Effects of Neutron Irradiation of Ti_3SiC_2 and Ti_3AlC_2 in the 121–1085 °C Temperature Range

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Abstract

Herein we report on the formation of defects in response to neutron irradiation of polycrystalline Ti_3SiC_2 and Ti_3AlC_2 samples exposed to total fluences of $\approx 6 \times 10^{20} \text{ n/m}^2$, $5 \times 10^{21} \text{ n/m}^2$ and $1.7 \times 10^{22} \text{ n/m}^2$ at irradiation temperatures of 121(12), 735(6) and 1085(68) °C. These fluences correspond to 0.14, 1.6 and 3.4 dpa, respectively. After irradiation to 0.14 dpa at 121 °C and 735 °C, black spots are observed via transmission electron microscopy in both Ti_3SiC_2 and Ti_3AlC_2 . After irradiation to 1.6 and 3.4 dpa at 735 °C, basal dislocation loops, with a Burgers vector of $\mathbf{b} = \frac{1}{2} [0001]$ are observed in Ti_3SiC_2 , with loop diameters of 21(6) and 30(8) nm after 1.6 dpa and 3.4 dpa, respectively. In Ti_3AlC_2 , larger dislocation loops, 75(34) nm in diameter are observed after 3.4 dpa at 735 °C, in addition to stacking faults. Impurity particles of TiC, as well as stacking fault TiC platelets in the MAX phases, are seen to form extensive dislocation loops under all conditions. Cavities were observed at grain boundaries and within stacking faults after 3.4 dpa irradiation, with extensive cavity formation in the TiC regions at 1085 °C. Remarkably, denuded zones on the order of 1 μm are observed in Ti_3SiC_2 after irradiation to 3.4 dpa at 735 °C. Small grains, 3-5 μm in diameter, are damage free after irradiation at 1085 °C at this dose. The results shown herein confirm once again that the presence of the A-layers in the MAX phases considerably enhance their irradiation tolerance. Based on these results, and up to 3.4 dpa, Ti_3SiC_2 remains a promising candidate for high temperature nuclear applications as long as the temperature remains > 700 °C.

Keywords: Ti_3SiC_2 ; Ti_3AlC_2 ; MAX phases; neutron irradiation; dislocation loops

1 Introduction

Recently, the $M_{n+1}AX_n$, MAX, phases – where M is an early transition metal, A is a group 13 to 16 element, and X is C and/or N – have been considered as potential materials for use in current and future nuclear applications, such as impeller blades, fuel claddings, and barrier coatings for existing cladding materials. These layered, ternary carbides possess a combination of metallic and ceramic properties that render them attractive materials for such applications [1, 2]. Some of the MAX phase family, including its leading candidate, Ti_3SiC_2 , possess high stiffness but are relatively soft, with high fracture toughness values due to their layered structure and metal-like bonding [1-5]. Additionally, these carbides are thermally and electrically conductive, resistant to thermal shock, and readily machinable with conventional steel tooling [6-11].

The MAX phases are quite strong in compression at room temperature, and undergo a plastic-to-brittle transition at around 1000 °C in both compression and tension [2, 4, 12]. Furthermore, some of the Al-containing MAX phases, notably, Ti_2AlC or Cr_2AlC , show excellent oxidation resistance in both air and water vapor [13-17]. They also possess the ability to repeatedly seal cracks at high temperature by the selective formation of alumina, Al_2O_3 , which fills in the cracked regions [18-21].

Neutron activation of Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC compares well with SiC, a more widely studied candidate material for use in next generation reactors [22]. Studies on the reactivity of Zircaloy-4, Zr-4, with bulk Ti_3SiC_2 and Ti_2AlC , and cold sprayed Ti_2AlC , have shown that the MAX phases form good diffusion bonds at temperatures in excess of 1100 °C [23]. Cold spray coatings of Ti_2AlC are seen to adhere strongly to Zircaloy-4 substrates and behave well under hydrothermal conditions, with improved oxidation resistance as compared to uncoated Zr-4 [24]. The combination of oxidation tolerance, thermal conductivity, high temperature strength and stability, and thermal shock resistance renders these MAX

phases, notably Ti_3SiC_2 , potential candidates for use in fuel cladding and accident tolerant fuel applications.

In recent years, many reports have investigated the effect on ion irradiation on a few MAX phases, including Ti_3SiC_2 , Ti_3AlC_2 , and $\text{Ti}_3(\text{Si,Al})\text{C}_2$ solid solutions [25-44]. A consensus has been reached that the MAX phases are resistant to irradiation damage and amorphization. In most cases, the response to ion irradiation, especially at temperatures $< 500^\circ\text{C}$, has been an increase in the c-lattice parameters, c-LP, and a decrease in the a-LP together with an increase in microstrain [27, 34, 36, 38]. In some cases, the layered structure was disturbed by ion irradiation, and a β -MAX polymorph was observed via X-ray diffraction, XRD [28, 30, 37, 38, 43]. More recently, Clark *et al.* observed similar lattice distortions in Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC after heavy ion irradiation (5.8 MeV Ni) to 10 and 30 dpa at 400 and 700 $^\circ\text{C}$ [44]. The aluminum containing MAX phases showed grain boundary, GB, cracking after 400 $^\circ\text{C}$ irradiation, which was attributed to anisotropic swelling in the lattice[44]. Ti_3SiC_2 , however, did not exhibit microcracking at any irradiation conditions. The authors also showed, in all three materials, evidence of point defect clusters after 400 $^\circ\text{C}$ irradiation, and larger defect structures within the basal planes after 700 $^\circ\text{C}$ irradiation [44]. Their results suggested that the aluminum MAX phases are unfit for nuclear applications in the 400 $^\circ\text{C}$ regime, while Ti_3SiC_2 was more damage tolerant overall[44].

Several recent density functional theory, DFT, studies [45-49] have concluded that the presence of the A-layers could render MAX phases irradiation tolerant. The calculations showed that Frenkel pairs, FPs, of M, A, and X elements can readily form as interstitials within the A-layer and/or in the space between the A and M layers. While varying in values due to differences in calculation methods, the energies of formation, E_f 's, for point defects, e.g. carbon interstitials, C_i , or A-layer vacancies, V_A , in the A-layers were consistently $\sim 1\text{-}3$ eV lower compared to defects within the TiC blocks, which cost more at > 9 eV [45-49]. Antisite defects, e.g. Ti_{Al} , were also shown to have E_f 's that were comparable to the

formation of A atom Frenkel pairs. Middleburgh *et al.* showed that the lowest energy C_i in hexagonal coordination with 3 basal Si and 2 Ti forms bond lengths similar to those found in TiC and SiC [48].

In comparing various A-elements, Wang *et al.* showed that C_{FP} and Si_{FP} , with $E_f = 1.5$ and 2.1 eV, respectively, were the lowest energy defects in Ti_3SiC_2 [46]. In contrast, the $Ti_{Al}-Al_{Ti}$ antisite defects, requiring 1.6 eV to form, were the lowest energy defects in Ti_3AlC_2 [46]. At 2.96 eV, the same antisite defect was also the lowest energy defect in Ti_2AlC [45]. As irradiation defect growth is heavily dependent on defect migration, energies of migration, E_m 's, were also reported, and were also shown to be quite low for several defect types. For example, Middleburgh *et al.* [48] calculated the migration energies for V_c , V_{Si} , C_i and Si_i to be, 4.3 , 0.61 , 0.45 and 2 eV, respectively. Interestingly, when Si_i was coupled to an adjacent vacancy, the migration energy for this interstitialcy migration mechanism was as low as 0.02 eV [48]. These results suggest rapid Frenkel defect recombination for Si defects in the Si-layer. Similarly, the migration energies of V_{Al} , Al_i , C_i and V_c in Ti_3AlC_2 , were calculated to be 0.6 , 0.4 , 0.55 and 0.46 eV [48].

Xiao *et al.* further described the effect of bond character between various MAX compositions, predicting that the more ionic character of the Ti-Al bonds found in Ti_3AlC_2 and Ti_2AlC would lead to enhanced irradiation tolerance compared to Ti_3SiC_2 by allowing for easier recovery of lattice damage [45]. With a higher Al:TiC block ratio, and thus a larger volume of point defect sinks, Ti_2AlC was predicted to have greater tolerance to irradiation damage than its 312 counterpart [45]. It was then theorized that the Al-containing phases would have better irradiation tolerance, due to the ease of forming stable antisite defects over Frenkel pairs, which would allow them to recover irradiation damage more easily. In general, the consensus seems to be that the low energies needed for the formation of antisite and point defects within the A-layer suggest that these layers could act as potent defect sinks within each nanolaminated layer.

Recently, the neutron irradiation up to 0.1 displacements per atom, dpa, of several MAX phases was reported, including Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , and Ti_2AlN [50]. It was shown that Ti_3SiC_2 and Ti_2AlC maintained phase stability after irradiation, while Ti_3AlC_2 and Ti_2AlN dissociated into their binary MX counterparts, viz. TiC and TiN , respectively. Lattice distortions mirroring those observed in ion irradiations were observed after irradiation at 350(40) °C, while irradiation at 710(50) °C resulted in a relaxed lattice with LPs that were near their pristine values [50].

In our previous work, TEM was used to characterize the defects formed after Ti_3SiC_2 and Ti_2AlC samples were irradiated to 0.4 dpa at different temperatures [51]. With about 1.5 orders of magnitude lower defect densities, Ti_3SiC_2 appeared to be more irradiation tolerant than Ti_2AlC . Ti_2AlC also showed extensive microcracking due to anisotropic expansion, after irradiation to 0.4 dpa at 350(40) °C. In both materials, the only irradiation dislocation loops observed were within the basal planes, with a Burgers vector, $\mathbf{b} = \frac{1}{2} [0001]$. Said otherwise, they were interstitial dislocation loops, IDLs. In a more recent neutron study by Ang *et al.*, commercially available Ti_3AlC_2 material, that contained $\text{Ti}_5\text{Al}_2\text{C}_3$ as an impurity phase, was irradiated up to ~2 dpa at ~400 °C [52]. The authors reported that, while crystallinity was maintained, extensive microcracking was seen throughout the sample, and was also attributed to anisotropic LP swelling. The swelling reduced the mechanical strength of the material by 90 % [52]. Based on these results, it is reasonable to assume that if the problem of anisotropic swelling - at intermediate temperatures - of the MAX phases is not solved, it is unlikely that these phases can be used in LWR applications.

The purpose of this work is to thus to shed more light on the effects of higher neutron irradiation doses and temperatures on polycrystalline Ti_3SiC_2 and Ti_3AlC_2 , henceforth referred to as TSC and TAC, respectively. Our focus is on temperatures higher than 600 °C in a first attempt to determine whether

these materials could in principle be used for Gen IV reactors. The irradiations were carried out at the Idaho National Laboratory, INL, and some of the irradiated samples were characterized.

2 Experimental Details

TSC samples were prepared by ball milling stoichiometric mixtures of Ti (99.9%, -325 mesh) Si (99.5%, -325 mesh) and C powders (99.9%) - all procured from Alfa Aesar, Ward Hill, MA, USA - for 24 h, after which were then poured into graphite dies and hot pressed, HPed, at 1450 °C for 6 h under a load corresponding to a stress of ~ 40 MPa. The vacuum was 10^{-1} Pa. Samples of TAC were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti_2AlC (Kanthal, Hallstahammar, Sweden) and TiC powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h. The mixture was HPed, as above, at 1400 °C for 4 h.

To fit into the irradiation capsules, three types of test specimens were electro-discharged machined, EDM, from the HPed blanks: $1.5 \times 1.5 \times 25.4$ mm³ resistivity bars, $16 \times 6 \times 0.7$ mm³ tensile dogbones and discs, 3 mm in diameter that were 0.3 mm thick, for TEM observation. All samples were polished with a final surface preparation of 1200 grit SiC to remove the EDM residue, and then cleaned in hydrochloric acid before loading into the capsules. It is worth noting that all post-irradiation characterization work in this paper was carried out on the resistivity bars, due to limited time and access to samples.

The irradiation was carried out at the 125 MW INL Advanced Test Reactor (ATR) in multiple phases depending on the target dose of the sample sets. The high dose irradiations were carried out in the East Flux Trap position 5 and the inboard location A-3 of the ATR, with a high fast neutron flux (average peak fast flux $\sim 1.7 \times 10^{14}$ n/cm²s, $E > 1.0$ MeV). The low dose irradiations utilized the ATR Hydraulic Shutter Irradiation System (HSIS), also referred to as the Rabbit system, at the B-7 position (average peak fast flux $\sim 8.1 \times 10^{13}$ n/cm²s, $E > 1.0$ MeV). The capsules at the EFT, A-3 and B-7

positions were in direct contact with coolant water, and were filled with a mixture of helium, He, and argon, Ar, to provide the necessary thermal conductivity to achieve the desired irradiation temperatures.

A general purpose Monte Carlo N-Particle transport code, MCNP [53], full core physics model was used to calculate the as-run heat rates, flux, and fluences for each specimen within each irradiation capsule. All materials within the experiment employed the ENDF-V.II data library and MCNP standard cross-section data libraries [53] were used in the full core models. The fluence analysis was performed using four model splits per cycle based on the as-run ATR power history. Each split described an MCNP model that adjusted for the shift in neck shims, control drums, and fuel loading, impacting the local neutron flux [54-56]. As-run heating rates were obtained using the ATR power history, core loading, and shim position data for each cycle in which the experiment capsules were irradiated [57, 58]. In this work, the dpa rate was estimated using a tally multiplier card with a standard flux tally in MCNP. As a result, the dpa conversion factor for the MAX phase samples irradiated in this work was $4.2 \times 10^{21} \text{ n/cm}^2 = 1 \text{ dpa}$, which was comparable to that used in our previous study, based on calculations of SiC [51].

The irradiation conditions of each capsule are compiled in Table 1, being the average of all values calculated for the MAX phase specimens irradiated in each capsule. For comparison, an average for each dose and temperature regime, i.e. D1 or T1, was calculated. This work thus explored the neutron irradiation response of TSC and TAC at 0.14(1), 1.6(1) and 3.4(1) dpa, denoted henceforth as D1, D2, and D3, respectively. The irradiation temperatures of 121(12), 735(6), and 1085(68) °C, will henceforth be denoted as T1, T2 and T3. We note that the listed irradiation temperatures are calculated design temperatures that have not been verified by post irradiation temperature monitor tests.

Table 1: Neutron irradiation parameters for TSC and TAC samples used herein. Not all samples were examined post-irradiation. The ones examined are listed in the last column. One standard deviation is denoted in parentheses representing one standard deviation of the last significant digit. The second column lists the acronyms used throughout this paper. The number 1, 2 and 3 denote low, medium and high conditions, respectively.

Capsule	Condition	Specific Temp. (°C)*	Total Fluence (n/cm ²)	Specific dpa‡	Explored herein
D	D1-T1	114(5)	$6.36(5) \times 10^{20}$	0.136(3)	TSC, TAC
E	D1-T2	735(27)	$6.15(5) \times 10^{20}$	0.138(3)	TSC, TAC
F	D1-T3	1143(8)	$6.18(5) \times 10^{20}$	0.140(3)	TSC
G	D2-T1	135(6)	$4.87(4) \times 10^{21}$	1.55(2)	-
H	D2-T2	740(10)	$4.98(4) \times 10^{21}$	1.59(2)	TSC, TAC
I	D2-T3	1010(19)	$5.00(5) \times 10^{21}$	1.56(2)	-
J	D3-T1	115(4)	$1.72(2) \times 10^{22}$	3.42(5)	TSC
K	D3-T2	730(9)	$1.66(1) \times 10^{22}$	3.44(8)	TSC, TAC
L	D3-T3	1100(23)	$1.6(3) \times 10^{22}$	3.39(6)	TSC

* Calculated design temperatures have not been verified by post irradiation temperature monitor tests.

‡ The fluence to dpa conversion factor was $4.2 \times 10^{21} \text{ n/cm}^2 = 1 \text{ dpa}$.

The surface microstructures of pristine and irradiated samples were imaged in a scanning electron microscope, SEM, (Quanta 3D FEG, FEI Company, USA). Irradiated samples were mounted and polished with 1200 grit SiC paper to remove possible friable contamination before proceeding with post-irradiation characterization.

XRD diffraction patterns of the irradiated samples were obtained, and analyzed, using the methods described in [50]. In short, XRD patterns from TSC and TAC irradiated surfaces were obtained using a XRD diffractometer (PANalytical Empyrean, Westborough, MA, USA) set up in the Bragg–Brentano configuration. The diffractograms were collected using continuous scan mode in the 5°–120° 2θ range with a 0.2° step size and 0.4 rad Soller slits. Samples were rotated at 4 revolution/s on a horizontal sample stage. Scans were made with Cu Kα radiation, with $\lambda = 0.15418 \text{ nm}$. The accuracy of the diffractometer in determining LPs, and its instrumental peak-shape function parameters was calibrated

using a LaB₆ standard (NIST 660A). A systematic shift of 0.01% was found in the LPs' evaluation as compared to the LaB₆ standard's reported values and was accounted for throughout.

All diffractograms were analyzed by the Rietveld refinement method, using the FULLPROF code [59, 60]. For each data set a model, assuming the presence of TiC, was refined. The Thompson-Cox-Hastings pseudo-Voigt model was used to refine the peak-shape of each phase's reflections. Lattice strains were also estimated assuming isotropic Lorentzian contributions to the peak shape function [61]. The microstrain, ϵ , in %, was calculated from the full width half maximum (FWHM) Lorentzian component, X , from each sample, assuming [62]:

$$\epsilon(\%) = \frac{\pi}{1.8} X \quad (1)$$

The neutron induced defects were imaged using a transmission electron microscope, TEM (Tecnai TF30-FEG STwin STEM, FEI Company, Hillsboro, OR, USA) equipped with an electron energy loss spectroscope, EELS (GIF System, Gatan, Inc., Pleasanton, CA, USA), and an energy dispersive X-ray spectroscope, EDX (EDAX Inc., Mahwah, NJ, USA). TEM lamellas were prepared using a Ga⁺ focused ion beam, FIB, (Quanta 3D FEG, FEI, Hillsboro, OR, USA) by milling out $\sim 25 \times 2 \times 15 \text{ } \mu\text{m}^3$ sections from the irradiated resistivity bars, which were then lifted onto TEM Cu grids. Samples were thinned in the FIB down to a final milling step using a voltage of 5 kV and a 77 pA ion emission current until small perforations were observed in the foils. FIB damage was cleaned with a final polish using a voltage of 2 kV and a 27 pA ion emission current. Previous work has shown the MAX phases to be resilient to Ga⁺ ion damage [63], and samples of pristine material were also prepared, which revealed no signs of implantation or Ga⁺ induced defects. Brightfield, BF, and darkfield, DF, TEM micrographs, at various tilts, as well as selected area electron diffraction (SAED) patterns, were collected to characterize the irradiation defects.

Log-ratio measurements of EELS spectra were collected to generate a relative mean free path that was then used to calculate lamella thicknesses following the equation developed by Iakoubovskii *et al.* [64]. The diameters and lengths of more than 200 loops, from multiple regions when possible, were measured, and averaged, using image analysis software (ImageJ, NIH, Bethesda, MD, USA).

To quantify the effect of irradiation-induced defects on the electrical properties, post-irradiation room temperature, RT, resistivity, ρ_{RT} , measurements were carried out using a 4-point probe technique. A 100 mA current was used. Voltages were recorded once per second for 300 s, until a steady voltage was recorded, and averaged over time. A resistivity jig was constructed to house the standard metallographic mount used for each sample. The jig consisted of 4 gold-plated, spring-loaded brass pins secured along an acrylic plate. The plate was aligned to the jig frame using guide pins, and was locked in place in contact with the sample surface using thumbscrews. The jig ensured that consistent contact was achieved between the sample surface and the probe leads. As described above, the samples were lightly polished with 1200 grit SiC polishing paper to remove any surface contamination. The entire apparatus was shielded with lead bricks to protect the users during data sampling. Due to limitations to sample access, only 1 bar was prepared for each irradiation condition.

3 Results

SEM micrographs of the 1200 grit SiC polished surfaces of the irradiated samples of TSC and TAC are compiled in Figs. 1a-l. For a list of acronyms used to describe the various samples after irradiation refer to the second column in Table 1. SEM micrographs of pristine TSC (Fig. 1a) and TAC (Fig. 1b) show dense and predominately single phase surfaces with limited pullouts and cracking. Like in our previous work, SEM micrographs of TSC irradiated to 0.14 dpa at 121 °C, henceforth denoted as TSC-

D1-T1 (also see Table 1) were microcracked as indirectly evidenced by the increased propensity for grain pullout (Fig. 1c). When the dose was increased to 3.4 dpa, at 121°C, viz. sample TSC-D3-T1, significantly more microcracking and pullouts were observed as shown in Fig. 1i.

After irradiation at 735 °C, for all doses, the extent of microcracking in the TSC samples is reduced compared to those irradiated at the lower temperature (compare Figs. 1c and d and Figs. 1i and j). That trend continues for the 1085 °C irradiations (Figs. 1e and 1k); in this case the samples appear to be fully dense with no apparent cracks. Said otherwise its surface was indistinguishable to the pristine samples (Fig. 1a).

The response of the TAC samples vis-à-vis neutron dose and temperature is comparable to that of TSC. Higher doses and low temperatures (Figs. 1f) are more detrimental than irradiations at higher temperatures (Figs. 1g and l). However, as a comparison of Figs. 1c and f makes clear, all else being equal, the TAC-D1-T1 samples were more cracked than their TSC counterparts.

Pristine	<div><div>Ti₃SiC₂</div><div><div>a)</div><div>25 μm</div></div></div>	<div><div>Ti₃AlC₂</div><div><div>b)</div></div></div>	
dpa	<div>121 °C</div> <div>735 °C</div> <div>1085 °C</div>		
0.14	<div><div>Ti₃SiC₂</div><div><div>c)</div></div></div>	<div><div>Ti₃SiC₂</div><div><div>d)</div></div></div>	<div><div>Ti₃SiC₂</div><div><div>e)</div></div></div>
	<div><div>Ti₃AlC₂</div><div><div>f)</div></div></div>	<div><div>Ti₃AlC₂</div><div><div>g)</div></div></div>	
1.6	<div><div>Ti₃SiC₂</div><div><div>h)</div></div></div>	<div><div>Ti₃SiC₂</div><div><div>i)</div></div></div>	
3.4	<div><div>Ti₃SiC₂</div><div><div>j)</div></div></div>	<div><div>Ti₃SiC₂</div><div><div>k)</div></div></div>	
	<div><div>Ti₃AlC₂</div><div><div>l)</div></div></div>	<div><div>Ti₃AlC₂</div><div><div>m)</div></div></div>	

Figure 1: a)-l) SEM micrographs of 1200 grit polished surfaces of pristine Ti_3SiC_2 and Ti_3AlC_2 , and after irradiation to 0.14, 1.6, and 3.4 dpa at temperatures of 121, 735 and 1085 °C. Increased pullout and microcracks are observed after irradiation at 121 °C. At higher irradiation temperatures, notably 1085 °C, the sample morphologies are indistinguishable from pre-irradiated samples. The scale bar shown in (a) is the same for all micrographs shown.

TEM micrographs of unirradiated TSC and TAC samples were taken to provide a baseline for comparison with those after irradiation (Fig. 2). The pristine samples were handled in exactly the same way as the irradiated samples to ensure an accurate comparison could be made. The majority of grains observed were - with the presence of occasional growth dislocations or stacking faults - generally defect free. Grains near the top surface of the TEM liftouts - i.e. near the polished surface - exhibit more complex defect networks, as seen in TSC (Fig. 2a) and TAC (Fig. 2b). These were attributed to deformation induced by the mechanical polishing used prior to FIBing the liftouts. When imaged directly on zone parallel to the basal planes, in the $[11\bar{2}0]$ direction, these defects appear as short line segments, and were similar in appearance to previously reported dislocation loops found in Ti_3SiC_2 and Ti_2AlC [51]. However, by tilting away from zone, it is revealed that these defects are curved arcs within the basal plane, sometimes appearing faceted, depending on sample orientation (Fig. 2a). It is worth noting that the density of these defects was considerably lower when grains far removed from the polished surfaces were imaged.

It is important to note that unlike interstitial dislocation loops, IDLs, which lie in the basal planes, with a $\mathbf{b} = \frac{1}{2} [0001]$ [51], the defects observed in the MAX phases – long assumed to be basal dislocations - do *not* lose diffraction contrast in a 2 beam conditions with $g \ 1\bar{1}00$ which strongly suggests that they are not dislocations, but ripplocations [65]. In the remainder of this paper, basal defects that did *not* disappear under a $g \cdot \mathbf{b} = 0$ condition in which they should have disappeared – had they been classic basal dislocations - are referred to as bulk ripplocations, BRs.

Figure 2: Brightfield TEM micrographs of, a) Ti_3SiC_2 and, b) Ti_3AlC_2 prior to irradiation, exhibiting pre-existing bulk ripplocations, BRs. These BRs – previously erroneously described as basal dislocations - are sometimes observed in the MAX phases as growth defects and/or after deformation, and are presented for comparison with irradiation induced defects.

Figure 3 shows TEM micrographs of TSC and TAC samples irradiated to 0.14 dpa, at various temperatures. If defects formed after irradiations at 121 °C (Figs. 3a and d), they were below the resolution of our TEM. That does not imply that no defects were found, however. Basal perturbations believed to be BRs were observed in both TSC-D1-T1 and TAC-D1-T1 (Figs. 3a and d). After irradiation at 735 °C, BRs were observed in both the TSC (Fig. 3b) and TAC (Fig. 3e) samples and denoted by white arrows. Occasionally, some small loops were observed, but insufficient observations were made to calculate their dimensions and/or density. Irradiation to 0.14 dpa at 1085 °C resulted in the formation of IDLs in sample TSC-D1-T3 (Fig. 3c). The nature of these loops, like all others of their type, were confirmed to be basal dislocation loops, with a $\mathbf{b} = \frac{1}{2} [0001]$, by tilting to several g excitations to meet the $g \cdot \mathbf{b} = 0$ criterion. These loops were seen to occur in the vicinity of stacking faults, SF.

Figure 3: Brightfield TEM micrographs of samples irradiated to 0.14 dpa, a) Ti_3SiC_2 at 121 °C, b) 735 °C, and, c) 1085 °C and, d) Ti_3AlC_2 at 121 °C and, e) 735 °C. In all cases, BRs (denoted by white arrows) - similar to those observed in the as-received samples – are observed. At 735 °C, some small loops are observed dispersed throughout the TAC grain in (e). In (c), IDLs are observed within the basal planes, with $\mathbf{b} = \frac{1}{2} [0001]$. Insets are SAED patterns of the imaged regions.

Irradiation to 1.6 dpa at 735°C of TSC (TSC-D2-T2) resulted in the formation of IDLs throughout this sample (Fig. 4a). The average loop diameter was 21(6) nm and the loop density was estimated to be $6(1) \times 10^{20}$ loops/m³ (Fig. 4a). Remarkably, a denuded zone, DZ, roughly 430(60) nm wide, completely free of all defects, was observed at a GB between a TSC and an impurity TiC grain (Fig. 4a). HRTEM micrographs of a single loop (Fig. 4b) revealed black/white strain contrast lobes, typical of IDLs [66].

The TSC-D3-T1 sample, on the other hand, was riddled with a significant number of defect clusters throughout the grains (Fig. 4c, d). Not surprisingly, given the low temperature, no discernable DZ was observed near the GB imaged (Fig. 4c). HRTEM of a nearby grain imaged on the $[11\bar{2}0]$ zone axis reveals a relatively large number of basal perturbations and basal defect clusters (Fig. 4d). The linear diffusion streaks in the SAED pattern (inset of Fig. 4d) confirm the presence a high density of defects.

Figure 4: Brightfield TEM micrographs of, a) Ti_3SiC_2 samples irradiated to 1.6 dpa at 735 °C showing IDLs imaged on the $[11\bar{2}0]$ zone axis, i.e. parallel to the basal planes, with an average loop diameter of 21(6) nm and a loop density of $6(1) \times 10^{20}$ loops/m³. A denuded zone, DZ, of 430(60) nm can be seen at a GB adjacent to a TiC particle. b) a single loop in (a), showing black/white lobed strain contrast. c) GB in the Ti_3SiC_2 sample irradiated to 3.4 dpa at 121 °C revealing small black spots and defect clusters throughout. d) a nearby grain imaged - in high resolution - on the $[11\bar{2}0]$ zone axis that reveals basal perturbations and defect clusters within the basal planes. Insets in (a) and (d) are SAED patterns of the micrographs shown in the same panels.

After irradiation of the TAC samples to 3.4 dpa at 735 °C, IDLs were observed (Figs. 5a and b). In this case, their density was $3(1) \times 10^{20}$ loops/m³ and their average diameter was 75(34) nm. The loops were seen to form throughout the grain (Fig. 5c). An 829(117) nm wide DZ was observed (Fig. 5a). HRTEM micrographs of this sample also showed extensive basal perturbations in addition to the basal IDLs (Fig. 5d). This sample exhibited a combination of defect clusters, IDLs, and SF. The SFs observed at this condition, denoted by arrows (Fig. 5c) are seen to form small defect clusters and loops within them, and were confirmed - via STEM EDX - to be deficient in Al (Fig. 5b).

Figure 5: a) Brightfield TEM micrographs of Ti_3AlC_2 irradiated to 3.4 dpa at 735 °C showing basal dislocation loops imaged near the $[11\bar{2}0]$ zone axis with an average loop diameter of 75(34) nm and a loop density of $3(1)\times 10^{20}$ loops/ m^3 . A denuded zone, DZ, of 829(117) nm is observed near the GB. A band of TiC is observed between the Ti_3AlC_2 grains in this area. b) Drift corrected STEM/EDX line scan (orange line) across the stacking fault, SF, within the black box in (a) reveals Al deficiency in the white contrast band. c) Higher magnification of a region in (a) reveals IDLs, short SFs, and defect clusters dispersed throughout the grain. d) HRTEM micrograph of the loops in this region show extensive perturbations and defect clusters within the basal planes in addition to IDLs. Insets are SAED patterns of imaged regions.

After irradiation to 3.4 dpa at 735 °C, TEM micrographs of a TSC sample showed the existence of IDLs, 30(8) nm in diameter with a density of $2.4(2) \times 10^{20}$ loops/m³ (Fig. 6a). HRTEM micrographs of the loops revealed a complex interaction of several IDLs stacked along the c-axis (Fig. 6b). More significantly and remarkably, a large DZ – 860(90) nm wide - was observed, and was notably isotropic along both the a- and c-directions of the grain's orientation (Fig. 6c). Cavities 7(2) nm wide were also observed at the GBs (Fig. 6d). Near the cavities and GBs, TSC nanograins were also observed (Fig. 6d inset). The nanograins were crystalline, with orientations that were different from the parent TSC grains surrounding them (inset in Fig. 6d).

Figure 6: TEM micrographs of Ti_3SiC_2 irradiated at 735 °C to 3.4 dpa. a) BF micrograph showing IDLs imaged near the $[11\bar{2}0]$ zone axis, with an average loop diameter of 30(8) nm and a loop density of $2.4(2) \times 10^{20}$ loops/ m^3 . b) High resolution micrograph of several loops in (a). c) DF micrograph showing a denuded zone, DZ (arrows), of 860(90) nm wide along both a and c-lattice directions. d) BF micrograph showing cavities - with an average diameter of 7(2) nm - observed at some GBs. Inset of (d) shows small Ti_3SiC_2 nanograins - observed at some GBs - that grew with different orientations to either parent grains (white arrows denote a-axis directions). Insets in (a) and (c) are SAED patterns of imaged regions.

After irradiation to 3.4 dpa at 1085 °C, the TSC sample contained a range of defects (Fig. 7). In one large grain, with basal planes oriented perpendicular to the polishing surface (denoted by white arrow), a relatively large concentration of short BRs (denoted by black arrows) was observed (Fig. 7a). These BRs are most likely not irradiation induced because they were only found near the polished surface and are therefore more likely than not a result of polishing.

Dispersed throughout this grain and agglomerated along, or decorating, the SFs and BRs, IDLs were readily identified (Figs. 7a and b). The loops were, on average, 63(25) nm in diameter with a defect density of $4(1) \times 10^{19}$ loops/m³, restricted to this grain. HRTEM micrographs reveal a large strain field around the IDLs, as they agglomerate near the SFs or BRs (Fig 7b). Tilting the micrograph shown in Fig. 7a to $g\ 1\bar{1}00$ resulted in all IDLs losing diffraction contrast, while the ripplocations dispersed throughout the grain remained in contrast (Fig. 7c). Arguably one of the most important results of this work is that the smaller TSC grains, after irradiation to 3.4 dpa at 1085 °C, appeared to be quite defect free (Fig. 7d).

Figure 7: BF TEM micrographs of Ti_3SiC_2 irradiated to 3.4 dpa at 1085 °C reveal: a) basal ripplocations (BRs) (vertical arrows) and basal dislocation loops (BDLs) (horizontal arrows) pinned at stacking faults dispersed throughout a large grain, on average 63(25) nm in dia. with a density of $4(1) \times 10^{19}$ loops/ m^3 . b) HRTEM micrographs of the loops in (a) reveal the c-axis strain contrast of the loop. c) Tilting of this sample to $g\ 1\bar{1}00$ results in the loss of contrast for the $\mathbf{b} = \frac{1}{2} [0001]$ IDLs; the BRs remain visible under all tilting conditions. d) Smaller grains, without SFs, appear to be defect free. Insets in (a) and (c) are SAED patterns of the imaged regions.

For the TAC-D3-T2 sample (Fig. 8a), SFs, confirmed to be TiC in composition, were observed with defect clusters throughout each faulted region. At the highest temperature, in sample TSC-D3-T3, cavities were observed at some of the GBs (Fig. 8b). More extensive cavity formation, however, was observed in preexisting TiC platelets or wide TiC SFs (Fig. 8b). A through focus study of region A in Fig. 8b - shown in Figs. 8c-e - reveals that the cavities within this TSC SF region are 3.8(7) nm in diameter and faceted. These cavity networks were observed in several regions, all of which were TiC in composition, as confirmed via STEM/EDS.

Figure 8: a) Brightfield TEM micrographs of SFs in Ti_3AlC_2 irradiated to 3.4 dpa at 735 °C, which formed defect clusters within. b) Near a delaminated region in Ti_3SiC_2 irradiated to 3.4 dpa at 1085 °C, cavities of 3.8(7) nm dia. were observed along a series of TiC impurity platelets, confirmed via EDS to be TiC in composition. Through-focus TEM micrographs of region A in (b) taken c) 300 nm under-focus, d) in focus and, e) 300 nm over-focus detail the faceted nature of the cavities.

Like in our previous work [51], under all irradiation conditions, the impurity TiC grains were significantly more defective than their surrounding TSC and TAC matrices (Fig. 9). A typical TiC grain in the TSC-D1-T3 sample with a high density of defect clusters and small loops, as well as a small DZ

of 70(5) nm was observed near a GB (Fig. 9a). Similar defect clusters and loops were also observed in TiC impurity grains in samples TSC-D2-T2 (Fig. 9b) and TSC-D3-T2 (Fig. 9c). Dislocation loops were also observed in the TiC grains found in the TAC-D1-T2 sample (Fig. 9d).

Figure 9: Brightfield TEM micrographs of TiC impurity particles in, a) Ti_3SiC_2 irradiated to 0.14 dpa at 1085 °C, b) 1.6 dpa at 735 °C and, c) 3.4 dpa at 735 °C and, d) Ti_3AlC_2 irradiated to 0.14 dpa at 735°C. All TiC particles observed contained defect clusters and dislocation loops in concentrations that were significantly higher than their surrounding MAX phase matrices. Insets are SAED patterns of imaged regions.

The Rietveld refinement results of the XRD data collected herein are summarized in Table 2. As noted above, TiC was included in the refinements to obtain the best fits. The as-received TiC content, in TSC samples, was estimated to be 7.7(3) wt. %. After irradiation, the TiC content fluctuated around the values found in the pristine samples (Table 2).

The XRD patterns of the as-received TAC did not have peaks that could be ascribed to TiC. After 121 °C irradiation the TiC content in the TAC-D1-T1 sample was 5.5(3) wt.%. After irradiation at 735 °C, the TiC contents were determined to be 2.0(2), 2.8(2) and 3.5(2) wt. %, after D1, D2 and D3, respectively. These results are strikingly different from our previously work at the MIT reactor [50], for which the TiC content - after irradiation to 0.1 dpa at 350(40) °C - was ~ 50 wt.% (see discussion).

Table 2: Summary of Rietveld refinement results of XRD patterns collected from the TSC and TAC surfaces studied herein, including microstrain values, ϵ %, calculated from FWHM parameter X (Eq. 1).

Sample	χ^2	a-LP (Å)	c-LP (Å)	Ti _{II} z position†	C z position†	TiC content wt. %	TiC a-LP (Å)	X	ϵ %
TSC-as-received	2.7	3.0665(1)	17.667(1)	0.36352(1)	0.5820(1)	7.7(3)	4.3183(3)	0.32(3)	0.55(5)
TSC-D1-T1	14.4	3.0543(5)	18.062(1)	0.3659(2)	0.5771(7)	4.7(3)	4.3376(1)	0.074(1)	0.13(2)
TSC-D1-T2	28.8	3.0680(2)	17.674(1)	0.3668(2)	0.5733(7)	9(1)	4.3239(2)	0.06(1)	0.10(1)
TSC-D1-T3	11.1	3.0682(2)	17.679(1)	0.3649(3)	0.576(9)	10.1(2)	4.3228(3)	0.04(1)	0.07(1)
TSC-D2-T2	20.6	3.0675(3)	17.673(1)	0.3656(2)	0.572(1)	4.4(1)	4.3167(5)	0.08(1)	0.15(2)
TSC-D3-T3	17.2	3.0679(2)	17.669(3)	0.3618(2)	0.568(1)	12(3)	4.3197(1)	0.05(1)	0.08(1)
TAC-as-received	2.78	3.073(1)	18.562(2)	0.1309(3)	0.577(1)	*	-	0.37(3)	0.65(5)
TAC-D1-T1	17.9	3.0365(4)	19.179(1)	0.1278(4)	0.574(1)	5.5(3)	4.3257(3)	0.06(1)	0.10(2)
TAC-D1-T2	18.2	3.0733(2)	18.562(1)	0.1282(1)	0.5729(4)	2.0(2)	4.3256(2)	0.08(1)	0.13(1)
TAC-D2-T2	22.3	3.0723(4)	18.549(1)	0.1287(2)	0.574(1)	2.8(2)	4.3195(2)	0.07(1)	0.13(1)
TAC-D3-T2	26.4	3.0722(4)	18.551(1)	0.1288(2)	0.572(1)	3.5(2)	4.3237(2)	0.04(1)	0.07(2)

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

† Z-height atomic position of atom in unit cell.

* Below detectability limit.

Rietveld refinement of sample TSC-D1-T1 showed an increase in the c-LP, from the as-received 17.667(1) Å to 18.062(1) Å, and a decrease in the a-LP, from 3.0665(1) Å to 3.0543(5) Å. Interestingly,

and in all cases, the microstrains after irradiation were smaller than in the as-received samples. For example, the TSC-D1-T2 resulted in a slight lattice distortion, with $a\text{-LP} = 3.0680(2) \text{ \AA}$, $c\text{-LP} = 17.674(1) \text{ \AA}$, and a 0.1 % microstrain. The TSC-D1-T3 lattice was further relaxed with a microstrain of 0.07% and LPs of $a\text{-LP} = 3.0682(1) \text{ \AA}$ and $c\text{-LP} = 17.679(1) \text{ \AA}$. The TSC-D2-T2 sample had the highest post-irradiation microstrain at 0.15 %, but maintained near pristine LPs with $a\text{-LP} = 3.0675(3) \text{ \AA}$ and $c\text{-LP} = 17.673(3) \text{ \AA}$. With an $a\text{-LP} = 3.0679(2) \text{ \AA}$ and $c\text{-LP} = 17.669(3) \text{ \AA}$ and 0.08% microstrain, distortions in the D3-T3 sample were also minimal. It is clear that for TSC irradiation at 745 °C, and above, results in significant recovery of the LPs. This is best seen in Fig. 10a.

Figure 10: a) Effect of irradiation temperatures on the a- and c-LPs of TSC samples. Uncertainties are smaller than symbols size. A similar trend was observed for TAC samples (not shown). b) Plot of log ρ_{RT} as a function of irradiation temperature.

Rietveld refinement of the XRD patterns of TAC revealed a similar trend. The sample irradiated at 121 °C, TAC-D1-T1, exhibited the greatest lattice distortion, as the a-LP decreased from 3.0728(1) Å to 3.0365(4) Å, and c-LP increased from 18.562(2) Å to 19.179(1) Å. At 0.1%, the microstrain decreased significantly from the 0.65 % of the as-received samples. After irradiation at 735 °C and 1085 °C, however, the LPs return to their values before irradiation. The microstrains are also significantly lowered.

In concurrence with previous studies [50, 51] the post-irradiation ρ_{RT} results show an increase in electron scattering after irradiation at low temperatures (Fig. 10b). At 9.1 and 9.6(1) $\mu\Omega\cdot m$, the ρ_{RT} of the TSC-D1-T1 and TAC-D1-T1 samples, respectively, were 50 times higher than their respective pristine values, at 0.17 and 0.21(1) $\mu\Omega\cdot m$. At 0.24 and 0.25 $\mu\Omega\cdot m$, ρ_{RT} of the TSC-D1-T2 and TSC-D1-T3 samples, respectively, are seen to saturate at values near their pristine values. Increasing the neutron dose, at 735 °C, did not greatly alter ρ_{RT} (compare ρ_{RT} of TSC-D2-T2 and TSC-D3-T2 samples in Fig. 10b, at 0.27(1) and 0.29(1) $\mu\Omega\cdot m$, respectively). At 0.41(1) and 0.43(1) $\mu\Omega\cdot m$, ρ_{RT} for the TAC-D1-T2 and TAC-D3-T2 samples, respectively, show a similar saturation in ρ_{RT} values at 735 °C, though twice that of TSC. At 18.1(1) $\mu\Omega\cdot m$, the ρ_{RT} of the TSC-D3-T1 sample was greatly increased. Lastly, the TSC-D3-T3 sample showed an increase in ρ_{RT} to 0.55(1) $\mu\Omega\cdot m$, a value ~ 3 times that of pristine.

4 Discussion

This work reports on the effects of neutron irradiations of two MAX phases to the highest temperatures and highest neutron doses ever carried out to date. The most important finding of this work is the presence of DZs of the order of $\approx 1 \mu m$ after irradiations at ≈ 735 °C in TSC (Fig. 11). For the

TAC composition, DZs of the order of 830 nm after irradiations at the same temperature were observed (Fig. 11). As far as we are aware, these values are among the highest reported for ceramics, e.g., $\sim 1\mu\text{m}$ DZ seen in MgAl_2O_4 irradiated to 35 dpa at 650 °C with 2.4 MeV Mg^+ ions [67]. This is especially true given the relatively low irradiation temperatures. In contrast, SiC irradiated to ~ 2 dpa at 1380 °C resulted in DZs on the order of 57 nm that, despite the much higher temperatures, are roughly an order of magnitude narrower than observed here [68]. The fact that DZs of the order of 1 μm are observed at ≈ 735 °C in TSC suggests that a microstructure with grains of that order could remain defect free even after high neutron doses. The fact that grains of the order of 2 to 3 μm are totally defect free after irradiations at the highest temperatures, even after 3.5 dpa, is also significant and consistent with the aforementioned conjecture. Spark plasma sintering has been shown to produce fine grained MAX phases. For example, Lapauw *et al.* produced Ti_2SnC samples with a grain size of $\approx 1\mu\text{m}$ using this technique [69].

a) Irradiation Defects and Denuded Zones

In agreement with our previous study [51], IDLs were observed in TSC and TAC at 735 °C and above (Figs. 4a, 5, 6, 7). The irradiation defects are summarized in Table 3. Simultaneously, defect-free DZs adjacent to most GBs in both TSC and TAC (Fig. 5a) at these conditions were observed, and their width seemed to increase with irradiation dose (Fig. 11). For example, at 860(90) nm, the DZs in TSC irradiated to 3.4 dpa (Fig. 6c) were twice as wide as those in irradiated to 1.6 dpa at the same temperature, viz. 430(60) nm (Fig. 4a). The increase in DZ width with dose can be attributed to an increase in mobility of point defects due to ionization-enhanced diffusion, similarly observed in ion irradiated UO_2 [70]. We note that this is not the first report of relatively large DZs in the MAX phases at intermediate temperatures. In our previous work [51] we observed ≈ 300 nm wide DZs a for a TSC sample irradiated to 0.1 dpa at 710 °C, also plotted in Fig. 11. At 829(117) nm (Fig. 5a), sample TAC-

D2-T2 showed lower but similar DZ width to TSC at this condition (Fig. 11). As the width of a DZ can be heavily dependent on GB structure, it is hereby acknowledged that a more comprehensive characterization of the GBs is needed before any general conclusions concerning the DZs can be reached. Furthermore, as DZ width is known to depend on irradiation temperature and dose rate [71], the increase in DZ width with dose seen here is contrary to conventional modeling expectations and needs further investigation to understand its origin. However, if these results are reproducible, and shown not to be due to experimental error or the particular combination of irradiation conditions used herein, then the importance of this observation cannot be overemphasized.

Table 3. Summary of defects observed in Ti_3SiC_2 and Ti_3AlC_2 after irradiation up to 3.4 dpa and 1085 °C.

Material	Dose (dpa)	Total Fluence (n/cm ²)	Temp. (°C)	IDL size (nm)	IDL density (loops/m ³)	Denuded Zone (nm)	Cavity size (nm)
Ti_3SiC_2	1.6	$4.98(4) \times 10^{21}$	735(6)	21(6)	$6(1) \times 10^{20}$	430(60)	-
	3.4	$1.66(1) \times 10^{22}$	735(6)	30(8)	$2.4(2) \times 10^{20}$	860(90)	7(2)
	3.4	$1.6(3) \times 10^{22}$	1085(68)	63(25)	$4(1) \times 10^{19}$	~1000*	3.8(7)
Ti_3AlC_2	3.4	$1.66(1) \times 10^{22}$	735(6)	75(34)	$3(1) \times 10^{20}$	829(117)	-

*Several grains on the order of 2-3 μm were free of defects, indicating that the denuded zones are at least half the grain width.

As, or even, more important, is that the smaller TSC grains after irradiation to 3.4 dpa at 1085 °C appear to be defect free (Fig. 7d). Given the size of the DZ shown in Fig. 6c this is not too surprising. The DZs in this case could be on the order ~1-2 μm , or larger than half the grain size observed to be defect free. At this time, it is unclear whether the lack of defects is due to the smaller size of the grains and/or the lack of SFs within them. This comment notwithstanding, it is more likely than not that the two are related.

Figure 11: Effect of neutron irradiation dose, in dpa, on width of denuded zones in Ti_3SiC_2 and Ti_3AlC_2 samples irradiated at 735 °C. The datum point at 0.1 dpa was taken from Ref. [49] where the irradiation was carried out at 710 °C.

At temperatures > 700 °C, the mobility of interstitials and vacancies is presumably increased to the point that they annihilate, as observed in the majority of smaller grains throughout the sample (Fig. 7d). One grain, however, shows IDLs to be trapped near SFs (Fig. 7a). Here it is presumed that the SFs are preexisting, and somehow interfere with point defect mobility. In general, the basal planes throughout the grain provide fast diffusion paths along the A-layers. Presumably, the TiC-rich SFs, lacking the high mobility A-layer, are slower diffusion paths for point defects. In Figure 7a, the migration of point defects appears to have been limited or restricted around the SFs, resulting in their agglomeration and subsequent coalescence into loops. Upon reevaluation of our previous work, this can be observed in Figure 9 of Ref. [51]. Many loops - observed around the SFs - can be rendered invisible when tilted to $g_{1\bar{1}00}$. It is hypothesized that the SF boundary acts as a defect sink, but is unable to accommodate defects as easily as the A-planes. The result is the formation of dislocation loops that are clustered in, or around, the SFs, while the remaining MAX grains are defect free. In our previous work it was not clear

whether the irradiation created the SFs or whether they were pre-existing. And while the results shown herein for TSC do not unequivocally answer that question, the much-reduced SF density suggests that they were pre-existing in our previous work [51]. More work is needed to answer this question, especially if it is confirmed that the SFs interfere with the annealing out of defects.

Unique to the samples irradiated to the highest dose, cavities were observed at the GBs of the TSC-D3-T2 (Fig. 6d) and TSC-D3-T3 (Fig. 8b) samples. In light of the large DZs observed, it is apparent that point defects are easily absorbed to the GBs from relatively far distances away. From this evidence, it is clear that vacancies have diffused towards the GB and their agglomeration resulted in formation of small faceted cavities (Figs. 8c-e). Additionally, nanocrystalline grains of TSC were also seen to form at some GBs (Fig. 6d inset). How or why these form is unclear at this time.

Like in most post-irradiation studies, tilting experiments in the TEM are essential to differentiate between irradiation-induced and pre-existing defects (Fig. 2). This is especially important here because we are proposing a new micromechanism in layered solids, bulk ripplations, BRs [72]. The challenge here is thus how to differentiate between IDLs, normal basal plane dislocations and BRs. This is particularly tricky since like IDLs, BRs are characterized by c-axis strain. Let us consider each separately:

- i) Basal dislocations disappear upon tilting when $\mathbf{g} \cdot \mathbf{b} = 0$ and are relatively easy to recognize. None were observed in this work.
- ii) IDLs: When tilted to the $g \ \bar{l}l00$ family of planes, the interstitial loops lose diffraction contrast, in accordance with the $\mathbf{g} \cdot \mathbf{b} = 0$ criterion. This is best seen when Figs. 7a and c are compared. In the latter, the IDLs are no longer visible.
- iii) BRs simply do not disappear under any tilting conditions, as shown herein (compare Figs. 7a and c). In our previous work on a mechanically deformed TSC sample [72] we showed that c-lattice strain is associated with BRs. Given that non-basal dislocations in the MAX phases

do not exist because of the latter's high c/a ratios, the only possible source of c -strain is the presence of BRs.

b) Irradiation tolerance due to the A-layer

Similar to our previous work [51], the TiC impurity grains - present in the pristine TSC samples or generated due to neutron irradiations in their TAC counterparts - were highly damaged upon irradiation (Fig. 9). These results once again point to the importance of the A-layer in the MAX phases for improving their irradiation tolerance. This is especially apparent when comparing TSC and TiC after irradiation to 3.4 dpa at 1085 °C. As noted above, most TSC grains were defect free, with a few IDLs clustered around the SFs (Fig. 7). Under the same conditions, the TiC regions are not only highly damaged relative to their surrounding MAX phase (Fig. 9), but also formed small, faceted cavities in their vicinity regardless of whether the matrix is TSC (Figs. 6d) or TAC (Fig. 8b-d). This is attributed to the accumulation of vacancies within these regions. The lack of such cavities in the MAX phases, on the other hand, implies that such preferential vacancy accumulation does not occur as readily.

Neutron irradiation leads to the formation of point defects and Frenkel pairs, most of which annihilate rapidly after generation from cascade events. With sustained irradiation fluence, some of these defects can either annihilate, or accumulate within the lattice into larger defect structures. Recent first principle studies [45-48] have illustrated the benefit of the presence of the A-layer in the MAX phases in terms of point defect accommodation. Most reports have shown that Frenkel pair defects of the M, A, and X atoms in the MAX phase structures are most favorably formed as interstitials within the free volume spaces between the M and the A layers. Furthermore, the A-layer was shown to be capable of accommodating antisite defects, which in Ti_2AlC and Ti_3AlC_2 had lower energies of formation, E_f 's, compared to the Al_{FP} . It was thus proposed that due to the low E_f 's of point defects in the A-layers,

every A-layer could in principle act as a defect sink during irradiation. By readily forming stable Frenkel pairs and antisites, the MAX phases were predicted to maintain structural stability under irradiation.

This hypothesis, of structural stability, is further confirmed by the results shown in this work. SAED patterns show that both TSC and TAC remain fully crystalline up to 3.4 dpa irradiation, with no diffuse halos indicative of amorphization. There are differences between the two compounds, however. For example, in TSC after irradiation to 3.4 dpa at 735 °C, the diameters of the IDLs and their density are 30(8) nm and $2.4(2) \times 10^{20}$ loops/m³, respectively. Under the same conditions, the respective values for TAC are 75(34) nm and $3(1) \times 10^{20}$ loops/m³. Since the only significant difference between the two ternaries is the nature of the A element, these results suggest that the Si-layer in TSC, as well as the nature of the Ti-Si and/or Si-Si bonds, allow for a higher mobility of Si defects. The increased DZ-widths in TSC compared to those in TAC (Fig. 11), lead to the same conclusion. This is counter to the DFT calculations, that predict that at 2 eV, the migration energy of Si_i in Ti₃SiC₂ is significantly higher than the 0.4 eV of the Al_i defects in Ti₃AlC₂ [48]. That said, it is possible that the answer resides in an interstitialcy mechanism.

c) Phase stability

The TiC impurity content in the TSC samples was 7.7(3) wt. % before irradiation, ~ 5 wt. % in the T1 and T2 samples and ~ 10 wt. % in the T3 samples. Given that irradiation cannot decrease the TiC content, these results imply that the TiC distribution in the pristine samples was inhomogeneous. This comment notwithstanding - and based on only two data points - it is possible that the TiC content for samples irradiated at 1085 °C was slightly higher than pristine.

The situation in the TAC case is different since, before irradiation, the TiC content was below our XRD's detectability limit. Thus the increase in TiC content – corresponding to 2-5.5 wt. % after

irradiation - has to be irradiation induced. In our previous work, TAC samples irradiated to 0.1 dpa at 350(40) °C resulted in a significantly higher increase in TiC content (up to ~ 50 wt.%) [50]. At present, it is unclear why the two sets of TAC samples – those irradiated at MIT and INL - behaved so differently. The only nominal difference between the two sets was the precursor Ti_2AlC powders – sourced from Kanthal used to make TAC. Our experience over the years with Kanthal powders has been that various nominally identical batches behaved differently. It is thus likely that this variability could be responsible for the two different outcomes observed herein. This is an important result since it implies that: i) the decomposition previously reported [50] is probably not intrinsic to TAC. That some decomposition does occur, however, is clear from the results shown in Table 2 and, ii) for nuclear applications much purer, and more single-phase, powders/samples are required. This is especially true here if indeed the TiC impurities are responsible for the cavities formed. Although not measured, it is reasonable to assume that such cavitations would adversely impact the mechanical properties and thus should be minimized.

d) Microcracking

As previously observed [44, 51], neutron irradiation of the MAX phases at lower temperatures resulted in extensive microcracking (Figs. 1a, d and g) due to the anisotropic expansion/contraction of the LPs (see Table 2). We attributed the latter to the formation of low mobility defects that increased the c-LP and shortened the a-LPs (Table 2). These anisotropic dimensional changes, in turn, result in internal stresses that ultimately result in microcracking and swelling. Clark *et al.* confirmed this to be the source through quantitative analysis of anisotropic lattice expansion and its effect on misfit strain [44]. The fact that the lattice distortions for the TAC samples (-1.2% a-LP, 3.3% c-LP) are significantly greater than those in the TSC samples (-0.4% a-LP, 2.2% c-LP) explains why the former is more microcracked and is consistent with our conjecture.

A perusal of the results shown in Table 2, reveal that these lattice distortions are limited to the irradiations carried out at 121 °C for both materials. At higher temperatures, the LPs return to values comparable to their pre-irradiated values (Fig. 10a), presumably because defect mobilities are higher. Recovery of the lattice distortions ultimately reduces microcracking.

Interestingly, at 0.55% and 0.65% the microstrains in the as-received TSC and TAC samples, respectively, were quite high, and likely due to the residual strains induced during fabrication. In all cases, the microstrain is seen to decrease from as-received values after neutron irradiation. The increased flux of migrating defects and/or microcracking can both result in reducing the microstrains.

e) Electrical Resistivity

The variations in ρ_{RT} with irradiation temperature and dose (Fig. 10b) are similar to what we have previously shown [50]. The low temperature irradiations result in the most drastic increases in ρ_{RT} because: i) the point defects and black spots generated (Fig. 4c) are presumably potent scatterers of electrons and, ii) of microcracking (Figs. 1d, g). After irradiations at 735 °C, the ρ_{RT} values decrease dramatically, and are not much higher than the pristine values (Fig. 10b) presumably because the point defects are either annihilated and/or exist in the form of IDLs, or larger defect structures, that are more coherent with the lattice and cause less electron scattering. The healing/absence of microcracks must also play an important role. The increase in ρ_{RT} after the irradiation to 3.4 dpa at 1085 °C is most probably due to cavity formation at the GBs and near TiC particles (Figs. 6d, 8). The fact that irradiation to 0.14 dpa at 1085 °C did not result in an increase in ρ_{RT} is consistent with the fact that cavities are not nucleated under those conditions.

f) Activation of Al-containing MAX

During post-irradiation examination, it was noted that at < 30 mR/h, the activity counts for most samples were low enough for us to conduct extended length tasks. However, at 160 and 190 mR/h, the TAC-D1-T1 and TAC-D1-T2 samples, respectively, showed a 10-fold increase in activity compared to their TSC counterparts irradiated at the same conditions. Further, the TAC-D3-T2 sample had an activity - 1860 mR/h - that was 3 orders of magnitude higher than TSC, even after > 2 years of decay in storage. Surveying the hot samples, the source of the radioactivity was identified to be Cobalt-60, Co-60. At this time, the Co source remains unknown. However, it has been shown that elemental Al can contain parts per million traces of Co from natural occurring sources [73]. It is plausible then, that trace amounts of Co-59 were present in the starting powders used in the fabrication of the TAC samples sourced from Kanthal. This result further emphasizes the need to carefully source the raw materials and their chemistries.

5 Summary and Conclusions

The impetus for this work was our conjecture a few years ago, that the presence of pure A-layers in the MAX phases would result in extraordinary damage tolerance to neutrons. As shown here the A-layers do indeed endow these phases with an extraordinary ability to mitigate neutron damage at relatively low temperatures. These benefits only accrue, however, at temperatures > 700 °C; irradiations at lower temperatures result in expansion along the c-axis and shrinkage along the a-axis that in turn results in microcracking.

TEM investigations of Ti_3SiC_2 and Ti_3AlC_2 samples exposed to neutron irradiation reveal the existence of several defect morphologies. After irradiation to 0.14 dpa at 121 °C, black spots formed which led to substantial increases in resistivity, and lattice distortions. Irradiation to 0.14 dpa at 735 °C resulted in small basal interstitial dislocation loops, with $\mathbf{b} = \frac{1}{2}[0001]$, interspersed amongst basal

ripplocations. With increasing dose for Ti_3SiC_2 irradiated at 735 °C, the basal dislocation loops grew in size, 21(6) nm and $6(1) \times 10^{20}$ loops/m³ at 1.4 dpa, and 30(8) nm and $2.4(2) \times 10^{20}$ loops/m³ at 3.4 dpa. Further, at 63(25) nm, the largest loops in Ti_3SiC_2 were observed after irradiation to 3.4 dpa at 1085 °C. The latter, however, were only observed near stacking faults; the majority of grains imaged showed no signs of irradiation damage. At 75(34) nm, the dislocations loops in Ti_3AlC_2 were larger, and slightly more numerous with a density of $3(1) \times 10^{20}$ loops/m³. Basal perturbation and defect clusters were also observed in Ti_3AlC_2 at these conditions.

After irradiation to 3.4 dpa, both at 735 and 1085 °C, cavities were observed within the GBs, growing in size at the latter temperature. Additionally, large stacking faults and TiC platelets were seen to form extensive cavity networks, showing faceted features at 1085 °C.

The TiC impurity particles present in the Ti_3SiC_2 samples were significantly more damaged than the matrix they were embedded in, forming extensive defect clusters and dislocation loop networks. These results provide, once again, unambiguous evidence for the benefit of the A-layer in the MAX phases, in mitigating neutron irradiation damage.

Most significant was the presence of large, defect-free denuded zones, nearing 1 μm in size, in Ti_3SiC_2 irradiated to 3.4 dpa at 735 °C. Furthermore, at 1085 °C, most grains on the order of 3-5 μm appeared to be free of damage altogether. However, since the denuded zone widths appeared to be isotropic regardless of the GB orientation with respect to the basal planes, the enhanced defect migration along the basal planes cannot be the only explanation. If the latter were the only operative mechanism, one would have expected the denuded zones to be narrower at GBs perpendicular to a grain's c-axis. More work is needed to fully understand the dynamics of defect mobility and damage recovery in the MAX phases.

Lastly the results presented in this work suggest that Ti_3SiC_2 could be a useful nuclear material at temperatures $> 700\text{ }^\circ\text{C}$, provided the TiC volume fraction and stacking faults densities in the starting materials are eliminated or minimized. Along the same lines the stability of this phase under irradiation has to be confirmed. Fabricating, testing, and characterizing samples with significantly smaller grain sizes should also prove quite instructive. In that respect, the fact that the mechanical properties of the MAX phases are better the smaller the grain size is a plus. These comments notwithstanding, it is hereby acknowledged that much more work will be required to understand the response of this compound to higher neutron irradiation doses.

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