Microstructure and mechanical properties of titanium aluminum carbides neutron irradiated at 400-700°C

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This work reports the first mechanical properties of Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ materials neutron irradiated at ~400, 630 and 700°C at a fluence of $2 \times 10^{25} \text{ n}\cdot\text{m}^{-2}$ ($E > 0.1 \text{ MeV}$ or a displacement dose of ~2 dpa). After irradiation at ~400°C, anisotropic swelling and loss of 90% flexural strength was observed. After irradiation at ~630-700°C, properties were unchanged. Microcracking and kinking-delamination had occurred during irradiation at ~630-700°C. Further examination showed no cavities in Ti_3AlC_2 after irradiation at ~630°C, and lamellar of MX_6 and A were preserved. However, disturbance of (0004) reflections corresponding to M-A layers was observed, and the number density of line/planar defects was $\sim 10^{23} \text{ m}^{-3}$ of size 5-10 nm. HAADF identified these defects as antisite Ti_{Al} atoms. Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ shows abrupt dynamic recovery of A-layers from ~630°C, but a higher temperature appears necessary for full recovery.

Introduction

Ti_3AlC_2 is a material known as a $\text{M}_{n+1}\text{AX}_n$ (MAX) phase, where M is an early transition metal, A is an A-group element (e.g., Al, Si) and X is either C or N[1]. The combination of metallic and ceramic properties is associated with the nanolamellar structure of M-X and M-A layers. The high fracture toughness values (of up to $10 \text{ MPa}\cdot\text{m}^{1/2}$ (compared to values of $\sim 4 \text{ MPa}\cdot\text{m}^{1/2}$ in monolithic SiC, for example)[2] are the result of dislocation-based kink bands that delaminate from the M-A layers within grains, coupled with diffuse intragranular microcracking, high-aspect ratio grain interlocking and push/pull-out mechanisms.[3-5] The key properties of interest for

fission and fusion applications are the A-layer derived electronic thermal conductivity, high monolithic fracture toughness, and potential radiation resistance.[6-8]

As a result, extensive ion irradiations of Ti_3AlC_2 and Ti_3SiC_2 have been supplemented by recent neutron irradiations. The results have been broadly consistent. *Ab initio* studies predicted that defect accumulation would occur in M-A layers[9], and this is confirmed by a ~20% decrease in electrical conductivity attributed to A-layer damage even at 0.1 displacements per atom (dpa) at ~360(20)°C.[10] The defect accumulation caused anisotropic lattice parameter (LP) expansion in Ti_3SiC_2 . [11] For Ti_3AlC_2 anisotropic LP expansion is 50% higher at room temperature ion irradiations and neutron irradiations at 400°C, and a-axis shrinkage is also observed.[10, 12-14] Mechanical properties are highly influenced by defect induced swelling. Ti_3AlC_2 and Ti_2AlC after neutron irradiation at ~400°C at 2 dpa and 0.1 dpa respectively report microcracking, and irradiated Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ reported low fracture strengths of ~30 MPa.[15, 16] Additional mechanical data is lacking due to the small size of ion-irradiated samples (<10 x 10 mm).[17, 18]

After neutron irradiation at ~695(20)°C, Ti_3AlC_2 and Ti_2AlC showed no lattice parameter changes, and electrical properties appeared unchanged.[10] This manuscript focuses on Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ irradiated at the dynamic recovery range of 400-700°C, and discusses the effect of neutron irradiation to ~2 dpa on elastic modulus, fracture strength, swelling, density and phase stability. In particular, the effect of A-atom displacement on fracture strength, macroscopic swelling behaviour and the early “recovery” microstructure is discussed.

Experimental

The experimental details have been previously published [11, 16], and the materials characterization is included in the results. Materials were machined into beams (25 x 2 x 1.5 mm) for dimensional swelling, density and elastic modulus measurements. Square discs (6 x 6 x 0.5 mm) were used for X-Ray Diffraction (XRD), equibiaxial fracture, density and electron microscopy. Samples were inserted into previously described irradiation capsules; due to non-symmetry, the beams may have experienced a higher temperature (+25°C). Samples were exposed to a neutron fluence of $2 \times 10^{25} \text{ n}\cdot\text{m}^{-2}$ ($E > 0.1 \text{ MeV}$) or ~2 dpa at ~400°C, ~630°C and 700°C at a damage rate of $4.5 - 6 \times 10^{-7} \text{ dpa}\cdot\text{s}^{-1}$ based on the conversion for SiC.[19]

Volumetric swelling was measured using beams. Length was measured from vertexes and the

average value taken to be equal to the length of the specimen. Four measurements were also taken of the height and width, and the lowest standard deviation (usually not the length value) was $\pm 3 \mu\text{m}$. Dynamic Young's modulus was determined using the impulse excitation and vibration method (by ASTM C1259) on beam specimens. Poisson's ratio is typically 0.2 (c.f. Tzenov and Barsoum et al) but their material was $>95\%$ Ti_3AlC_2 with Al_2O_3 impurities.[20] Due to the presence of softer intermetallics, a value of 0.21 was used.

XRD patterns were acquired using Cu K α (40 kV, 40 mA) radiation with a Scintag Pad V system on square discs placed on a zero-background (SiO_2 Optical Grade from MTIXTI) mount. Due to substantial difficulties in characterization, a Bruker D2 Phaser and a Phillips X'pert Diffractometer were also used in conjunction with three software suites: PANanalytical HighScore Plus (HS+), Bruker TOPAS 4.2 and GSAS.[21] Independent lattice parameters (without structure) were obtained using TOPAS 4.2 using a Le Bail (1988) fit for all phases.[22] Samples used an internal Si SRM640b for lattice parameter refinements. Microstrain and crystallite size for Ti_3AlC_2 and $\text{TiC}_{(1-x)}$ were determined by Williamson-Hall method from GSAS data.[23]

Archimedes density (by ASTM B962) used 3M Fluorinet Liquid FC-43 as the suspension and immersion medium. Room temperature equibiaxial flexural strength (by ASTM C1499) was conducted to obtain Weibull statistics on 32 unirradiated specimens. The probability of failure due to flaws in processing is given by;

$$P = 1 - \exp\left(-\frac{1}{V} \int_V \left(\frac{\sigma}{\sigma_0}\right)^m dV\right)$$

where V is the characteristic volume, m is the Weibull shape parameter, σ_0 is the characteristic strength or scale parameter. In order to obtain m, a population of 32 unirradiated specimens was plotted to:

$$\ln \left(\ln \frac{1}{(1 - P(f))} \right) = m \ln (\sigma_i)$$

where P_f is the probability of failure (using the median $(i - 0.3)/(n + 0.4)$ i^{th} ordered failure specimen and n is the population), and σ_i is the failure stress of the i^{th} specimen.[24] After irradiation, the equibiaxial strength was conducted on a minimum of 3 specimens. The crosshead speed was $0.1 \text{ mm} \cdot \text{min}^{-1}$, with slack (minimum) load of 5 N. Tests were validated as

per Kondo et al; as biaxial testing removes edge effects from relatively small specimens, avoidance of tensile stress magnification in the region between load ring and outer support ring is necessary.[24] Prevention of outer overhang of the sample from moving toward the center causes lower failure stresses with cracks initiating from the overhang, and thus validation of the test should be demonstrated by fractures initiating in the central load area.[24] Scanning Electron Microscopy (SEM) was conducted on polished and fracture surfaces with a JEOL 6500F.[24, 25]

Unirradiated materials were analyzed in high-angle annular dark-field (HAADF) mode on the FEI Titan G2 aberration-corrected STEM at North Carolina State University, Analytical Instrumentation Facility. The instrument was operated at 200 kV accelerating voltage. On irradiated samples, STEM was conducted using an FEI Talos F200X S/TEM at 300 kV, equipped with four detectors ((HAADF), medium-angle annular dark field, low angle annular dark field, and bright field). The annular detectors are collectively referred to as HAADF. Foil thickness was derived using “Absolute Thickness” method by Egerton et al.[26, 27] Number densities (N_d) were counted using a 50 x 50 nm region. All images were captured using a high-speed, high-resolution (4096x4096 pixel) TEM camera system.

Results

Density and swelling

Table 1 shows density and dimensional data for all three irradiation temperatures. Dimensional swelling is (L)ength, (W)idth and (H)eight components and the multiple represents the (V)olumetric swelling. Archimedes density decreased after irradiation at ~400°C and was unchanged after irradiation at ~630 and ~700°C based on two samples per irradiation condition.

	ASTM B962		Dimensional and volume swelling			
Condition	(g·cm ⁻³)	% Δρ	% ΔL, W, H and V			
Initial	3.964(20)	-	Length	Width	Height	Volumetric
~400°C	3.849(3)	-2.9%	1.3(0.08)%	1.35(0.14)%	1.32(0.13)%	4.02%

~630°C	4.004(7)	1.0%	0.1(0.04)%	-0.24(0.04)%	-0.23(0.10)%	-0.37%
~700°C	3.979(6)	-0.4%	0.49(0.05) %	0.52(0.03)%	0.63(0.09)%	1.65%

Table 1. Macroscopic density, linear (L, W, H) and volumetric swelling (V) (%) after irradiation at selected temperatures. Parenthesis show $\pm\sigma\bar{x} = 1$ standard deviation.

It can be observed from Table 1 that:

- Density and swelling have the correct negative relationship as expected, there are significant margins; at ~400, 630 and 700°C, there are differences of 1.1%, 0.6% and 1.2% respectively.
- These differences can be caused by porosity, densification and phase changes, but are difficult to verify due to limited pattern fitting in the XRD data.
- All materials are polycrystalline without preferred orientation since they were pressurelessly sintered, so the L, W, H and V components of the 25 x 2 x 1 ½ mm beams show the same trend.

After irradiation at ~400 °C, density decreased and volumetric swelling increased, consistent with open pore volume from swelling and microcracking.[16] From irradiations at 630 to 700°C densification of the intermetallic could be responsible for the changes in density and swelling.

Morphology

Figure 1(a) shows the morphology of the $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ as-machined and polished. Back-Scattered Electron (BSE) images are provided for phase differentiation. The MAX phase is the high-aspect ratio grains up to ~50 μm in length. A slight change in channeling contrast in MAX grains reveals the c-axis contrast. Channeling contrast is indicative of a chemistry and stacking change, such as Ti_3AlC_2 to $\text{Ti}_5\text{Al}_2\text{C}_3$. The intermetallic phase is the darker intergranular regions.

Figure 1. BSE images of Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ at 2500X in (a) as received condition, and after irradiation at (b) $\sim 400^\circ\text{C}$. After irradiation at (c) $\sim 630^\circ\text{C}$ and (d) $\sim 700^\circ\text{C}$ intragranular deformations are observed; white arrows show delaminations, yellow arrows indicate microcracks and red arrows show pores that appear to have formed in the intermetallic after irradiation.

Figure 1(b) shows transgranular microcracking after irradiation at $\sim 400^\circ\text{C}$ as previously reported.[16] Figure 1(c) shows the material after irradiation at $\sim 630^\circ\text{C}$. Microcracking was confined within grains, and the major difference in morphology to the unirradiated material was delaminations indicated by the white arrows. The delamination and microcracks increased in density after irradiation at $\sim 700^\circ\text{C}$ (Figure 1(d)).

X-Ray Diffraction (XRD)

The XRD patterns are shown in Figure 2. The grey line is the Rietveld pattern fit, and major reflections of each phase are marked. Figure 2(a) shows the pre-irradiation HighScorePlus (HS+) identification of the phases. The material contained mostly Ti_3AlC_2 (312) and $\text{Ti}_5\text{Al}_2\text{C}_3$ (523) phases. $\text{Ti}_5\text{Al}_2\text{C}_3$ phase is purportedly from the thermodynamically favorable toptactic transformation in two unit cells of Ti_2AlC , leading to a 312 cell on top of a 211, caused by Al depletion during processing.[28] The material was purchased as “ Ti_2AlC ” (211), and would be consistent with the high vapor pressure of Al during sintering. For the purpose of this study, $\text{Ti}_5\text{Al}_2\text{C}_3$ classified as a distinct phase.[29] A previous publication indexed the material to either Ti_2AlC or Ti_3AlC_2 using GSAS as it was unable to incorporate $\text{Ti}_5\text{Al}_2\text{C}_3$. Both TOPAS and HS+ were able to identify the peak positions and thus lattice parameters (LPs), but it was difficult to de-convolute crystallite size, microstrain and preferred orientation in $\text{Ti}_5\text{Al}_2\text{C}_3$. HS+ was able to provide crude Quantitative Phase Analysis (QPA) within the constraint of optical and SEM observations indicating ~80 vol% MAX phase. This analysis is confident of lattice parameters, but output values of scale factors and preferred orientation (required for QPA) should be treated with caution (e.g. up to $\pm 5\text{-}10\text{ wt}\%$). No $\text{TiC}_{(1-x)}$ was detected in the diffraction pattern of the unirradiated material.

Figure 2. XRD patterns from HighScorePlus for **(a)** as-received materials, **(b)** after irradiation at ~400°C and **(c)** at ~630 °C. In **(b)**, a possible pattern fit to $\text{TiC}_{(1-x)}$ is shown, with peak shifts for (0008) and (000(21)/(23)) for Ti_3AlC_2 and “toptactic” $\text{Ti}_5\text{Al}_2\text{C}_3$ are respectively noted with blue and magenta arrows.

Figure 2(b) shows the pattern after irradiation at ~400°C. Note the low angle reflections have

disappeared, while basal planes (0008 – blue) and (000(21), 000(23) – magenta) for Ti_3AlC_2 and “toptactic” $\text{Ti}_5\text{Al}_2\text{C}_3$ have respectively shifted left to higher d-spacing, indicative of c-axis expansion. The (0008) reflection for Ti_3AlC_2 (blue arrow) can be seen as an extra peak for Ti_3AlC_2 between the 101₃ and 101₄. [13] The (000(21)) and (000(23)) of $\text{Ti}_5\text{Al}_2\text{C}_3$ shift left (magenta arrows) and causes substantial reinforcement of the $\sim 37^\circ$ and $\sim 42^\circ$ 2θ regions. This appeared to cause problems with shape profile parameters and preferred orientation on the sample irradiated at $\sim 400^\circ\text{C}$. The difference plot shows that peak broadening is more evident, with lower intensities and countering preferred orientation problems. Finally, a possible fit to $\text{TiC}_{(1-x)}$ is shown assuming preferred orientation to (200) is permitted. Figure 2(c) shows that after irradiation at $\sim 630^\circ\text{C}$, the pattern is similar to the as-received material; basal reflections are unchanged, peak intensities increase and the preferred orientation problem returns.

Table 2 shows the initial lattice parameters (LPs) and after irradiation at $\sim 400^\circ\text{C}$, $\sim 630^\circ\text{C}$ and 700°C . TOPAS and HS+ were able to fit all phases, with values that agreed on Ti_3AlC_2 and $\text{Ti}_5\text{Al}_2\text{C}_3$. No lattice swelling was observed on MAX phases after irradiation at $\sim 630^\circ\text{C}$ and $\sim 700^\circ\text{C}$. $\text{Ti}_5\text{Al}_2\text{C}_3$ swelling has not previously been published, but it appears to be consistent with literature suggesting that swelling of $(n = 1, 2, \dots)$ $\text{M}_{n+1}\text{AX}_n$ phases of identical atomic composition are the same. [10] Since 523 is effectively 312 and 211 unit cells ($n = 1.5$ (average)), it is not unexpected that defect accumulation and thus swelling is similar if irradiated below dynamic recovery temperatures.

Condition	$\text{Ti}_5\text{Al}_2\text{C}_3$	Δ [%]	Ti_3AlC_2	Δ [%]	TiC	$\text{Ti}_5\text{Al}_{11}$	Δ [%]
a-axis lattice parameters ($\pm 0.001 \text{ \AA}$)							
Initial	3.0679	-	3.0721	-	-	3.912	-
400°C	3.0302	-1.20%	3.0391	-1.10%	4.277	3.825	-2.20%
630°C	3.0628	-0.20%	3.0693	-0.10%	-	3.842	-1.80%
700°C	3.0625	-0.20%	3.0683	-0.10%	-	3.845	-1.70%
c-axis lattice parameters ($\pm 0.001 \text{ \AA}$)							
Initial	48.326		18.5415	-	-	16.812	-
400°C	49.776	3.00%	19.1038	3.00%	-	16.873	0.40%
630°C	48.294	-0.10%	18.5274	-0.10%	-	16.821	0.10%
700°C	48.269	-0.10%	18.5427	0.00%	-	16.833	0.10%

Table 2. Lattice parameters (LPs) of all identified phases, and sub-cells showing $\Delta c/c$ and $\Delta a/a$ values as a percentage of the initial lattice parameters after ~2 dpa. (using HS+ and TOPAS, GSAS for $\text{TiC}_{(1-x)}$.) $\Delta[\%]$ denotes the change in value after irradiation.

The far right of Table 2 includes the LPs of intermetallics; data is included for posterity as LPs were not previously obtained on irradiation of Ti-Al intermetallics.[30-33] Irradiation of intermetallic joints have reported differential swelling (in morphology) with their parent carbides.[34] This could explain the increased damage from Figure 1(c) to (d) in the polished materials.

As noted, an LP value for $\text{TiC}_{(1-x)}$ is included for after irradiation at ~400°C; GSAS was only able to fit Ti_3AlC_2 and $\text{TiC}_{(1-x)}$. It is consistent with X-ray analysis of Ti_3AlC_2 decomposition to TiC from Tallman et al after irradiation at 360(20)°C [10]. However, on closer examination, $\text{TiC}_{(1-x)}$ should be ruled out when crystallite size is examined. TOPAS could not accept $\text{TiC}_{(1-x)}$ within these constraints (lattice parameter, shape profile, etc). In GSAS, fitting to Ti_3AlC_2 and $\text{TiC}_{(1-x)}$ on Figure 2(b) leads to an *increase* in crystallite size; this is consistent when HS+ was used to fit the (200) preferred orientation for $\text{TiC}_{(1-x)}$. It seems that without proper constraints, a $\text{TiC}_{(1-x)}$ (200) is an acceptable solution. However, empirical evidence showed that neutron irradiations on $\text{TiC}_{(1-x)}$ at this same temperature[10] cannot result in such highly annealed crystallites. Furthermore, the observed Ti_3AlC_2 decomposition to TiC from X-ray patterns indicate that it should be nanocrystalline.[12, 13, 35] A change in preferred orientation of a MAX phase e.g. Ti_3AlC_2 (10 $\bar{1}$ 5) seems more likely to explain the position of this reflection that represents $\text{TiC}_{(1-x)}$ (200).

Table 3 shows the microstrain and crystallite size for data using GSAS that fitted Ti_3AlC_2 and $\text{TiC}_{(1-x)}$. Crystallite sizes and microstrain were not able to be obtained on $\text{Ti}_5\text{Al}_2\text{C}_3$.

Condition	$\mu\epsilon$ (%)		Crystallite size (nm)			
	Ti_3AlC_2	TiC	Ti_3AlC_2	TiC (GSAS)	TiC (HS+)	TiC (TOPAS)
Initial	0.49(1)	0.09(1)	794(1)	77.8(1)	n/a	n/a
400°C ~2 dpa	0.024(1)	0.25(1)	13.3(0.5)	542(1)	808(1)	n/a

630°C ~2 dpa	0.02(1)	0.21(1)	25.9(2.3)	28.6(1)	n/a	n/a
700°C ~2 dpa	0.02(1)	0.20(1)	22.2(1.8)	78.0(1)	n/a	n/a

Table 3. This shows microstrain ($\mu\epsilon$) and crystallite size of Ti_3AlC_2 and TiC phases from data fitted using GSAS. Largest deviations from each Williamson-Hall plot shown. Parenthesis show $\pm\sigma\bar{x} = 1$ standard deviation. Example solutions of $\text{TiC}_{(1-x)}$ are shown, where GSAS, HS+ and TOPAS appear to assign preferred (200) orientation with substantial crystallite size, which seems unlikely.

For Ti_3AlC_2 fitted using GSAS, the Williamson-Hall correction has some uncorrected trigonometric functions due to anisotropic strain (not shown), but this did not appear significant if corrected.[23] Microstrain decreases after irradiation, likely due to annealing stresses from machining.[10, 15] As expected, crystallite size decreases after irradiation. Overall, the data for Ti_3AlC_2 is consistent with general understanding of irradiated ceramics as dynamic recovery occurs.

In summary, the materials were ~80% vol MAX phase, consisting of Ti_3AlC_2 , $\text{Ti}_5\text{Al}_2\text{C}_3$ and $\text{Ti}_5\text{Al}_{11}$. Decomposition to $\text{TiC}_{(1-x)}$ may have occurred as a nanometric phase within the convoluted reflections < 5-10 wt% or subsumed into background, but a highly crystalline phase was not considered a solution. The quality of profile fitting for QPA was poor due to inability to compensate for convolution of $\text{Ti}_5\text{Al}_2\text{C}_3$ reflections and preferred orientation. However, lattice parameters were able to be obtained. Anisotropic swelling in Ti_3AlC_2 and $\text{Ti}_5\text{Al}_2\text{C}_3$ occurred after irradiation at ~400°C, but after irradiation at ~630 and ~700°C, lattice parameters are unchanged from as-received values. This indicated that swelling of $\text{Ti}_5\text{Al}_2\text{C}_3$ is identical to the sub-cells of Ti_3AlC_2 and Ti_2AlC .

Fracture surfaces

Figure 3(a) shows the fracture surface of as-received materials after room temperature equibiaxial testing. There is delamination within grains, ligaments buckling, and likely grain interlocking based on surface roughness.[3-5] Some transgranular cracks are also present. Figure 3(b) shows that after irradiation at 400°C, the morphology is dominated by large microcracks such as that marked by the arrows. The brittle fracture was not accompanied by toughening since the surfaces appear flat. An inset photograph shows the test depression. It appears that no cohesion occurred in the ceramic. Activated powder and debris was ejected

during capsule deconstruction, suggesting that these samples had behaved like pressed green compacts. All tests were considered valid due to the absence of crack initiation from the outer fulcrum.[24]

Figure 3(c) shows the fracture surface after irradiation at $\sim 700^\circ\text{C}$. The fracture surface is similar to the fracture of as-received material; they show delamination (white arrows) within grains, buckling, and grain interlocking. The intermetallic phase (red arrows) is between the MAX phase ligaments. As seen in Figure 3(c), the formation of pores suggests a morphology change in the $\text{Ti}_5\text{Al}_{11}$ and indicates the possibility of differential swelling (Table 2), densification or growth. If the intermetallic applied stress on the MAX phase, delamination could have occurred during irradiation.

Figure 3. Fracture surfaces **(a)** before irradiation, and after **(b)** irradiation at $\sim 400^{\circ}\text{C}$. An photograph of the sample shows that deformation occurred as if the material was a powder compact rather than elastic deflection. After irradiation at $\sim 700^{\circ}\text{C}$, **(c)** morphology returns to normal; delaminations noted with white arrows and pores in the intermetallic shown with red arrows. General morphology of fracture surface is shown **(d)** after irradiation at $\sim 700^{\circ}\text{C}$.

Figure 3(d) shows that a significant surface area is added by kinking-delamination and hanging ligaments, similar in fracture morphology to Ti_3SiC_2 . [36] $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ maintains high strength after irradiation at $\sim 700^{\circ}\text{C}$ due to its operational kinking-delamination, grain interlocking and diffuse microcracking mechanisms, but the mechanism does not appear to be viable at $\sim 400^{\circ}\text{C}$.

Elastic modulus

The stockpile contained 11 modulus bars for planned irradiation campaign. The average modulus was 250.8 ± 6.5 GPa. Young's modulus of the actual beams inserted into the irradiation capsules were respectively 241, 254 and 285 GPa (subset average 260 ± 22 GPa). After irradiation at $\sim 400^{\circ}\text{C}$ the recorded modulus was 203 GPa. Modulus was unchanged (254 GPa) after $\sim 630^{\circ}\text{C}$, but dropped to 214 GPa at $\sim 700^{\circ}\text{C}$. The reported change in elastic modulus after $\sim 700^{\circ}\text{C}$ is unusual given the absence of lattice swelling. For both $\sim 400^{\circ}\text{C}$ and $\sim 700^{\circ}\text{C}$ irradiations, diffuse microcracking and delaminations may have affected the sonic modulus technique.

Equibiaxial fracture strength

The pre-irradiation equibiaxial strength distribution in a Weibull plot is shown in Figure 4(a). The characteristic 62% P_f strength was 315 MPa, with a calculated Weibull modulus of 22, justifying the use of a small irradiated sample set. The as-received strength was 308 ± 16 MPa ($\pm \sigma_X = 1$ standard deviation).

Figure 4. (a) Weibull modulus and flexural strength distribution of that $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ pre-irradiated **(b)** The average strength of pre-irradiation specimens and after irradiation at the selected temperatures.

Figure 4(b) shows the sample set of unirradiated materials, and all the irradiated samples in one plot. The material showed 90% reduced strength after irradiation at $\sim 400^\circ\text{C}$. [16] After irradiation at $\sim 630^\circ\text{C}$ and $\sim 700^\circ\text{C}$, strength values were 307 ± 7 MPa and 332 ± 18 MPa respectively.

Recovery microstructure

STEM imaging was conducted on the specimens irradiated at $\sim 630^\circ\text{C}$. All STEM images were within $\sim 4^\circ$ of $[11\bar{2}0]$ zone axis. As-received materials were verified to be both Ti_3AlC_2 and $\text{Ti}_5\text{Al}_2\text{C}_3$ as modeled by the XRD pattern. A STEM image of the 523 variant before irradiation is shown in Figure 5(a). The “211” and “312” alternating layers is shown by the bright chevrons indicative of higher Z-weight Ti atoms. Al atoms are visible as marked in the STEM image, although they are faint. SAED confirms that the material is $\text{Ti}_5\text{Al}_2\text{C}_3$.

In the irradiated materials, FIB extraction only yielded Ti_3AlC_2 . The SAED inset in Figure 5(b) confirms the diffraction pattern of Ti_3AlC_2 down the $[11\bar{2}0]$ zone axis. The irradiated Ti_3AlC_2 -region has no cavities and shows some thickness contrast and stacking faults (SFs). Consistent

with other work, SFs were present before irradiation.[10, 15] The inset of the irradiated Ti_3AlC_2 in Figure 5(b) indicates an inability to obtain a coherent indexed (0004) adjacent to the primary beam. This suggests defects associated with the Ti_1 -Al layers. In contrast, SAED patterns from Tallman et al appear closer to theoretical after irradiation at 0.1 dpa [15]; when correlated with swelling (1.6 vs 3.1% c-axis LP expansion) this suggested progressive structural damage due to the higher dose in this study. Nanometric “black spots” aligned along the basal plane, coupled with the inability to obtain a (0004) suggested destructive interference associated with Ti_1 and Al layers, consistent with the most favorable interstitial and antisite defect sites.[9, 37]

Figure 5. (a) Unirradiated material in HAADF STEM showing $\text{Ti}_5\text{Al}_2\text{C}_3$ microstructure; note the contrast between Ti (chevrons pattern of Ti_1 - Ti_2) and Al (arrows); inset SAED indicates shows indexing of $\text{Ti}_5\text{Al}_2\text{C}_3$ as viewed down the $\langle 11\bar{2}0 \rangle$ direction. **(b)** STEM images of Ti_3AlC_2 lift out from Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ material irradiated to ~ 2 dpa at $\sim 630^{\circ}\text{C}$ and viewed down the $\langle 11\bar{2}0 \rangle$ direction showing the absence of voids, presence of short length stacking faults and a weaker (0004) reflection in the SAED; **(c)** STEM dark field image shows line/planar defects from the white contrast with a density of $\sim 10^{23} \text{ m}^{-3}$ of size ~ 5 -10 nm, with an inset showing a schematic unit cell orientation. **(d)** HAADF images showing chevrons of the Ti atoms in Ti_3AlC_2 . Elliptical distortion indicates strain fields and noted with arrows. The inset shows evidence of antisite line/planar defects along one of the basal planes occupied by Ti instead of Al atoms.

Figure 5(c) shows a STEM image in dark field condition near the $[11\bar{2}0]$ zone axis. Since the bright spots represent the diffracted beam, it suggests distortions such as strain fields in the crystal structure. It appears the defects are of size 5-10 nm. The densities were calculated as 1.4 , 2.1 and $2.2 \times 10^{23} \text{ m}^{-3}$ following irradiations at $\sim 630^\circ\text{C}$ at ~ 2 dpa. The microstructure is consistent with densities of defects in the Burgers vector $\frac{1}{2}\langle 0001 \rangle$ [10, 15] previously reported. Insets to Figure 5(c) and (d) are provided as a guide to interpretation.

Figure 5(d) shows a high resolution HAADF image. As suggested by prior TEM after ion irradiations at 600°C (2, 5 and 10 dpa) and 695°C (0.1 dpa), lamellae are intact along the a -axis, which is the vertical axis in the image.[12, 15] The bright echelon or chevron points in the horizontal direction show the TiC_6 octahedra as viewed down the $[11\bar{2}0]$ zone axis representing $\text{Ti}_1\text{-Ti}_2\text{-Ti}_1$. It is known that electrical conductivity was restored at this irradiation temperature, suggesting Al atoms were present.[10] Based on the matching contrast of rows of Al atoms in Figure 5(a) to Figure 5(d), this is in agreement with substantial dynamic recovery at $\sim 630^\circ\text{C}$. Defects with an elliptical shaped strain field populate the image (marked with arrows), while some appear to be Ti antisites on Al (Ti_{Al}). Figure 5(d) includes a highlight of six Ti_{Al} defects, which likely represents a cross-section of a planar defect. A schematic explanation is shown in the inset. This is strong evidence of antisite defects and incomplete recovery.

Discussion

Ti-based antisite defects (M-M)

Prior irradiations at 600 , $695\text{-}700^\circ\text{C}$ [12, 15, 18] appear to show line/planar defects after mitigation of swelling. This is an indication of self-interstitial point defects accumulating to line defects and collapsing to form planar defects. The density of these defects appears to be affected by dose rate ($1.9 \times 10^{11} \text{ ions/cm}^2\text{s}$ from Huang et al and $3 \times 10^{11} \text{ ions/cm}^2\text{s}$ from Clark et al) and temperature; these appear to produce a higher density of defects or defect growth from enhanced diffusion. Even lower dose specimens (0.1 dpa) at $695(20)^\circ\text{C}$ showed “interstitial dislocation loops” (IDLs) with a Burgers vector $\frac{1}{2}\langle 0001 \rangle$ and average size 5-15 nm in Ti_2AlC with N (number density) of 1×10^{23} (tilted to $[3\bar{3}01]$). [15] These specimens were irradiated at $\sim 630^\circ\text{C}$ at ~ 2 dpa, and Ti_3AlC_2 has defects of size of 5-10 nm, with a bias toward ~ 5 nm based on Figure 5(d) and a density of $\sim 2(1) \times 10^{23}$. Thus both ~ 0.1 and 2 dpa at 695 and $\sim 630^\circ\text{C}$

appear to show the early recovery microstructures; evolved microstructures at the same temperatures ($\sim 700^\circ\text{C}$) at higher dose rates (3×10^{11} ions/ cm^2s (1.4×10^{-4} dpa/s)) or dose seems to nucleate such a high concentration of planar defects that they appear to form into chevrons of zero-stress configurations. However, consistent with all the above data is that these are likely the same defects, aligned along the (0001) basal plane and with a prismatic strain field component.

HAADF data appeared to show that the origin of the line/planar defects is a core of antisite Ti atoms after irradiation at $\sim 630^\circ\text{C}$. Since electrical properties were dependent on Al, and lattice parameters and strength appeared to be unaffected, it implied that the majority of C and Al atoms returned to their respective sites. The stability of the Ti_{Al} defect site was predicted by Middleburgh et al. Further work is now needed to identify other species (if any) in these planar defects apart from Ti. The defects near the entrance surface of the foil provide enough channeling that strain is observed. However, defects nearer the bottom of the foil are visible from their HAADF compared to the local Al, but the strain around them is swamped by the channeling of the perfect Ti, Al and C layers above them. Starting with Ti_{Al} (1) the possible configurations are shown in Figure 6.

Figure 6. Observed HAADF simulation of Ti_{Al} cluster (1) in the [1120] zone axis. This is confirmed. Thus at least two types of possible clusters are proposed around these Ti antisites: (2) $\text{Ti}_{\text{Al}} + \text{I}_{\text{C}}$ and (3) $\text{Ti}_{\text{Al}} + \text{I}_{\text{Al}}$ (shown with a strain field in $\frac{1}{2}$ $\langle 0001 \rangle$ direction).

Since the radiation tolerance of MAX phase is based on antisite and interstitial accommodation of defects, it indicates that:

- If C occupies an interstitial site, this is considered a stacking fault in MAX phase.[10, 38] This early defect configuration may be the basis for the nanometric TiC(1-x) observed at low irradiation temperatures.
- Al in Figure 6 as an interstitial is more stable, has a low migration energy and explains the maintained electrical conductivity.[9, 10, 37]
- Tallman et al observed “interstitial dislocation loops”, which could refer to I_{Ti} simply between Ti_1 and Ti_2 layers.[10, 15] This would indicate that there are at least two types of line/planar defect; those in the M-A layers and those in the M-X layers. These are the subject of future investigations.

Intragranular TiC (M-X)

Irradiation induced decomposition of MAX phase to an MX crystal structure is noted in literature.[10, 12, 35, 39, 40] This is sub-stoichiometric $MX_{(1-x)}$ with NaCl-type structure that has been separated from the MAX (101x) and MX (200) reflections. This has generally been confirmed for room temperature irradiations where: [10, 12, 16, 35]

- Wang et al irradiated with 50 keV He ions to ~4, 11, 31 and 52 dpa, showing shift of the (0008) plane at 11 and 52 dpa, with only slight shift at 4 and 31 dpa. Peak broadened reflections of TiC are observed at all doses and no TiC reflections were in the starting material.[13]
- Song et al also used He ions but at 0.5 MeV to ~2.5, 5 15 and 50 dpa, with (111), (200) and (220) reflections of TiC observed. No (0008) shift is noted in MAX, and authors acknowledged their data included the implantation region. No TiC reflections were in the starting material.[35]
- Huang et al irradiated with 7 MeV Xe ions and shows a broad reflection corresponding to TiC (111) and (200). No TiC reflections were in either Al- or Si- material.[12]

It is also observed in neutron irradiations:

- Tallman et al had material with an impurity of TiC from the mid-angle data, but the increase in a peak intensity corresponding to the (200) is obvious after irradiation, leading to QPA of 48 wt% TiC.[10, 15] Such a large decomposition to TiC after 0.1 dpa would seem to suggest relatively poor thermodynamic stability of MAX compared to MX and the authors continue to follow up this data.

It appears that $\text{TiC}_{(1-x)}$ formation by irradiation is associated with point defect configuration at lower irradiation temperatures, but is nanocrystalline. While higher temperatures should provide annealing and larger crystallites, it is not observed after ion irradiations at 300, 500 (Song et al) and 600 °C (Haung et al).[10, 12, 16, 35, 39, 40] This is because point-defect swelling is also mitigated above ~500°C and is not observed in neutron irradiations above ~700°C.[16] Furthermore, $\text{TiC}_{(1-x)}$ phase fitted to the Rietveld solution after irradiation at ~400°C has an improbable crystallite size because TEM of $\text{TiC}_{(1-x)}$ irradiated at 0.1 dpa showed “black spot” radiation damage (exceeding the authors’ ability to count[10, 15]). It is not possible to conclude that MX decomposed from MAX phase in this study, as a preferred orientation change or c-axis expansions can also explain the presence of reflections matching that of $\text{TiC}_{(1-x)}$.

Mechanical feasibility (M-A)

In $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ materials, it appears that irradiation imposes a significant stress on the MAX phase either at all irradiation temperatures. At low temperature, high strains from swelling need to be mitigated but dislocation-based kink bands needed for delamination are defective. This is problematic for applications at LWR-temperatures, where the point defect clusters causing swelling appear to be immobile and result in low strength.[16] This agrees with low temperature indentation hardness results.[17, 18] After irradiation at ~700°C, the strength appears to be maintained, but there is a 1.65% macroscopic swelling, and reduction in sonic-method derived modulus indicated microcracking. This could be caused by phase changes induced by irradiation of intermetallics, as cracking and pre-delaminations were observed after irradiation at ~630-700°C. Consider that MAX phases appear to be difficult to purify, so this differential swelling may be unavoidable. Excess Al or Ti (from the intermetallic) is not detrimental to strength (Figure 4), and correlates to strategies used to eliminate TiC impurities.[12, 13, 35] Therefore, it appears that higher irradiation temperatures are more feasible for MAX phases, and impurities have yet to demonstrate a detrimental effect.

The damage tolerance of $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ materials is apparent from the Weibull data. Damage tolerance is generally defined as two components; (1) the maximum size of critical crack translating to a stress concentration that causes the crack to propagate in an uncontrolled manner and begins affecting bulk strength, and (2) the energy absorption capacity of the material.[41] The reliability of the Ti_3AlC_2 materials can be inferred from the lack of data spread

in Figure 4(b) after irradiation at ~630-700°C, and it is clear that the ligaments from kinking-delamination in Figure 3(d) are operative after irradiation at ~700°C, despite the presence of antisites. The swelling, delamination and microcracking would still need to be considered in light of geometric tolerances, coolant environments or radionuclide containment for nuclear applications. While high temperature fracture tests are needed to observe the pseudoductility, it does appear that $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ materials are mechanically promising after irradiation from least ~630°C, due to functionality of M-A (or M-M) atoms on the (0004) plane.

Conclusions

$\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ materials were neutron-irradiated at $2 \times 10^{25} \text{ n}\cdot\text{m}^{-2}$ ($E > 0.1 \text{ MeV}$) or a displacement dose of ~ 2 dpa at ~400, 630 and 700 °C. Anisotropic lattice swelling of Ti_3AlC_2 and $\text{Ti}_5\text{Al}_2\text{C}_3$ was significant after ~400°C, resulting in transgranular cracking and loss of 90% strength. Microcracks reduced the Archimedes density and affected elastic modulus measurements. After irradiation at ~630-700°C, no lattice swelling was observed, and equibiaxial strength, modulus and density appeared unchanged. Volumetric swelling of 1.65% was still observed between 630-700°C and is attributed to differential swelling and kinking-delamination processes, which indirectly confirmed Al-atom recovery. STEM investigations showed significant number density ($\sim 10^{23} \text{ m}^{-3}$) of line/planar defects after irradiation at ~630°C, which consisted of Ti_{Al} . No cavities were observed. Significant dynamic recovery of the A-layer atoms occurred between 400-630°C, which explains the unchanged strength, modulus and absence of defect-based swelling. The presence of intermetallics and residual M-M layers after irradiation at ~630°C does not appear detrimental at this dose. $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ appears mechanically promising at ~700°C but a higher temperature appears necessary for full recovery.

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List of Figures, Tables and Captions

Table 1. Macroscopic density, linear (L, W, H) and volumetric swelling (V) (%) after irradiation at selected temperatures. Parenthesis show $\pm\sigma\bar{x} = 1$ standard deviation.

Figure 1. BSE images of $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ at 2500X in **(a)** as received condition, and after irradiation at **(b)** $\sim 400^\circ\text{C}$. After irradiation at **(c)** $\sim 630^\circ\text{C}$ and **(d)** $\sim 700^\circ\text{C}$ intragranular deformations are observed; white arrows show delaminations, yellow arrows indicate microcracks and red arrows show pores that appear to have formed in the intermetallic after irradiation.

Figure 2. XRD patterns from HighScorePlus for **(a)** as-received materials, **(b)** after irradiation at $\sim 400^\circ\text{C}$ and **(c)** at $\sim 630^\circ\text{C}$. In **(b)**, a possible pattern fit to $\text{TiC}_{(1-x)}$ is shown, with peak shifts for (0008) and (000(21)/(23)) for Ti_3AlC_2 and “toptactic” $\text{Ti}_5\text{Al}_2\text{C}_3$ are respectively noted with blue and magenta arrows.

Table 2. Lattice parameters (LPs) of all identified phases, and sub-cells showing $\Delta c/c$ and $\Delta a/a$ values as a percentage of the initial lattice parameters after ~ 2 dpa. (using HS+ and TOPAS, GSAS for $\text{TiC}_{(1-x)}$.) $\Delta[\%]$ denotes the change in value after irradiation.

Table 3. This shows microstrain ($\mu\epsilon$) and crystallite size of Ti_3AlC_2 and TiC phases from data fitted using GSAS. Largest deviations from each Williamson-Hall plot shown. Parenthesis show $\pm\sigma\bar{x} = 1$ standard deviation. Example solutions of $\text{TiC}_{(1-x)}$ are shown, where GSAS, HS+ and TOPAS appear to assign preferred (200) orientation with substantial crystallite size, which seems unlikely.

Figure 3. Fracture surfaces **(a)** before irradiation, and after **(b)** irradiation at $\sim 400^\circ\text{C}$. An photograph of the sample shows that deformation occurred as if the material was a powder compact rather than elastic deflection. After irradiation at $\sim 700^\circ\text{C}$, **(c)** morphology returns to normal; delaminations noted with white arrows and pores in the intermetallic shown with red arrows. General morphology of fracture surface is shown **(d)** after irradiation at $\sim 700^\circ\text{C}$.

Figure 4. **(a)** Weibull modulus and flexural strength distribution of that $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ pre-irradiated **(b)** The average strength of pre-irradiation specimens and after irradiation at the

selected temperatures.

Figure 5. (a) Unirradiated material in HAADF STEM showing $\text{Ti}_5\text{Al}_2\text{C}_3$ microstructure; note the contrast between Ti (chevrons pattern of $\text{Ti}_1\text{-Ti}_2$) and Al (arrows); inset SAED indicates shows indexing of $\text{Ti}_5\text{Al}_2\text{C}_3$ as viewed down the $\langle 11\bar{2}0 \rangle$ direction. **(b)** STEM images of Ti_3AlC_2 lift out from $\text{Ti}_3\text{AlC}_2\text{-Ti}_5\text{Al}_2\text{C}_3$ material irradiated to ~ 2 dpa at $\sim 630^\circ\text{C}$ and viewed down the $\langle 11\bar{2}0 \rangle$ direction showing the absence of voids, presence of short length stacking faults and a weaker (0004) reflection in the SAED; **(c)** STEM dark field image shows line/planar defects from the white contrast with a density of $\sim 10^{23} \text{ m}^{-3}$ of size $\sim 5\text{-}10$ nm, with an inset showing a schematic unit cell orientation. **(d)** HAADF images showing chevrons of the Ti atoms in Ti_3AlC_2 . Elliptical distortion indicates strain fields and noted with arrows. The inset shows evidence of antisite line/planar defects along one of the basal planes occupied by Ti instead of Al atoms.

Figure 6. Observed HAADF simulation of Ti_{Al} cluster (1) in the $[1120]$ zone axis. This is confirmed. Thus at least two types of possible clusters are proposed around these Ti antisites: (2) $\text{Ti}_{\text{Al}} + \text{I}_{\text{C}}$ and (3) $\text{Ti}_{\text{Al}} + \text{I}_{\text{Al}}$ (shown with a strain field in $\frac{1}{2} \langle 0001 \rangle$ direction).