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, Ti3AlC, Ti3SiC2 and Ti3AlN. Rietveld refinement of X-ray diffraction patterns of the irradiated samples showed irradiation-enhanced dissociation into TiC of the Ti3AlC2 and Ti3SiC2 phases, most prominently in the former. Ti3AlN also showed an increase in TiN content, as well as Ti3AlN3 after irradiation. In contrast, Ti3AlC was quite stable under these irradiation conditions. Dislocation loops are seen to form in Ti3AlC 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 Ti3AlC and Ti3SiC2 are the more promising materials for high-temperature nuclear applications.

Keywords: Ti3AlC; 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 Mnx+1AXn−x (MAX) phases are a class of layered, machinable, ternary carbides and/or nitrides, where M is an early transition metal, A is a group 13–16 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 m1/2) 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 Ti3SiC2, showing surface layer amorphization of the Ti3SiC2 and impurity phases, as well as selective grain boundary sputtering due to nuclear interactions [11]. Liu et al. characterized Al-doped Ti3SiC2, 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-Ti3SiC2 phase to explain the presence of new peaks found in the post-irradiated XRD patterns [17]. With increasing dose, diffraction peaks were found to disappear due to lattice disturbances. In 2010, Bugnet et al. explored the effect of 100 keV Ar2+ ion irradiation on multilayered (Ti,Al)N/Ti3AlN 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 Ti3AlC2 and Ti3SiC2 possess very high resistance to amorphization, even up to 25 dpa, irradiated with 1 MeV Kr2+ and 1 MeV Xe2+ [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 Ti3SiC2 [12]. Also in 2011, Nappé et al. investigated the structural changes of Ti3SiC2 under a variety of ions and energies, concluding that...
Ti$_3$SiC$_2$ 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 $^{129}$I$^{132}$ irradiation of Ti$_3$SiC$_2$, 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$_3$SiC$_2$ [19]. Also in 2013, Bugnet et al. revealed a loss of chemical ordering along the c axis in Ti$_3$AlC$_2$ induced by 150 keV Ar$^{2+}$ ions [18]. While the aluminum layers were highly disordered, the TiC octahedra layers remained unperturbed, and no amorphization was observed for fluences up to $1.5 \times 10^{15}$ Ar/cm$^2$ ($\sim$1.7 dpa).

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$_3$AlC$_2$ [22]. More recently, Wang et al. irradiated Ti$_3$AlC$_2$ samples with 50 keV He ions with fluences ranging from $8 \times 10^{16}$ cm$^{-2}$ to $1 \times 10^{18}$ 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$_3$AlC$_2$ 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$_3$AlC$_2$ 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$_3$AlC$_2$ 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$_3$AlC$_2$ structure, and a transition to β-Ti$_3$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$_3$SiC$_2$, Ti$_3$AlC$_2$ and Ti$_2$AlC 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$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_3$AlC and Ti$_3$AIN. As far as we are aware, and with the exception of a report that has just been published, on the neutron irradiation of Ti$_3$SiC$_2$ 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$_2$AlC were prepared by pouring pre-reacted Ti$_2$AlC 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 $\sim$40 MPa and a vacuum of 10$^{-4}$ Pa at a temperature of 1300°C. The Ti$_3$AlC$_2$ samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti$_2$AlC 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$_3$AlN samples were fabricated by milling stoichiometric mixtures of Ti and AlIN powders (Alfa Aesar, Ward Hill, Massachusetts, USA) as above, and then HPing them at 1300°C for 4 h. Fine-grained samples of Ti$_3$SiC$_2$, henceforth referred to as Ti$_3$SiC$_2$-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$_3$SiC$_2$, henceforth referred to as Ti$_3$SiC$_2$-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 μm 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$_3$AlC$_2$ (Fig. 1b) and Ti$_3$SiC$_2$ (Fig. 1d and e) with well-exposed grain boundaries. In these micrographs, the TiC grains appear bright white, highlighted in Fig. 1 by white arrows. The length, $d_o$, 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. $\sqrt[3]{d_o \cdot d_t}$. Test specimens were electro-discharged machined into $1.5 \times 1.5 \times 25.4$ mm$^3$ resistivity bars, 16 x 4 x 0.7 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 $3.4 \times 10^{20}$ n cm$^{-2}$ at 360(20)°C, denoted henceforth as LT, and to $4.8 \times 10^{20}$ n cm$^{-2}$ at 695(25)°C, henceforth 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$^\text{TM}$ show that the temperature variation across the sample capsule is less than $\pm 10$ 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 \(4 \times 10^{21} \text{n cm}^{-2}\) total fluence = 1 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\(_2\)AlC, Ti\(_3\)AlC\(_2\), Ti\(_2\)AlN, Ti\(_3\)SiC\(_2\)-FG and Ti\(_3\)SiC\(_2\)-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 5–70° 2\(\theta\) range, with a step time of 2 s. Scans were made with 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 diffractograms 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 LaB\(_6\) standard’s reported value. For each data set, a model containing TiC and each specific MAX phase, e.g., Ti\(_3\)SiC\(_2\), Ti\(_3\)AlC\(_2\) or Ti\(_2\)AlC, was refined. For Ti\(_2\)AlN, the model was refined with the TiN and Ti\(_4\)AlN\(_3\) 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 Lorenzian 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:

\[
\%\mu e = \frac{\pi}{1.8} \left( \sqrt{U_{\text{sample}}} - U_{\text{std}} \right)
\]

where \(U_{\text{std}}\) was refined from the LaB\(_6\) standard. If \(U_{\text{sample}}\) refined lower than the \(U_{\text{std}}\), the microstrain was unresolvable for that specimen. The \(U_{\text{std}}\) 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 Ti\(_2\)AlC and Ti\(_3\)AlC\(_2\) samples using a TEM (JEOL 2010, Japan). TEM disks were mechanically polished with 1200 grit SiC paper down to a thickness of <50 \(\mu\)m and electropolished (Model 110 Twin 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 g\(^3\)g condition 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 \(\text{m}^2\) 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 (\(\rho\)) measurements were carried out 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$_3$AlC$_2$ and Ti$_2$AlC 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$_3$SiC$_2$-FG and Ti$_3$SiC$_2$-CG, were 8(3) and 50(20) μm, respectively, with uncertainty listed in parentheses. The average grain sizes of Ti$_2$AlC, Ti$_2$AlN and Ti$_3$AlC$_2$ were 10(4), 15(2) and 16(6) μm, respectively.

The XRD patterns collected from the Ti$_3$SiC$_2$-FG, Ti$_3$SiC$_2$-CG, Ti$_3$AlC$_2$, Ti$_2$AlC and Ti$_2$AlN 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$_2$AlC, Ti$_3$AlC$_2$, Ti$_3$SiC$_2$-FG and Ti$_3$SiC$_2$-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$_4$AlN$_3$ phase was observed in pristine Ti$_2$AlN, 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$_3$AlC$_2$ 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$_3$SiC$_2$-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$_3$SiC$_2$-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).

Rietveld refinement of the XRD pattern of the Ti$_3$SiC$_2$-FG sample irradiated at 360(20) °C, denoted henceforth as Ti$_3$SiC$_2$-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. 2 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$_3$SiC$_2$-FG sample irradiated at 695(25) °C, henceforth referred to as Ti$_3$SiC$_2$-FG-HT, was only slightly perturbed, with a c-LP of 17.668(1) and an a-LP of 3.0674(1) Å.
The microstrain level was below that of the standard used to calibrate the diffractometer. The Ti$_3$SiC$_2$-CG samples behaved similarly to their fine-grained counterparts (Fig. 3). Refinement of the XRD patterns of the Ti$_3$SiC$_2$-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)$^\circ$C, the Ti$_3$SiC$_2$-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$_3$AlC$_2$-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$_3$AlC$_2$-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$_3$AlC 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$_2$AlC-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.

Rietveld refinement of the Ti$_3$AlN samples revealed a similar trend in distorted LPs (Figs. 6 and 7). The best fit, however, was achieved when TiN and Ti$_4$AlN$_3$ were refined as well. Ti$_2$AlN-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, 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$_2$AlN-HT samples were least distorted of all samples irradiated to 360(20) °C (Fig. 7). At 0.58%, the microstrain found in the Ti$_2$AlN-HT sample was significantly higher than all other samples irradiated at this condition. Unique among all MAX phases tested herein, Ti$_2$AlN-HT resulted in the
formation of 36(3) wt.% Ti₃AlN₃. An additional phase, with peaks at ~36°, 41° and 58.6° 2θ, was unidentified, due to the low intensity of these peaks 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 Ti₂AlC (Fig. 8) and Ti₃AlC₂ (Fig. 9) samples. TEM micrographs of Ti₂AlC-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 Ti₂AlC-HT sample revealed the presence of dislocation loops with an average diameter of 51(21) nm, having an areal density of 7.7 × 10¹⁴ m⁻², lying within the (0001) habit plane, as determined by SAED (Fig. 8c and d). The defect density decreased with increasing temperature for both Ti₂AlC₂ and Ti₂AlC. However, the formation of triangular defects appears to be unique to Ti₃AlC₂. 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 Ti₃AlC₂ samples with 2.84(2) μΩ·m after irradiated as compared to 0.262(8) μΩ·m before. At 2.2(1) μΩ·m, the Ti₃SiC₂-CG samples had a higher ρ compared to Ti₃SiC₂-FG, at 1.1(1) μΩ·m, both of which increased from the pristine values of 0.21(1) and 0.21(1), respectively. The ρ of the Ti₃AlN samples increased from 0.37(1) μΩ·m pristine to 1.2 × 10¹⁴ 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 Ti₃AlC₂ samples also retain their crystallinity, though with a slightly diffuse background. The Ti₃AlC₂-HT samples formed triangular defects with an average edge length of 27(7) nm and areal density of 8.9 × 10¹⁴ 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 Ti₃AlC₂ and Ti₂AlC. However, the formation of triangular defects appears to be unique to Ti₃AlC₂. The defect dimensions are summarized in Table 2.

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experienced only a slight increase in $q$, ranging from 0.23(1) for Ti$_3$SiC$_2$-FG to 0.44(1) for Ti$_2$AlC (Table 2).

4. Discussion

Rietveld refinement of the XRD patterns revealed a distortion of LPs under neutron irradiation of all compositions (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$_3$AlC$_2$ and Ti$_2$AlC showed the largest increase in c-LP, while Ti$_3$AlN showed the least (Fig. 7a). The a-LPs decreased after LT irradiation, with Ti$_3$AlC showing the largest deviation from pristine (Fig. 7b). In contradiction, 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$_3$SiC$_2$ samples, both of which showed less extensive distortion than Ti$_3$AlC$_2$.

What is noteworthy and completely unexpected, however, was the dissociation of $\sim 50$ wt.% of the Ti$_3$AlC$_2$ into TiC. One of the reasons this was unexpected is that it was never observed or reported 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$_3$AlC$_2$ may not be as resistant to neutrons as previously assumed. Clearly, the dissociation of Ti$_3$AlC$_2$ into TiC appears to be enhanced by the neutron irradiation, the extent of which is higher 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:

$$T_2 - T_1 = \frac{\left(\frac{E_f}{\Delta E} + 2E_f\right) \ln \left(\frac{\phi_2}{\phi_1}\right)}{1 - \left(\frac{E_f}{\Delta E} + 2E_f\right) \ln \left(\frac{\phi_2}{\phi_1}\right)}$$  (2)

where $E_f, E_m, \phi, T$ 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 $4.7 \times 10^{-9}$ dpa s$^{-1}$. As Ti$_3$AlC$_2$ dissociated into TiC by
way of Al migration out of the layered structure, the correlation was calculated based on Al vacancies with $E_f = 4 \text{ eV}$ and $E_m = 0.61 \text{ eV}$, 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$_3$AlC$_2$ was $\sim 2.5 \times 10^{-3} \text{ dpa s}^{-1}$, in good agreement with typical heavy ion irradiation studies [38]. The irradiation temperatures of the study herein were 360 $^\circ\text{C}$ and 695 $^\circ\text{C}$. 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 defect complexes and phase decomposition reported in Ref. [15], which was conducted at room temperature. Such high-temperature ion irradiation studies are 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$_3$SiC$_2$ 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$_3$AlC$_2$ case. 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$_3$AlC$_2$ showed the largest increase in c-LP, with Ti$_2$AlN showing the least. Ti$_2$AlN had the largest reduction in a-LP, while the Ti$_3$SiC$_2$ samples had the least. Unsurprisingly, the Ti$_3$SiC$_2$-FG and CG samples responded similarly (Fig. 7). For most samples, irradiation at HT resulted in LPs that were only slightly distorted from their pristine values. Ti$_2$AlN 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$_2$AlC showed good resistance to lattice distortions and/or dissociation. It is unclear at this time why Ti$_2$AlC is so much more stable vis-à-vis dissociation than Ti$_3$AlC$_2$. 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 formed.

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Fig. 6. Rietveld analysis of XRD data of (a) pristine Ti$_2$AlN, and (b) Ti$_2$AlN irradiated to 0.1 dpa at 360(20) $^\circ\text{C}$ and (c) 0.1 dpa at 695(25) $^\circ\text{C}$. Open circles, solid lines and solid green lines 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$_2$AlN (first row), TiN (second). In (c), the best fit for Ti$_2$AlN-HT was achieved my including Ti$_2$AlN$_3$ in the refinement (third row). Dissociation of the parent Ti$_2$AlN phase resulted in the formation of TiN and Ti$_4$AlN$_3$. Peaks at $\sim 36, 41$ and $58.6^\circ$ 20 were unidentified. The large amorphous background was due to the mounting putty.
**Table 1.** Irradiation-induced structural and compositional changes in Ti$_3$SiC$_2$-FG, Ti$_3$SiC$_2$-CG, Ti$_2$AlC$_2$, Ti$_2$AlC and Ti$_2$AlN for irradiation up to 0.1 dpa at 360(20) °C (LD-LT) and at 695(25) °C (LD-HT).

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\chi^2$</th>
<th>a-LP (Å)</th>
<th>c-LP (Å)</th>
<th>Ti$_{II_z}$ position</th>
<th>C$_{z}$ position</th>
<th>TiC content (wt.%)</th>
<th>TiC a-LP (Å)</th>
<th>FWHM parameter, $U$%</th>
<th>µ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$SiC$_2$-FG-pristine</td>
<td>16.4</td>
<td>3.0668(7)</td>
<td>17.669(6)</td>
<td>0.3652(5)</td>
<td>0.569(2)</td>
<td>20.0(5)</td>
<td>4.3186(1)</td>
<td>0.005(3)</td>
<td>–</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$-FG-LD-LT</td>
<td>3.08</td>
<td>3.0648(1)</td>
<td>17.812(9)</td>
<td>0.3661(3)</td>
<td>0.571(1)</td>
<td>22.7(5)</td>
<td>4.3192(1)</td>
<td>0.0385(7)</td>
<td>0.27</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$-FG-LD-HT</td>
<td>1.83</td>
<td>3.0667(2)</td>
<td>17.675(1)</td>
<td>0.3675(7)</td>
<td>0.556(3)</td>
<td>25(1)</td>
<td>4.3195(2)</td>
<td>0.0133(5)</td>
<td>–</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$-CG-pristine</td>
<td>16.7</td>
<td>3.0688(7)</td>
<td>17.680(1)</td>
<td>0.3662(4)</td>
<td>0.572(2)</td>
<td>18.2(5)</td>
<td>4.3185(1)</td>
<td>0.0042(1)</td>
<td>–</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$-CG-LD-LT</td>
<td>1.84</td>
<td>3.0647(1)</td>
<td>17.840(1)</td>
<td>0.3664(3)</td>
<td>0.556(2)</td>
<td>23.3(5)</td>
<td>4.3238(2)</td>
<td>0.0488(1)</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$-CG-LD-HT</td>
<td>2.79</td>
<td>3.0674(8)</td>
<td>17.669(1)</td>
<td>0.3660(4)</td>
<td>0.556(2)</td>
<td>17.0(4)</td>
<td>4.3235(2)</td>
<td>0.0150(2)</td>
<td>0.06</td>
</tr>
<tr>
<td>Ti$_2$AlC$_2$-pristine</td>
<td>1.88</td>
<td>3.0736(2)</td>
<td>18.562(2)</td>
<td>0.1291(5)</td>
<td>0.564(2)</td>
<td>19(6)</td>
<td>4.3114(2)</td>
<td>0.0094(7)</td>
<td>0.10</td>
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<tr>
<td>Ti$_2$AlC$_2$-LD-LT</td>
<td>2.63</td>
<td>3.0542(2)</td>
<td>18.896(1)</td>
<td>0.1251(3)</td>
<td>0.600(1)</td>
<td>52.6(9)</td>
<td>4.3197(3)</td>
<td>0.0641(3)</td>
<td>0.39</td>
</tr>
<tr>
<td>Ti$_2$AlC$_2$-LD-HT</td>
<td>3.73</td>
<td>3.0699(2)</td>
<td>18.543(2)</td>
<td>0.1314(4)</td>
<td>0.599(1)</td>
<td>44.4(8)</td>
<td>4.3082(3)</td>
<td>0.05(1)</td>
<td>0.34</td>
</tr>
<tr>
<td>Ti$_2$AlC$_2$-pristine</td>
<td>3.2</td>
<td>3.0616(2)</td>
<td>13.652(2)</td>
<td>0.588(1)</td>
<td>a/a</td>
<td>6.7(8)</td>
<td>4.3106(7)</td>
<td>0.0236(8)</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti$_2$AlC$_2$-LD-LT</td>
<td>3.17</td>
<td>3.0367(2)</td>
<td>13.882(1)</td>
<td>0.5843(5)</td>
<td>a/a</td>
<td>8.3(3)</td>
<td>4.3168(3)</td>
<td>0.157(1)</td>
<td>0.66</td>
</tr>
<tr>
<td>Ti$_2$AlC$_2$-LD-HT</td>
<td>2.44</td>
<td>3.0583(3)</td>
<td>13.659(3)</td>
<td>0.5853(3)</td>
<td>a/a</td>
<td>4.3(1)</td>
<td>4.3128(1)</td>
<td>0.0176(2)</td>
<td>0.11</td>
</tr>
<tr>
<td>Ti$_2$AlN-pristine</td>
<td>1.6</td>
<td>2.9886(3)</td>
<td>13.640(2)</td>
<td>0.587(2)</td>
<td>a/a</td>
<td>3.23(2)</td>
<td>4.2239(2)</td>
<td>0.015(1)</td>
<td>0.16</td>
</tr>
<tr>
<td>Ti$_2$AlN-LD-LT</td>
<td>2.2</td>
<td>2.9808(6)</td>
<td>13.714(4)</td>
<td>0.590(1)</td>
<td>a/a</td>
<td>11.6(1)</td>
<td>4.2336(1)</td>
<td>0.0262(2)</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti$_2$AlN-LD-HT</td>
<td>2.6</td>
<td>3.0086(3)</td>
<td>13.664(3)</td>
<td>0.570(2)</td>
<td>a/a</td>
<td>13(1)</td>
<td>4.2223(3)</td>
<td>0.125(2)</td>
<td>0.58</td>
</tr>
</tbody>
</table>

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

*a* In M$_2$AX compounds, the C-atom $z$ position is fixed at the origin.

*b* In the case of Ti$_2$AlN, at high temperature, 36(3) wt.% Ti$_4$AlN$_3$ 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.

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**Fig. 7.** Plots comparing (a) c-LPs and (b) a-LPs as a function of irradiation temperature for Ti$_3$SiC$_2$-FG and -CG, Ti$_2$AlC$_2$, Ti$_2$AlC and Ti$_2$AlN, show a significant temperature dependence on irradiation-induced lattice deformation after low dose irradiation (0.1 dpa). Pristine values are plotted for reference. Colors of axes labels and data points are correlated. Ti$_3$AlC$_2$ showed the highest expansion in c-LP at 360(20) °C irradiation, while Ti$_2$AlN was least expanded. In all cases, the c-LP was close to that of the pristine lattice when irradiated at 695(25) °C. The a-LPs decreased with irradiation at 360(20) °C, with Ti$_2$AlC showing the most distortion. Similar to the c-LP, irradiation at 695(25) °C resulted in a-LPs that were close to those of the pristine samples.

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**Fig. 8.** Bright field TEM micrographs of Ti$_2$AlC (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) Two regions irradiated to 0.1 dpa at 695(25) °C, resulting in larger dislocation loops of 51(21) nm agglomerating in ordered arrays 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.
and Ti₂AlC₂ relieves the lattice strains. Note that the removal sample at LT (Fig. 9 a and b) were samples. It is possessed the highest RT reveal a often contain into TiC may be detrimental (Fig. 9). The majority of the dislocation loops of Ti₃AlC₂ sample irradiated to 0.1 dpa at 695(25) °C. (c) Tilted to the (0001) zone axis, and (d) 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 planes. 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 2. Room temperature resistivity and irradiation defect size after neutron (>0.1 MeV) irradiation of up to 0.1 dpa at 360(20) °C or 695(25) °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\rho$ (\mu\Omega m)</th>
<th>Reference</th>
<th>360(20) °C</th>
<th>695(25) °C</th>
<th>Mean dislocation loop size (nm) [areal density] (defects m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti₃AlC</td>
<td>0.31(4)</td>
<td>0.32 [34]</td>
<td>0.75(1)</td>
<td>0.44(1)</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Ti₃AlC₂</td>
<td>0.262(8)</td>
<td>0.353 [34]</td>
<td>2.84(2)</td>
<td>0.39(1)</td>
<td>75(25) [1.2 × 10¹⁴]</td>
</tr>
<tr>
<td>Ti₂AlN</td>
<td>0.37(1)</td>
<td>0.25 [34]</td>
<td>1.46(1)</td>
<td>0.25(1)</td>
<td>–</td>
</tr>
<tr>
<td>Ti₃SiC₂-FG</td>
<td>0.21(1)</td>
<td>0.23 [33]</td>
<td>1.1(1)</td>
<td>0.23(1)</td>
<td>–</td>
</tr>
<tr>
<td>Ti₃SiC₂-CG</td>
<td>0.21(1)</td>
<td>0.23 [33]</td>
<td>2.2(1)</td>
<td>0.24(1)</td>
<td>–</td>
</tr>
</tbody>
</table>

Ti₂AlN prepared with elemental powder mixture.
Ti₂AlN prepared with commercially available pre-reacted powder from Kanthal, Sweden.
Triangular defects form at high temperature in Ti₃AlC₂, edge length is listed.

Also of note is the resiliency of TiC after irradiation at these conditions. While Ti₃AlC₂ and Ti₂AlC 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 Ti₃AlC₂ samples. It is plausible then that the TiC which forms via dissociation of Ti₃AlC₂ relieves the lattice strains. Note that the removal of the Al-layer would result in the de-twinning of the Ti₆C octahedra layers, forming bulk TiC [41]. While the large scale dissociation of Ti₃AlC₂ 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 Ti₃AlC and Ti₃SiC₂ 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 $\rho$ values of samples irradiated at LT conditions were found to be almost an order of magnitude higher than those for the pristine samples (Table 2), confirming that LT neutron irradiation generated a significant amount of point defects. After irradiation, Ti₃AlC₂ possessed the highest RT $\rho$ at 2.84(2) \mu\Omega m. TEM was used to confirm the increase in defect density as a result of neutron irradiation of Ti₃AlC (Fig. 8) and Ti₃AlC₂ (Fig. 9). The majority of the dislocation loops were seen to form in the basal planes of the MAX phases (Figs. 8c, 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 $\rho$ (Table 2) compared to their $\rho$ values prior to irradiation. HT irradiation resulted in the agglomeration of the small defect clusters seen in the Ti₂AlC-LT sample (Fig. 8a) into larger dislocation loop structures (Fig. 8c and d). The dislocation loops seen in the Ti₃AlC₂ 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 Ti₃SiC₂, Ti₃AlC₂, Ti₂AlC and Ti₂AlN remain fully crystalline under neutron irradiation up to 0.1 dpa at 360(20) and 695(25) °C. However, Rietveld analysis of the XRD spectra for Ti₂AlC and Ti₃AlC₂ reveal a drastic difference in irradiation tolerance between the two
compounds. Roughly 50 wt.% of the Ti$_3$AlC$_2$ 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 and were close to pristine. This same trend in lattice parameters is seen in Ti$_2$AlC; however, the extent of dissociation into TiC is not observed. Ti$_2$AlN was seen to dissociate into 13(1) wt.% TiN and 36(3) wt.% Ti$_4$AlN$_3$, resulting in significant lattice strains after irradiation at HT.

Ti$_3$SiC$_2$ also showed lattice distortion, but to a lesser extent than Ti$_3$AlC$_2$ or Ti$_3$AlC, 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$_2$AlC and Ti$_3$AlC$_2$. 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$_3$AlC$_2$, 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.

Room temperature p measurements of Ti$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_2$AlC, and Ti$_3$AlN show roughly an order of magnitude increase in resistivity after LT irradiation, but only a 25% increase at HT. The low resistivity values of samples after HT irradiation are evidence for the MAX phases’ dynamic recovery at temperatures as low as 695(25) °C. TEM micrographs of the defects formed in Ti$_2$AlC and Ti$_3$AlC$_2$ correlate the effect of irradiation temperature with the resistivity values. At 2.2(1) μm, the RT p of Ti$_3$SiC$_2$-CG was twice that of Ti$_3$SiC$_2$-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$_3$SiC$_2$.

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.

Acknowledgments

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References


