22 MeV. Irradiation experiments were performed at room temperature (RT), 300°C and 600°C ($\pm 20^\circ\text{C}$). The sample holder was fixed with thermocouples to allow for the temperature to be monitored during the experiments. There was no cooling during the room temperature experiments, but due to the low ion flux, temperatures did not exceed 40°C. For high temperature experiments, a dedicated in-situ heating holder was fitted. Samples were locked onto the stage with stainless steel clips and a sheet of aluminium foil between the sample and the heater to maximise surface contact; this allowed the homogeneous transfer of heat. Once the irradiation was completed, the chamber was allowed to cool to room temperature and was vented with nitrogen gas. A full list of the irradiation experiments is summarised in Table 2.

The ion damage levels in Zr₂AlC were estimated by the Monte Carlo simulation programme SRIM 2008. The results from the simulation estimated the dpa values and an estimation of the ion implantation depth below the surface. The Kinchin-Pease quick calculation method was used with threshold displacement energies of 40, 25, and 28 for Zr, Al and C respectively. The dpa profile for 22 MeV Au⁷⁺ ions against the penetration depth is presented in Fig. 2. It should be noted that the reported damage is the maximum damage in the analysed region and is not uniform throughout the sample.

Table 2

Conditions of the irradiation experiments.

Midrange dose (dpa)	Fluence ($\times 10^{13}$ ions/cm ²)	Temperature (°C)
1.0	7.2	RT
1.0	7.2	300
1.0	7.2	600
3.5	22.0	RT
3.5	22.0	300
3.5	22.0	600

Fig. 2. Estimated damage (dpa) profile induced by 22 MeV Au⁷⁺ irradiation on Zr₂AlC for high and low irradiation doses as a function of ion penetration depth.

2.3. Analytical procedures

A FEI Nova NanoSEM SEM fitted with an Energy Dispersive X-ray (EDX) spectroscope was used to collect backscattered electron and secondary electron images. Thin film lamellae were extracted using a Focused Ion Beam (FIB) instrument (FEI Helios Nanolab Dual Beam FIB SEM). Samples were milled and transferred to copper grids, following the standard lift-out procedure [23]. The lamella were then milled with Ga ions to a thickness of 100 nm using a 2 kV, 8 pA probe. The very low currents used in the final cleaning step ensured that ion beam artefacts were minimised and did not overshadow effects caused from the irradiation experiments. A JEOL 200CX TEM was used to obtain bright and dark field images, and selected area diffraction (SAED) patterns. This instrument is fitted with a tungsten electron source and has a maximum operating voltage of 200 kV. The smallest area of analysis was equivalent to that of a circle with a diameter of 500 nm. A Bruker D8 X-ray diffractometer was used for X-ray diffraction (XRD) measurements, which operated in reflection mode at 40 kV and 40 mA with both CuK_{α1} and CuK_{α2} radiation of wavelength 1.5406 Å and 1.5433 Å respectively. An angle of incidence of 4° was chosen for the incident X-ray beams. This allowed the X-rays to target the top surface of sample (approx. 10 μm below the surface) and reduce reflections from the unirradiated bulk material. This X-ray penetration depth was estimated by the Highscore Plus programme assuming the density of Zr₂AlC to be 4.5 g/cm³. The detector was fitted with a long parallel collimator and 8200 steps at three seconds per step were recorded between 30° and 60° 2θ. In order to analyse the patterns, the PANalytical HighScore Plus software package was used. Lattice parameter measurements were recorded from the two-theta positions. It should be noted that the penetration of the X-rays is deeper than the stopping

range of Au^{7+} in Zr_2AlC , but the contribution from the non-irradiated bulk is not expected to have affected the comparison between irradiated samples.

3. Results

3.1. Irradiation-induced microcracking

The microstructure of the pristine material is shown in the backscattered SEM image in Fig. 3. The microstructure mainly consists of Zr_2AlC with large grains $\sim 10\ \mu\text{m}$ in size, and clusters of smaller ZrC grains. Characteristic MAX phase cracks parallel to the (0001) basal planes are observed in some Zr_2AlC grains.

Fig. 3. (a) and (b) Backscattered SEM images of the microstructure of the pristine surface at different magnifications.

Topographical disparities developed as a result of irradiation. The irradiated surfaces for six conditions with various ion dosage and temperatures are presented in Fig. 4 (a-f): (a) 3.5 dpa at RT, (b) 3.5 dpa at 300°C , (c) 3.5 dpa at 600°C , (d) 1.0 dpa at RT, (e) 1.0 dpa at 300°C , and (f) 1.0 dpa at 600°C . The most prominent effect observed across all conditions is the development of microcracks; this effect is most substantial as a result of irradiating at 300°C . By comparison, no microcracks were observed at either RT or 600°C irradiation conditions. The microcracks that formed as a result of ion irradiation at 300°C were all intergranular. In an attempt to establish whether the microcracking was induced by the ion irradiation or by the annealing treatment, unirradiated samples were annealed at identical rates (i.e. heating and cooling rates and dwell times) to the 300°C irradiation experiment but were shown not to crack. This suggests that the microcracks arose as the result of the combined phenomena of irradiation and high temperature. To quantify the degree of surface cracking induced by the heat treatments and irradiation, randomly oriented lines were drawn on the SEM images. The average number of

interceptions between the line and the cracks were then measured. Measurements on the 300°C sample were shown to be 0.092 and 0.093 cracks/ μm for 1.0 and 3.5 dpa conditions respectively, i.e. very similar. A distribution of the average crack length was also measured from the SEM images. A random surface area equivalent to 100 μm^2 was chosen and the total length of all the cracks were measured. The average crack length from both samples irradiated at 300°C 1.0 and 3.5 dpa was shown to be 12.3 ($\pm$ 0.5) and 11.6 ($\pm$ 0.5) μm respectively, also very similar.

Fig. 4. Backscattered SEM images of Zr_2AlC at different ion irradiation conditions (a) 3.5 at dpa-RT, (b) 3.5 dpa at 300°C, (c) 3.5 dpa at 600°C, (d) 1 dpa at RT, (e) 1.0 dpa at 300°C, and (f) 1.0 dpa at 600°C.

3.2. XRD analysis

The XRD patterns collected from Zr_2AlC before and after irradiation at RT, 300°C and 600°C, irradiated to 1.0 and 3.5 dpa respectively are presented in Fig. 5. The patterns are displayed between 30 and 60° 2 θ : this range covers the majority of the intense diffraction reflections in Zr_2AlC , while maintaining a reasonably stable X-ray interaction volume in the sample. Reflections from the secondary phase ZrC are also labelled. It should be noted that there are no obvious Bragg reflections relating to other phases.

3.2.1. Room temperature irradiation

It is evident that RT irradiation changes in the crystal structure of the Zr_2AlC . At both 1.0 and 3.5 dpa, a major drop in the intensity of the reflections and peak broadening were observed. The drop in intensity indicates a loss in crystallinity and the peak broadening suggests the accumulation of micro-strain within the Zr_2AlC grains. The most prominent modification is the decrease in intensity of the 013 and 006 reflections at 1.0 dpa, which are suppressed further at 3.5 dpa. In addition, a very broad peak, characteristic of scattering from amorphous material, forms between 32 and $40^\circ 2\theta$. Again, the hump-like peak is more significant at 3.5 dpa. This further suggested that higher irradiation doses resulted in greater damage to the crystalline material. The secondary phase ZrC , marked with a blue circle in Fig. 5, does not seem to be affected by irradiation. The effect of irradiation on the crystalline peaks at RT is also notably much greater than at higher temperatures. RT irradiation does not appear to suggest a phase transformation but rather the direct amorphisation of the Zr_2AlC .

3.2.2. High temperature irradiation

In comparison with RT experiments, the crystallinity of Zr_2AlC is better maintained upon irradiation at 300°C at both doses. This implies that Zr_2AlC exhibits an enhanced crystal recovery upon irradiation at high temperatures. As expected, irradiation at 3.5 dpa suggests a suppression in crystallinity relative to 1.0 dpa: a drop in intensity of the 013 and 006 reflections is apparent and an enhanced amorphous hump which is visible between 32° and $40^\circ 2\theta$. Most obviously, irradiation at this temperature produces substantial peak broadening of the 101, 006, 013 and 104 reflections. The broadening infers a build-up of micro-strain, consistent with an increase in the density of defects along these planes. At the highest irradiation temperature, 600°C , the phase remains almost unaltered at both doses, with only minor modifications to the intensities and a slight peak broadening. The 006 reflection is the most suppressed. The pattern suggests that any amorphous hump present would be incorporated in the background. These observations imply that temperature has a substantial effect on the recrystallisation of Zr_2AlC upon irradiation. Lattice parameter measurements from all the XRD patterns are summarised in Table 3. Measurements reveal that there is little distortion in both a and c parameters at all doses, precluding a subtle change upon irradiation at 600°C at both 1.0 and 3.5 dpa.

Fig. 5. XRD patterns collected from the material before and after irradiation to 1.0 and 3.5 dpa at RT, 300°C, and 600°C respectively. The peaks marked with a blue circle correspond to the secondary ZrC phase.

Table 3

Lattice parameter measurements of Zr_2AlC at different irradiation conditions.

dpa	°C	a (Å)	c (Å)	% change a	% change c
0	RT	3.323(6)	14.566(6)	-	-
0	300	3.319(9)	14.561(1)	-0.1136	-0.0378
0	600	3.321(6)	14.565(9)	-0.0619	-0.0045
1.0	RT	3.323(2)	14.562(4)	-0.0117	-0.0286
1.0	300	3.325(5)	14.574(3)	0.0571	0.0530
1.0	600	3.310(8)	14.653(3)	-0.3860	0.5950
3.5	RT	3.325(4)	14.576(7)	0.0528	0.0691
3.5	300	3.322(5)	14.565(5)	-0.0333	-0.0095
3.5	600	3.313(1)	14.626(5)	-0.3177	0.4113

3.3. TEM analysis

SAED patterns from lamellae extracted from Zr_2AlC irradiated at different conditions are shown in Fig. 6. The lamellae were extracted from the irradiated region at a depth of between 2-4 μm below the surface, which corresponds to the maximum nominal midrange dose (Fig. 2). The selected zone axes were taken to show the diffraction spots along the (000l) set of reflections. Diffuse scattering halo rings were observed at both RT irradiation conditions. These distinct halo rings are indicative of the loss of long-range atomic order and amorphisation. These observations compliment the XRD patterns, which also suggest an extensive loss in crystallinity and the formation of amorphous material. SAED patterns from Zr_2AlC irradiated at 300°C and 600°C reveal that the phase remains highly crystalline following irradiation, again consistent with interpretations from XRD patterns.

Fig. 6. SAED patterns of Zr_2AlC grains irradiated with 22 MeV Au^{7+} ions at different irradiation conditions (a) 3.5 dpa at RT, (b) 3.5 dpa at 300°C, (c) 3.5 dpa at 600°C, (d) 1.0 dpa at RT, (e) 1.0 dpa at 300°C, (f) 1.0 dpa at 600°C. The patterns are obtained from different samples and are taken at different zone axes but mostly presenting the [000l] systematic row of reflections.

The pristine region of Zr_2AlC revealed the grains to be distinctively featureless from defects. Very few dislocations and stacking faults were observed, which is typical of unirradiated MAX phase ceramics. The irradiation of the MAX phase introduces a high density of dislocations and stacking faults, most notably upon irradiation at high temperature. The defects observed in Zr_2AlC were mainly dislocations and stacking faults. Dislocations (500 nm long in projection) were most usually scattered 500 nm apart in the irradiated region and were scarce. Stacking faults can either propagate across a grain between two grain

boundaries, propagate partially across the grain to a cluster of dislocations, or be bound by two dislocations within the grain (Fig. 7).

Fig. 7. Schematic of defect types observed in irradiated Zr_2AlC

At both doses irradiated at RT, the Zr_2AlC became partially amorphous and developed a low density of dislocations. At 300°C amorphous regions were not evident, but there was a noticeable increase in dislocation density. The defects present were arranged in large clusters, predominantly along the basal planes: these are consistent with defects observed in other irradiated MAX phases [17]. Large stacking faults decorated with dislocations were seen in some irradiated regions.

The micrographs in Fig. 8 show dislocations and stacking faults in Zr_2AlC irradiated to 3.5 dpa at 600°C . Parallel arrays of stacking faults were observed. The majority of the MAX phase grains were decorated with a low density of large dislocations (Fig. 8 a). The contrast from these faults is not uniform along a given line. Upon observation at different orientations, distinctive stacking faults along the basal plane are seen to be bound by perpendicular dislocations (Fig. 8 b). As marked on the figure, the partial dislocations are labelled D1-D4 and stacking faults labelled SF1-SF4. Trace analysis showed that the dislocations lie on the basal planes. Two beam conditions were used to determine the Burgers vector $\mathbf{b}$ of the dislocations through the invisibility condition $\mathbf{g} \cdot \mathbf{b} = \mathbf{0}$ for suitable diffracting reciprocal lattice vectors $\mathbf{g}$ (Fig. 9). When $\mathbf{g}$ vectors lying in the $[11\bar{2}0]$ zone were selected for these two beam conditions, the contrast of the dislocations relative to the background of the grains was always weak (similar to the contrast seen in Fig. 9 c), consistent with what is expected for the invisibility criteria. Conversely for $\mathbf{g}$ vectors not in this zone, the same dislocations gave strong contrast, such as in the $[1\bar{2}10]$ zone in Fig. 10 (a). Hence it can be concluded that the Burgers vector of these dislocations are $\frac{1}{3}[11\bar{2}0]$.

Fig. 8. Defects in Zr_2AlC irradiated to 3.5 dpa at 600°C: **(a)** (A) arrays of parallel stacking faults across the whole grain, (B) faceted grain boundary and (C) stacking fault bound by dislocations. **(b)** Stacking faults labelled SF1-SF4 are bound by dislocations labelled D1-D4 are situated within the grain and are on the (0001) planes.

Fig. 9. Defects in Zr_2AlC irradiated to 3.5 dpa at 300°C: **(a)** showing dislocations **(b)** Arrays of dislocations (approx. 0.5 μm in length in projection).

Fig. 10. Features along the (000l) axis on Zr_2AlC irradiated to 3.5 dpa at 600°C: (a) Stacking faults and dislocations on the 000l planes, its corresponding SAED is indexed (b). (c) The same defects imaged at the orientation from the SAED (d), showing weak contrast.

4. Discussion

4.1. Defect evolution in Zr_2AlC

Irradiation temperature normally has a great influence on the microstructural response of a material to irradiation. At low temperatures, defects created by energetic ions have very low mobility and tend to accumulate until newly created defects annihilate pre-existing ones. The defect accumulation is characteristically proportional to the dose. Prolonged irradiation of ceramics at low temperatures typically leads to amorphisation [24–26]. This is observed upon the irradiation of Zr_2AlC at room temperature, where the phase only

retained partial crystallinity. As a result of the lack of thermal energy in the Zr_2AlC crystal system at room temperature, defects did not diffuse or combine into particular low energy defect zones. These zones are along the basal planes (0001) for the hexagonal close packed (hcp) crystal structure of Zr_2AlC . As a result of this poor dynamic defect recovery, there is an overall net accumulation of defects localised in the damaged region.

The XRD and TEM results show the susceptibilities of Zr_2AlC to irradiation-induced amorphisation. Prolonged irradiation causes the damage instigated by the ion particles to become increase and the multilayer crystal structure of Zr_2AlC eventually disappears, becoming amorphous. This is observed in RT irradiation at 1.0 dpa in Fig. 5. This analysis is further supported by the decrease in crystallinity observed at 3.5 dpa relative to 1.0 dpa irradiation. The drop in intensity from XRD reflections reveals that there is a substantial decrease in crystal order, at both 1.0 and 3.5 dpa. Further, the formation of the broad hump-like peak suggests that the phase becomes amorphous. This is also supported by the TEM SAED micrographs from Fig. 7, which reveal a distinctive amorphous halo ring. Bugnet et al. [27] observed amorphisation in Cr_2AlC upon RT irradiation, and Wang et al. [9] showed that the prolonged irradiation of Cr_2AlC exhibited a decrease in phase crystallinity at room temperature. Wang et al. also reported that V_2AlC gradually transformed into face-centred cubic (fcc) structure from the original (hcp) structure without amorphisation [9]. Contrary to the findings of previous studies on other MAX phases, the XRD and SAED results of this study showed no evidence of irradiation-induced crystalline phase transformations in Zr_2AlC .

Defects with the lowest formation energies are the most likely to be created as a result of ion bombardment. *Ab initio* simulations of defect formation in Zr_2AlC have been reported by Shah et al. [28]. Although these calculations can only suggest the irradiation tolerance of this phase, they can give an indication on the likelihood of certain elements to form defects, as well as their corresponding defect types. They report that the preferred defects in Zr_2AlC are a Frenkel pair of an Al vacancy and Al interstitial (V_{Al} and Al_{I}) but also energetically favourable antisites of Zr and Al (Zr_{Al} + Al_{Zr}). This means that the Al component is most likely to form interstitial defects and that Zr and Al are likely to exchange sites in the layered structure. Zr_2AlC is a low-density layered crystal structure that has sufficient space between its layers, which can easily accommodate interstitial atoms. Their findings suggest that these defects preserve the lattice coherence and offers a viable recovery mechanism during irradiation which makes the material highly radiation tolerant.

Irradiation of Zr_2AlC at higher temperatures offers defects created by the irradiation much higher mobility, consequently allowing defects migrate to recombine with sessile vacancies or agglomerate to form dislocations and stacking faults. After irradiation above 300°C, the microstructure of Zr_2AlC revealed a higher degree of crystallinity, and TEM showed the presence of a number of crystal defects in the irradiated zone (Fig. 9). These were mainly dislocation lines and stacking faults. At 300°C and 600°C defect mobility was

high and defects were able to relax into lower energy zones. Both XRD reflections and TEM micrographs revealed that the structure remained highly ordered but with an increased density of crystal defects, mostly dislocations lines.

4.2. Crack development

Clark et al. [19] observed an interesting crack-development phenomenon upon irradiating Ti_3AlC_2 . They reported the appearance of surface cracks at 400°C irradiation conditions, but not at either RT or 700°C. These cracks were described to form as a result of the anisotropic swelling of the material and were shown to be highly correlated with lattice parameter distortions, which were highest at 400°C. The cause of intergranular cracks here on irradiated Zr_2AlC at only 300°C conditions follows similar trends to work by Clark et al. but the cause of the cracks is thought to be different. Firstly, in Zr_2AlC , it is apparent that the highest distortions in lattice parameters are upon irradiation at 600°C (Table 3). The slight increase in c parameter and decrease in a parameter is consistent with other irradiated MAX phase work [29–31]. However, the distortions are still relatively low at 600°C and consequently no cracks appeared. Secondly, as opposed to Zr_2AlC , Ti_3AlC_2 shows no sign of amorphisation even after RT irradiation. Clark et al. describe the changes in lattice parameters and swelling at 400°C to be in the ‘point defect swelling regime’: a stage of temperature and irradiation-related volumetric swelling whereby the magnitude of swelling is significantly higher at a material-specific temperature range. The lack of amorphisation at 300°C in our work here suggests that structured defects contribute to the microstructural strain in Zr_2AlC .

While cracking was observed in Zr_2AlC at 300°C but not at RT or 600°C (Fig. 5), there was no correlation between the bulk swelling of the material and the formation of cracks. Therefore, it is suggested that lattice parameter distortions are not the cause of crack development. XRD reflections broaden when crystal imperfections are introduced. The large peak broadening from XRD patterns at 300°C suggests that lattice defects are present in abundance, which is also apparent from TEM micrographs. This abundance of dislocations and other strain fields such as stacking faults, twin faults or layer disorder develops excessive micro-strain in the grains. In Zr_2AlC the excessive strain lead to the swelling of the grains and resulted in the development of intergranular cracks exclusive to the grain boundaries. In an experiment to study the effects of irradiation of bulk Mo at various temperatures, Birmhall et al. [32] showed that swelling in their material was formed as a consequence of the build-up of immobile defects. They found that swelling decreased as the defects become more mobile and fell into sinks at temperatures above 300°C. This is what is suggested to be the case in Zr_2AlC , whereby Al interstitials and vacancies diffuse to form dislocation lines.

The increase in XRD peak broadening is suggestive of micro-strain, which is thought to be the cause of crack formation in Zr_2AlC at 300°C. It is important to note that the influence of thermal expansion between the two phases, Zr_2AlC

and ZrC (33 wt. %), has been disregarded in this analysis. As the differential swelling of the two phases in this material would have resulted in crack formation at both 300 °C and 600 °C, but this is not the case. It is thought that the cracking forms solely as a result of the micro-strain development from Zr₂AlC, though this does not explain the lack of crack formation at 600°C.

Linking the defect density observed through TEM micrographs, there was an obvious increase in the density of defects at 300°C irradiation conditions. However, it was difficult to quantify and compare the defect densities with 600°C irradiation conditions. XRD reflections revealed that the micro-strain at 600°C was much less noticeable than at 300°C irradiation conditions, which further supports the hypothesis that the microcracking arises as a consequence of internal micro-strain.

5. Conclusions

Zr₂AlC-rich material was irradiated with 22 MeV Au⁷⁺ ions reaching estimated damage levels of 1.0 and 3.5 dpa. Results from XRD and SAED analysis in the damaged region between 1 and 4 µm below the irradiated surface suggested a high post-irradiation stability of the Zr₂AlC phase, but the phase became predominantly amorphous at RT at both 1.0 and 3.5 dpa. The degree of crystallinity was higher upon irradiating at 300°C and 600°C. TEM analysis showed that Zr₂AlC has a higher density of crystal defects following irradiation at high temperatures, and that there was an increase in (0001) stacking faults across most MAX phase material. XRD revealed that at 300°C defects agglomerated to form defect clusters, reducing amorphisation but increasing lattice strain. This indicated that the temperature of the point defect annihilation region for Zr₂AlC is around 300°C: above this range, the mobility of defects is sufficient to suppress amorphisation. The temperature-dependent microcracking phenomenon observed at 300°C suggested that the defects, mainly Al interstitials agglomerated into defect zones along the basal planes in Zr₂AlC. However, these defect clusters caused high lattice strains as they were not able to relax into optimum low energy clusters. This build-up of defects resulted in intergranular cracking that was exclusively observed at the grain boundaries. According to the results from these particular irradiation experiments, Zr₂AlC does not have a high resistance to irradiation damage at low temperatures. The microcracking observations show that it could only be considered fit for structural applications at continuous operating temperatures above 300°C. Under these circumstances, the irradiation tolerance and low neutron absorption cross-section of this phase may be very advantageous.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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