Project No. 09-790

Neutron Damage and MAX Phase Ternary Compounds

Integrated University Programs

Dr. Michael Barsoum
Drexel University

In collaboration with:
Massachusetts Institute of Technology
Savannah River National Laboratory

Sue Lesica, Federal POC
Doug Marshall, Technical POC

NEUP Nuclear Energy University Programs
U.S. Department of Energy

Final Report

Project Title: Neutron Damage and MAX Phase Ternary Compounds

Covering Period: 2010-2013

Date of Report: Friday, January 31, 2014

Recipient: Name: Drexel University
Street: 3141 Chestnut St.
City: Philadelphia
State: Pennsylvania
Zip: 19104

Award Number: 90309

Project Number: 09-790

Principal Investigator: Michel Barsoum – 215 895 2338 – barsoumw@drexel.edu

Collaborators: Elizabeth Hoffman, Robert Sindelar, Brenda Garcia-Diaz (SRNL); Gordon Kohse (MIT)

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+ ºC) 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 x 10^{25} n/m^2 (En> 0.1 MeV) or 1.9 dpa at 60 ºC and 650 ºC at the MIT Research Reactor.

Table of Contents

Executive Summary: 3
Background: 3
Objectives: Accomplishments and Failures 6
Sample Fabrication 6
Sample Irradiation 7
X-ray Diffraction Refinement 8
Transmission Electron Microscopy 13
Room Temperature Resistivity 15
In situ Resistivity Jig 16
Tensile Testing 17
Fiber Reinforced Creep of Ti_3SiC_2 17
Summary: 18
References 21

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 > 1MeV) 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 Ti_3AlC_2, Ti_2AlC, Ti_3SiC_2 and Ti_2AlN. X-ray diffraction refinement of the irradiated samples showed irradiation-enhanced dissociation into TiC of the Ti_3AlC_2 phase, and possibly in Ti_3SiC_2. . Ti_2AlN also showed an increase in TiN content, as well as Ti_4AlN_3 after irradiation. In contrast, Ti_2AlC was quite stable under these irradiation conditions. Dislocation loops are seen to form in Ti_2AlC and Ti_3AlC_2 after irradiation at 360(20) °C. While these loops coarsen in Ti_2AlC at 695(25) °C, stacking fault tetrahedra are observed in Ti_3AlC_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 at 695(25) °C. Based on these preliminary results, it appears that several of the MAX phases, most notably Ti_2AlC and possibly Ti_3SiC_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 > 1MeV) 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 $M_{n+1}AX_n$ (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_3SiC_2, showing surface layer amorphization of the Ti_3SiC_2 and impurity phases, as well as, selective grain boundary sputtering due to nuclear interactions [9]. Liu *et al.* characterized Al-doped Ti_3SiC_2, 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 β-Ti_3SiC_2 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 $Ti_3(Si,Al)C_2$ 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^{2+} ion irradiation on multilayered (Ti,Al)N/Ti_2AlN_x nitrogen-deficient thin films, reporting that the multilayered structure was preserved up to a dose of 12 dpa, likely due to nitrogen vacancies acting as sinks for interstitial point defects [19].

Along the same lines, Whittle *et al.* reported that Ti_3AlC_2 and Ti_3SiC_2 possess very high resistance to amorphization, even up to 25 dpa, irradiated with 1 MeV Kr^{2+} and 1 MeV Xe^{2+} [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_3SiC_2 [10]. Also in 2011, Nappé *et al.* investigated the structural changes of Ti_3SiC_2 under a variety of ions and energies, concluding that Ti_3SiC_2 is not sensitive to electrical interactions, and confirmed that nuclear collisions lead to an increase in c-LP and a decrease in the a lattice parameter, a-LP, and a concomitant increase in lattice microstrains [12].

In 2012, Zhang *et al.* reported that a TiC and/or 3C-SiC (cubic β) 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 8×10^{16} cm^{-2} to 1×10^{18} 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 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 β-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_2AlC and Ti_2AlN. As far as we are aware, and with the exception of a report that has just been published, on the neutron irradiation of Ti_3SiC_2 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_2AlC were prepared by pouring pre-reacted Ti_2AlC 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^{-1} Pa at a temperature of 1300 °C. The Ti_3AlC_2 samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti_2AlC 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_2AlN 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_3SiC_2, henceforth referred to as Ti_3SiC_2-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_3SiC_2, henceforth referred to as Ti_3SiC_2-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_3AlC_2 (Fig. 1b) and Ti_3SiC_2 (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_l, and width, d_t, 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 x 1.5 x 25.4 mm^3 resistivity bars, 16 x 4 x 0.7 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 Ti_3SiC_2-FG and Ti_3SiC_2-CG, were 8(3) and 50(20) μm, respectively, with standard deviations listed in parentheses. The average grain sizes of Ti_2AlC, Ti_2AlN and Ti_3AlC_2 were 10(4), 15(2) and 16(6) μm, respectively.

Ti_3SiC_2/SiC fiber composites were fabricated by layering 140 μm 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 2x2.5mm^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 x 10^{20} n/cm^2 to 2.8 x 10^{21} n/cm^2 (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 4x10^{21} n/cm^2 = 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_2AlC and Ti_3AlC_2 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_2SC 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_2SC was abandoned early on.

X-ray Diffraction Refinement

XRD patterns from the surfaces of samples of Ti_2AlC, Ti_3AlC_2, Ti_2AlN, Ti_3SiC_2-FG and Ti_3SiC_2-CG were obtained using one of two diffractometers (Bruker D8, Madison, WI, USA) in the Bragg–Brentano configuration, for pristine and irradiated conditions, respectively. The diffractograms were collected using step scans of 0.02° in the 5–70° 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_6 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_6 standard's reported value. For each data set, a model containing TiC and each specific MAX phase, *e.g.*, Ti_3SiC_2, Ti_3AlC_2, or Ti_2AlC was refined. For Ti_2AlN, the model was refined with the TiN and Ti_4AlN_3 phases. The Thompson-Cox-Hastings pseudo-Voigt model was used to refine the peak-shape of each phase's reflections. Lattice strains and particle sizes were also estimated assuming isotropic Lorenzian and Gaussian contributions to the peak shape function [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_{std} was refined from the LaB_6 standard. If U_{sample} refined lower than the U_{std}, the microstrain was unresolvable for that specimen. The U_{std} 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_3SiC_2-FG, Ti_3SiC_2-CG, Ti_3AlC_2, Ti_2AlC and Ti_2AlN 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_2AlC, Ti_3AlC_2, Ti_3SiC_2-FG and Ti_3SiC_2-CG samples, were found to be 6.7(8) wt.%, 1.9(6) wt.%, 20.0(5) wt.% and 18.2(5) wt.%, respectively. While no Ti_4AlN_3 phase was observed in pristine Ti_2AlN, 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_3AlC_2 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_3SiC_2-FG also yielded an increase in TiC content, going from 20.0(5) wt. % initially to 22.7(5) and 25(1) wt.% after the LT and HT irradiations, respectively. The TiC

content in the Ti_3SiC_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 Ti_3SiC_2-FG irradiated at 360(20) °C, denoted henceforth as Ti_3SiC_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 Ti_3SiC_2-FG-HT, the Ti_3SiC_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 Ti_3SiC_2-CG samples behaved similarly to their fine-grained counterparts (Fig. 5). Refinement of Ti_3SiC_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 Ti_3SiC_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 Ti_3AlC_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 Ti_3AlC_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 Ti_2AlC 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 Ti_2AlC-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_2AlC-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_3AlC_2-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_2AlN samples revealed a similar trend of distorted LPs (Figs. 8 and 9). The best fit, however, was achieved when TiN and Ti_4AlN_3 were refined as well. Ti_2AlN-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_2AlN-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_2AlN-HT was significantly higher than all other samples irradiated at this condition. Unique among all MAX phases tested herein, Ti_2AlN-HT resulted in the formation of 36(3) wt.% Ti_4AlN_3. 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_3SiC_2-FG, Ti_3SiC_2-CG, Ti_3AlC_2, Ti_2AlC and Ti_2AlN 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_3AlC_2 and Ti_2AlC showed the largest increase in c-LP, while Ti_2AlN showed the least (Fig. 9a). The a-LPs decreased after LT irradiation, with Ti_2AlC 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 Ti_3SiC_2, both of which showed less extensive distortion than Ti_3AlC_2.

What is noteworthy and completely unexpected however, was the dissociation of roughly 50 wt. % of the Ti_3AlC_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 Ti_3AlC_2 may not be as resistant to neutrons as previously assumed. Clearly, the dissociation of Ti_3AlC_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-Ti_3SiC_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 Ti_3AlC_2 case.

After LT irradiation, the Ti_2AlN followed a similar trend in lattice distortion but to a lesser extent (Fig. 9). In contrast to all other samples at HT condition however, Ti_2AlN 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.% Ti_4AlN_3. With a microstrain of 0.58%, it is plausible that the formation of TiN and Ti_4AlN_3 prevented the Ti_2AlN lattice from relaxing, even during high temperature irradiation.

In sharp contrast, Ti_2AlC 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 Ti_2AlC-LT, and only 4.3(1)% was observed in Ti_2AlC-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 Ti_2AlC is so much more stable vis-à-vis dissociation than Ti_3AlC_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 Ti_3AlC_2 and Ti_2AlC 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 Ti_3AlC_2 samples. It is plausible then that the TiC which forms via dissociation of Ti_3AlC_2 relieves strain on the lattice, as the removal of the Al-layer would result in the de-twinning of the Ti_6C octahedra layers, forming bulk TiC. While the large scale dissociation of Ti_3AlC_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 Ti_2AlC and Ti_3SiC_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 Ti_2AlC and Ti_3AlC_2 samples using a TEM (JEOL 2010, Japan). TEM discs were mechanically polished with 1200 grit SiC paper down to a thickness of < 50 μm 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 Ti_2AlC (Fig. 10) and Ti_3AlC_2 (Fig. 11) samples. TEM micrographs of Ti_2AlC-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 Ti_2AlC-HT revealed the presence of dislocation loops with an average

diameter of 51(21) nm, having an areal density of 7.7 x 10^{13} 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 Ti_2AlC lattice. SAED patterns of the regions in Fig. 10c revealed that Ti_2AlC samples maintained their crystallinity when irradiated to 0.1 dpa at 695(25) °C.

Irradiation of the Ti_3AlC_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 x 10^{14} 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 Ti_3AlC_2 samples also retain their crystallinity, though with a slightly diffuse background. The Ti_3AlC_2-HT samples formed stacking fault tetrahedra (SFT) with an average edge length of 27(7) nm and areal density of 8.9 x 10^{13} m^{-2}, lying within the (0001) habit plane, as determined by SAED (Fig. 11c). The defect density decreases with increasing temperature for both Ti_3AlC_2 and Ti_2AlC. However, the formation of SFT appears to be unique to Ti_3AlC_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 Ti_2AlC (Fig. 10) and Ti_3AlC_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 Ti_2AlC-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, Ti_3AlC_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 Ti_3AlC_2 (Fig. 11c) and 50(21) nm dislocation loops in Ti_2AlC (Fig. 10c). It is therefore plausible that Al-vacancy mobility in Ti_3AlC_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 (ρ) 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:

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

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 Ti_3AlC_2 and Ti_2AlC 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 ρ of the pristine MAX phases in this work compare well with those previously reported (Table 3) [30-34]. After LT irradiation, the ρ values were 4-10 times greater than before irradiation (Table3). The largest increase in RT ρ was seen in Ti_3AlC_2, with 2.84(2) μΩ-m after irradiated as compared to 0.262(8) μΩ-m before. At 2.2(1) μΩ-m, Ti_3SiC_2-CG had a higher ρ compared to Ti_3SiC_2-FG, at 1.1(1) μΩ-m, both of which increased from the pristine values of 0.21(1) and 0.21(1), respectively. The ρ of the Ti_2AlN samples increased from 0.37(1) μΩ-m pristine to 1.46(1) μΩ-m after irradiation at LT. At 0.75(1) μΩ-m, Ti_2AlC yielded the lowest increase in ρ compared to 0.31(4) μΩ-m as pristine. In contradistinction to the low temperature irradiations, samples irradiated to at HT conditions experienced only a slight increase in ρ, ranging from 0.23(1) for Ti_3SiC_2-FG to 0.44(1) for Ti_2AlC (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 ρ 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. Ti_3AlC_2 was shown to have the highest RT ρ at 2.84(2) μΩ-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 ρ (Table 3) compared to their ρ 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 Ti_3SiC_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 22nd 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 lead 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 Ti_3SiC_2 (Fig. 10b) [37]. Creep testing of the uniaxial Ti_3SiC_2/SiC fiber composites was abandoned.

Summary:

The first ever reported neutron irradiation of bulk MAX phases show that Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC and Ti_2AlN 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 Ti_2AlC and Ti_3AlC_2 reveal a drastic difference in irradiation tolerance between the two related compounds. Ti_3AlC_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 Ti_2AlC, however the extent of dissociation into TiC was not observed. Ti_2AlN was seen to dissociate into 13(1) wt.% TiN and 36(3) wt.% Ti_4AlN_3, resulting in significant lattice strains after irradiation at HT.

Ti_3SiC_2 also showed lattice distortion, but to a lesser extent than Ti_3AlC_2 or Ti_2AlC, 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 Ti_2AlC and Ti_3AlC_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 Ti_3AlC_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 ρ measurements of Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC, and Ti_2AlN 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 at 695(25) °C. TEM micrographs of the defects formed in Ti_2AlC and Ti_3AlC_2 correlate the effect irradiation temperature on the resistivity values. At 2.2(1) μΩ-m, the RT ρ of Ti_3SiC_2-CG was twice that of Ti_3SiC_2-FG, which is attributed to the increase in grain boundary fraction present in the fine-grained samples, likely resulting in fewer residual defects after irradiation. While defects are known to annihilate at grain boundary sinks, more TEM analysis is required to quantify the effect of decreased grain size on defect formation for Ti_3SiC_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.

Acknowledgements

This work is funded by the Department of Energy's Nuclear Energy University Program (DOE-NEUP). The authors would like to thank Dr. David Carpenter of MIT for his assistance

with irradiations and fluence calculations for the irradiated samples. The authors would also like to thank Mike Tosten, Gregg Creech, and David Missimer of SRNL for their help with characterizing the irradiated samples.

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
- 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" Materials Research Society Boston, MA, 02 December 2013
- 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". American Nuclear Society Winter Meeting and Technology Expo, Washington, D. C., 12 November 2013
- (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.

Condition	Temperature, °C	Irradiation Dates	Exposure, MWh	Fluence (>0.1 MeV), n/cm^2	Total Fluence, n/cm^2	dpa (4x10^{21} n/cm^2=1dpa)
Low Dose - Low T	360(20)	10/13-12/4 2010	5,000	2.40x10^{20}	3.40x10^{20}	0.1
Low Dose - High T	695(25)	10/13-12/4 2010	5,000	3.50x10^{20}	4.80x10^{20}	0.1
Med Dose - Low T	340(20)	3/8-12/22-2011	20,200	9.80x10^{20}	1.40x10^{21}	0.4
Med Dose - High T	740(20)	3/8-12/22-2011	20,200	1.40x10^{21}	1.90x10^{21}	0.5
High Dose - Low T	380(10) *300(10)	10/13/2010-12/22/2011	29,300	1.40x10^{21}	2.00x10^{21}	0.5
High Dose - High T	750(30) *650(15)	10/13/2010-12/22/2011	29,300	2.00x10^{21}	2.80x10^{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_3SiC_2FG, Ti_3SiC_2CG, Ti_3AlC_2, Ti_2AlC, and Ti_2AlN for irradiation up to 0.1 dpa at 360(20) °C (LD-LT) and at 695(25) ° C (LD-HT).

Condition	χ^2	a-LP, Å	c-LP, Å	Ti_{II}_z position	C_z position	TiC content, wt.%	TiC a-LP, Å	FWHM Parameter, U	με, %
Ti_3SiC_2FG-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_3SiC_2FG-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_3SiC_2FG-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_3SiC_2CG-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_3SiC_2CG-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_3SiC_2CG-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_3AlC_2-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_3AlC_2-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_3AlC_2-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
				Ti_I_z position					
Ti_2AlC-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_2AlC-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_2AlC-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
						TiN wt.%	TiN a-LP		
Ti_2AlN-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_2AlN-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_2AlN-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_2AX compounds, the C-atom z position is fixed at the origin.

§- In the case of Ti_2AlN, at high temperature, 36(3) wt.% Ti_4AlN_3 content was detected. With a-LP of 2.9931 and c-LP of 22.986, the lattice was distorted from pristine, at 2.988 and 23.372, for a-LP and c-LP, respectively.

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	**ρ, μΩ-m**				**Mean Dislocation Loop Size, nm [Areal Density], defects/m^{-2}**		**UTS, MPa**
	Pristine	Reference	360(20) °C	695(25) °C	360(20) °C	695(25) °C	Pristine
Ti_2AlC	0.31(4)	0.32 [31] 0.23 [33] 0.39 [34]	0.75(1)	0.44(1)	<15 [-]	51(21) [7.7x10^{13}]	155(22)
Ti_3AlC_2	0.262(8)	0.353 [31] 0.287 [33]	2.84(2)	0.39(1)	75(25) [1.2x10^{14}]	27(7)† [8.9x10^{13}]†	138(1)
Ti_2AlN	0.37(1)	a0.25 [31] b0.343 [31]	1.46(1)	0.25(1)	-	-	154(16)
Ti_3SiC_2-FG	0.21(1)	0.23 [30] 0.23 [32]	1.1(1)	0.23(1)	-	-	104(27)
Ti_3SiC_2-CG	0.21(1)	0.23 [30] 0.23 [32]	2.2(1)	0.24(1)	-	-	165(18)

a- Ti_2AlN prepared with elemental powder mixture
b- Ti_2AlN prepared with commercially available pre-reacted powder from Kanthal, Sweden.
†- Stacking fault tetrahedra form at high temperature in Ti_3AlC_2, 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 mini-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 (1st row), TiC (2nd). 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 (1st row), TiC (2nd). 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 (1st row), TiC (2nd). 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 (1st row), TiC (2nd). 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 (1st row), TiN (2nd). In c), the best fit for Ti_2AlN-HT was achieved my including Ti_4AlN_3 in the refmement(3rd 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° 2θ 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 Ti_3SiC_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) Ti_3SiC_2CG, b) Ti_3SiC_2FG, c) Ti_3AlC_2, d) Ti_2AlC, and e) Ti_2AlN. 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 Ti_3SiC_2/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(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 Ti_3SiC_2, at 458 kJ/mol [32]. This deviation is attributed to defects in fabrication, as the majority of samples tested failed prematurely.

References

[1] DOE US. A Technology Roadmap for Generation IV Nuclear Energy Systems. In: Forum USDNERACatGII, editor, 2002.

[2] Barsoum MW. The $M_{n+1}AX_n$ Phases and their Properties. In: Riedel R, I.-W. Chen, editor. Ceramics Science and Technology. Weinheim, German: Wiley-VCH Verlag GmbH & Co. KGaA, 2010. p.299.

[3] Barsoum M, El-Raghy T. Metallurgical and Materials Transactions A 1999;30:363.

[4] Radovic M, Barsoum MW, El-Raghy T, Seidensticker J, Wiederhorn S. Acta Materialia 2000;48:453.

[5] Radovic M, Barsoum MW, El-Raghy T, Wiederhorn SM, Luecke WE. Acta Materialia 2002;50:1297.

[6] Barsoum MW, Radovic M, Finkel P, El-Raghy T. Applied Physics Letters 2001;79:479.

[7] Barsoum MW, Radovic M. Mechanical Properties of the MAX Phases. In: Buschow KHJ, Robert WC, Merton CF, Bernard I, Edward JK, Subhash M, Patrick V, editors. Encyclopedia of Materials: Science and Technology. Oxford: Elsevier, 2004. p.1.

[8] Barsoum MW. MAX Phases: Properties of Machinable Carbides and Nitrides: Wiley VCH GmbH & Co. , 2013.

[9] Nappé JC, Grosseau P, Audubert F, Guilhot B, Beauvy M, Benabdesselam M, Monnet I. Journal of Nuclear Materials 2009;385:304.

[10] Nappé JC, Maurice C, Grosseau P, Audubert F, Thomé L, Guilhot B, Beauvy M, Benabdesselam M. Journal of the European Ceramic Society 2011;31:1503.

[11] Nappé JC, Monnet I, Audubert F, Grosseau P, Beauvy M, Benabdesselam M. Nucl Instrum Meth B 2012;270:36.

[12] Nappé JC, Monnet I, Grosseau P, Audubert F, Guilhot B, Beauvy M, Benabdesselam M, Thome L. Journal of Nuclear Materials 2011;409:53.

[13] Whittle KR, Blackford MG, Aughterson RD, Moricca S, Lumpkin GR, Riley DP, Zaluzec NJ. Acta Materialia 2010;58:4362.

[14] Liu XM, Le Flem M, Béchade JL, Monnet I. Journal of Nuclear Materials 2010;401:149.

[15] Liu XM, Le Flem M, Bechade JL, Onimus F, Cozzika T, Monnet I. Nucl Instrum Meth B 2010;268:506.

[16] Le Flem M, Liu X, Doriot S, Cozzika T, Monnet I. International Journal of Applied Ceramic Technology 2010;7:766.

[17] Le Flem M, Monnet I. Journal of Nuclear Materials 2013;433:534.

[18] Zhang L, Qi Q, Shi LQ, O'Connor DJ, King BV, Kisi EH, Venkatachalam DK. Applied Surface Science 2012;258:6281.

[19] Bugnet M, Cabioc'h T, Mauchamp V, Guérin P, Marteau M, Jaouen M. J Mater Sci 2010;45:5547.

[20] Xiao J, Wang C, Yang T, Kong S, Xue J, Wang Y. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2013;304:27.

[21] Wang C, Yang T, Kong S, Xiao J, Xue J, Wang Q, Hu C, Huang Q, Wang Y. Journal of Nuclear Materials 2013;440:606.

[22] Patel MK, Tallman DJ, Valdez JA, Aguiar J, Anderoglu O, Tang M, Griggs J, Fu E, Wang Y, Barsoum MW. Scripta Materialia 2014;77:1.

[23] Hoffman EN, Vinson DW, Sindelar RL, Tallman DJ, Kohse G, Barsoum MW. Nuclear Engineering and Design 2012;244:17.

[24] Barsoum M, El-Raghy T, Ali M. Metallurgical and Materials Transactions A 2000;31:1857.

[25] Heinisch HL, Greenwood LR, Weber WJ, Williford RE. Journal of Nuclear Materials 2004;327:175.

[26] Rodríguez-Carvajal J. Physica B: Condensed Matter 1993;192:55.

[27] Rietveld H. J Appl Crystallogr 1969;2:65.

[28] Rodriguez-Carvajal J, Fernandez-Diaz MT, Martinez JL. Journal of Physics: Condensed Matter 1991;3.
[29] Snead LL, Nozawa T, Katoh Y, Byun T-S, Kondo S, Petti DA. Journal of Nuclear Materials 2007;371:329.
[30] Barsoum MW, Yoo HI, Polushina IK, Rud' VY, Rud' YV, El-Raghy T. Physical Review B 2000;62:10194.
[31] Scabarozi T, Ganguly A, Hettinger JD, Lofland SE, Amini S, Finkel P, El-Raghy T, Barsoum MW. Journal of Applied Physics 2008;104:073713.
[32] Finkel P, Hettinger JD, Lofland SE, Barsoum MW, El-Raghy T. Physical Review B 2001;65:035113.
[33] Wang XH, Zhou YC. Acta Materialia 2002;50:3143.
[34] Wang P, Mei B-c, Hong X-l, Zhou W-b. Transactions of Nonferrous Metals Society of China 2007;17:1001.
[35] Snead LL. Journal of Nuclear Materials 2004;329–333, Part A:524.
[36] Was GS. Fundamentals of radiation materials science: metals and alloys: Springer, 2007.
[37] Radovic M, Barsoum MW, El-Raghy T, Wiederhorn SM. Journal of Alloys and Compounds 2003;361:299.
[38] Magnuson M, Palmquist JP, Mattesini M, Li S, Ahuja R, Eriksson O, Emmerlich J, Wilhelmsson O, Eklund P, Högberg H, Hultman L, Jansson U. Physical Review B 2005;72:245101.