Effect of neutron irradiation on select MAX phases

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Abstract

Herein we report on the effect of neutron irradiation – of up to 0.1 displacements per atom at 360(20)°C or 695(25)°C – on polycrystalline samples of Ti₃AlC₂, Ti₂AlC, Ti₃SiC₂ and Ti₂AlN. X-ray diffraction refinement of the irradiated samples showed irradiation-enhanced dissociation into TiC of the Ti₃AlC₂ and Ti₃SiC₂ phases, most prominently in the former. Ti₂AlN also showed an increase in TiN content, as well as Ti₄AlN₃ after irradiation. In contrast, Ti₂AlC was quite stable under these irradiation conditions. Dislocation loops are seen to form in Ti₂AlC and Ti₃AlC₂ after irradiation at 360(20)°C. The room temperature electrical resistivity of all samples increased by an order of magnitude after irradiation at 360(20)°C, but only by 25% after 695(25)°C, providing evidence for the MAX phases' dynamic recovery at temperatures as low as 695(25)°C. Based on these preliminary results, it appears that Ti₂AlC and Ti₃SiC₂ are the more promising materials for high-temperature nuclear applications.

Keywords: Ti₂AlC; Ti₃SiC₂; Ti₃AlC₂; Neutron irradiation; Rietveld refinement

1. Introduction

Gen IV nuclear reactor designs require materials that can withstand long-term operation in extreme environments of elevated temperatures, corrosive media and fast neutron fluences with up to 100 displacements per atom (dpa) [1]. A full understanding of the irradiation response in selected materials is paramount to long-term, reliable service. The $M_{n+1}AX_n$ (MAX) phases are a class of layered, machinable, ternary carbides and/or nitrides, where M is an early transition metal, A is a group 13 to 16 element and X is C and/or N. These compounds possess a unique set of properties, both metallic and ceramic in nature. For example, some of them exhibit relatively high fracture toughness values (8-12 MPa $\sqrt{m}$) and are elastically stiff like their binary carbide and nitride counterparts, and yet are readily machinable, lightweight and relatively soft [2-6]. The MAX phases also undergo plastic-to-brittle transitions at high temperatures, and the materials can withstand high compressive stresses at room temperature (RT) [2,5]. Al-containing MAX phases also show excellent oxidation resistance in air and in the presence of water vapor [7-10].

Many recent studies have explored the damage tolerance and amorphization resistance of several MAX phases irradiated with heavy ions [11-21]. In 2009, Nappé et al. explored the effect of 90 MeV Xe ions on Ti_3SiC_2 , showing surface layer amorphization of the Ti_3SiC_2 and impurity phases, as well as selective grain boundary sputtering due to nuclear interactions [11]. Liu et al. characterized Al-doped Ti_3SiC_2 , irradiated to a maximum dose of 3.25 dpa with high-energy Kr and Xe ions, via X-ray diffraction (XRD) and nanoindentation showing an expansion of the c-lattice parameter, c-LP, and irradiation-induced hardness that could be annealed out at 800°C [16,17]. They also reported the possible existence of a β - Ti_3SiC_2 phase to explain the presence of new peaks found in the post-irradiated XRD patterns [17]. Soon after, Le Flem et al. reported on selected area diffraction (SAD) patterns in a transmission electron microscope (TEM) of $Ti_3(Si,Al)C_2$ irradiated with 92 MeV Xe ions up to 6.67 dpa, which further

confirmed this MAX phases' resistance to amorphization [18]. With increasing dose, diffraction peaks were found to disappear due to lattice disturbances. In 2010, Bugnet et al. explored the effect of 100 keV Ar^{2+} ion irradiation on multilayered $(\text{Ti,Al})\text{N}/\text{Ti}_2\text{AlN}_x$ nitrogen-deficient thin films, reporting that the multilayered structure was preserved up to a dose of 12 dpa, likely due to nitrogen vacancies acting as sinks for interstitial point defects [21].

Along the same lines, Whittle et al. reported that Ti_3AlC_2 and Ti_3SiC_2 possess very high resistance to amorphization, even up to 25 dpa, irradiated with 1 MeV Kr^{2+} and 1 MeV Xe^{2+} [15]. Nappé et al. reported that nuclear collisions with 4 MeV Au ions, up to a dose of 4.3 dpa, resulted in a 2.2% swelling in Ti_3SiC_2 [12]. Also in 2011, Nappé et al. investigated the structural changes of Ti_3SiC_2 under a variety of ions and energies, concluding that Ti_3SiC_2 is not sensitive to electrical interactions, and confirmed that nuclear collisions lead to an increase in c-LP and a decrease in the a lattice parameter, a-LP, and a concomitant increase in lattice microstrains [14]. In 2012, Zhang et al. reported that a TiC and/or 3C-SiC (cubic β) nanocrystalline phase formed under 2 MeV I^{2+} irradiation of Ti_3SiC_2 , though the material did not fully decompose, even up to 10.3 dpa [20]. In 2013, Le Flem and Monnet reported on a saturation in irradiation damage at 3.2 dpa via hardness measurements and cell volume expansion due to defect formation under 92 MeV Xe ions in Ti_3SiC_2 [19].

It is important to note that, in contrast to neutrons, which pass through the bulk, the penetration depth of heavy ion and He irradiation is limited to the subsurface, and He atoms tend to accumulate and form bubbles inside the material after momentum transfer. This has been illustrated by Xiao et al. via ab initio methods, showing the He most energetically favors Al-site interstitials in Ti_3AlC_2 [22]. More recently, Wang et al. irradiated Ti_3AlC_2 samples with 50 keV He ions with fluences ranging from $8 \times 10^{16} \text{ cm}^{-2}$ to $1 \times 10^{18} \text{ cm}^{-2}$, resulting in the formation of spherical He bubbles, string-like bubbles and faulting zones [23]. Grazing incidence XRD analysis and selected area electron diffraction (SAED) confirmed

significant structural disorder without amorphization, even up to 52 dpa. Patel et al. irradiated Ti_3AlC_2 samples with 200 keV He ions to a maximum dose of 5.5 dpa at 500°C, and showed, by careful analysis of XRD patterns, that the Ti_3AlC_2 structure was maintained, but with an increased c-LP and a decreased a-LP, together with a highly disordered Al layer [24]. If He bubbles exist, they were < 1 nm in diameter and did not agglomerate, as observed by Wang et al. at RT [23]. Very recently, Yang et al. reported on the structural transitions of Ti_3AlC_2 irradiated with 50 keV He ions over a wide fluence range. While no amorphization was detected up to 31 dpa, antisite defects readily destroyed the nanolamellar Ti_3AlC_2 structure, and a transition to $\beta\text{-Ti}_3\text{AlC}_2$ was observed above 2.61 dpa [25].

In addition to heavy ion and He irradiation studies, Hoffman et al. have shown that neutron activation of Ti_3SiC_2 , Ti_3AlC_2 and Ti_2AlC compare well to SiC and are three orders of magnitude lower than alloy 617, two candidate materials for use in next generation reactors [26].

Based on these preliminary results it has been proposed that the MAX phases could be used in demanding nuclear environments either as fuel matrices or as coating materials, with the potential for significant improvements in performance due to their high-temperature capabilities, high damage tolerance, chemical resistance and versatile manufacturing techniques. The purpose of this work is to understand the effects of neutron irradiation on the microstructural stability and electrical resistivity of polycrystalline samples of Ti_3AlC_2 , Ti_3SiC_2 , Ti_2AlC and Ti_2AlN . As far as we are aware, and with the exception of a report that has just been published, on the neutron irradiation of Ti_3SiC_2 formed at joints between SiC parts, this is the first report on the neutron irradiation of bulk MAX phases in the open literature.

2. Experimental details

Details of the synthesis and processing conditions of the MAX phases are discussed elsewhere [5,27]. In short, samples of Ti_2AlC were prepared by pouring pre-reacted Ti_2AlC powders (Kanthal,

Hallstahammar, Sweden) into graphite dies, which were loaded into a vacuum hot press and hot pressed (HPed) for 4 h under a load corresponding to a stress of ~ 40 MPa and a vacuum of 10^{-1} Pa at a temperature of 1300°C . The Ti_3AlC_2 samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti_2AlC and TiC powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h. The latter were, in turn, HPed at 1400°C for 4 h. The Ti_2AlN samples were fabricated by milling stoichiometric mixtures of Ti and AlN powders (Alfa Aesar, Ward Hill, Massachusetts, USA) as above, and then HPing them at 1300°C for 4 h. Fine-grained samples of Ti_3SiC_2 , henceforth referred to as $\text{Ti}_3\text{SiC}_2\text{-FG}$, were prepared by ball milling stoichiometric mixtures of Ti, Si and C powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h, which were then HPed at 1450°C for 6 h. Coarse-grained Ti_3SiC_2 , henceforth referred to as $\text{Ti}_3\text{SiC}_2\text{-CG}$, was prepared from elemental mixtures as above, and HPed at 1500°C for 4 h, followed by an anneal at 1600°C for 8 h in an argon atmosphere in order to grow the grains.

Samples of each phase were sectioned, mounted in epoxy and polished with a final surface preparation of $3\ \mu\text{m}$ diamond suspension for observation under an optical microscope (OM). The MAX phase microstructure was exposed with an etchant composed of 1:1:1 parts by volume solution of hydrofluoric acid (50 vol.%), nitric acid (70 vol.%) and water, which was applied to the surface for < 30 s and rinsed. This etchant resulted in vibrantly colored MAX phase grains, notably in Ti_3AlC_2 (Fig. 1b) and Ti_3SiC_2 (Fig. 1d and e) with well-exposed grain boundaries. In these micrographs, TiC appears as bright white grains, highlighted in Fig. 1 by white arrows. The length, d_l , and thickness, d_t , of >100 grains per sample were measured from OM micrographs. The equivalent grain size was calculated as the geometric mean value of the grain dimensions, i.e. $\sqrt[3]{d_l^2 \cdot d_t}$. Test specimens were electro-discharged machined into $1.5 \times 1.5 \times 25.4\ \text{mm}^3$ resistivity bars, $16 \times 4 \times 0.7\ \text{mm}^3$ tensile dogbones and 0.5 mm thick and 3 mm diameter disks for TEM observation. In all cases, the initial dimensions were recorded.

Specimens were irradiated in a 6 MW research reactor at the Massachusetts Institute of Technology Nuclear Reactor Laboratory in a neutron spectrum similar to that of a light water power reactor. Samples were irradiated to a total fluence of $3.4 \times 10^{20} \text{ n cm}^{-2}$ at 360(20)°C, denoted henceforth as LT, and to $4.8 \times 10^{20} \text{ n cm}^{-2}$ at 695(25)°C, denoted as HT. The samples were irradiated in an inert gas atmosphere consisting of a mixture of high-purity (>99.99%) helium and neon and were in contact only with clean titanium (CP Grade 2). The effluent gas was periodically monitored for impurities using a residual gas analyzer, with typical values for oxygen and water of a few ppm. The irradiation temperature was monitored using a thermocouple in each capsule. Calculations using Fluent™ show that the temperature variation across the sample capsule is less than $\sim \pm 10 \text{ K}$. Note that the fluences are based on the actual integrated MWh for each set of specimens and Monte Carlo N-Particle Transport Code (MCNP) calculated flux levels at the irradiation positions. Using the SiC damage cross-sections reported in Ref. [28] as a function of neutron energy and spectral data from MCNP for a similar in-core experimental position, the dpa in each energy bin per neutron of total fluence was calculated for SiC [29]. Integrating over all neutron energies leads to a dpa conversion of $4 \times 10^{21} \text{ n cm}^{-2} \text{ total fluence} = 1 \text{ dpa}$. Using this damage rate for MAX phases, in the absence of other damage cross-section data, this work explores the irradiation response in the 0.1 dpa regime, henceforth denoted as low dose. Characterization of samples irradiated up to $20 \times 10^{20} \text{ n cm}^{-2}$ and $30 \times 10^{20} \text{ n cm}^{-2}$ is underway, and is not covered herein.

XRD patterns from the surfaces of samples of Ti_2AlC , Ti_3AlC_2 , Ti_2AlN , $\text{Ti}_3\text{SiC}_2\text{-FG}$ and $\text{Ti}_3\text{SiC}_2\text{-CG}$ were obtained using one of two diffractometers (Bruker D8, Madison, WI, USA) in the Bragg–Brentano configuration, for pristine and irradiated conditions, respectively. The diffractograms were collected using step scans of 0.02° in the $5\text{--}70^\circ 2\theta$ range, with a step time of 2 s. Scans were made with $\text{Cu K}\alpha$ radiation (45 kV and 40 mA). The accuracy of the diffractometer in determining lattice parameters, and its instrumental peak-shape function parameters, were calibrated using a LaB_6 standard (NIST 660A).

All diffraction patterns were analyzed by the Rietveld refinement method, using the FULLPROF code [30,31]. A systematic shift of 0.02 % was found, and corrected for, in the lattice parameters' (LPs'), evaluation as compared to the LaB₆ standard's reported value. For each data set, a model containing TiC and each specific MAX phase, e.g., Ti₃SiC₂, Ti₃AlC₂ or Ti₂AlC, was refined. For Ti₂AlN, the model was refined with the TiN and Ti₄AlN₃ phases. The Thompson–Cox–Hastings pseudo-Voigt model was used to refine the peak shape of each phase's reflections. Lattice strains and particle sizes were also estimated assuming isotropic Lorentzian and Gaussian contributions to the peak shape function [32]. The microstrain was calculated from the full width half maximum (FWHM) parameter U from each sample, according to the following equation:

$$\% \mu \epsilon = \frac{\pi}{1.8} (\sqrt{U_{\text{sample}} - U_{\text{std}}}) \quad (1)$$

where U_{std} was refined from the LaB₆ standard. If U_{sample} refined lower than the U_{std} , the microstrain was unresolvable for that specimen. The U_{std} values were 0.006(2) and 0.014(2) for the standards scanned on the diffractometers for pristine and irradiated samples, respectively.

Microstructural analysis of irradiation defects was carried out on the Ti₂AlC and Ti₃AlC₂ samples using a TEM (JEOL 2010, Japan). TEM disks were mechanically polished with 1200 grit SiC paper down to a thickness of < 50 μm and electropolished (Model 110 T win Jet, Fischione Instruments, Exton, PA, USA) in a 95 vol.% methanol, 5 vol.% perchloric acid solution to produce electron transparent edges around perforations that formed in the samples. Bright field (BF) and weak beam dark field TEM micrographs, as well as SAED patterns, were collected to characterize the irradiation defects. Lacking detailed information on the lamella thicknesses, the defect density per m² was measured to compare the defect density qualitatively between sample conditions in this study. Rigorous TEM characterization of the defects found in these materials is the focus of a future study.

Pre- and post-irradiation RT resistivity (ρ) measurements were obtained for all samples using a four-point probe technique using a current of 100 mA. Three resistivity bars of each material were irradiated at each condition, and the recorded values were averaged from the multiple bars tested. Since some resistivity bars were broken upon retrieval, in some cases the average of only two resistivity bars is reported. Voltages were recorded once per second for 3 min to allow the scans to reach steady state, and averaged over time. For most samples a time-independent voltage signal was recorded. Occasionally, a Ti_3AlC_2 and Ti_2AlC sample would exhibit a noisy signal. Lightly polishing the surfaces with 600 grit grinding paper solved the problem and resulted in steady voltage measurements.

3. Results

OM micrographs of the resulting samples showed them to be fully dense and predominately single phase, with randomly aligned plate-like grains (Fig. 1a–e). The average grain sizes of the Ti_3SiC_2 -FG and Ti_3SiC_2 -CG, were 8(3) and 50(20) μm , respectively, with uncertainty listed in parentheses. The average grain sizes of Ti_2AlC , Ti_2AlN and Ti_3AlC_2 were 10(4), 15(2) and 16(6) μm , respectively.

The XRD patterns collected from the Ti_3SiC_2 -FG, Ti_3SiC_2 -CG, Ti_3AlC_2 , Ti_2AlC and Ti_2AlN samples before and after the LT and HT irradiations are shown in Figs. 2–6, respectively. The results of the Rietveld analyses of these patterns are summarized in Table 1. According to these results, the TiC contents of the pristine Ti_2AlC , Ti_3AlC_2 , Ti_3SiC_2 -FG and Ti_3SiC_2 -CG samples were found to be 6.7(8) wt.%, 1.9(6) wt.%, 20.0(5) wt.% and 18.2(5) wt.%, respectively. While no Ti_4AlN_3 phase was observed in pristine Ti_2AlN , the TiN content was found to be 3.2(2) wt.%.

In all cases, the neutron irradiations resulted in structural as well as compositional changes compared to their pristine conditions (Table 1). The best fit of the XRD patterns was achieved by including TiC during refinement of the carbide phases. Irradiation of the Ti_3AlC_2 samples resulted in the significant increase in the TiC content from 1.9(6) wt.% before irradiation, to 52.6(9) and 44.4(8) wt.% after the LT

and HT irradiations, respectively. Cross-sections of these samples were also scanned by XRD (not shown), confirming that the dissociation into TiC was not a surface phenomenon. Irradiation of Ti_3SiC_2 -FG also yielded an increase in TiC content, going from 20.0(5) wt.% initially to 22.7(5) and 25(1) wt.% after the LT and HT irradiations, respectively. The TiC content in the Ti_3SiC_2 -CG changed from 18.2(5) wt.% as received to 23.3(6) and 17.0(4) wt.% after LT and HT irradiations, respectively (Table 1).

The Rietveld refinement of the XRD pattern of the Ti_3SiC_2 -FG sample irradiated at 360(20)°C, denoted henceforth as Ti_3SiC_2 -FG-LT, showed an increase in the c-LP from 17.681(1) to 17.812(9) Å and a decrease in the a-LP from 3.0686(8) to 3.0648(1) Å (Figs. 2a and 7). A microstrain of 0.27% was calculated for the distorted lattice; an increase from 0.08% in the pristine sample (Table 1). The lattice of the Ti_3SiC_2 -FG sample irradiated at 695(25)°C, henceforth referred to as Ti_3SiC_2 -FG-HT, was only slightly perturbed, with a c-LP of 17.668(1) and an a-LP of 3.0674(1) (Figs. 2c and 7 and Table 1). The microstrain level was below that of the standard used to calibrate the diffractometer.

The Ti_3SiC_2 -CG samples behaved similarly to their fine-grained counterparts (Fig. 3). Refinement of the XRD patterns of the Ti_3SiC_2 -CG-LT sample revealed an increase in the c-LP from 17.680(8) to 17.840(8) Å and a decrease in the a-LP from 3.0688(7) to 3.0647(8) Å. There was a simultaneous increase in microstrain to 0.33% (Table 1). After irradiation at 695(25)°C, the Ti_3SiC_2 -CG lattice was slightly distorted, with a c-LP of 17.669(6) Å, an a-LP of 3.0674(8) Å (Fig. 7); the microstrain was only 0.06%.

The Rietveld refinement of Ti_3AlC_2 -LT XRD patterns (Fig. 4a and b) also showed an increase in the c-LP from 18.562(2) to 18.896(1) Å and a decrease in a-LP from 3.0736(2) to 3.0542(2) Å (Table 1). Concomitantly there was an increase in microstrain from 0.1% to 0.39% (Fig. 4b and Table 1). At 18.543(2) Å and 3.0699(2) Å, the c- and a-LPs, respectively, of the Ti_3AlC_2 -HT samples were less distorted than those at LT (Figs. 4c and 7). After irradiation at 695(25)°C, the microstrain was 0.34%.

As noted above, pristine Ti_2AlC samples were fabricated using commercially available MAX powders (Kanthal, Sweden), resulting in an initial TiC volume fraction of 6.7(8) wt.%. At 8.3(3) wt.%, the TiC composition did not change after the LT irradiation and was within the variability in TiC content obtained for these samples. The lattice parameters of the Ti_2AlC -HT samples were similar to the dimensions of the pristine samples (Fig. 5c). Refinement also revealed that these samples contained 4.3(1) wt.% TiC, a value lower than in the pristine samples. Since this is unlikely, it confirms the somewhat inhomogeneous distribution of TiC in these samples.

While the a- and c-LPs for each MAX phase discussed above were distorted at LT conditions (Fig. 7), the a-LP for the TiC phase remained relatively constant at all conditions, showing at most an increase of $\sim 0.2\%$ in the Ti_3AlC_2 -LT samples (Table 1); while the TiC content increased in some cases, its LPs remained quite close to their values in the pristine samples.

Rietveld refinement of the Ti_2AlN samples revealed a similar trend in distorted LPs (Figs. 6 and 7). The best fit, however, was achieved when TiN and Ti_4AlN_3 were refined as well. Ti_2AlN -LT showed an increase in the c-LP from 13.640(2) to 13.714(4) Å and a decrease in a-LP from 2.9886(3) to 2.9808(6) Å (Figs. 6a and b and 7). Unsurprisingly, there was an increase in microstrain from 0.16% to 0.2% (Fig. 6b and Table 1). At 13.664(4) Å and 3.0086(3) Å, the c- and a-LPs, respectively, of the Ti_2AlN -HT samples were the least distorted of all samples irradiated to 360(20)°C (Fig. 7). At 0.58 %, the microstrain found in the Ti_2AlN -HT sample was significantly higher than all other samples irradiated at this condition. Unique among all MAX phases tested herein, Ti_2AlN -HT resulted in the formation of 36(3) wt.% Ti_4AlN_3 . An additional phase with peaks at $\sim 36, 41$ and $58.6^\circ 2\theta$ was unidentified, due to these peaks' low intensity and the high background noise.

It is also important to note that the relative atomic positions of each MAX phase tested herein did not change significantly under the studied irradiation conditions (Table 1).

Post irradiation TEM analysis was completed for the Ti_2AlC (Fig. 8) and Ti_3AlC_2 (Fig. 9) samples. TEM micrographs of Ti_2AlC -LT showed a large concentration of small black spots, on the order of 15 nm in size, with an areal density too large to quantify (Fig. 8a and b). SAED patterns from these regions showed a crystalline microstructure, with an increased diffuse background. TEM micrographs of the Ti_2AlC -HT sample revealed the presence of dislocation loops with an average diameter of 51(21) nm, having an areal density of $7.7 \times 10^{13} \text{ m}^{-2}$ (Fig. 8c and d). Seen edge on, the loops formed parallel to the basal planes and were arrayed coherently along the [0001] direction within the Ti_2AlC lattice. SAED patterns of the regions in Fig. 8c revealed that the Ti_2AlC samples maintained their crystallinity when irradiated to 0.1 dpa at 695(25)°C.

Irradiation of the Ti_3AlC_2 samples at LT resulted in larger dislocation loops, with an average diameter of 75(25) nm (Fig. 9a and b). Having an areal density of $1.2 \times 10^{14} \text{ m}^{-2}$, the loops were randomly dispersed, and appear to lie within the (0001) habit plane. SAED patterns of the region shown in Fig. 9b revealed that the Ti_3AlC_2 samples also retain their crystallinity, though with a slightly diffuse background. The Ti_3AlC_2 -HT samples formed triangular defects with an average edge length of 27(7) nm and areal density of $8.9 \times 10^{13} \text{ m}^{-2}$, lying within the (0001) habit plane, as determined by SAED (Fig. 9c and d). The defect density decreased with increasing temperature for both Ti_3AlC_2 and Ti_2AlC . However, the formation of triangular defects appears to be unique to Ti_3AlC_2 . The defect dimensions are summarized in Table 2.

The measured RT ρ of the pristine MAX phases in this work compare well with those previously reported (Table 2) [33-37]. After LT irradiation, the ρ values were 4-10 times greater than before irradiation (Table 2). The largest increase in RT ρ was seen in the Ti_3AlC_2 samples, with 2.84(2) $\mu\Omega \text{ m}$ after irradiated as compared to 0.262(8) $\mu\Omega \text{ m}$ before. At 2.2(1) $\mu\Omega \text{ m}$, the Ti_3SiC_2 -CG samples had a higher ρ compared to Ti_3SiC_2 -FG, at 1.1(1) $\mu\Omega \text{ m}$, both of which increased from the pristine values of

0.21(1) and 0.21(1), respectively. The ρ of the Ti_2AlN samples increased from 0.37(1) $\mu\Omega\text{ m}$ pristine to 1.46(1) $\mu\Omega\text{ m}$ after irradiation at L T. At 0.75(1) $\mu\Omega\text{ m}$, Ti_2AlC yielded the lowest increase in ρ compared to 0.31(4) $\mu\Omega\text{ m}$ as pristine. In contradistinction to the low temperature irradiations, samples irradiated to HT experienced only a slight increase in ρ , ranging from 0.23(1) for $\text{Ti}_3\text{SiC}_2\text{-FG}$ to 0.44(1) for Ti_2AlC (Table 2).

4. Discussion

Rietveld refinement revealed a distortion of LPs under neutron irradiation of the $\text{Ti}_3\text{SiC}_2\text{-FG}$, $\text{Ti}_3\text{SiC}_2\text{-CG}$, Ti_3AlC_2 , Ti_2AlC and Ti_2AlN samples (Fig. 7). This result concurs with previous work where heavy ions and He irradiations were shown to result in lattice distortions [11-16,18,19,21,23,24]. After LT irradiation, Ti_3AlC_2 and Ti_2AlC showed the largest increase in c-LP, while Ti_2AlN showed the least (Fig. 7a). The a-LPs decreased after LT irradiation, with Ti_2AlC showing the largest deviation from pristine (Fig. 7b). In contradistinction, after HT irradiation, the LPs for most materials tested were distorted by $\leq 0.1\%$, confirming the dynamic recovery capabilities of the MAX phases. There were little observable differences between the fine- and coarse-grained Ti_3SiC_2 samples, both of which showed less extensive distortion than Ti_3AlC_2 .

What is noteworthy and completely unexpected, however, was the dissociation of $\sim 50\text{ wt.}\%$ of the Ti_3AlC_2 into TiC. One of the reasons this was unexpected is that it was never observed or reported on in any of the heavy ion irradiation work [11-16,18,19,21,23,24]. This is an important result since it is clear that Ti_3AlC_2 may not be as resistant to neutrons as previously assumed. Clearly, the dissociation of Ti_3AlC_2 into TiC appears to be enhanced by the neutron irradiation, the extent of which increased at the lower irradiation temperature. The differences between charged particles and neutrons for irradiation are well known, each varying in energy range, penetration depth, volume of interaction and length of irradiation exposure [38]. The correlation between irradiation temperature and damage rate is also well

known, allowing for comparison of various particles used for irradiation at a fixed dose, assuming a recombination dominant regime [39]. In this case, the solution for the correlation which assumes that the ratio of defects lost to sinks, $R_s = N_{sv}/N_{si}$, is invariant is more accepted for comparing defect structures, shown by the following equation:

$$T_2 - T_1 = \frac{\left(\frac{kT_1^2}{E_m^v + 2E_f^v}\right) \ln\left(\frac{\phi_2}{\phi_1}\right)}{1 - \left(\frac{kT_1^2}{E_m^v + 2E_f^v}\right) \ln\left(\frac{\phi_2}{\phi_1}\right)} \quad (2)$$

where E_f^v , E_m^v , ϕ , T and k are the energy of formation of a vacancy, energy of migration of a vacancy, damage rate in dpa s^{-1} , irradiation temperature in K and Boltzmann's constant, respectively. Based on the irradiation dose rate herein, the damage rate for this study is assumed to be 4.7×10^{-9} dpa s^{-1} . As Ti_3AlC_2 dissociated into TiC by way of Al migration out of the layered structure, the correlation was calculated based on Al vacancies with $E_f = 4$ eV and $E_m = 0.61$ eV, based on density functional theory calculations [40]. According to the dose rates reported in Ref. [15], the damage rate for 1 MeV Xe irradiation of Ti_3AlC_2 was $\sim 2.5 \times 10^{-3}$ dpa s^{-1} , in good agreement with typical heavy ion irradiation studies [38]. The irradiation temperatures of the study herein were 360°C and 695°C. Based on this alone, to expect similar defect structures at 0.1 dpa, heavy ion irradiation studies would need to be conducted at $\sim 420^\circ\text{C}$ and $\sim 840^\circ\text{C}$, respectively. This required increase in irradiation temperature could explain the lack of irradiation defects and phase decomposition shown in Ref. [15], which was conducted at room temperature. Such high-temperature ion irradiation studies were lacking in the literature. More work is required to better understand the correlations between these particles in relation to MAX phase irradiation, and high-temperature ion irradiation should more thoroughly be explored. Based on the results shown in Table 1, both the FG and CG- Ti_3SiC_2 samples showed a slight increase in TiC content when irradiated under LT conditions. Given the fluctuations in the TiC contents of the pristine and irradiated samples, it is difficult to conclude if any dissociation occurred at all. If it did

occur, however, it is far less extensive than in the Ti_3AlC_2 case, and longer exposure times will clarify the issue.

Fig. 7 summarizes the effect of irradiation temperature on the LPs of each MAX phase tested herein. In all cases, irradiation at LT resulted in an expansion in the c-LP and a reduction in the a-LP. The Ti_3AlC_2 showed the largest increase in c-LP, with Ti_2AlN showing the least. Ti_2AlC had the largest reduction in a-LP, while the Ti_3SiC_2 samples had the least. Unsurprisingly, the Ti_3SiC_2 -FG and CG samples responded similarly (Fig. 7). For most samples, irradiation at HT resulted in LPs that were only slightly distorted from pristine dimensions. Ti_2AlN revealed an increase in a-LP at HT, in contrast to all other samples tested. This is attributed to the extensive distortion observed in the XRD spectrum (Fig. 6c) seen by the increased background intensity, and the formation of several impurity phases after irradiation.

In sharp contrast, Ti_2AlC showed superb resistance to lattice distortions and/or dissociation. It is unclear at this time why Ti_2AlC is so much more stable vis-à-vis dissociation than Ti_3AlC_2 . While XRD results confirmed the phase content for the samples tested, the question remains as to the fate of the Al and Si content in the cases where TiC and TiN were formed.

Also of note is the resiliency of TiC after irradiation at these conditions. While Ti_3AlC_2 and Ti_2AlC samples showed significant lattice distortion after LT irradiation, the a-LP of the TiC phase remained largely unperturbed, at most increasing by 0.19% in the Ti_3AlC_2 samples. It is plausible then that the TiC which forms via dissociation of Ti_3AlC_2 relieves the lattice strains. Note that the removal of the Al-layer would result in the de-twinning of the Ti_6C octahedra layers, forming bulk TiC [41]. While the large scale dissociation of Ti_3AlC_2 into TiC may be detrimental to its future in nuclear applications, it is unclear if the presence of small volume fractions will be problematic for other MAX phases, since

commercially available Ti_2AlC and Ti_3SiC_2 often contain ~ 10 wt.% TiC . More work is needed to ascertain the extent of influence the TiC impurity has on the irradiated properties of the MAX phases.

The collision of high-energy neutrons with lattice atoms is known to create point defects, increase the dangling bond density and result in an increase in resistivity [42]. Post-irradiation RT ρ values of samples irradiated at LT conditions were found to be almost an order of magnitude higher than seen for pristine samples (Table 2), confirming that LT neutron irradiation generated a significant amount of point defects. After irradiation, Ti_3AlC_2 possessed the highest RT ρ at $2.84(2) \mu\Omega \text{ m}$. TEM was used to confirm the increase in defect density as a result of neutron irradiation of Ti_2AlC (Fig. 8) and Ti_3AlC_2 (Fig. 9). The majority of the dislocation loops were seen to form in the basal planes of the MAX phases (Figs. 8c and d and 9).

With increasing temperatures, if the defect mobility is high enough, they can start to agglomerate and/or annihilate. Dislocation loops are also known to interact and coalesce into fewer but larger defect structures with increasing temperatures [38]. Annihilation of the point defects reduces the dangling bond density, resulting in a decrease in resistivity. This was confirmed herein for all HT samples; all showed only a slight increase in RT ρ (Table 2) compared to their ρ values prior to irradiation. HT irradiation resulted in the agglomeration of the small defect clusters seen in the Ti_2AlC -LT sample (Fig. 8a) into larger dislocation loop structures (Fig. 8c and d). The dislocation loops seen in the Ti_3AlC_2 sample at LT (Fig. 9a and b) were not observed at HT, where instead, triangular defects were identified (Fig. 9c and d). Further TEM of all samples is ongoing and is the focus of a future study.

5. Summary and conclusions

The first ever reported neutron irradiation of bulk MAX phases show that Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC and Ti_2AlN remain fully crystalline under neutron irradiation up to 0.1 dpa at $360(20)$ and $695(25)^\circ\text{C}$. However, Rietveld analysis of the XRD spectra for Ti_2AlC and Ti_3AlC_2 reveal a drastic difference in

irradiation tolerance between the two compounds. Roughly 50 wt.% of the Ti_3AlC_2 sample was converted to TiC with a 1.7% increase in c-LP and a 0.6% decrease in a-LP after LT irradiation (Fig. 7). This dissociation was not mitigated by irradiation at HT, though the lattice parameters showed less distortion, being close to pristine. This same trend in lattice parameters is seen in Ti_2AlC ; however, the extent of dissociation into TiC is not observed. Ti_2AlN was seen to dissociate into 13(1) wt.% TiN and 36(3) wt.% Ti_4AlN_3 , resulting in significant lattice strains after irradiation at HT.

Ti_3SiC_2 also showed lattice distortion, but to a lesser extent than Ti_3AlC_2 or Ti_2AlC , with only ~1% increase in c-LP and 0.6% decrease in a-LP. The Ti–Si bonding has been shown to be stronger than Ti–Al bonding in the MAX phases, which could explain the lesser distortion of the lattice [43]. There also appears to be no difference in the lattice response as a function of grain size.

Neutron irradiation resulted in the formation of dislocation loops in Ti_2AlC and Ti_3AlC_2 . In the former, irradiation at LT resulted in a high density of small dislocation loops on the order of 15 nm. Irradiation at HT resulted in agglomerated basal plane loops that grew to a size of 51(21) nm (Fig. 4c). In Ti_3AlC_2 , loops of 75(25) nm are seen after irradiation at LT, while triangular defects with edge lengths 27(7) nm form after irradiation at HT.

RT ρ measurements of Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC and Ti_2AlN show an order of magnitude increase in resistivity at LT, but only a 25% increase at HT. The low resistivity values of samples irradiated HT is strong evidence for the MAX phases' dynamic recovery at temperatures as low as 695(25)°C. TEM micrographs of the defects formed in Ti_2AlC and Ti_3AlC_2 correlate the effect irradiation temperature on the resistivity values. At 2.2(1) $\mu\Omega\text{ m}$, the RT ρ of Ti_3SiC_2 -CG was twice that of Ti_3SiC_2 -FG, which is attributed to the increase in grain boundary fraction present in the fine grained samples, likely resulting in fewer residual defects after irradiation. While defects are known to annihilate at grain boundary sinks,

more TEM analysis is required to quantify the effect of decreased grain size on defect formation for Ti_3SiC_2 .

Also of note is the difference in defect microstructure seen in this work compared to previous heavy ion and He studies. This work shows evidence for dislocation loops that have not been previously reported on in the MAX phases. Work is ongoing to fully characterize the defect microstructures, as more data at increasing dosage are compiled.

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Figure Captions

Fig. 1. Representative optical micrographs of (a) Ti_2AlC , (b) Ti_3AlC_2 , (c) Ti_2AlN , (d) Ti_3SiC_2 FG and (e) Ti_3SiC_2 CG microstructures after etching with a solution of hydrofluoric acid, nitric acid and water. The MAX phase samples were fully dense and predominately single phase, with randomly aligned plate-like grains, which are vibrantly colored after etching. TiC appears as bright white grains, denoted by white arrows.

Fig. 2. Rietveld analysis of XRD data of (a) pristine Ti_3SiC_2 -FG, and Ti_3SiC_2 -FG irradiated to (b) 0.1 dpa at 360(20)°C and (c) 0.1 dpa at 695(25)°C. Open circles, solid line and solid line at the bottom represent the observed data, calculated model and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_3SiC_2 -FG (first row), TiC (second). The large amorphous background was due to the mounting putty.

Fig. 3. Rietveld analysis of XRD data of (a) pristine Ti_3SiC_2 -CG, and Ti_3SiC_2 -CG irradiated to (b) 0.1 dpa at 360(20)°C and (c) 0.1 dpa at 695(25)°C. Open circles, solid line and solid line at the bottom, represent the observed data, calculated model and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_3SiC_2 (first row), TiC (second). The large amorphous background was due to the mounting putty.

Fig. 4. Rietveld analysis of XRD data of (a) pristine Ti_3AlC_2 , Ti_3AlC_2 irradiated to (b) 0.1 dpa at 360(20)°C and (c) 0.1 dpa at 695(25)°C. Open circles, solid line and solid line at the bottom represent the observed data, calculated model and variance between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_3AlC_2 (first row), TiC

(second). The large amorphous background was due to the mounting putty. Where peaks were not present, sections were excluded from analysis (shown in gray).

Fig. 5. Rietveld analysis of XRD data of (a) pristine Ti_2AlC , and Ti_2AlC irradiated to (b) 0.1 dpa at $360(20)^\circ\text{C}$ and (c) 0.1 dpa at $695(25)^\circ\text{C}$. Open circles, solid line and solid line at the bottom represent the observed data, calculated model and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_2AlC (first row), TiC (second). The large amorphous background was due to the mounting putty. Where peaks were not present, sections were excluded from analysis (shown in gray).

Fig. 6. Rietveld analysis of XRD data of (a) pristine Ti_2AlN , and Ti_2AlN irradiated to (b) 0.1 dpa at $360(20)^\circ\text{C}$ and (c) 0.1 dpa at $695(25)^\circ\text{C}$. Open circles, solid line and solid line at the bottom represent the observed data, calculated model and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_2AlN (first row), TiN (second). In (c), the best fit for $\text{Ti}_2\text{AlN-HT}$ was achieved by including Ti_4AlN_3 in the refinement (third row). Dissociation of the parent Ti_2AlN phase resulted in the formation of TiN and Ti_4AlN_3 . Peaks at $\sim 36, 41$ and $58.6^\circ 2\theta$ were unidentified due to their low intensity and the high background noise. The large amorphous background was due to the mounting putty.

Fig. 7. Plots comparing (a) c-LPs and (b) a-LPs as a function of irradiation temperature for the MAX phases $\text{Ti}_3\text{SiC}_2\text{-FG}$ and -CG , Ti_3AlC_2 , Ti_2AlC and Ti_2AlN show a significant temperature dependence on irradiation-induced lattice deformation after low dose irradiation (0.1 dpa). Pristine values are plotted for reference. (a) Ti_3AlC_2 showed the highest expansion in c-LP at $360(20)^\circ\text{C}$ irradiation, while Ti_2AlN was least expanded. In all cases, the c-LP was close to that of the pristine lattice when irradiated at $695(25)^\circ\text{C}$. (b) The a-LPs decreased with irradiation at $360(20)^\circ\text{C}$, with Ti_2AlC showing the most distortion. There appears to be no effect due to grain size with Ti_3SiC_2 . Similarly to the c-LP, irradiation

at 695(25)°C resulted in a-LPs that were close to that of the pristine sample. Ti₂AlN, however, showed an increase in a-LP after irradiation at 695(25)°C.

Fig. 8. Bright field TEM micrographs of Ti₂AlC (a) irradiated to 0.1 dpa at 360(20)°C on the (11-20) zone axis showing a large density of small defect clusters or loops on the order of 15 nm. (b) The same region as (a) tilted off zone for two beam kinematic where the defects become invisible. (c, d) Bright field TEM micrographs of two regions of Ti₂AlC irradiated to 0.1 dpa at 695(25)°C, resulting in larger dislocation loops of 51(21) nm agglomerating in ordered arrays along the c lattice forming parallel to the basal plane. SAED patterns from these regions (insets) reveal that the MAX samples maintain crystallinity, with an increased diffuse background in the 360(20)°C samples, indicating increased disorder.

Fig. 9. Bright field TEM micrographs of Ti₃AlC₂ irradiated to 0.1 dpa at 360(20)°C: (a) tilted off zone near (11-20) zone axis and (b) tilted to two beam kinematic condition near (0001) zone axis where dislocation loops of 75(25) nm appear to lie in the (0001) habit plane. Bright field TEM micrographs of a region in the Ti₃AlC₂ sample irradiated to 0.1 dpa at 695(25)°C. (c) Tilted to the (0001) zone axis, and (b) the same region off zone for two beam kinematic condition reveal the formation of triangular defects with edge length 27(7) nm forming on the basal plane. SAED patterns from these regions (insets) reveal that the MAX samples maintain crystallinity, with an increased diffuse background in the 360(20)°C samples, indicating increased disorder.

Table 1

Irradiation-induced structural and compositional changes in Ti₃SiC₂FG, Ti₃SiC₂CG, Ti₃AlC₂, Ti₂AlC and Ti₂AlN for irradiation up to 0.1 dpa at 360(20)°C (LD-LT) and at 695(25)°C (LD-HT)

Condition	χ^2	a-LP (Å)	c-LP (Å)	Ti _{II} _z	C_z	TiC	TiC a-	FWHM	με%
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				position	position	content (wt.%)	LP (Å)	Parameter, <i>U</i>	
Ti ₃ SiC ₂ FG-pristine	16.4	3.0668(7))	17.669(6)	0.3652(5)	0.569(2)	20.0(5)	4.3186(1))	0.0051(3)	-
Ti ₃ SiC ₂ FG-LD-LT	3.08	3.0648(1))	17.812(9)	0.3661(3)	0.571(1)	22.7(5)	4.3192(1))	0.0385(7)	0.27
Ti ₃ SiC ₂ FG-LD-HT	1.83	3.0667(2))	17.675(1)	0.3675(7)	0.556(3)	25(1)	4.3195(2))	0.0133(5)	-
Ti ₃ SiC ₂ CG-pristine	16.7	3.0688(7))	17.680(1)	0.3662(4)	0.572(2)	18.2(5)	4.3185(1))	0.0042(1)	-
Ti ₃ SiC ₂ CG-LD-LT	1.84	3.0647(1))	17.840(1)	0.3664(3)	0.565(1)	23.3(5)	4.3238(2))	0.0488(1)	0.33
Ti ₃ SiC ₂ CG-LD-HT	2.79	3.0674(8))	17.669(1)	0.3660(4)	0.556(2)	17.0(4)	4.3235(2))	0.0150(2)	0.06
Ti ₃ AlC ₂ -pristine	1.88	3.0736(2))	18.562(2)	0.1291(5)	0.564(2)	1.9(6)	4.3114(2))	0.0094(7)	0.10
Ti ₃ AlC ₂ -LD-LT	2.63	3.0542(2))	18.896(1)	0.1251(3)	0.648(1)	52.6(9)	4.3197(3))	0.064(1)	0.39
Ti ₃ AlC ₂ -LD-HT	3.73	3.0699(2))	18.543(2)	0.1313(4)	0.599(1)	44.4(8)	4.3082(3))	0.05(1)	0.34
				Ti _{i_z} position					

Ti ₂ AlC-pristine	3.2	3.0616(2))	13.652(2)	0.588(1)	^a n/a	6.7(8)	4.3106(7))	0.0236(8)	0.23
Ti ₂ AlC-LD-LT	3.17	3.0367(2))	13.882(1)	0.5843(5)	^a n/a	8.3(3)	4.3168(3))	0.157(1)	0.66
Ti ₂ AlC-LD-HT	2.44	3.0585(3))	13.659(3)	0.585(3)	^a n/a	4.3(1)	4.3128(1))	0.0176(2)	0.11
						TiN wt. %	TiN a- LP		
Ti ₂ AlN-pristine	1.6	2.9886(3))	13.640(2)	0.587(2)	^a n/a	3.23(2)	4.2329(2))	0.015(1)	0.16
Ti ₂ AlN-LD-LT	2.2	2.9808(6))	13.714(4)	0.590(1)	^a n/a	11.6(1)	4.2336(1))	0.0262(2)	0.20
^b Ti ₂ AlN-LD-HT	2.6	3.0086(3))	13.664(4)	0.570(2)	^a n/a	13(1)	4.2223(3))	0.125(2)	0.58

Numbers in parentheses represent one standard deviation of the last significant digit.

a In M₂AX compounds, the C-atom z position is fixed at the origin.

b In the case of Ti₂AlN, at high temperature, 36(3) wt.% Ti₄AlN₃ content was detected. With a-LP of 2.9931 and c-LP of 22.986, the lattice was distorted from pristine, at 2.988 and 23.372, for a-LP and c-LP, respectively.

Table 2

Room temperature resistivity and irradiation defect size of MAX phases after neutron (> 0.1 MeV) irradiation of up to 0.1 dpa at 360(20)°C or 695(25)°C

Composition	ρ ($\mu\Omega$ m)				Mean dislocation loop size (nm)	
	Pristine	Reference	360(20) $^{\circ}$ C	695(25) $^{\circ}$ C	360(20) $^{\circ}$ C	695(25) $^{\circ}$ C
Ti ₂ AlC	0.31(4)	0.32 [30] 0.23 [32] 0.39 [33]	0.75(1)	0.44(1)	<15 [-]	51(21) [7.7 $\times 10^{13}$]
Ti ₃ AlC ₂	0.262(8)	0.353 [30] 0.287 [32]	2.84(2)	0.39(1)	75(25) [1.2 $\times 10^{14}$]	^c 27(7) ^c [8.9 $\times 10^{13}$]
Ti ₂ AlN	0.37(1)	^a 0.25 [30] ^b 0.343 [30]	1.46(1)	0.25(1)	–	–
Ti ₃ SiC ₂ -FG	0.21(1)	0.23 [29] 0.23 [31]	1.1(1)	0.23(1)	–	–
Ti ₃ SiC ₂ -CG	0.21(1)	0.23 [29] 0.23 [31]	2.2(1)	0.24(1)	–	–

a Ti₂AlN prepared with elemental powder mixture.

b Ti₂AlN prepared with commercially available pre-reacted powder from Kanthal, Sweden.

c Triangular defects form at high temperature in Ti₃AlC₂, edge length is listed.

Figure 1.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 6.

Figure 7.

Figure 8.

Figure 9.