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# Neutron Damage and MAX Phase Ternary Compounds

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## Integrated University Programs

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Project Objective (Initial):

The demands of Gen IV nuclear power plants for long service life under neutron radiation at high temperature are severe. Advanced materials that would withstand high temperatures (up to 1000+ °C) to high doses in a neutron field would be ideal for reactor internal structures and would add to the long service life and reliability of the reactors. The objective of this work is to investigate the response of a new class of machinable, conductive, layered, ternary transition metal carbides and nitrides - the so-called MAX phases - to low and moderate neutron dose levels. The microstructures, tensile properties and electrical resistivities of select MAX phases will be characterized following irradiation up to  $2.5 \times 10^{25}$  n/m<sup>2</sup> (E<sub>n</sub> > 0.1 MeV) or 1.9 dpa at 60 °C and 650 °C at the MIT Research Reactor.

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## **Executive Summary:**

The demands of Gen IV nuclear power plants for long service life under neutron radiation at high-temperature are severe. Advanced nuclear reactor designs require materials that can withstand long term operation in extreme environments of elevated temperatures, corrosive media, and fast ( $E > 1\text{MeV}$ ) neutron fluences with up to 100 displacements per atom (dpa). Herein we report on the effect of neutron irradiation - of up to 0.1 dpa at 360(20) °C or 695(25) °C - on polycrystalline samples of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_2\text{AlN}$ . X-ray diffraction refinement of the irradiated samples showed irradiation-enhanced dissociation into TiC of the  $\text{Ti}_3\text{AlC}_2$  phase, and possibly in  $\text{Ti}_3\text{SiC}_2$ .  $\text{Ti}_2\text{AlN}$  also showed an increase in TiN content, as well as  $\text{Ti}_4\text{AlN}_3$  after irradiation. In contrast,  $\text{Ti}_2\text{AlC}$  was quite stable under these irradiation conditions. Dislocation loops are seen to form in  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$  after irradiation at 360(20) °C. While these loops coarsen in  $\text{Ti}_2\text{AlC}$  at 695(25) °C, stacking fault tetrahedra are observed in  $\text{Ti}_3\text{AlC}_2$  at the same conditions. The room temperature electrical resistivity of all samples increased by an order of magnitude after irradiation at 360(20) °C, but only by 25% after 695(25) °C, providing evidence for the MAX phases' dynamic recovery at temperatures as low as 695(25) °C. Based on these preliminary results, it appears that several of the MAX phases, most notably  $\text{Ti}_2\text{AlC}$  and possibly  $\text{Ti}_3\text{SiC}_2$ , are promising materials for high temperature nuclear applications. This work provides a solid base of information to characterize the irradiation response of the MAX phases and provides an initial comparison to leading ceramics proposed for Gen IV in-core components.. The irradiated tensile specimens could not be tested within the time frame of the project. Medium (0.4 dpa) and high (0.7 dpa) dose samples are in storage at SRNL, as funding and time ran out before characterization could be completed. With additional irradiation characterization, the MAX phases may prove to be superior materials for in-reactor component design, especially with their creep resistance well beyond 1000 °C.

## **Background:**

Gen IV nuclear reactor designs require materials that can withstand long term operation in extreme environments of elevated temperatures, corrosive media, and fast ( $E > 1\text{MeV}$ ) neutron fluences with up to 100 displacements per atom (dpa) [1]. Full understanding of the irradiation response in selected materials is paramount to long-term, reliable service. The  $\text{M}_{n+1}\text{AX}_n$  (MAX) phases are a class of layered, machinable, ternary carbides and/or nitrides,

where M is an early transition metal, A is a group 13 to 16 element, and X is C and/or N. These compounds possess a unique set of properties both metallic and ceramic in nature. For example, some of them exhibit relatively high fracture toughness values (8-12 MPa $\sqrt{m}$ ) and are elastically stiff like their binary carbide and nitride counterparts, and yet are readily machinable, lightweight, and relatively soft [2-8]. The MAX phases also undergo plastic-to-brittle transitions at high temperatures, and the materials can withstand high compressive stresses at room temperatures, RT [2, 7].

Many recent studies have explored the damage tolerance and amorphization resistance of several MAX phases irradiated with heavy ions [9-19]. In 2009, Nappé *et al.* explored the effect of 90 MeV Xe ions on Ti<sub>3</sub>SiC<sub>2</sub>, showing surface layer amorphization of the Ti<sub>3</sub>SiC<sub>2</sub> and impurity phases, as well as, selective grain boundary sputtering due to nuclear interactions [9]. Liu *et al.* characterized Al-doped Ti<sub>3</sub>SiC<sub>2</sub>, irradiated to a maximum dose of 3.25 dpa with high energy Kr and Xe ions, via X-ray diffraction (XRD) and nanoindentation showing an expansion of the c-lattice parameter, c-LP, and irradiation induced hardness that could be annealed out at 800 °C [14, 15]. They also reported the possible existence of a  $\beta$ -Ti<sub>3</sub>SiC<sub>2</sub> phase to explain the presence of new peaks found in the post-irradiated XRD patterns [15]. Soon after, Le Flem *et al.* reported on selected area diffraction (SAD) patterns in a transmission electron microscope (TEM) of Ti<sub>3</sub>(Si,Al)C<sub>2</sub> irradiated with 92 MeV Xe ions up to 6.67 dpa, which further confirmed this MAX phases' resistance to amorphization [16]. With increasing dose, diffraction peaks were found to disappear due to lattice disturbances. In 2010, Bugnet *et al.* explored the effect of 100 keV Ar<sup>2+</sup> ion irradiation on multilayered (Ti,Al)N/Ti<sub>2</sub>AlN<sub>x</sub> nitrogen-deficient thin films, reporting that the multilayered structure was preserved up to a dose of 12 dpa, likely due to nitrogen vacancies acting as sinks for interstitial point defects [19].

Along the same lines, Whittle *et al.* reported that Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>SiC<sub>2</sub> possess very high resistance to amorphization, even up to 25 dpa, irradiated with 1 MeV Kr<sup>2+</sup> and 1 MeV Xe<sup>2+</sup> [13]. Nappé *et al.* reported that nuclear collisions with 4 MeV Au ions, up to a dose of 4.3 dpa, resulted in a 2.2% swelling in Ti<sub>3</sub>SiC<sub>2</sub> [10]. Also in 2011, Nappé *et al.* investigated the structural changes of Ti<sub>3</sub>SiC<sub>2</sub> under a variety of ions and energies, concluding that Ti<sub>3</sub>SiC<sub>2</sub> is not sensitive to electrical interactions, and confirmed that nuclear collisions lead to an increase in c-LP and a decrease in the a lattice parameter, a-LP, and a concomitant increase in lattice microstrains [12].

In 2012, Zhang *et al.* reported that a TiC and/or 3C-SiC (cubic  $\beta$ ) nanocrystalline phase formed under 2 MeV  $I^{2+}$  irradiation of  $Ti_3SiC_2$ , though the material did not fully decompose, even up to 10.3 dpa [18]. In 2013, Le Flem reported on a saturation in irradiation damage at 3.2 dpa via hardness measurements and cell volume expansion due to defect formation under 92 MeV Xe ions in  $Ti_3SiC_2$  [17].

It is important to note, that in contrast to neutrons, which pass through the bulk, the penetration depth of heavy ion and helium, He, irradiation is limited to the surface, and He atoms tend to accumulate and form bubbles inside the material after momentum transfer. This has been illustrated by Xiao *et al.* via *ab initio* methods, showing the He most energetically favors Al-site interstitials in  $Ti_3AlC_2$  [20]. More recently, Wang *et al.* irradiated  $Ti_3AlC_2$  samples with 50 keV He ions with fluences ranging from  $8 \times 10^{16} \text{ cm}^{-2}$  to  $1 \times 10^{18} \text{ cm}^{-2}$ , resulting in the formation of spherical He bubbles, string-like bubbles and faulting zones [21]. Grazing incidence XRD analysis and SAED confirmed significant structural disorder without amorphization, even up to 52 dpa. Patel *et al.* irradiated  $Ti_3AlC_2$  samples with 200 keV He ions to a maximum dose of 5.5 dpa at 500 °C, and showed, by careful analysis of XRD patterns, that the  $Ti_3AlC_2$  structure was maintained, but with an increased c-LP and a decreased a-LP together with a highly disordered Al layer [22]. If He bubbles exist, they were  $< 1 \text{ nm}$  in diameter and did not agglomerate as observed by Wang *et al.* at RT [21]. Very recently, Yang *et al.* reported on the structural transitions of  $Ti_3AlC_2$  irradiated with 50 keV He ions over a wide fluence range. While no amorphization was detected up to 31 dpa, antisite defects readily destroyed the nanolamellar  $Ti_3AlC_2$  structure, and a transition to  $\beta$ - $Ti_3AlC_2$  was observed above 2.61 dpa.

In addition to heavy ion and He irradiation studies, Hoffman *et al.* have shown that neutron activation of  $Ti_3SiC_2$ ,  $Ti_3AlC_2$ , and  $Ti_2AlC$  compare well to SiC and are three orders of magnitude lower than alloy 617, two candidate materials for use in next generation reactors [23].

Based on these preliminary results it has been proposed that the MAX phases could be used in demanding nuclear environments either as fuel matrices or as coating materials, with potential for significant improvements in performance due to their high temperature capabilities, high mechanical deformation tolerance, chemical resistance, and versatile manufacturing techniques. The purpose of this work is to understand the effects of neutron irradiation on the microstructural stability and electrical resistivity of polycrystalline samples of  $Ti_3AlC_2$ ,  $Ti_3SiC_2$ ,

Ti<sub>2</sub>AlC and Ti<sub>2</sub>AlN. As far as we are aware, and with the exception of a report that has just been published, on the neutron irradiation of Ti<sub>3</sub>SiC<sub>2</sub> formed at joints between SiC parts, this is the first report on the neutron irradiation of bulk MAX phases in the open literature.

## **Objectives: Accomplishments and Failures**

### **Sample Fabrication**

Details of the synthesis and processing conditions of the MAX phases are discussed elsewhere [7, 24]. In short, samples of Ti<sub>2</sub>AlC were prepared by pouring pre-reacted Ti<sub>2</sub>AlC powders (Kanthal, Hallstahammar, Sweden) into graphite dies, which were loaded into a vacuum hot press and hot pressed (HPed) for 4 h under a load corresponding to a stress of ~ 40 MPa and a vacuum of 10<sup>-1</sup> Pa at a temperature of 1300 °C. The Ti<sub>3</sub>AlC<sub>2</sub> samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti<sub>2</sub>AlC and TiC powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h which, in turn, were HPed at 1400 °C for 4 h. The Ti<sub>2</sub>AlN samples were fabricated by milling stoichiometric mixtures of Ti and AlN powders (Alfa Aesar, Ward Hill, Massachusetts, USA) as above, and then HPing at 1300 °C for 4 h. Fine grained samples of Ti<sub>3</sub>SiC<sub>2</sub>, henceforth referred to as Ti<sub>3</sub>SiC<sub>2</sub>-FG, were prepared by ball milling stoichiometric mixtures of Ti, Si, and C powders (Alfa Aesar, Ward Hill, Massachusetts, USA) for 24 h, which were then HPed at 1450 °C for 6 h. Coarse grained Ti<sub>3</sub>SiC<sub>2</sub>, henceforth referred to as Ti<sub>3</sub>SiC<sub>2</sub>-CG, were prepared from elemental mixtures as above, and HPed at 1500 °C for 4 h, followed by an anneal at 1600 °C for 8 h in an argon atmosphere.

Samples of each phase were sectioned, mounted in epoxy, and polished to a final surface preparation of 3 μm diamond suspension for optical microscopy (OM). The MAX phase microstructure was exposed with an etchant composed of 1:1:1 parts by volume solution of hydrofluoric acid (50 vol.%), nitric acid (70 vol.%), and water, which was applied to the surface for < 30 seconds and rinsed. This etchant resulted in vibrantly colored MAX phase grains, notably in Ti<sub>3</sub>AlC<sub>2</sub> (Fig. 1b) and Ti<sub>3</sub>SiC<sub>2</sub> (Figs. 1d and e) with well exposed grain boundaries. TiC impurities appear as bright white grains, highlighted in Fig. 1 by white arrows. The length, d<sub>l</sub>, and width, d<sub>t</sub>, of >50 grains per sample were measured by OM, and the equivalent grain size was calculated as the geometric mean value of the grain dimensions, i.e.  $\sqrt[3]{d_l^2 \cdot d_t}$ .

Test specimens were electro-discharged machined into  $1.5 \times 1.5 \times 25.4 \text{ mm}^3$  resistivity bars,  $16 \times 4 \times 0.7 \text{ mm}^3$  tensile dog-bones, and 3 mm dia. x 0.5 mm discs for TEM observation (Fig. 2). Initial dimensions were recorded.

OM micrographs of the resulting samples showed to be fully dense, with some evidence of pull out, and predominately single phase, with randomly aligned plate like grains (Figs. 1a-e). The average grain sizes of the  $\text{Ti}_3\text{SiC}_2$ -FG and  $\text{Ti}_3\text{SiC}_2$ -CG, were 8(3) and 50(20)  $\mu\text{m}$ , respectively, with standard deviations listed in parentheses. The average grain sizes of  $\text{Ti}_2\text{AlC}$ ,  $\text{Ti}_2\text{AlN}$  and  $\text{Ti}_3\text{AlC}_2$  were 10(4), 15(2) and 16(6)  $\mu\text{m}$ , respectively.

$\text{Ti}_3\text{SiC}_2/\text{SiC}$  fiber composites were fabricated by layering 140  $\mu\text{m}$  dia. SiC fibers arrayed longitudinally with prereacted powders into graphite dies for hot pressing as above. Samples were HPed at 1500 °C for 4 h under a load corresponding to 30 MPa. Creep dog-bone specimens with a test cross section of  $2 \times 2.5 \text{ mm}^2$  were machined using EDM. Issues with the SiC arrays led to curved fiber sections, appearing almost like wood grains. The samples had areas of porosity and large cracks, which impeded sample cutting. Only 6 samples were of good enough quality to commence testing.

## Sample Irradiation

The irradiation occurred in three phases at the 6 MW MIT Nuclear Research Reactor at the Massachusetts Institute of Technology in a neutron spectrum similar to that of a light water power reactor (Fig. 3): Phase I 10/13-12/4 2010, Phase II 12/4/2010-3/8/2011, Phase III 3/8-12/22 2011. For the purposes of this report, the six sample sets are designated Low Fluence Low T, Low Fluence High T, Med Fluence Low T, Med Fluence High T, High Fluence Low T and High Fluence High T. The Low Fluence sample sets were exposed only in Phase I, the Med Fluence sample sets only in Phase III and the High Fluence in all three Phases. While 60 and 650 °C were the initial temperature targets for this experiment, the capsule designs and their positions within the reactor resulted in higher temperatures being reached, as given in Table 1. Depending on the particular capsule, the temperature ranged from 340 to 380 °C and from 695 to 750 °C for the low and high temperatures, respectively, further denoted at LT and HT (Table 1).

The total irradiation exposures expressed in MWh (reactor power multiplied by time at power) are: Phase I, 5,000; Phase II, 4,100; and Phase III, 20,200. Specimens were irradiated to a



maximum fluence ranging from  $2.0 \times 10^{20}$  n/cm<sup>2</sup> to  $2.8 \times 10^{21}$  n/cm<sup>2</sup> (E>1 MeV) at LT and HT, respectively. Note that the fluences are based on the actual integrated MWh for each set of specimens and Monte Carlo N-Particle Transport Code, MCNP, calculated flux levels at the irradiation positions. Based on the SiC damage cross-sections reported in [25] and the neutron spectrum in another in-core experimental facility, the damage rate for SiC has been previously calculated to be  $4 \times 10^{21}$  n/cm<sup>2</sup> = 1 dpa. Using this damage rate for the MAX phases, in the absence of other damage cross-sectional information, this work explores the irradiation response in the 0.1, 0.5, and 0.7 dpa regimes, henceforth denoted as low, medium and high dose, respectively. All proposed samples were successfully irradiated and are being stored at SRNL for post-irradiation characterization.

Contained in this report are results of the characterization of the low dose samples. Delays in irradiation, and increased cooling periods led to a ripple effect in the majority of the characterization experiments. At this time, resistivity testing and XRD refinement has been completed for all low dose samples. TEM characterization of irradiation defects has been performed on the pristine and low dose samples of Ti<sub>2</sub>AlC and Ti<sub>3</sub>AlC<sub>2</sub> irradiated at both LT and HT.

Tensile testing was completed for all pristine samples. All remaining samples are in storage at SRNL for future testing. Ti<sub>2</sub>SiC was found to be problematic during this project due to the significantly higher activation compared to all other samples. Impurities in the starting materials resulted in hafnium formation, which lead to unsafe dose counts for the RAD workers. In concurrence with the TPOC Douglas Marshall, Ti<sub>2</sub>SiC was abandoned early on.

## **X-ray Diffraction Refinement**

XRD patterns from the surfaces of samples of Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>2</sub>AlN, Ti<sub>3</sub>SiC<sub>2</sub>-FG and Ti<sub>3</sub>SiC<sub>2</sub>-CG were obtained using one of two diffractometers (Bruker D8, Madison, WI, USA) in the Bragg–Brentano configuration, for pristine and irradiated conditions, respectively. The diffractograms were collected using step scans of 0.02° in the 5–70° 2θ range, with a step time of 2s. Scans were made with Cu Ka radiation (45 kV and 40 mA). The accuracy of the diffractometer in determining lattice parameters, and its instrumental peak-shape function parameters were calibrated using a LaB<sub>6</sub> standard (NIST 660A).

All diffractograms were analyzed by the Rietveld refinement method, using the FULLPROF code [26, 27]. A systematic shift of 0.02% was found, and corrected for, in the lattice parameters', LP, evaluation as compared to the LaB<sub>6</sub> standard's reported value. For each data set, a model containing TiC and each specific MAX phase, *e.g.*, Ti<sub>3</sub>SiC<sub>2</sub>, Ti<sub>3</sub>AlC<sub>2</sub>, or Ti<sub>2</sub>AlC was refined. For Ti<sub>2</sub>AlN, the model was refined with the TiN and Ti<sub>4</sub>AlN<sub>3</sub> phases. The Thompson-Cox-Hastings pseudo-Voigt model was used to refine the peak-shape of each phase's reflections. Lattice strains and particle sizes were also estimated assuming isotropic Lorentzian and Gaussian contributions to the peak shape function [28]. The micro strain was calculated from the full width half max (FWHM) parameter U from each sample, according to the following equation:

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

where U<sub>std</sub> was refined from the LaB<sub>6</sub> standard. If U<sub>sample</sub> refined lower than the U<sub>std</sub>, the microstrain was unresolvable for that specimen. The U<sub>std</sub> values were 0.006(2) and 0.014(2) for the standards scanned on the diffractometers for pristine and irradiated samples, respectively.

The XRD patterns collected from the Ti<sub>3</sub>SiC<sub>2</sub>-FG, Ti<sub>3</sub>SiC<sub>2</sub>-CG, Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>2</sub>AlC and Ti<sub>2</sub>AlN samples before and after the LT and HT irradiations are shown in Figs. 4, 5, 6, 7 and 8, respectively. The results of the Rietveld analyses of these patterns are summarized in Table 2. According to these results, the TiC contents of the pristine Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>3</sub>SiC<sub>2</sub>-FG and Ti<sub>3</sub>SiC<sub>2</sub>-CG samples, were found to be 6.7(8) wt.%, 1.9(6) wt.%, 20.0(5) wt.% and 18.2(5) wt.%, respectively. While no Ti<sub>4</sub>AlN<sub>3</sub> phase was observed in pristine Ti<sub>2</sub>AlN, the TiN content was found to be 3.2(2) wt.%.

In all cases, the neutron irradiations resulted in structural, as well as compositional changes compared to their pristine conditions (Table 2). The best fit was achieved by including TiC during refinement of the carbide phases. Irradiation of the Ti<sub>3</sub>AlC<sub>2</sub> resulted in the significant increase in the TiC content from 1.9(6) wt.% before irradiation, to 52.6(9) and 44.4(8) wt.%, after the LT and HT irradiations, respectively. Cross sections of these samples were also scanned by XRD (not shown), confirming that the dissociation into TiC was not a surface phenomenon. Irradiation of Ti<sub>3</sub>SiC<sub>2</sub>-FG also yielded an increase in TiC content, going from 20.0(5) wt. % initially to 22.7(5) and 25(1) wt.% after the LT and HT irradiations, respectively. The TiC

content in the  $\text{Ti}_3\text{SiC}_2$ -CG changed from 18.2(5) wt.% as received to 23.3(6) and 17.0(4) wt.% after LT and HT irradiations, respectively (Table 2). At this time it is not clear whether the TiC content increased as a result of the irradiations or if the changes are simply due to sample to sample variabilities.

The Rietveld refinement of  $\text{Ti}_3\text{SiC}_2$ -FG irradiated at 360(20) °C, denoted henceforth as  $\text{Ti}_3\text{SiC}_2$ -FG-LT, showed an increase in the c-LP from 17.681(1) to 17.812(9) Å and a decrease in the a-LP from 3.0686(8) to 3.0648(1) Å (Figs. 4 and 9). A microstrain of 0.27% was calculated for the distorted lattice, increased from 0.08% in the pristine sample (Table 2). After irradiation at 695(25) °C, denoted as  $\text{Ti}_3\text{SiC}_2$ -FG-HT, the  $\text{Ti}_3\text{SiC}_2$ -FG lattice was only slightly perturbed, with c-LP of 17.668(1) and a-LP of 3.0674(1), with a microstrain level below that of the standard used to calibrate the diffractometer (Figs. 4c and 9 and Table 2).

The  $\text{Ti}_3\text{SiC}_2$ -CG samples behaved similarly to their fine-grained counterparts (Fig. 5). Refinement of  $\text{Ti}_3\text{SiC}_2$ -CG-LT, showed an increase in the c-LP from 17.680(8) to 17.840(8) Å and a decrease in the a-LP from 3.0688(7) to 3.0647(8) Å. There was a simultaneous increase in microstrain to 0.33% (Table 2). After irradiation at 695(25) °C, the  $\text{Ti}_3\text{SiC}_2$ -CG lattice was slightly distorted, with a c-LP of 17.669(6) Å, and an a-LP of 3.0674(8) Å (Fig. 9); the microstrain was only 0.06%.

The Rietveld refinement of  $\text{Ti}_3\text{AlC}_2$ -LT (Figs. 6a,b) also showed an increase in the c-LP from 18.562(2) to 18.896(1) Å and a decrease in a-LP from 3.0736(2) to 3.0542(2) Å (Table 2). Concomitantly there was an increase in microstrain from 0.1% to 0.39% (Fig. 6b and Table 2). At 18.543(2) Å and 3.0699(2) Å, the c- and a-LPs, respectively, the unit cell parameters of the  $\text{Ti}_3\text{AlC}_2$ -HT samples were less distorted than those at LT (Figs. 6c and 9). After irradiation at 695(25) °C, the microstrain was 0.34 %.

As noted above, the pristine  $\text{Ti}_2\text{AlC}$  samples were fabricated using commercially available MAX powders (Kanthal, Sweden), resulting in a higher initial TiC volume fraction of 6.7(8) wt. %. The c- and a-LPs, of the pristine samples were found 13.652(2) Å and 3.0616(2) Å, respectively (Fig. 7a and Table 2). Refinement of the XRD patterns of the  $\text{Ti}_2\text{AlC}$ -LT samples revealed a distorted unit cell with an increased c-LP of 13.882(1) and decreased a-LP of 3.0367(2) (Figs. 7b and 9). At 8.3(3) wt.%, the TiC composition did not change after the LT

irradiation and was within the variability in TiC content obtained for these samples. With a c-LP of 13.359(3) Å and an a-LP of 3.05851(3), the lattice parameters of the Ti<sub>2</sub>AlC-HT samples were similar to their values in the pristine samples (Fig. 7c). Refinement also revealed that these samples contained 4.3(1) wt.% TiC, a value lower than in the pristine samples. Since this is unlikely, it confirms the somewhat inhomogeneous distribution of TiC in these samples.

While the a- and c-LPs for each MAX phase discussed above were distorted at LT conditions (Fig. 9), the a-LP for the TiC phase remained relatively constant at all conditions, showing at most an increase of ~ 0.2 % in the Ti<sub>3</sub>AlC<sub>2</sub>-LT samples (Table 2). While the TiC content increased in some cases, the LPs of the TiC phase remained very close to their values in the pristine samples.

Rietveld refinement of the Ti<sub>2</sub>AlN samples revealed a similar trend of distorted LPs (Figs. 8 and 9). The best fit, however, was achieved when TiN and Ti<sub>4</sub>AlN<sub>3</sub> were refined as well. Ti<sub>2</sub>AlN-LT showed an increase in the c-LP from 13.640(2) to 13.714(4) Å and a decrease in a-LP from 2.9886(3) to 2.9808(6) Å (Figs. 8a,b and 9). Unsurprisingly, there was an increase in microstrain from 0.16% to 0.2% (Fig. 8b and Table 2). At 13.664(4) Å and 3.0086(3) Å, the c- and a-LPs, respectively, of the Ti<sub>2</sub>AlN-HT samples were the least distorted of all samples irradiated to 360(20) °C (Fig. 9). At 0.58 %, the micro-strain found in Ti<sub>2</sub>AlN-HT was significantly higher than all other samples irradiated at this condition. Unique among all MAX phases tested herein, Ti<sub>2</sub>AlN-HT resulted in the formation of 36(3) wt.% Ti<sub>4</sub>AlN<sub>3</sub>. An additional phase with peaks around 36, 41, and 58.6° 2θ was unidentified, due to these peaks' low intensity and the high background noise.

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

Rietveld refinement revealed a distortion of LPs under neutron irradiation of the Ti<sub>3</sub>SiC<sub>2</sub>-FG, Ti<sub>3</sub>SiC<sub>2</sub>-CG, Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>2</sub>AlC and Ti<sub>2</sub>AlN samples (Fig. 9). This result concurs with previous work where heavy ions and He irradiations were shown to result in lattice distortions [9-14, 16, 17, 19, 21, 22]. After LT irradiation, Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>2</sub>AlC showed the largest increase in c-LP, while Ti<sub>2</sub>AlN showed the least (Fig. 9a). The a-LPs decreased after LT irradiation, with Ti<sub>2</sub>AlC showing the largest deviation from pristine (Fig. 9b). In contradistinction, after HT

irradiation, the LPs for most materials tested were distorted by  $\leq 0.1\%$ , confirming the dynamic recovery capabilities of the MAX phases. There was little observable difference between fine- and coarse-grained  $\text{Ti}_3\text{SiC}_2$ , both of which showed less extensive distortion than  $\text{Ti}_3\text{AlC}_2$ .

What is noteworthy and completely unexpected however, was the dissociation of roughly 50 wt. % of the  $\text{Ti}_3\text{AlC}_2$  into TiC. One of the reasons this was unexpected is that it was never observed or reported on in any of the heavy ion irradiation work [9-14, 16, 17, 19, 21, 22]. This is an important result since it is clear that  $\text{Ti}_3\text{AlC}_2$  may not be as resistant to neutrons as previously assumed. Clearly, the dissociation of  $\text{Ti}_3\text{AlC}_2$  into TiC appears to be enhanced by the neutron irradiation, the extent of which increased at the lower irradiation temperature.

Based on the results shown in Table 2, both the FG and CG- $\text{Ti}_3\text{SiC}_2$  showed a slight increase in TiC content when irradiated LT conditions. Given the fluctuations in the TiC contents of the pristine and irradiated samples, it is difficult to conclude that the dissociation of this compound is also catalyzed by the neutron irradiation. If it is, however, it is far less extensive than in the  $\text{Ti}_3\text{AlC}_2$  case.

After LT irradiation, the  $\text{Ti}_2\text{AlN}$  followed a similar trend in lattice distortion but to a lesser extent (Fig. 9). In contrast to all other samples at HT condition however,  $\text{Ti}_2\text{AlN}$  remained distorted with a 0.2% increase in c-LP, and a 0.7% increase in a-LP. This is attributed to the significant change in phase composition with 13(1) % TiN and 36(3) wt.%  $\text{Ti}_4\text{AlN}_3$ . With a microstrain of 0.58%, it is plausible that the formation of TiN and  $\text{Ti}_4\text{AlN}_3$  prevented the  $\text{Ti}_2\text{AlN}$  lattice from relaxing, even during high temperature irradiation.

In sharp contrast,  $\text{Ti}_2\text{AlC}$  showed excellent resistance to lattice distortions and/or dissociation. While the lattice parameters showed a similar trend of increasing c-LP and decreasing a-LP (Fig. 9), the TiC content only slightly increased from 6.7(8) to 8.3(3) wt.% in  $\text{Ti}_2\text{AlC-LT}$ , and only 4.3(1)% was observed in  $\text{Ti}_2\text{AlC-HT}$ , all values almost within the range of the TiC content in the pristine samples, viz. 6.7(8) wt. %. It is unclear at this time why  $\text{Ti}_2\text{AlC}$  is so much more stable vis-à-vis dissociation than  $\text{Ti}_3\text{AlC}_2$ . While XRD results confirmed the phase content for the samples tested, the question remains as to the fate of the Al and Si content in the cases where TiC and TiN were formed. Most likely, the A-group layers have become highly

disordered after irradiation, providing less contribution to the XRD patterns, as seen by Patel *et al.* [22].

Also of note is the resiliency of TiC after irradiation at these conditions. While  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_2\text{AlC}$  showed significant lattice distortion after LT irradiation, the a-LP of the TiC phase remained largely unperturbed, at most increasing by 0.19 % in the  $\text{Ti}_3\text{AlC}_2$  samples. It is plausible then that the TiC which forms via dissociation of  $\text{Ti}_3\text{AlC}_2$  relieves strain on the lattice, as the removal of the Al-layer would result in the de-twinning of the  $\text{Ti}_6\text{C}$  octahedra layers, forming bulk TiC. While the large scale dissociation of  $\text{Ti}_3\text{AlC}_2$  into TiC may be detrimental to its future in nuclear applications, it is unclear if the presence of small volume fractions will be problematic for other MAX phases, since commercially available  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  often contain ~10 wt.% TiC. More work is needed to ascertain the effect, if any, of the presence of a TiC impurity on the irradiated properties.

XRD refinement of the medium and high dose samples was not completed in the timeframe of this project. Further work is ongoing to continue to gather XRD patterns for each remaining samples

## **Transmission Electron Microscopy**

Microstructural analysis of irradiation defects was carried out on the  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$  samples using a TEM (JEOL 2010, Japan). TEM discs were mechanically polished with 1200 grit SiC paper down to a thickness of < 50  $\mu\text{m}$  and electropolished (Model 110 Twin Jet, Fischione Instruments, Exton, PA, USA) in a 95 vol.% methanol, 5 vol.% perchloric acid solution to produce electron transparent edges around perforations that formed in the samples. Brightfield (BF) and weak beam g3g condition TEM micrographs, as well as selected area electron diffraction (SAED) patterns, were collected to characterize the irradiation defects. The TEM characterization of the other MAX phases is ongoing.

Post irradiation TEM analysis was completed for the  $\text{Ti}_2\text{AlC}$  (Fig. 10) and  $\text{Ti}_3\text{AlC}_2$  (Fig. 11) samples. TEM micrographs of  $\text{Ti}_2\text{AlC}$ -LT showed a large concentration of small black spots, on the order of 15 nm in size with an areal density too large to count (Fig. 10b). SAED patterns from these regions showed a crystalline microstructure, with an increased diffuse background. TEM micrographs of  $\text{Ti}_2\text{AlC}$ -HT revealed the presence of dislocation loops with an average

diameter of 51(21) nm, having an areal density of  $7.7 \times 10^{13} \text{ m}^{-2}$  (Fig. 10c). Seen edge on, the loops formed parallel to the basal planes and were arrayed coherently along the [0001] direction within the  $\text{Ti}_2\text{AlC}$  lattice. SAED patterns of the regions in Fig. 10c revealed that  $\text{Ti}_2\text{AlC}$  samples maintained their crystallinity when irradiated to 0.1 dpa at 695(25) °C.

Irradiation of the  $\text{Ti}_3\text{AlC}_2$  samples to LT conditions resulted in larger dislocation loops with an average diameter of 75(25) nm (Fig. 11b). Having an areal density of  $1.2 \times 10^{14} \text{ m}^{-2}$ , the loops were randomly dispersed, mostly within the (0001) habit plane. SAED patterns of the region shown in Fig. 11b revealed that the  $\text{Ti}_3\text{AlC}_2$  samples also retain their crystallinity, though with a slightly diffuse background. The  $\text{Ti}_3\text{AlC}_2$ -HT samples formed stacking fault tetrahedra (SFT) with an average edge length of 27(7) nm and areal density of  $8.9 \times 10^{13} \text{ m}^{-2}$ , lying within the (0001) habit plane, as determined by SAED (Fig. 11c). The defect density decreases with increasing temperature for both  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_2\text{AlC}$ . However, the formation of SFT appears to be unique to  $\text{Ti}_3\text{AlC}_2$ . The defect dimensions are summarized in Table 3.

TEM was used to confirm the increase in defect density as a result of neutron irradiation in  $\text{Ti}_2\text{AlC}$  (Fig. 10) and  $\text{Ti}_3\text{AlC}_2$  (Fig. 11). The majority of the dislocation loops were seen to form in the (0001) habit plane, along the basal planes of the MAX phases (Figs. 10b, 11b). The  $\text{Ti}_2\text{AlC}$ -LT samples contained a large concentration of small defect clusters or loops > 15 nm in size, with an areal density that was too high to count (Fig. 10b). At the same irradiation conditions,  $\text{Ti}_3\text{AlC}_2$  exhibited larger dislocation loops interspersed with smaller spot defects, which were disordered and randomly dispersed within the lattice (Fig. 11b).

HT irradiation resulted in 27(7) nm SFT in  $\text{Ti}_3\text{AlC}_2$  (Fig. 11c) and 50(21) nm dislocation loops in  $\text{Ti}_2\text{AlC}$  (Fig. 10c). It is therefore plausible that Al-vacancy mobility in  $\text{Ti}_3\text{AlC}_2$  is high enough at 695(25) °C to allow for vacancy agglomeration into clusters which could then collapse into SFT under irradiation doses as low as 0.5 dpa. This is in contradistinction to SiC, which requires irradiation conditions of > 1000 °C and > 2 dpa to exhibit void formation from vacancy agglomeration [29].

TEM analysis for the remaining samples will not be completed at SRNL. Instead, plans were made to ship the remaining TEM samples from the MITR experiment to INL for PIE

alongside a sister project with the ATR, where the student from Drexel University – Darin Tallman - will have access to the FIB and TEM equipment..

## Room Temperature Resistivity

Pre- and post-irradiation room temperature (RT) resistivity ( $\rho$ ) measurements were obtained for all samples using a 4-point probe technique using a current of 100 mA. Three resistivity bars of each material were irradiated at each condition, and the recorded values were averaged from the multiple bars tested. Resistivity was calculated using the following formula:

$$\rho = \frac{VA}{IL} \quad \text{Eq. (1),}$$

where A is the cross sectional area, L is the lead separation, I is the applied current, and V is the measured voltage. Due to complications with handling, some resistivity bars were broken upon retrieval and thus in some cases the average of only 2 resistivity bars is reported. Voltages were recorded once per second for 3 minutes to allow the scans to reach steady state, and averaged over time. For most samples a time independent voltage signal was recorded. Occasionally, a  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_2\text{AlC}$  sample would exhibit a noisy signal. Lightly polishing the surfaces with 600 grit grinding paper solved the problem and resulted in steady voltage measurements.

The measured RT  $\rho$  of the pristine MAX phases in this work compare well with those previously reported (Table 3) [30-34]. After LT irradiation, the  $\rho$  values were 4-10 times greater than before irradiation (Table 3). The largest increase in RT  $\rho$  was seen in  $\text{Ti}_3\text{AlC}_2$ , with 2.84(2)  $\mu\Omega\text{-m}$  after irradiated as compared to 0.262(8)  $\mu\Omega\text{-m}$  before. At 2.2(1)  $\mu\Omega\text{-m}$ ,  $\text{Ti}_3\text{SiC}_2\text{-CG}$  had a higher  $\rho$  compared to  $\text{Ti}_3\text{SiC}_2\text{-FG}$ , at 1.1(1)  $\mu\Omega\text{-m}$ , both of which increased from the pristine values of 0.21(1) and 0.21(1), respectively. The  $\rho$  of the  $\text{Ti}_2\text{AlN}$  samples increased from 0.37(1)  $\mu\Omega\text{-m}$  pristine to 1.46(1)  $\mu\Omega\text{-m}$  after irradiation at LT. At 0.75(1)  $\mu\Omega\text{-m}$ ,  $\text{Ti}_2\text{AlC}$  yielded the lowest increase in  $\rho$  compared to 0.31(4)  $\mu\Omega\text{-m}$  as pristine. In contradistinction to the low temperature irradiations, samples irradiated to at HT conditions experienced only a slight increase in  $\rho$ , ranging from 0.23(1) for  $\text{Ti}_3\text{SiC}_2\text{-FG}$  to 0.44(1) for  $\text{Ti}_2\text{AlC}$  (Table 3).

The collision of high energy neutrons with lattice atoms is known to create point defects, increasing the dangling bond density, resulting in an increase in resistivity [35]. Post-irradiation



RT  $\rho$  values of samples irradiated at LT conditions were found to be almost an order of magnitude higher than seen for pristine samples (Table 3), confirming that LT neutron irradiation generated a significant amount of point defects.  $\text{Ti}_3\text{AlC}_2$  was shown to have the highest RT  $\rho$  at 2.84(2)  $\mu\Omega\cdot\text{m}$ . With increasing temperatures, if the defect mobility is high enough, they can start to agglomerate and/or annihilate. Dislocation loops are also known to interact and coalesce into fewer but larger defect structures with increasing temperatures [36]. Annihilation of the point defects reduces the dangling bond density, resulting in a decrease in resistivity. This was confirmed herein for all HT samples; all showed only a slight increase in RT  $\rho$  (Table 3) compared to their  $\rho$  values prior to irradiation.

At the end of the project term, only the low dose resistivity values have been measured.

### ***In situ* Resistivity Jig**

In an attempt to record resistivity during dose an *in situ* resistivity jig was constructed using silver contact wires wrapped around a  $\text{Ti}_3\text{SiC}_2$  resistivity sample, which was then encased in protective alumina sheathing (Fig. 12). The leads for the resistivity measurements fed out of the top of the jig, ready to be connected once inserted into the MITR. There were issues in getting the *in situ* resistivity device installed due to interference from the four thermocouples for the capsules already in place. The scheduled end of the irradiation for the four capsules in the core at the end of the last scheduled operating period for 2011, on December 22<sup>nd</sup> was reached. During the first week of January 2012, the procedure to transfer the capsules from the core to the hot box for extraction of the samples commenced. The capsules were removed one at a time because of the activity levels and the length of the sample stack. As the top capsule (low temperature, intermediate fluence) was lifted, the thermocouples from the lower capsules became entangled with the top capsule and its thermocouple. MITR personnel were eventually successful in getting the top capsule into the shielded transfer cask and into the hot box, but in the process the sheath of one of the thermocouples from the lower capsules broke off somewhere in the in-core section, resulting in the release of activated insulation material (Hf oxide) from the thermocouple with serious contamination of the transfer cask and some areas of the reactor. As a result, they were unable to transfer the other three capsules. Though the thermocouple snags lead to delays with capsule retrieval, no samples were lost due to this issue.

The *in situ* work was abandoned because of unanticipated difficulty in inserting an additional capsule on top of the four capsules already in the irradiation rig. Each capsule had an associated thermocouple and the clearance between the capsules and the irradiation tube wall is necessarily small in order to maintain accurate gas gap widths to maintain the desired temperatures. MITR personnel were concerned that further attempts to install the *in situ* measurement rig would risk damaging the existing thermocouples or capsules, which could have resulted in a premature end to irradiation of all the samples. They were also forced to abandon the backup plan to install the *in situ* rig for a short run after removing all the other capsules because of the severe contamination that occurred due to the aforementioned breakage of a thermocouple during removal of the top capsule at the end of the scheduled irradiation.

## **Tensile Testing**

Tensile testing of pre-irradiated samples was performed on a uniaxial load frame (Instron, Norwood, MA) equipped with a 500 N load cell. The small tensile samples were attached to pin and hole grips, and a preload of 5N was applied. Tests were conducted at strain rates of 0.01 and 0.1 mm/min to explore the effect of strain rate. Samples were loaded to failure, and ultimate tensile strengths, UTS, were recorded (Table 3). Strain gauges were not available for the very small tensile specimens, so strain was calculated from total displacement of the ram head during testing. The initial upward curving segments of the load vs displacement curves were attributed to machine compliance as the grip assembly adjusted under load (Figs. 13a-d). The differences in UTS between the strain rate of 0.01 and 0.1 mm/min were negligible. The small tensile samples were difficult to test, more often than not snapping simply from handling prior to loading. It was clear that the small tensile bars were quite brittle/fragile. Timing and funding ran out before testing of the irradiated samples could commence, though the brittleness may pose a problem in the future. The samples are in storage at SRNL.

## **Fiber Reinforced Creep of $Ti_3SiC_2$**

Creep testing of the  $Ti_3SiC_2/SiC_f$  composite samples proved problematic. The samples were significantly marred after EDM, where gouges and cutouts in the samples were likely caused by the SiC fibers deflecting the cutting wire (Fig. 14a). Also, the bulk of the samples had several regions with small cracks and voids. This led to most of the creep tests to end

prematurely before the minimum strain rate regime was achieved. Using the few data points that were collected, a log plot of minimum strain rate versus inverse temperature revealed an activation energy of 293 kJ/mol, which was found to be much lower than previously reported bulk  $\text{Ti}_3\text{SiC}_2$  (Fig. 10b) [37]. Creep testing of the uniaxial  $\text{Ti}_3\text{SiC}_2/\text{SiC}$  fiber composites was abandoned.

## Summary:

The first ever reported neutron irradiation of bulk MAX phases show that  $\text{Ti}_3\text{SiC}_2$ ,  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_2\text{AlN}$  remain fully crystalline under neutron irradiation up to 0.1 dpa at 360(20) and 695(25) °C. However, Rietveld analysis of the XRD spectra for  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$  reveal a drastic difference in irradiation tolerance between the two related compounds.  $\text{Ti}_3\text{AlC}_2$  was seen to dissociate into ~ 50 wt.% TiC with a 1.7% increase in c-LP and a 0.6% decrease in a-LP after LT irradiation (Fig. 7). This dissociation was not mitigated by irradiation at HT, though the lattice parameters showed less distortion, being close to pristine. This same trend in lattice parameters is seen in  $\text{Ti}_2\text{AlC}$ , however the extent of dissociation into TiC was not observed.  $\text{Ti}_2\text{AlN}$  was seen to dissociate into 13(1) wt.% TiN and 36(3) wt.%  $\text{Ti}_4\text{AlN}_3$ , resulting in significant lattice strains after irradiation at HT.

$\text{Ti}_3\text{SiC}_2$  also showed lattice distortion, but to a lesser extent than  $\text{Ti}_3\text{AlC}_2$  or  $\text{Ti}_2\text{AlC}$ , with only ~1% increase in c-LP and 0.6% decrease in a-LP. The Ti-Si bonds have been shown to be stronger than Ti-Al bonds in the MAX phases, which could explain the lesser distortion of the lattice [38]. There also appears to be no difference in the lattice response as a function of grain size.

Neutron irradiation of bulk MAX phases shows the formation of dislocation loops in  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$ . In the former, irradiation at LT resulted in a high density of small dislocation loops on the order of 15 nm. Irradiation at HT resulted in agglomerated loops that grew to a size of 51(21) nm and appear in ordered arrays within the lattice along the c-axis direction (Fig 4c). In  $\text{Ti}_3\text{AlC}_2$ , loops of 75(25) nm are seen after irradiation at LT, while SFT with edge lengths 27(7) nm form after irradiation at HT.

RT  $\rho$  measurements of  $\text{Ti}_3\text{SiC}_2$ ,  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$ , and  $\text{Ti}_2\text{AlN}$  show an order of magnitude increase in resistivity at LT, but only 25 % increase at HT. The low resistivity values of samples irradiated HT is strong evidence for the MAX phases' dynamic recovery at temperatures as low as 695(25) °C. TEM micrographs of the defects formed in  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$  correlate the effect irradiation temperature on the resistivity values. At 2.2(1)  $\mu\Omega\text{-m}$ , the RT  $\rho$  of  $\text{Ti}_3\text{SiC}_2\text{-CG}$  was twice that of  $\text{Ti}_3\text{SiC}_2\text{-FG}$ , which is attributed to the increase in grain boundary fraction present in the fine-grained samples, likely resulting in fewer residual defects after irradiation. While defects are known to annihilate at grain boundary sinks, more TEM analysis is required to quantify the effect of decreased grain size on defect formation for  $\text{Ti}_3\text{SiC}_2$ .

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

Tensile testing of the pristine condition has been completed, however, the small size of the test specimens lead to considerable premature failures during loading of the samples. Testing of the irradiated specimens was not completed in the time frame of this project. Work is continuing at SRNL to collect tensile strength data of the samples, with an emphasis on high temperature testing.

Due to delays with irradiation and PIE start, the remaining characterization was incomplete at the end of this project timeframe. Further work is required to more accurately correlate previous ion irradiation with neutron irradiation. The team at Drexel University was rewarded a second NEUP grant that follows the work in this report. Work is ongoing to fully characterize the defect microstructures, as more data at increasing dosage is compiled. Medium dose resistivity and XRD work is still on going. The high dose samples are in storage and await future proposals to continue characterization.

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## Information Release

- D. J. Tallman, E. N. Hoffman, E. N. Caspi, B. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum. "Effect of Neutron Irradiation on MAX phases". *Acta Materialia*. (Submitted for publication) June 16, 2014.
- D. J. Tallman, E. N. Hoffman, E. N. Caspi, B. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum. "Effect of Neutron Irradiation on  $M_{1+n}AX_n$  phases". The Metals, Minerals, and Materials Society (TMS) Annual Meeting and Exposition, San Diego, Ca, 17 February 2014
- D. J. Tallman, E. N. Hoffman, E. N. Caspi, B. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum. "Effect of Neutron Irradiation on  $M_{1+n}AX_n$  phases". International Conference and Exposition on Advanced Ceramics and Composites (ICACC), Daytona Beach, FL, 29 January 2014
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- (Invited) D. J. Tallman, E. N. Hoffman, E. N. Caspi, G. Kohse, R. L. Sindelar, M. W. Barsoum. "The Effect of Neutron Irradiation on MAX phases for Gen IV reactors". International Conference and Exposition on Advanced Ceramics and Composites (ICACC), Daytona Beach, FL, 31 January 2013
- D. J. Tallman, E. N. Hoffman, G. Kohse, R. L. Sindelar, M. W. Barsoum. "On The Potential Use of the MAX Phases in Nuclear Reactors". FCRD Advanced Fuels Campaign: Integration Meeting, Los Alamos National Lab, Los Alamos, NM, 11 September 2012
- D. J. Tallman, E. N. Hoffman, G. Kohse, R. L. Sindelar, M. W. Barsoum. "Effect of Neutron Irradiation on Select MAX Phases". The Metals, Minerals, and Materials Society (TMS) Annual Meeting and Exposition, Orlando, Fl, 15 March 2012
- D. J. Tallman, E. N. Hoffman, G. Kohse, R. L. Sindelar, M. W. Barsoum. "MAX Ceramics for Nuclear Applications: A New Material for a New Generation of Power". The Metals, Minerals, and Materials Society (TMS) Annual Meeting and Exposition, San Diego, Ca, 03 February 2011

Table 1. Irradiation exposure parameters for the Drexel University MAX phase project at MITR.

<b>Condition</b>	<b>Temperature, °C</b>	<b>Irradiation Dates</b>	<b>Exposure, MWh</b>	<b>Fluence (&gt;0.1 MeV), n/cm<sup>2</sup></b>	<b>Total Fluence, n/cm<sup>2</sup></b>	<b>dpa (<math>4 \times 10^{21}</math> n/cm<sup>2</sup>=1dpa)</b>
Low Dose - Low T	360(20)	10/13-12/4 2010	5,000	$2.40 \times 10^{20}$	$3.40 \times 10^{20}$	0.1
Low Dose - High T	695(25)	10/13-12/4 2010	5,000	$3.50 \times 10^{20}$	$4.80 \times 10^{20}$	0.1
Med Dose - Low T	340(20)	3/8-12/22-2011	20,200	$9.80 \times 10^{20}$	$1.40 \times 10^{21}$	0.4
Med Dose - High T	740(20)	3/8-12/22-2011	20,200	$1.40 \times 10^{21}$	$1.90 \times 10^{21}$	0.5
High Dose - Low T	380(10) *300(10)	10/13/2010-12/22/2011	29,300	$1.40 \times 10^{21}$	$2.00 \times 10^{21}$	0.5
High Dose - High T	750(30) *650(15)	10/13/2010-12/22/2011	29,300	$2.00 \times 10^{21}$	$2.80 \times 10^{21}$	0.7

\*-The reactor was operated at a lower temperature for a several weeks awaiting permission to increase reactor temperature after phase 2 shut down, denoted in parentheses.

Table 2. Irradiation induced structural and compositional changes in Ti<sub>3</sub>SiC<sub>2</sub>FG, Ti<sub>3</sub>SiC<sub>2</sub>CG, Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>2</sub>AlC, and Ti<sub>2</sub>AlN for irradiation up to 0.1 dpa at 360(20) °C (LD-LT) and at 695(25) °C (LD-HT).

Condition	$\chi^2$	a-LP, Å	c-LP, Å	Ti <sub>II</sub> z position	C z position	TiC content, wt. %	TiC a-LP, Å	FWHM Parameter, U	$\mu\epsilon$ , %
Ti <sub>3</sub> SiC <sub>2</sub> FG-Pristine	16.4	3.0668(7)	17.669(6)	0.3652(5)	0.569(2)	20.0(5)	4.3186(1)	0.0051(3)	-
Ti <sub>3</sub> SiC <sub>2</sub> FG-LD-LT	3.08	3.0648(1)	17.812(9)	0.3661(3)	0.571(1)	22.7(5)	4.3192(1)	0.0385(7)	0.27
Ti <sub>3</sub> SiC <sub>2</sub> FG-LD-HT	1.83	3.0667(2)	17.675(1)	0.3675(7)	0.556(3)	25(1)	4.3195(2)	0.0133(5)	-
Ti <sub>3</sub> SiC <sub>2</sub> CG-Pristine	16.7	3.0688(7)	17.680(1)	0.3662(4)	0.572(2)	18.2(5)	4.3185(1)	0.0042(1)	-
Ti <sub>3</sub> SiC <sub>2</sub> CG-LD-LT	1.84	3.0647(1)	17.840(1)	0.3664(3)	0.565(1)	23.3(5)	4.3238(2)	0.0488(1)	0.33
Ti <sub>3</sub> SiC <sub>2</sub> CG-LD-HT	2.79	3.0674(8)	17.669(1)	0.3660(4)	0.556(2)	17.0(4)	4.3235(2)	0.0150(2)	0.06
Ti <sub>3</sub> AlC <sub>2</sub> -Pristine	1.88	3.0736(2)	18.562(2)	0.1291(5)	0.564(2)	1.9(6)	4.3114(2)	0.0094(7)	0.10
Ti <sub>3</sub> AlC <sub>2</sub> -LD-LT	2.63	3.0542(2)	18.896(1)	0.1251(3)	0.648(1)	52.6(9)	4.3197(3)	0.064(1)	0.39
Ti <sub>3</sub> AlC <sub>2</sub> -LD-HT	3.73	3.0699(2)	18.543(2)	0.1313(4)	0.599(1)	44.4(8)	4.3082(3)	0.05(1)	0.34
				<b>Ti<sub>II</sub> z position</b>					
Ti <sub>2</sub> AlC-Pristine	3.2	3.0616(2)	13.652(2)	0.588(1)	*n/a	6.7(8)	4.3106(7)	0.0236(8)	0.23
Ti <sub>2</sub> AlC-LD-LT	3.17	3.0367(2)	13.882(1)	0.5843(5)	*n/a	8.3(3)	4.3168(3)	0.157(1)	0.66
Ti <sub>2</sub> AlC-LD-HT	2.44	3.0585(3)	13.659(3)	0.585(3)	*n/a	4.3(1)	4.3128(1)	0.0176(2)	0.11
						<b>TiN wt. %</b>	<b>TiN a-LP</b>		
Ti <sub>2</sub> AlN-Pristine	1.6	2.9886(3)	13.640(2)	0.587(2)	*n/a	3.23(2)	4.2329(2)	0.015(1)	0.16
Ti <sub>2</sub> AlN-LD-LT	2.2	2.9808(6)	13.714(4)	0.590(1)	*n/a	11.6(1)	4.2336(1)	0.0262(2)	0.20
Ti <sub>2</sub> AlN-LD-HT §	2.6	3.0086(3)	13.664(4)	0.570(2)	*n/a	13(1)	4.2223(3)	0.125(2)	0.58

\*- In M<sub>2</sub>AX compounds, the C-atom z position is fixed at the origin.

§- In the case of Ti<sub>2</sub>AlN, at high temperature, 36(3) wt.% Ti<sub>4</sub>AlN<sub>3</sub> content was detected. With a-LP of 2.9931 and c-LP of 22.986, the lattice was distorted from pristine, at 2.988 and 23.372, for a-LP and c-LP, respectively.

Table 3. Room temperature resistivity, irradiation defect size, and tensile strength of MAX phases after neutron (> 0.1MeV) irradiation of up to 0.1 dpa at 360(20)°C or 695(25) °C.

Composition	$\rho$ , $\mu\Omega\cdot\text{m}$				Mean Dislocation Loop Size, nm [Areal Density], defects/m <sup>-2</sup>		UTS, MPa
	Pristine	Reference	360(20) °C	695(25) °C	360(20) °C	695(25) °C	
Ti <sub>2</sub> AlC	0.31(4)	0.32 [31] 0.23 [33] 0.39 [34]	0.75(1)	0.44(1)	<15 [-]	51(21) [7.7x10 <sup>13</sup> ]	155(22)
Ti <sub>3</sub> AlC <sub>2</sub>	0.262(8)	0.353 [31] 0.287 [33]	2.84(2)	0.39(1)	75(25) [1.2x10 <sup>14</sup> ]	27(7) <sup>†</sup> [8.9x10 <sup>13</sup> ] <sup>†</sup>	138(1)
Ti <sub>2</sub> AlN	0.37(1)	a0.25 [31] b0.343 [31]	1.46(1)	0.25(1)	-	-	154(16)
Ti <sub>3</sub> SiC <sub>2</sub> -FG	0.21(1)	0.23 [30] 0.23 [32]	1.1(1)	0.23(1)	-	-	104(27)
Ti <sub>3</sub> SiC <sub>2</sub> -CG	0.21(1)	0.23 [30] 0.23 [32]	2.2(1)	0.24(1)	-	-	165(18)

a- Ti<sub>2</sub>AlN prepared with elemental powder mixture

b- Ti<sub>2</sub>AlN prepared with commercially available pre-reacted powder from Kanthal, Sweden.

†- Stacking fault tetrahedra form at high temperature in Ti<sub>3</sub>AlC<sub>2</sub>, edge length is listed.



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

Figure 2. a) Sample geometries for MAX irradiation testing, showing the miniature tensile bar, resistivity bar, and TEM disc. b) A photograph of an example of  $Ti_3SiC_2$  FG after being hot pressed, with the miniature tensile bars machined by electrical discharge machining.

Figure 3. Neutron spectra of typical PWR and of ICSA configurations of a) ICSA thimble with aluminum dummy element (standard), b) 3mm  $H_2O$  annulus introduced outside ICSA thimble. Note that the MAX phase irradiation took place with an approximately 1-mm water gap with the spectrum corresponding to curve (a).

Figure 4. Rietveld analysis of XRD data of a) pristine  $Ti_3SiC_2$ -FG, and  $Ti_3SiC_2$ -FG irradiated to b) 0.1 dpa at 360(20) °C and c) 0.1 dpa at 695(25) °C. Open circles, solid line, and solid line at the bottom, represent the observed data, calculated model, and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the  $Ti_3SiC_2$ -FG (1<sup>st</sup> row), TiC (2<sup>nd</sup>). The large amorphous background was due to the mounting putty.

Figure 5. Rietveld analysis of XRD data of a) pristine  $Ti_3SiC_2$ -CG, and  $Ti_3SiC_2$ -CG irradiated to b) 0.1 dpa at 360(20) °C and c) 0.1 dpa at 695(25) °C. Open circles, solid line, and solid line at the bottom, represent the observed data, calculated model, and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the  $Ti_3SiC_2$  (1<sup>st</sup> row), TiC (2<sup>nd</sup>). The large amorphous background was due to the mounting putty.

Figure 6. Rietveld analysis of XRD data of, a) pristine  $Ti_3AlC_2$ ,  $Ti_3AlC_2$  irradiated to b) 0.1 dpa at 360(20) °C and c) 0.1 dpa at 695(25) °C. Open circles, solid line, and solid line at the bottom, represent the observed data, calculated model, and variance between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the  $Ti_3AlC_2$  (1<sup>st</sup> row), TiC (2<sup>nd</sup>). The large amorphous background was due to the mounting putty. Where peaks were not present, sections were excluded from analysis (shown in grey).

Figure 7. Rietveld analysis of XRD data of a) pristine  $Ti_2AlC$ , and  $Ti_2AlC$  irradiated to b) 0.1 dpa at 360(20) °C and c) 0.1 dpa at 695(25) °C. Open circles, solid line, and solid line at the bottom, represent

the observed data, calculated model, and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the  $Ti_2AlC$  (1<sup>st</sup> row),  $TiC$  (2<sup>nd</sup>). The large amorphous background was due to the mounting putty. Where peaks were not present, sections were excluded from analysis (shown in grey).

Figure 8. Rietveld analysis of XRD data of a) pristine  $Ti_2AlN$ , and  $Ti_2AlN$  irradiated to b) 0.1 dpa at 360(20) °C and c) 0.1 dpa at 695(25) °C. Open circles, solid line, and solid line at the bottom, represent the observed data, calculated model, and the difference between the two, respectively. The two rows of vertical tags represent the calculated Bragg reflections' positions of the  $Ti_2AlN$  (1<sup>st</sup> row),  $TiN$  (2<sup>nd</sup>). In c), the best fit for  $Ti_2AlN$ -HT was achieved by including  $Ti_4AlN_3$  in the refinement(3<sup>rd</sup> row). Dissociation of the parent  $Ti_2AlN$  phase resulted in the formation of  $TiN$  and  $Ti_4AlN_3$ . Peaks around 36, 41, and 58.6° 2 $\theta$  were unidentified due to their low intensity and the high background noise. The large amorphous background was due to the mounting putty.

Figure 9. Plots comparing a) c-LPs and b) a-LPs as a function of irradiation temperature for the MAX phases  $Ti_3SiC_2$ -FG and -CG,  $Ti_3AlC_2$ ,  $Ti_2AlC$ , and  $Ti_2AlN$  show a significant temperature dependence on irradiation induced lattice deformation after low dose irradiation (0.1 dpa). Pristine values are plotted for reference. a)  $Ti_3AlC_2$  showed the highest expansion in c-LP at 360(20) °C irradiation, while  $Ti_2AlN$  was least expanded. In all cases, the c-LP was close to that of the pristine lattice when irradiated at 695(25) °C. b) The a-LPs decreased with irradiation at 360(20) °C, with  $Ti_2AlC$  showing the most distortion. There appears to be no effect due to grain size with  $Ti_3SiC_2$ . Similarly to the c-LP, irradiation at 695(25) °C resulted in a-LPs that were close to that of the pristine sample.  $Ti_2AlN$ , however, showed an increase in a-LP after irradiation at 695(25) °C.

Figure 10. TEM micrographs of  $Ti_2AlC$  a) pristine, irradiated to b) 0.1 dpa at 360(20) °C showing a large density of small defect clusters or loops on the order of 15 nm, and c) 0.1 dpa at 695(25) °C resulting in larger dislocation loops of 51(21) nm agglomerating in ordered arrays along the c lattice forming parallel to the basal plane. SAED patterns from these regions (insets) reveal that the MAX samples maintain crystallinity, with an increased diffuse background in the 360(20) °C samples, indicating increased disorder.

Figure 11. TEM micrographs of  $Ti_3AlC_2$  a) pristine, and irradiated to b) 0.1 dpa at 360(20) °C where dislocation loops of 75(25)nm can be seen in the (0001) habit plane, and c) 0.1 dpa at 695(25) °C showing the formation of stacking fault tetrahedra (SFT) with edge length 27(7) nm forming on the basal plane. SAED patterns from these regions (insets) reveal that the MAX samples maintain crystallinity, with an increased diffuse background in the 360(20)°C samples, indicating increased disorder.

Figure 12. a) The *in situ* resistivity jig composed of silver wires wrapped around a  $\text{Ti}_3\text{SiC}_2$  FG resistivity bar within alumina sheathing. The wire leads were fed through the top of the alumina sheathe, for connecting to the assembly in the MITR core.

Figure 13. Stress vs. strain plots for pristine samples of a)  $\text{Ti}_3\text{SiC}_2\text{CG}$ , b)  $\text{Ti}_3\text{SiC}_2\text{FG}$ , c)  $\text{Ti}_3\text{AlC}_2$ , d)  $\text{Ti}_2\text{AlC}$ , and e)  $\text{Ti}_2\text{AlN}$ . Subsequent samples have been shifted to the right for clarity. Initial upwards curvature in the plots is due to machine compliance of the load frame used. The samples were too small to incorporate an extensometer, so strain was calculated using total displacement of the load frame. Ultimate tensile strength (UTS) was measured as the highest load reached prior to failure. As these materials are ceramics, the strains were small, and no necking was experienced at room temperature.

Figure 14. a) Photographs of the  $\text{Ti}_3\text{SiC}_2/\text{SiC}_f$  6 vol.% composites reveal that the samples were not successfully fabricated by pressing layers of uniaxially aligned SiC fiber arrays. The wood grain like appearance is due to the fiber arrays not staying horizontal in the die during hot pressing. b) An Arrhenius plot of  $\ln(\text{strain rate})$  vs  $1/T$  of samples crept in tension at 40 MPa in the 1000-1200 °C range reveals a straight line, the slope of which is the activation energy,  $Q$ , over the constant  $R$ . At 293 kJ/mol,  $Q$  for the fiber composite is lower than previously reported for coarse grained  $\text{Ti}_3\text{SiC}_2$ , at 458 kJ/mol [32]. This deviation is attributed to defects in fabrication, as the majority of samples tested failed prematurely.

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