Phase stability, swelling, microstructure and strength of Ti_3SiC_2 -TiC ceramics after low dose neutron irradiation

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Abstract

$\text{M}_{n+1}\text{AX}_n$ (MAX) phase Ti_3SiC_2 materials were neutron irradiated at ~ 400 , ~ 630 , and 700°C to a fluence of $\sim 2 \times 10^{25} \text{ nm}^{-2}$ ($E > 0.1 \text{ MeV}$). After irradiation at $\sim 400^\circ\text{C}$, anisotropic c-axis dilation of $\sim 1.5\%$ was observed. Room temperature strength was reduced from $445 \pm 29 \text{ MPa}$ to $315 \pm 33 \text{ MPa}$ and the fracture surfaces showed flat facets and transgranular cracks instead of typical kink-band deformation and bridging ligaments. XRD phase analysis indicated an increase of 10-15 wt% TiC. After irradiation at $\sim 700^\circ\text{C}$ there were no lattice parameter changes, $\sim 5 \text{ wt\%}$ decomposition to TiC occurred, and strength was $391 \pm 71 \text{ MPa}$ and $378 \pm 31 \text{ MPa}$. The fracture surfaces indicated some kink-band based deformation but with lesser extent of delamination than as-received samples. Ti_3SiC_2 appears to be radiation tolerant at $\sim 400^\circ\text{C}$, and progressively radiation resistant at ~ 630 - 700°C , but a higher temperature may be necessary for full recovery.

Introduction

Ti_3SiC_2 is a MAX phase named after their chemical formula ($\text{M}_{n+1}\text{AX}_n$) where M is an early transition metal, A is an A-group element and X is either C or N^{1,2}. In Ti_3SiC_2 , lamellar atomic planes of “Si” atoms alternate between crystalline “Ti-C” ceramic unit cells. Their proposed use in nuclear applications are all derived from the phenomenon associated with the metallic A-layer. First, high thermal conductivity is essential in heat transfer systems and mitigates internal stresses. Fracture toughness values up to $\sim 10 \text{ MPa}\cdot\text{m}^{1/2}$ have been reported, caused by reversible dislocation-based incipient kink bands and diffuse microcracking.^{3,4} Finally, the alternating A and MX layers offer the possibility of dispersing atomic-level clusters between the nanoscale interfaces.⁵ According to kinetic rate theory, this may suppress development of extended defects that are often responsible for undesirable property changes such as radiation-induced hardening and degradation of high temperature strength.

Recent ion irradiations of both Ti_3SiC_2 and Ti_3AlC_2 have been accompanied by transmission electron microscopy (TEM), and acquisition of crystallographic data by Low or Grazing Incidence X-ray Diffraction (XRD).⁶⁻⁹ The intact lamellae after irradiation represent undisturbed “A-layers” and MX layers; this proposes confinement defect growth, satisfying a criteria of irradiation performance.⁹⁻¹² However, Ti_3SiC_2

and Ti_3AlC_2 still undergo anisotropic lattice parameter expansion, a possible strain-related α -to- β transition, and in Ti_3AlC_2 , a 90% loss of strength after irradiation at $\sim 400^\circ\text{C}$ was reported.^{9,13-15} Electrical conductivity measurements by Tallman et al were one of the first indications that disruptions to the “A-layer” were occurring in Ti_3AlC_2 , Ti_2AlC , Ti_3SiC_2 and Ti_2AlN .¹³ These displacements of the Al and Si atoms appear to cause swelling, and degrade mechanical and electrical properties.

Early studies by Nappe et al reported swelling up to $\sim 1\text{-}2\%$ in Ti_3SiC_2 .¹⁶ Like Ti_3AlC_2 , disruption of the “A-layer occurs” between room temperature and $\sim 400^\circ\text{C}$, however, the swelling of Ti_3SiC_2 seems to be less than Ti_3AlC_2 .^{9,13,15,17} Lower anisotropic swelling and only *partial* grain boundary separations have been reported in Ti_3SiC_2 .^{18,19} Reduced swelling, intact lamellae and confined microcracks suggest Ti_3SiC_2 is more feasible than Ti_3AlC_2 for current reactor-relevant temperatures. In both Al/Si-containing materials, the decomposition to $\text{TiC}_{(1-x)}$ is consistently reported – up to a significant $\sim 48\text{ wt}\%$ at 0.1 dpa after irradiation at $360(20)^\circ\text{C}$ for Ti_3AlC_2 .¹³ Quantifying the radiation induced decomposition of Ti_3SiC_2 to $\text{TiC}_{(1-x)}$ as a distinct phase is complicated by the presence of $\text{TiC}_{(1-x)}$ as an impurity in MAX phases.^{13,18} Irradiation induced $\text{TiC}_{(1-x)}$ regions have not been isolated.¹⁹⁻²²

At irradiation temperatures of $695\text{-}700^\circ\text{C}$, both Ti_3AlC_2 and Ti_3SiC_2 have no lattice parameter dilation and unchanged electrical resistivity.^{9,13,15,17} Thus between 400°C and 700°C , a process occurs to return metallic atoms to their sites (and Ti and C atoms). The mechanical properties between these temperatures are unknown, and are key issues for feasibility of Ti_3SiC_2 . This paper discusses additional questions. First, is there a similarity in swelling behaviour of MAX phases and their parent carbides? Does Ti_3SiC_2 have the same vulnerability to microcracking as Ti_3AlC_2 , which represents a generic problem with HCP ceramics? What aspects of toughness (diffuse microcracking, crack deflection, grain push and pull-out, and buckling/kinking of individual grains above yield stress)^{3,4} are retained after irradiation? This manuscript reports volumetric swelling, phase analysis, equibiaxial strength, modulus and fracture surfaces after irradiation at temperatures of $400\text{-}700^\circ\text{C}$.

Experimental

Materials and capsule design

Commercially available MAX phase materials (3-ONE-2, LLC (Willow Grove, PA)) were machined into disc coupons ($6 \times 6 \times 0.5\text{ mm}$) and multipurpose beams ($25 \times 2 \times 1.5\text{ mm}$). A brief section is included due to the non-conventional capsule configuration. Specimens were placed into holders along with mechanical support springs and passive Temperature Monitors (TMs). Figure 1 shows the configuration is not typical of irradiation capsules. Figure 1 shows the TMs, disc coupons ($6 \times 6 \times 0.5\text{ mm}$) and multipurpose beams ($25 \times 2 \times 1.5\text{ mm}$) for this paper. The irradiation experiment is simulated using ANSYS

14.0. A simple two-dimensional model in the r- θ plane provided estimates of operating temperatures using finite element methods. The thermal design assumes 12.7 μm gas gaps between the adjacent parts. Thermal expansion is also included in the analysis that simulates the irradiation environment.

Figure 1. MAX phase capsule specimen configuration showing thermal analysis cross-section

A fast neutron fluence of $\sim 2 \times 10^{25} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$) produced an estimated atomic displacement damage of $\sim 2 \text{ dpa}$ (displacements per atom) based on a typical dpa conversion for SiC, with a calculated damage rate²³ of $4.5 - 6.0 \times 10^{-7} \text{ dpa}\cdot\text{s}^{-1}$ in the mixed spectrum High Flux Isotope Reactor (HFIR) at ORNL.

Irradiation temperature

The irradiation temperature (T_{irr}) was determined from the nuclear-grade stoichiometric CVD SiC temperature monitors (TMs). A recent technique has been developed to increase precision and Table 1 shows the output SiC TM values.²⁴

Capsule #	1	4	7	Comments
TMs edge T_{irr} min ($^{\circ}\text{C}$)	328	564	599	Ref. ²⁴
TMs edge T_{irr} max ($^{\circ}\text{C}$)	370	615	641	Ref. ²⁴
TMs edge T_{irr} mid-point ($^{\circ}\text{C}$)	349(21)	584(26)	621(21)	Ref. ²⁴
Modeled	382-438	584-655	641-718	ANSYS (Figure 2)
CVD SiC $\Delta V/V$ (%)	2.18(0.04)	1.03(0.02)	1.20(0.04)	Multipurpose beam
Snead, Kato et al ($^{\circ}\text{C}$)	350	700	650	Ref. ²⁵
CVD SiC core TMs XRD LPs	0.83%	0.53%	0.54%	Central TMs – does not include axial temperature distribution
LP $\Delta V/V$	2.51%	1.60%	1.63%	
Snead, Katoh et al ($^{\circ}\text{C}$)	250	600	590	Lowest temperature in capsule

Table 1. Capsule number, minimum, maximum, mid-point, modeled irradiation temperatures.²⁴ CVD SiC swelling values are also able to show the approximate radiation temperatures.²⁵ Parenthesis show ($\pm\sigma_{\bar{x}}$) 1 standard deviation. Swelling shows the minimum value, with parenthesis showing the upper error (diagonal length measurement of non-adjacent vertices).

Thermal contour maps were developed for Figure 1 for the three capsules using the position of the recovered outer TMs. This is shown in Figure 2(a), (b) and (c). The model indicates that specimen temperatures are above that of the TMs.

Figure 2. Specimen configuration and temperature contour maps of capsules designated values of (a) 400°C, (b) 630°C and (c) 700°C.

The swelling of various CVD SiC materials at locations in the capsule can also gauge the irradiation temperatures. Redundant TM systems are more crucial in non-conventional capsule design. Table 1 also shows that the swelling of the CVD SiC materials correlate the temperature well to the TM calculated method. For convenience, the irradiation temperature (T_{irr}) values of $\sim 400^\circ\text{C}$, 630°C and 700°C were used in the manuscript.

Properties and characterization

Volumetric swelling was measured using one of the beams in each irradiation capsule. Length was measured at 90° intervals around the edges and the average value taken to be equal the length of the specimen. Four measurements were taken of the height and width, with the precision of all measurements being better than $\pm 3 \mu\text{m}$. Dynamic Young's modulus was determined using the impulse excitation and vibration method (by ASTM C1259) using the beam specimen and a Poisson's ratio of 0.21 due to the presence of intermetallics.²⁶ XRD patterns of both pre-irradiated and post-irradiated materials were acquired using Cu-K α (40 kV, 40 mA) radiation using a Scintag XRD. Samples were placed on a zero-background (SiO₂ Optical Grade from MTIXTI) mount. An internal Si SRM640b standard was used for lattice parameter refinements. Full profile fits of the XRD patterns were performed using GSAS.²⁷ Independent lattice parameters (without structure) were obtained using TOPAS 4.2 using a Le Bail (1988) fit.²⁸ Microstrain was determined by Williamson-Hall method.²⁹ Archimedes density on two specimens per capsule (by ASTM B962) used a proprietary 3M Fluorinet Liquid FC-43 as the suspension and immersion

medium. Samples were polished to a 1- μm finish with a series of diamond polishing pastes. Scanning Electron Microscopy (SEM) was conducted with a JEOL 6500F. Monotonic equibiaxial flexural strength (by ASTM C1499) was conducted on a minimum of 3 irradiated specimens. Weibull statistics were assembled on an unirradiated data set using;

where P_f is the probability of failure, m is the Weibull shape parameter, σ_0 is the characteristic strength or scale parameter and σ_u is the minimum strength or threshold parameter. In order to obtain m , a population of 32 unirradiated specimens was plotted to:

where P_f is the probability of failure (using the median $(i - 0.3)/(n + 0.4)$ i^{th} failure specimen and n is the population), and σ_i is the failure stress of the i^{th} specimen.³⁰

Results and Discussion

Phase analysis (XRD)

The general results of XRD analysis are as follows; c-axis expansion ($+\Delta c/c$) and negligible a-axis shrinkage ($-\Delta a/a$) was observed at $T_{\text{irr}} \sim 400^\circ\text{C}$. Lattice swelling did not occur at $T_{\text{irr}} \sim 630^\circ\text{C}$ and 700°C . An increase in TiC content was observed at all irradiation conditions.

In detail, the XRD pattern for pre-irradiated Ti_3SiC_2 material is shown in Figure 3(a). The residual plot accompanies the phases fitted with GSAS. The major phase of Ti_3SiC_2 (ICSD-180419) was identified, with minor phases $\text{TiC}_{(1-x)}$ (ICSD-5910091) and intermetallic TiSi_2 (ICSD-86810).

Figure 3(b) shows the XRD pattern from the specimen irradiated at $\sim 400^\circ\text{C}$. After irradiation, the residual plot became harder to minimize. A reduction in intensities of (0002) and (0004) reflections suggested increased disorder; the increase of (10 $\bar{1}$ 1), (10 $\bar{1}$ 3) and (10 $\bar{1}$ 5) relative to the basal reflections was consistent with results of ion irradiation to 10.3 dpa at $\sim 250^\circ\text{C}$.¹⁹

Figure 3(c) and (d) show that after irradiation at $\sim 630^\circ\text{C}$ and 700°C the residual plot improves in both patterns, fitting to reference crystal structures. The major difference between Figure 3(a) ($T_{\text{irr}} \sim 400^\circ\text{C}$) against (c) and (d) is that intensity of $\text{TiC}_{(1-x)}$ reflections does not change as much from as-received values. This was consistent literature using Rietveld models or published patterns with retained $\text{TiC}_{(1-x)}$ ^{6-9,13,15,16,18,31,32} suggesting irradiation induced decomposition, which is reduced at higher irradiation temperatures.

Figure 3. XRD pattern of Ti_3SiC_2 material (a) as-machined and after irradiation at (b) 400°C, (c) 630°C, (d) 700°C. TiC peaks are clearly noted in the original material.

The XRD pattern in Figure 3(a) shows distinct reflections of $\text{TiC}_{(1-x)}$, which are found in all samples. If discounted as $\text{TiC}_{(1-x)}$, only a peak shift and preferential orientation of (10 $\bar{1}$ 2) Ti_3SiC_2 phase could satisfy the model, which is an improbable anisotropic $\Delta a/a$ shrinkage of 1.8%. No large value (see Figure 4) of a -axis shrinkage has been reported for Ti_3SiC_2 .^{6-9,13,16,18,31,32}

The results of Quantitative Phase Analysis (QPA) are summarized in Table 2. The first line shows an attempt using a Mo-K α source (Xpert) analyzed with HighScorePlus (HS+). Most of the analysis used a Cu-K α source (Scintag) analyzed with GSAS (G). Results from the two techniques were consistent. They were also consistent with a batch used by Nappe et al.^{16,18} This indicated the vendor left residual intermetallics, and a consistent $\text{TiC}_{(1-x)}$ impurity. Table 2 shows that the $\text{TiC}_{(1-x)}$ phase was an impurity, and increased in relative intensity after $T_{\text{irr}} \sim 400^\circ\text{C}$ by $\sim 10\text{-}15\text{ wt}\%$ and $\sim 5\text{ wt}\%$ at $T_{\text{irr}} \sim 630^\circ\text{C}$ and 700°C .

Phase	Analysis package	Ti ₃ SiC ₂	TiC	TiSi ₂
Space group		P 63/m m c	F m -3 m	F d d d
Instrument		Wt. %		
Xpert Mo-Kα	HSP	70.4	23.8	5.7
Scintag Cu-Kα	G	76.6	20.2	3.2
Nappe et al (XRD)	-	74	19	7

Scintag T _{irr} ~400°C	G	65.7	34.3	Not fitted
Scintag T _{irr} ~630°C	G	73.2	26.8	Not fitted
Scintag T _{irr} ~700°C	G	72.6	27.4	Not fitted

Table 2. Result of quantitative phase analysis (QPA) of Ti-Si-C material; HSP = HighScorePlus, G = GSAS. Comparison QPA from vendor supplied material.^{16,18}

Table 3 shows lattice parameter (LP) changes of all phases. Since LPs changes are indicative of lattice relaxation from accumulated point defects and multiple phases were present, two methods were used. A Le Bail (structure-less) fit yielded TiSi₂ LPs that were not able to be refined with GSAS.²⁸ The QPA and lattice parameters of TiSi₂ are not analyzed in detail here.

		Phases				Lattice Parameters (Å)
Instrument / T _{irr}		Ti ₃ SiC ₂ [a; c]	%	TiC [a]	%	TiSi ₂ [a; b; c]
Scintag Cu Kα unirradiated	G	3.0706(1); 17.6940(6)	-	4.3243(1)	-	4.292(4); 4.789(6); 8.626(11)
Scintag Cu Kα unirradiated	T	3.0682(1); 17.679(1)	-	4.3220(1)	-	4.421(1); 4.887(1); 8.968(1)
Scintag T _{irr} ~400°C	G	3.0693(1); 17.9536(15)	-0.04; 1.5	4.3390(6)	0.34	Not fitted
Scintag T _{irr} ~400°C	T	3.0652(1); 17.9546(1)	-0.1; 1.6	4.3378(1)	0.37	4.3675(1); 4.9560(1); 9.2445(1)
Scintag T _{irr} ~630°C	G	3.0695(1); 17.7020(6)	-0.04; 0.05	4.3266(1)	0.05	Not fitted
Scintag T _{irr} ~630°C	T	3.0649(1); 17.6817(1)	-0.1; 0.02	4.3207(1)	-0.03	4.3825(1); 4.9500(1); 9.2474(1)
Scintag T _{irr} ~700°C	G	3.0697(1); 17.7011(9)	-0.03 0.04	4.3248(1)	0.01	Not fitted
Scintag T _{irr} ~700°C	T	3.0664(1); 17.6916(1)	-0.06 0.07	4.3204(1)	-0.03	4.3843(1); 4.9465(1); 9.247(1)

Table 3. Lattice parameters of phases fitted in Ti₃SiC₂-TiC material. ΔLPs are shown for Ti₃SiC₂ and TiC. Anisotropic swelling observed at T_{irr} ~ 400°C for Ti₃SiC₂. (G = GSAS, T = TOPAS) Parenthesis show (±σ_x) 1 standard deviation.

Table 3 shows that at T_{irr} ~ 400°C, Ti₃SiC₂ Δc/c increases by ~1.5%, with negligible Δa/a. The LPs do not dilate after T_{irr} ~ 630°C and 700°C. Figure 4 shows cumulative data from several irradiation studies as a

function of estimated displacement damage. Sets of markers are shown for T_{irr} , with trends approximated with dotted curves where data seems consistent (“25” (room temperature), 400 and 700°C). The line markers are ion irradiations supported by Grazing Incidence XRD, while the solid markers are neutron data (triangles and diamonds) that were able to use conventional Bragg-Brentano XRD configuration. The “cited” X-ray analysis region of some data is not well bracketed and large error bars or ranges of values are shown.^{16,18,20}

Figure 4 shows that the magnitude of $\Delta c/c$ monotonically decreases with increasing temperature. This indicated that defect microstructures affecting $\Delta c/c$ LPs were the same for ion and neutron irradiation within the point defect swelling regime. Saturation swelling at relatively low doses is suggested.

Figure 4. Compiled change in lattice parameter data versus reported displacement doses from all ion and neutron irradiations on Ti_3SiC_2 using GXRd (or XRD where noted).^{6-9,13,16,18,20,31,32} The value of c-axis lattice parameter swelling reduces with irradiation temperature.

Some low temperature (~120°C) or room temperature (25°C) ion irradiations appear to underestimate swelling, which may be caused by sample constraint. The XRD data from Huang et al was most consistent with temperature dependent mitigation of point defects in Ti_3SiC_2 .^{9,13,16,18,20,31} This trend was similar to observed data on Ti_3AlC_2 , except that no a-axis shrinkage is observed^{9-11,13,14} The difference

appears to be the use of conventional Bragg-Brentano XRD; furthermore, Huang et al proposed an α and “modified” β phases suggesting a strain-induced lattice transition of Ti_3SiC_2 , which could also explain prior underestimated LPs using $\alpha\text{-Ti}_3\text{SiC}_2$ phase; when fitting to $\alpha\text{-Ti}_3\text{SiC}_2$ no lattice swelling was observed by Huang et al.^{9,14} This transition should alter defect accommodation. It is particularly interesting given that this strain induced transition seems to occur in Ti_3AlC_2 at $\sim 5\% \Delta c/c$ and Ti_3SiC_2 at $\sim 3\% \Delta c/c$. This implied an intrinsic difference in defect accommodation solely due to a difference in A-type atoms. Figure 4 shows that only low temperature irradiations are likely to observe $\alpha\text{-}\beta$ transitions since a significant number density or size of defect clusters would be required to reach these values. Neutron data (all Bragg-Brentano XRD) and high temperature ion irradiation data (Clark et al) are consistent with sublinear swelling and temperature dependence.¹⁵ Qi et al noted no change to as-received LPs if $T_{\text{irr}} > 450^\circ\text{C}$.²⁰

This temperature-dependent saturation swelling was similar to another HCP ceramic BeO, which displays lattice swelling by positive $\Delta c/c$ values and minimal $\Delta a/a$ values.^{33,34} In BeO, data extrapolated to $T_{\text{irr}} \sim 400^\circ\text{C}$ revealed $\Delta c/c$ values that saturated at $\sim 2.5\%$, while $\Delta a/a$ was in the order of -0.1% .^{33,34} The theories to explain the c-axis increase in BeO show similarities to Ti_3SiC_2 ; Sabine, Austerman and Miller et al all proposed planar defect clusters but were unable to agree on configuration, but the reported size (7.5 nm) was consistent with low dose microstructures seen by Tallman et al.^{17,35,36} As T_{irr} increases, volumetric swelling ($\Delta V/V$) due to LP changes in BeO were reduced due to increased defect mobility (which promoted point defect recombination), and lattice swelling saturated to values that were dependent on temperature, because defects were thermally dissipated as they were produced.^{33,34} LP values in Figure 4 suggests that in Ti_3SiC_2 , this begins from $T_{\text{irr}} \sim 550\text{-}700^\circ\text{C}$, which was unfortunately below the radiation temperature in this study, and is the subject of future isochronal annealing. BeO also reported a threshold $\alpha\text{-}\beta$ transition, similar to these MAX phases.^{9,11,13,37} From a mechanical feasibility standpoint, the anisotropic c-axis lattice swelling was correlated to intergranular microcracking in BeO.⁴⁸ When $\Delta c/c$ of Ti_3AlC_2 (or $\Delta V/V$) reaches $\sim 3\text{-}4\%$ this is also observed.³⁸ Fracture and microcracking of Ti_3SiC_2 is addressed in the following section.

Polished and fracture surfaces

In general, the extent of microcracking decreased and delamination of kink bands increased with T_{irr} . This delamination was accompanied by prismatically oriented, brighter regions observed in Back Scatter Electron (BSE) imaging that were likely dislocation walls in kink bands. After $T_{\text{irr}} \sim 400^\circ\text{C}$, fracture surfaces were flat facets, without interlocking grains and delamination ligaments. These “toughening” morphologies were present after irradiation at $\sim 700^\circ\text{C}$.

In detail, Figure 5(a) shows the as-received material after machining and polishing. There are three phases under BSE contrast. The elongated grains that dominate the morphology are Ti_3SiC_2 . The

dispersed, equiaxed phase is $\text{TiC}_{(1-x)}$. The darker matrix region appear to be the intermetallic TiSi_2 based on *ad hoc* QPA (see Table 2). Pores are present in the material from intergranular pullout during polishing, and even revealed delaminations (red arrows).

Figure 5. (a) SEM image of an as-received and polished Ti_3SiC_2 -TiC materials and after post-irradiation at (b) $\sim 400^\circ\text{C}$ (c) $\sim 630^\circ\text{C}$ and (d) $\sim 700^\circ\text{C}$. Green arrows show microcracks; red arrows show regions of delamination or kink-band instability. Yellow arrows denote brighter regions in BSE which appear to be both along the (e) long a-axis ($T_{\text{irr}} \sim 400^\circ\text{C}$) and (f) short c-axis ($T_{\text{irr}} \sim 630^\circ\text{C}$).

Figure 5(b) shows the surface morphology after $T_{\text{irr}} \sim 400^\circ\text{C}$. Intragranular and intergranular cracks are observed (green arrows), accompanied by pullouts. Figure 5(c) shows that after $T_{\text{irr}} \sim 630^\circ\text{C}$ there continues to be microcracking. All microcracks are well below critical crack size for Ti_3SiC_2 .³⁹ Table 3 and Figure 4 showed that lattice swelling cannot be responsible for damage at this temperature. This indicated a different mechanism caused the damage after irradiation. In Figure 5(d) after $T_{\text{irr}} \sim 700^\circ\text{C}$, the extent of microcracking appears reduced and is similar to Figure 5(a) because more delaminations (red arrows) are observed. From El Raghy et al, since long axis of the grain represents the a-axis, the completely parallel intragranular striations were assumed to be kink bands in early delamination.^{4,26,40,41} After irradiation, brighter intragranular regions in Ti_3SiC_2 were observed in orientations parallel and normal to the a-axis.

Figures 5(e) and (f) show higher magnification images of the “intragranular regions” that have the same contrast as $\text{TiC}_{(1-x)}$ in the as-received material. Tallman et al observed basal plane $\frac{1}{2}\langle 0001 \rangle$ strain-field nanometric dislocation or antisite loops at 0.1 and 0.4 dpa.^{17,35,36} This is consistent with the planar component to defects in hcp ceramics. The parallel brighter regions are observed both before and after irradiation, and may be residual $\text{TiC}_{(1-x)}$ from processing. Figure 5(f) is unusual because it would imply Ti-rich regions are in the *prismatic* c-axis direction, since delamination parallel to a-axis is visible. This is addressed in Figure 6.

Figure 6 shows the fracture surfaces of Ti_3SiC_2 in SEI mode. In the unirradiated material (Figure 6(a)) the fracture surface consists of microcracks (green arrows) and delaminations (red arrows). Figure 6(b) shows that after irradiation at $\sim 400^\circ\text{C}$, delaminations are absent. The fracture surface is brittle fracture but is only flat facets. Some “stepping” is observed, but the surface consists mostly of large cracks (green arrows) on flat surfaces. Figure 6(c) shows the fracture surface after $T_{\text{irr}} \sim 700^\circ\text{C}$. No secondary microcracks were observed; instead the stepping improved to the point where it almost appears that delamination was possible. Thus (a) as-received and (c) $T_{\text{irr}} \sim 700^\circ\text{C}$ appear identical, but does show a difference in the extent of delamination. Delamination should provide more edge contrast as basal planes move apart; this is found in (a) but not in (c). It appears as though kink-bands are not rendered unstable during fracture. However, an improvement in fracture toughness compared to $T_{\text{irr}} \sim 400^\circ\text{C}$ can be implied by the increased surface area.

Figure 6(d) shows some of the prismatic, “brighter” BSE regions noted in Figure 5(f). No delamination was observed based on the spacing of the basal-layer morphology (red arrows) but there does appear to be orientation-contrast; the contrast disappeared during tilting (as shown), indicative of kink-band dislocation walls (marked by yellow arrows).⁴² This is consistent with bright BSE regions in the prismatic direction in Figure 5.

Figure 6. SEM fracture surfaces of (a) unirradiated $\text{Ti}_3\text{SiC}_2\text{-TiC}$ and after irradiation at (b) $\sim 400^\circ\text{C}$ and (c) $\sim 700^\circ\text{C}$. The brighter vertical regions (yellow arrows) in BSE in (d) appear to be related to channeling contrast that can be eliminated by sample tilting.

The fracture and polished surfaces appear similar, and indicate that kink-band related mechanisms were operational before and after irradiation at $\sim 700^\circ\text{C}$. No microcracking was observed in TEM phase-pure Ti_3SiC_2 at ~ 0.1 dpa after irradiation $\sim 400^\circ\text{C}$ at 0.9% c-axis swelling.¹⁷ Thus the microcracking may also be attributed to polishing artefacts due to suboptimum preparation available for irradiated materials. There is a lower extent of delamination after irradiation at $\sim 700^\circ\text{C}$ but more frequent appearance of dislocation walls. It appears that Ti_3SiC_2 behaved as other HCP ceramics when irradiated in the low temperature swelling regime, but damage can be mitigated by mechanisms (particularly at higher temperature) that other ceramics do not possess.

Mechanical properties and fracture strength

Briefly, Ti_3SiC_2 shows a gradual degradation of strength to 66% as the irradiation temperature falls from 700°C to $\sim 400^\circ\text{C}$. The pre-irradiation strengths in a Weibull modulus plot is shown in Figure 7(a) from 32 fractured Ti_3SiC_2 specimens. The characteristic 62% P_f strength was 458 MPa with a calculated Weibull modulus m of 17.

Figure 7. (a) Weibull modulus and strength distribution of the pre-irradiated Ti_3SiC_2 materials (b) The average strength of pre-irradiated (initial) and specimens irradiated at the selected temperatures.

The equibiaxial flexural strength (σ_{ef}) is shown in Figure 7(b). The first column of values shows the spread data from unirradiated samples (379-502 MPa). The average strength is 445 ± 29 MPa ($\pm \sigma_{\bar{x}} = 1$ standard deviation). Post-irradiation specimens fractured after $T_{\text{irr}} \sim 400^\circ\text{C}$, 630°C and 700°C are shown next. At $T_{\text{irr}} \sim 400^\circ\text{C}$, σ_{ef} was 315 ± 33 MPa, well outside two standard deviations and is interpreted as a 33% reduction in strength. The average strength after $T_{\text{irr}} \sim 630^\circ\text{C}$ and $\sim 700^\circ\text{C}$ is 391 ± 71 MPa and 378 ± 31 MPa. Due to the toughness of MAX phase requiring a substantial critical crack size to reduce strength, it was difficult to confirm a decreased reliability or toughness, except at $T_{\text{irr}} \sim 630^\circ\text{C}$ where the use of 3 specimens showed an upper and lower σ_{ef} exceeding the original sample set (Figure 7(b)).

The elastic modulus appeared to be reduced by 33% from 325 GPa to 205(6) GPa, although this was also attributed to microcracking. After irradiation at $\sim 630^\circ\text{C}$, modulus value shifted from 319 GPa to 312(1) GPa after irradiation and at $\sim 700^\circ\text{C}$, the modulus increased slightly from 285 GPa to 302(0.8) GPa. For $T_{\text{irr}} \sim 400^\circ\text{C}$, the decrease of strength correlates to flat fracture surfaces and agrees with the presence of microcracks. For $T_{\text{irr}} \sim 700^\circ\text{C}$, the surfaces in Figure 6(c) and (d) represent similar fracture surfaces to as-received materials (Figure 6(a)). There appears to be reduction in delamination morphologies compared to as-received materials, implying resistance to fracture depended more on interlocked grains buckling. It appears that mechanical properties are progressively degraded as the irradiation temperature is lowered from 700°C .

Swelling behavior

Table 4 shows the dimensional changes and density after irradiation. The “initial” density was $4.390 \pm 0.021 \text{ gcm}^{-3}$. After $T_{\text{irr}} \sim 400^\circ\text{C}$, the density was reduced to 4.344 gcm^{-3} . After $T_{\text{irr}} \sim 630^\circ\text{C}$ and 700°C , the densities were 4.359 and 4.386 gcm^{-3} . The linear swelling is included to compare to the volumetric swelling. No significant differences were expected or found between linear (L, W, H) and volumetric (V) data since they are polycrystalline. The volumetric swelling values are respectively 0.77%,

0.89% and 1.47% after T_{irr} ~400, 630 and 700°C respectively. The swelling reflects density changes; microcracks after irradiation at ~400°C reduce density. After irradiation at ~700°C there was substantial swelling without an overall change in density.

	ASTM B962	Dimensional and volume swelling (L = length, W = width, H = height)				ASTM B962	XRD (W-H)
Condition	(g·cm ⁻³)	(±σ _x = % single std dev.)				(g·cm ⁻³)	μ ε (%)
Initial	4.390(21)	ΔL/L	ΔW/W	ΔH/H	ΔV	Δρ	0.02%
~400°C	4.344(20)	0.40(0.03)%	0.29(0.11)%	0.08(0.32)%	0.77%	-1.05%	0.02%
~630°C	4.359(20)	0.37(0.04)%	0.25(0.01)%	0.27(0.03)%	0.89%	-0.71%	0.05%
~700°C	4.386(20)	0.56(0.01)%	0.47(0.04)%	0.43(0.16)%	1.47%	-0.09%	0.02%

Table 4. Archimedes density, linear and volumetric swelling (%) from dimensional changes microstrain (μ ε(%)) after irradiation at selected temperatures. Parenthesis show (±σ_x) 1 standard deviation of four measurements.

An increase in microstrain and then relaxation suggests a mechanism causes further mechanical damage during irradiation at ~400-630°C. It is not caused by lattice swelling (Table 3). The reduction in lattice swelling, accompanied by increase in volumetric swelling, indicated substantial free volume. The soaked weight was identical to the weight in air, which indicated no open pore volume. Further work is needed to explain the increased swelling observed after irradiation at ~700°C.

TiC_(1-x) and Ti₃(Al/Si)C₂ lattice parameters

The study also provided data on TiC_{1-x} under irradiation, which may provide some insight into irradiation of MX-derived ternary carbides. Figure 8(a) and (b) shows the compiled data for irradiations at 0.1 and 2 dpa (~2 × 10²⁵ nm⁻² (E > 0.1 MeV)) for the TiC impurity phases in Ti₃SiC₂ from Tallman et al and this work.¹³ Superimposed to the same displacement dose are SiC, Ti₃AlC₂, TiC_{1-x} and Ti₃SiC₂.^{13,14,25,43} The dpa conversion for ZrC and SiC were reportedly similar at E > 0.1 MeV threshold and TiC was assumed to be similar.^{23,44,45}

Figure 8. Change in lattice parameters of TiC (green) impurities in Ti_3SiC_2 at 0.1 and 2 dpa at (a) $T_{irr} \sim 400^\circ\text{C}$ and (b) $T_{irr} \sim 700^\circ\text{C}$.^{13,14} SiC lattice parameter (linear $\Delta a/a$) is shown as a comparison with the blue markers.^{25,43}

After $T_{irr} \sim 400^\circ\text{C}$, anisotropic swelling occurred in the MAX phases (minor in Ti_3SiC_2 and significant in Ti_3AlC_2). Linear swelling of SiC is known to be $\sim 0.7\%$ at $T_{irr} \sim 400^\circ\text{C}$.^{25,43} TiC_{1-x} showed increasing lattice swelling with dose, due to point defect damage (black spots were observed by Tallman et al).¹⁷ TiC_{1-x} in Figure 8 consists of data only with confirmed lattice parameter (thus known starting C/Ti ratios) that would affect Ti or C migration energies.^{13,46} An increase in LPs (~ 0.01 - 0.03 at 0.1 dpa, ~ 0.15 at 2 dpa) was observed after $T_{irr} \sim 360(20)/400^\circ\text{C}$.^{13,46} Figure 8(b) shows that at $T_{irr} \sim 700^\circ\text{C}$, point defect swelling Ti_3SiC_2 , Ti_3AlC_2 and TiC_{1-x} is mitigated.

The bond lengths in Ti-C based compounds vary: TiC_{1-x} is $2.164 \text{ \AA}$, compared with $2.188 \text{ \AA}$ for $\text{Ti}_1\text{-C}$ and $\sim 2.0975 \text{ \AA}$ for $\text{Ti}_2\text{-C}$ in Ti_3SiC_2 .⁴⁷ The vacancy migration energies of Ti and C are dependent on stoichiometry, ranging from ~ 2.44 - 4.15 eV (respectively)⁴⁸, but similar to values of 2.81 - 4.13 eV (Ti and C (respectively) at the edge of TiC_6 region⁴⁹). Vacancy migration has been observed after ion irradiations of TiC_{1-x} at $\sim 800^\circ\text{C}$ ⁵⁰, which is consistent with a migration energy near $\sim 3 \text{ eV}$.

In $\text{Ti}_3(\text{Al/Si})\text{C}_2$ LP swelling is not eliminated by interstitial migration but it does appear to be progressively mitigated.¹⁴ However, interstitial migration is already available from room temperature^{15,49,51}, and yet at $\sim 400^\circ\text{C}$, the A-atom interstitials are still not recovering, since there is a loss of kinking-delamination and electrical conductivity.^{13,14} When A-atoms are displaced, anisotropic swelling occurs.¹⁴ Therefore lattice parameter swelling at ~ 550 - 700°C implies that $\text{Ti}_3(\text{Al/Si})\text{C}_2$ A-atom recovery is dependent on a higher defect migration energy (either vacancy migration, or thermal dissolution of small vacancy clusters).

The above analysis describes the higher temperature behavior near recovery. At low temperature irradiations when defect mobility is lower, an α to "modified β " strain-induced transformation is consistent

with antisite defects in the M-A layers shifting the M position to Wyckoff 2b to 2d.¹¹ At low temperature, the ~1.5 eV energy barrier is a significant hurdle.^{49,51} The retention of TiC or MX content (usually at ~5-10 wt%) and only slight loss of electrical conductivity would indicate stable defect sites for Ti or C atoms in the M-A layers.¹³ This may also explain the difference in unirradiated and $T_{irr} \sim 700^\circ\text{C}$ fracture surfaces, if delamination morphologies are those of mixed M-M (Ti_{Al}) and M-A bonds rather than uninterrupted sheets of M-A atoms.

The separate low and high temperature irradiation behavior provides hypothesis for future work. If knock-on atoms (e.g. Al and Si) come to rest in the Ti-C region, then some A-atoms are trapped in the Ti-C region, mitigated only when A-atoms can return through a vacancy-assisted mechanism. Onset of vacancy migration is often shown as an inflection mitigating swelling in irradiated ceramics (e.g. MgO, Al_2O_3 , SiC and BeO).⁵ Trapped A-type atoms also explains why Ti_3AlC_2 has 50% higher $\Delta c/c$ than Ti_3SiC_2 , due to bigger atom/ion radii resting in the otherwise identical Ti-C region. Since Ti_2AlC and Ti_3AlC_2 $\Delta c/c$ was reportedly similar¹³, and $\Delta c/c$ of Cr_2AlC matches Ti_3AlC_2 , logically it is not the M or C atoms.⁵² Finally, if the M-X selection determines the “recovery”, then selection of the M-X atoms could engineer the “recovery” temperature by analogy to migration energies in $\text{MX}_{(1-x)}$. Sub-stoichiometry of M or X, or two types of M atoms may achieve this. Based on these extrapolations, annealing, positron annihilation studies and future compositions are being planned.

Conclusions

Ti_3SiC_2 was irradiated to ~ 2 dpa ($E > 0.1 \text{ MeV}$) ($2 \times 10^{25} \text{ nm}^{-2}$) at ~400, ~630 and ~700°C, and showed progressively reduced lattice parameter dilation as irradiation temperature increased. However, this was accompanied by an increase in volumetric swelling. This could only be explained by the presence of microcracking and kink-band based deformation that increased free volume. The decomposition of Ti_3SiC_2 to TiC of at least ~5 wt% occurred at all temperatures, but was particularly high after irradiation at ~400°C (~10-15 wt%). Lattice parameter changes of $\text{TiC}_{(1-x)}$ and Ti_3SiC_2 at 400°C and 700°C showed similar trend of recovery, suggesting a key mobility mechanism in the MX structure could be related to recovery of MAX phases. The fracture strength of Ti_3SiC_2 increased from 66% of as-received values after irradiation at ~400 to ~80% after irradiation at ~700°C. Fracture surfaces showed flat facets and microcracks after irradiation at ~400°C, but showed kink-band related fracture, grain interlocking and limited delamination at higher irradiation temperatures. Elastic modulus was unaffected after irradiation at ~630-700°C but appeared to validate the presence of microcracks after irradiation at ~400°C. Strength, swelling and fracture surfaces thus indicate that Si-layers were partially displaced by neutron irradiation and progressively recovered at higher irradiation temperatures. It appears that Ti_3SiC_2 undergoes a minor and gradual degradation of mechanical properties when irradiation temperature is decreased from 700°C.

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