Effect of Neutron Irradiation on Defect Evolution in Ti_3SiC_2 and Ti_2AlC

Darin J. Tallman,^{*}¹Lingfeng He,²Brenda L. Garcia-Diaz,³Elizabeth N. Hoffman,³Gordon Kohse,⁴Robert L. Sindelar,³ and Michel W. Barsoum¹

¹*Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104*

²*Idaho National Laboratory, Idaho Falls, ID 83415*

³*Savannah River National Laboratory, Savannah River Site, Aiken, SC 29808*

⁴*MIT Nuclear Reactor Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139*

**Corresponding author: tallman@drexel.edu*

Abstract

Herein we report on the characterization of defects formed in polycrystalline Ti_3SiC_2 and Ti_2AlC samples exposed to neutron irradiation - up to 0.1 displacements per atom (dpa) at $350 \pm 40^\circ\text{C}$ or $695 \pm 25^\circ\text{C}$, and up to 0.4 dpa at $350 \pm 40^\circ\text{C}$. Black spots are observed in both Ti_3SiC_2 and Ti_2AlC after irradiation to both 0.1 and 0.4 dpa at 350°C . After irradiation to 0.1 dpa at 710°C , small basal dislocation loops, with a Burgers vector of $\mathbf{b} = \frac{1}{2} [0001]$ are observed in both materials. At 9 ± 3 and 10 ± 5 nm, the loop diameters in the Ti_3SiC_2 and Ti_2AlC samples, respectively, were comparable. At 1×10^{23} loops/ m^3 , the dislocation loop density in Ti_2AlC was ≈ 1.5 orders of magnitude greater than in Ti_3SiC_2 , at 3×10^{21} loops/ m^3 . After irradiation at 350°C , extensive microcracking was observed in Ti_2AlC , but not in Ti_3SiC_2 . The room temperature electrical resistivities increased as a function of neutron dose for all samples tested, and appear to saturate in the case of Ti_3SiC_2 . The MAX phases are unequivocally more neutron radiation tolerant than the impurity phases TiC and Al_2O_3 . Based on these results, Ti_3SiC_2 appears to be a more promising MAX phase candidate for high temperature nuclear applications than Ti_2AlC .

Keywords: Ti_3SiC_2 ; Ti_2AlC ; MAX phases; neutron irradiation; dislocation loops

I. Introduction

The $M_{n+1}AX_n$ (MAX) phases - where M is an early transition metal, A is a group 13 to 16 element, and X is C and/or N - have recently been proposed as potential materials for use in future nuclear reactor designs (Gen IV, ITER) where increased operating temperatures, fast neutron fluences, and corrosive coolants require material innovations[1-3]. These layered, machinable, ternary carbides and/or nitrides possess a combination of properties, both metallic and ceramic. Ti_3SiC_2 , one of the leading candidate MAX phases for such applications, is both stiff[4] but relatively soft, with high fracture toughness[5]. Like other MAX phases, it is also thermally and electrically conductive[6-7], and resistant to thermal shock[8]. Depending on their grain size, the MAX phases are quite strong in compression at room temperatures, RT, and undergo a plastic-to-brittle transition at around 1000 °C[9-10]. Al-containing MAX phases, such as Ti_2AlC , also show excellent oxidation resistance in air and water vapor [11-14]. They also possess the ability to repeatedly heal cracks, by the selective formation of alumina[15-18].

The neutron activation of Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC has been shown to compare well to SiC and is about three orders of magnitude lower than Inconel 617, two candidate materials for use in next generation reactors [3]. A recent study on the reactivity of Zircaloy-4 with Ti_3SiC_2 and Ti_2AlC has shown the MAX phases to form diffusion bonds at temperatures in excess of 1100 °C, with the A-element being the dominant diffusing species[19]. Additionally, cold sprayed coatings of Ti_2AlC have been shown to adhere well to a Zircaloy-4 substrate, providing oxidation resistance after a 20 min. exposure to 1005 °C Ar/steam, followed by quenching[20]. The combination of these properties renders some of the MAX phases, notably Ti_3SiC_2 and Ti_2AlC , viable candidates for nuclear applications.

To date the majority of recent irradiation studies have investigated the effects of heavy ion irradiation and He on several MAX phases, notably Ti_3SiC_2 , Ti_3AlC_2 , and $Ti_3(Si,Al)C_2$ solid solutions [21-38]. The general conclusions from these studies are that the MAX phases are resistant to irradiation damage and amorphization, even up to 52 displacements per atom (dpa). Additionally, in all cases the irradiation resulted in an expansion in the c-lattice parameter, c-LP, and a reduction in the a-lattice parameter, a-LP, along with increased microstrains[23, 30, 32, 34]. Further, disruption of the layered MAX phase structure has been observed[24, 26, 33, 38], as well as the possible formation of a β -MAX phase polymorph after irradiation[33-34]. Interestingly, in none of the ion irradiation studies to date has

there been any mention of irradiation-induced dislocation loops. Irradiation with He ions resulted in the formation of bubbles, small stacking faults and defect clusters [23-24, 33].

In a recent paper, we reported preliminary results on the effect of 0.1 dpa neutron irradiation of Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , and Ti_2AlN at $360\pm 20^\circ\text{C}$ and $695\pm 25^\circ\text{C}$. Of these, Ti_3SiC_2 and Ti_2AlC were found to be the most stable [39]. In contrast, roughly half the Ti_3AlC_2 sample was converted to TiC . Similarly, the TiN and Ti_4AlN_3 contents of the Ti_2AlN samples increased after irradiation. After irradiation at $360\pm 20^\circ\text{C}$ and similar to the ion irradiation studies, Ti_3SiC_2 , Ti_3AlC_2 and Ti_2AlC all showed increases in their c-LPs and decreases in their a-LPs. After irradiation at $695\pm 25^\circ\text{C}$, however, their lattice parameters appeared to relax, and revert back to their unirradiated values [39]. Based on these results, Ti_3AlC_2 and Ti_2AlN were abandoned, and the focus of our work shifted to cataloguing and understanding the various irradiation defects that occurred in Ti_3SiC_2 and Ti_2AlC samples as a function of temperature and neutron dose.

II. Experimental Details

Details of the synthesis and processing conditions of the MAX phases are reported elsewhere [10, 40]. The same materials described in [39] were further characterized herein. In short, fine-grained samples of Ti_3SiC_2 , henceforth referred to as FG-312, were prepared by ball milling stoichiometric mixtures of Ti, Si, and C powders (Alfa Aesar, Ward Hill, Massachusetts, USA) for 24 h, pouring the mixture into graphite dies, and loading them into a vacuum hot press. The powders were then hot-pressed (HPed) at 1450°C for 6 h under a load corresponding to a stress of $\sim 40\text{ MPa}$ and a vacuum of 10^{-1} Pa . Coarse-grained samples of Ti_3SiC_2 , henceforth referred to as CG-312, 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, Ar, atmosphere to grow the grains. Samples of Ti_2AlC were prepared by pouring pre-reacted Ti_2AlC powders (Kanthal, Hallstahammar, Sweden) into graphite dies, which were then HPed at 1300°C for 4 h. Test specimens were electro-discharged machined into $1.5\times 1.5\times 25.4\text{ mm}^3$ resistivity bars, 3 mm dia. $\times 0.5\text{ mm}$ thick discs, and $16\times 5\times 0.7\text{ mm}^3$ tensile dogbones.

Details of the irradiation conditions were described previously [39]. In brief, samples were irradiated to a total fluence of $3.4\times 10^{20}\text{ n/cm}^2$ at an irradiation temperature of $360\pm 20^\circ\text{C}$, henceforth referred to as LD-LT; to $4.8\times 10^{20}\text{ n/cm}^2$ at a temperature of $695\pm 25^\circ\text{C}$, henceforth referred to as LD-HT; and to $14\times 10^{20}\text{ n/cm}^2$ at a temperature of $340\pm 20^\circ\text{C}$, henceforth referred to as MD-LT. The irradiation

temperatures were monitored using a thermocouple in each capsule. To simplify the discussion, however, and allow for comparisons, we averaged the two low irradiation temperatures (viz. 340 °C and 360 °C) to obtain 350 ± 40 °C.

In the absence of other damage cross-sectional data, we used the fluence conversion for SiC in the MITR assumed in [39]—viz. 4×10^{21} n/cm² total fluence = 1 dpa, based on fluence calculations using total energy spectrum referenced in a similar irradiation experiment at the MIT test reactor [41]. It follows that therein we characterize the post-neutron irradiation microstructures and electrical resistivities of polycrystalline samples of Ti₂AlC and Ti₃SiC₂ irradiated to 0.1 and 0.4 dpa at ≈ 350 °C and at 0.4 dpa at 695 °C. Samples were also irradiated to a total fluence of 20×10^{20} n/cm² at 740 ± 20 °C, to 20×10^{20} n/cm² at 340 ± 14 °C and to 28×10^{20} n/cm² at 700 ± 34 °C. Samples from the latter three conditions have yet to be characterized.

Surface microstructures of pristine and irradiated samples of FG-312 and Ti₂AlC were observed using a scanning electron microscope, SEM, (Quanta 3D FEG, FEI Company, USA). Irradiated samples were polished with 1200 grit SiC paper to remove possible friable contamination before proceeding with their post-irradiation characterization.

XRD analysis of the medium dose samples was conducted using the methods described in [39]. In short, XRD patterns from Ti₂AlC and FG-312 irradiated to MD-LT surfaces were obtained using a diffractometer (Bruker D8, Madison, WI, USA) in the Bragg–Brentano configuration. The diffractograms were collected using step scans of 0.02° in the 5°–70° 2θ range, with a step time of 2 s. Scans were made with Cu Kα 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 LaB₆ standard (NIST 660A).

All diffractograms were analyzed by the Rietveld refinement method, using the FULLPROF code [42–43]. A systematic shift of 0.02% was found, and corrected for, in the lattice parameters', LP, evaluation as compared to the LaB₆ standard's reported values. For each data set, a model assuming the presence of TiC was refined. The Thompson-Cox-Hastings pseudo-Voigt model was used to refine the peak-shape of each phase's reflections. Lattice strains were also estimated assuming isotropic Lorentzian and Gaussian contributions to the peak shape function [44]. The microstrain was calculated

from the full width half max (FWHM) parameter, U , from each sample, according to the following equation:

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

where U_{std} was refined from the LaB_6 standard. If U_{sample} refined is lower than the U_{std} , the microstrain was unresolvable for that specimen. The U_{std} values were 0.006 ± 0.002 and 0.014 ± 0.002 for the standards scanned on the diffractometer for pristine and irradiated samples, respectively. Results were compared with the as-received spectra from Ref.[39].

Microstructural analysis was carried also out on the FG-312 and Ti_2AlC samples using a transmission electron microscope, TEM (Tecnai TF30-FEG STwin STEM, FEI Company, Hillsboro, OR, USA) equipped with electron energy loss spectroscopy, EELS (GIF System, Gatan, Inc., Pleasanton, CA, USA), and an energy dispersive X-ray spectroscopy, EDX (EDAX Inc., Mahwah, NJ, USA). TEM lamellas were prepared using a focused ion beam, FIB, (Quanta 3D FEG, FEI Company, Hillsboro, OR, USA) by milling out $20 \times 2 \times 15 \mu\text{m}^3$ sections from the irradiated TEM samples with Ga^+ ions, which were then lifted out onto TEM copper grids. Samples were thinned in the FIB down to a final milling step of 5 kV at 77 pA ion emission current until small perforations were observed. FIB damage was cleaned with a final polish using 2 kV at 27 pA ion emission current. Brightfield, BF, and darkfield, DF, TEM micrographs at various tilts, as well as, selected area electron diffraction (SAED) patterns, were collected to characterize the irradiation defects.

The lamella thicknesses were calculated using the inelastic mean free path (IMFP) for transmission of electrons through a solid, following the equation developed by Iakoubovskii *et al.*[45],

$$\lambda = \frac{200 F E_0}{11 \rho^{0.3} \ln \left[\left(\frac{\alpha^2 + \beta^2 + 2\theta_E^2 + |\alpha^2 - \beta^2|}{\alpha^2 + \beta^2 + 2\theta_C^2 + |\alpha^2 - \beta^2|} \right) \times \left(\frac{\theta_C^2}{\theta_E^2} \right) \right]} , \quad (\text{Eq. 2})$$

where $F = (1 + E_0/1022)/(1 + E_0/511)^2$ is a relativistic factor, E_0 is the electron energy, α is the convergence angle, β is the collection semi-angle, $\theta_E = 5.5 \times \rho^{0.3}/(F E_0)$ and $\theta_C = 20$ mrad. ρ is the sample density assumed to be 4.5 g/cm^3 for FG-312 and 4.1 g/cm^3 for Ti_2AlC .

Log-ratio measurements of EELS spectra were collected for various regions with defects to generate a relative mean free path used to calculate lamella thicknesses for defect density calculations. The

diameters and lengths of more than 200 loops were measured and averaged using image analysis software (ImageJ, NIH, Bethesda, MD, USA).

Post-irradiation room temperature (RT) resistivity, ρ , measurements were obtained for the MD-LT samples using a 4-point probe technique using a current of 100 mA. As most of the resistivity bars were broken upon retrieval from the capsules, the average of only 2 resistivity bars is reported. Voltages were recorded once per second for 3 minutes, until a steady state voltage was obtained.

III. Results

The XRD patterns collected from the FG-312 and Ti_2AlC samples as received and after the MD-LT irradiations are shown in Fig. 1. The results of the Rietveld analyses are summarized in Table 1. Similar to the LD-LT results reported previously [39], irradiation at MD-LT conditions resulted in changes in the lattice parameters, LPs, while the MAX phase compositions were maintained. The best fits were achieved by including TiC during refinement, and the corrected as-received TiC content in FG-312 and Ti_2AlC samples were 23 ± 1 and 7.5 ± 1.0 wt. %, respectively [39]. As similarly reported for the low dose samples [39], the a-LP for the TiC phase after MD-LT remained close to the values in the pristine samples (Table 1). The TiC content in the FG-312 sample after MD-LT irradiation was 22 ± 1 wt. % (Table 1).

Figure 1. Rietveld analysis of XRD patterns of, a) pristine FG-312 [39] and, b) FG-312 irradiated to MD-LT. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_3SiC_2 (1st row), TiC (2nd). c) pristine Ti_2AlC [39], and d) Ti_2AlC irradiated to MD-LT. The two rows of vertical tags represent the calculated Bragg reflections' positions of the Ti_2AlC (1st row), TiC (2nd). The large amorphous background in a and c was due to scanning a single 1.5 mm wide resistivity

bar, resulting in more signal coming from the mounting putty. Open diamonds, solid red line, and solid green line at the bottom, represent the observed data, calculated model, and the difference between the two, respectively.

Rietveld refinement of the FG-312 irradiated to MD-LT XRD patterns (Fig. 1b), however, revealed an increase in the c-LP from 17.680 ± 0.005 Å to 17.887 ± 0.001 Å and a decrease in the a-LP from 3.0685 ± 0.0006 Å to 3.0637 ± 0.0002 Å. At 0.36%, the lattice microstrain was seen to increase from pristine condition, at 0.19%, and was also larger than the LD-LT sample, at 0.27%.

Rietveld refinement of Ti_2AlC irradiated to MD-LT XRD patterns (Fig. 1d) showed an increase in the c-LP from 13.650 ± 0.002 Å to 14.056 ± 0.003 Å and a decrease in the a-LP from 3.0614 ± 0.0002 Å to 3.0206 ± 0.0003 Å. At 1.14%, the microstrain in Ti_2AlC irradiated to MD-LT was higher than reported for both pristine – which was below that of the standard used to calibrate the diffractometer – and LD-LT [39], at 0.66%. At 2 ± 1 wt.%, the TiC content was below that of the pristine sample, which implies that the TiC distribution was inhomogeneous in these samples. After HPing, sample blanks commonly form an outer layer of TiC that is machined off prior to specimen fabrication. It is possible that the specimens scanned for the pristine condition were machined from the outer regions of the blank, possessing a higher TiC content. These comments notwithstanding, the fact that the TiC content does not increase drastically shows that the Ti_2AlC – in sharp contrast to the Ti_3AlC_2 [39] – remained stable after irradiation to MD-LT conditions.

TEM micrographs of unirradiated FG-312 (Figs. 2a and b) and Ti_2AlC (Figs. 2c and d) lamella reveal the types of defects present before irradiation. Stacking faults in the MAX phases occur only as growth defects, when missing A-layers leave close-packed MX stacking [46]. Basal dislocations can be seen throughout all the grains, as well as dislocation arrays and stacking faults. In Ti_2AlC , dislocations can be seen emanating from a grain boundary (Figs. 2c and d). The samples are fully crystalline and contain some impurity phases, such as TiC or Al_2O_3 particles.

Figure 2. TEM micrograph of unirradiated, a) Ti_3SiC_2 , bright-field, using a 2-beam condition near the $[11\bar{2}0]$ zone; b) Ti_3SiC_2 from another region on zone showing dislocation arrays commonly observed in pristine samples; c) Ti_2AlC taken on zone down the $[11\bar{2}0]$ axis, and, d) Ti_2AlC tilted off zone to a 2 beam condition - revealing dislocation arrays and SFs. Dislocations appear to be straight lines when viewed on zone in (c), but in fact are curved within the basal planes, and some appear to emanate from a grain boundary, GB, as seen when tilted in (d).

This paper is divided into sections detailing the type of defect structures observed in the post-irradiated samples.

i) Black Spots and/or Defect Clusters

Samples of FG-312 irradiated to LD-LT revealed no signs of irradiation induced defects, and remained fully crystalline with no amorphization as observed in the SAEDs (shown as insets in Figs. 3a and b). If any defect clusters formed, they were beyond the resolution of the TEM. Stacking faults and basal dislocations (Fig. 3a), closely resembling preexisting defects observed in the unirradiated samples (Fig. 2a), were observed in a grain tilted near the $[11\bar{2}0]$ zone axis. Within the stacking faults, small defect clusters can be observed. Arrays of basal dislocations are observed, which are most likely preexisting as well (Fig 3b).

Samples of FG-312 remain crystalline after irradiation to MD-LT (inset in Figs. 3c and d). HRTEM of the sample near a kink boundary reveals the presence of black spots and defect clusters (Fig. 3d). The latter are uniformly distributed throughout all grains. With the sample viewed edge-on, i.e. down the $[11\bar{2}0]$ zone axis, no missing spots were observed in the SAED patterns (inset in Fig. 3d) indicating no loss of long range structural ordering.

Figure 3. Representative brightfield TEM micrograph of FG-312, a) irradiated to LD-LT reveals limited signs of irradiation induced defects. Defect clusters are observed within the stacking faults throughout the grain (top inset); b) in another region after showing dislocations commonly observed in pristine samples; c) irradiated to MD-LT shows preexisting kink boundaries (red arrows) in grains near the $[11\bar{2}0]$ orientation, with no signs of larger irradiation defects; d) at high resolution of a region near (c) showing disorder in the layered structure and defect clusters and/or black spots.

Examples of larger dislocations, similar to those seen in the unirradiated samples (Figs. 2c and d) are also observed in the Ti_2AlC samples irradiated at LD-LT (Fig. 4a) and MD-LT (Fig. 4c). HRTEM micrographs of Ti_2AlC irradiated to LD-LT reveal distorted basal planes

and irradiation induced black spots (Fig. 4b). The size and density of these black spots increase in the MD-LT samples (Fig. 4d).

Figure 4. Brightfield TEM micrograph of Ti_2AlC sample irradiated to, a) LD-LT reveals dislocations threading through the grain as seen in pristine MAX phases; b) LD-LT imaged at high resolution of a grain edge-on reveals disorder of the basal planes and the presence of defect clusters and/or black spots, c) MD-LT taken in 2 beam condition near the $[0001]$ zone axis showing overlapping basal plane dislocation networks; d) Same region as (c) tilted further removing contrast from dislocation arrays, and revealing only black spots and defect clusters.

ii) Microcracking

SEM micrographs of unirradiated, as-received FG-312 and Ti_2AlC samples shown in Figs. 5a and 5e, respectively, were essentially fully dense and crack free. The dark spots seen in the micrographs are either pullouts and/or small pores. Post-irradiation SEM micrographs of roughly polished FG-312 and Ti_2AlC samples reveal an increase of grain pullouts and microcracking in both samples, but more prominently in the Ti_2AlC samples. In both materials, after irradiation to 0.1 dpa, more microcracking is observed in samples irradiated at LT (Figs. 5b and f) compared to those irradiated at HT, (compare Figs. 5c and g). In the FG-312 samples irradiated to MD-LT (Fig. 5d), the extent of microcracking and grain pullout is similar to that of LD-LT (Fig. 5b). In contrast, the Ti_2AlC sample irradiated to MD-LT exhibited extensive grain pullout, with cracks and pores surrounding most grains (Fig. 5h). These pullouts are an indirect manifestation of the extent of neutron-induced microcracking. Note that as the irradiation temperature is increased, the extent of microcracking, and concomitant grain pullouts, decreases suggesting that microcracks may either not form, or heal at higher temperatures.

Figure 5. SEM micrographs of (1200 grit polished surfaces of) FG-312, a) as-received, and irradiated to, b) LD-LT, c) LD-HT, and d) MD-LT, and Ti₂AlC, e) as-received, and irradiated to f) LD-LT, g) LD-HT, and h) MD-LT. The extent of cracking between grains is highest after irradiation to MD-LT (white arrows denoting cracks). For both materials, an increase in pullout and microcracking is observed with increased irradiation dose, i.e. from top to bottom. Irradiation of FG-312 at LD-HT, i.e. the highest temperature, results in a microstructure similar to that of the pristine material.

TEM micrographs taken near the (0001) zone axis of Ti_2AlC samples irradiated to LD-LT reveal microcracks that extend across entire lamella (Fig. 6a). Intragranular cracking was often seen to extend beyond grain boundaries (e.g. region A in Fig. 6b). Based on the zone axis of the micrograph taken of the lamella, for the most part, these cracks were parallel to the basal planes, and propagate throughout (Fig. 6a). The cracks were seen to interact and overlap at the lamella edges (Fig. 6a, region B). Occasional microcracking was observed in the FG-312 samples, though not to the extent seen in Ti_2AlC .

Figure 6. a) Composite TEM micrograph of a Ti_2AlC lift-out irradiated to LD-LT. Networks of long microcracks (red trace) are seen to traverse the entire liftout. b) Enlarged region of square outlined in a, where several cracks (white arrows) are seen to extend beyond a grain boundary (region A). Cracks are seen to overlap and interact near the edge of the lamella (region B)

iii) Dislocation Loops

TEM micrographs of FG-312 samples irradiated to LD-HT reveal the presence of dislocation loops (Fig. 7). Extensive tilting experiments revealed that their Burgers vector is $\mathbf{b} = 1/2[0001]$, i.e. perpendicular to the basal planes. In some cases, the loops can be seen to accumulate along stacking faults (Fig. 7a). The dislocation loops observed in FG-312 were found to be 9 ± 3 nm long, with a density of 3×10^{21} loops/m³. The loops appear in the bulk of the grains with black and white lobe contrast (Fig. 7b). HRTEM of an individual loop shows significant strain contrast all around the affected region (Fig. 7c), and a Fourier filtered image of the region shows the presence of extra atomic layers (Fig. 7d). A ~ 300 nm loop-denuded zone, labeled DZ in Fig. 7a, was also observed.

Figure 7. Brightfield TEM micrograph of, a) FG-312 lift-out irradiated to LD-HT showing dislocation loops imaged near the $[11\bar{2}0]$ zone axis, i.e. parallel to the basal plane. A denuded zone, DZ, ~ 300 nm wide was observed near a grain boundary. b) a region in the vicinity of region shown in (a) showing an even distribution of loops - with black/white lobe contrast due to strain induced in the surrounding lattice - with an average loop diameter of 9 ± 3 nm and a density of 3×10^{21} loops/m³. The loops are aligned along the basal planes. c) a single loop at high resolution with, d) Fourier filtered image - of dotted square in c confirming interstitial character of the loop.

Brightfield and darkfield TEM micrographs of a region in the Ti_2AlC sample irradiated to LD-HT also showed evidence of dislocation loops (Figs. 8a and b). Taken near the $[11\bar{2}0]$ zone, the loops appear with bright white contrast in a darkfield image (Fig. 8b). Imaged near the $[\bar{3}301]$ zone axis, the loops appear as open ellipses (Fig. 8c). Viewed edge on, near the

$[11\bar{2}0]$ zone axis, the basal plane loops appear as parallel lines lying in the basal planes, with a high density throughout the grain (Fig 8d). The average length of these loops was 10 ± 5 nm. In this case there does not seem to be any preferred accumulation near stacking faults. At 1×10^{23} loops/m³, the loop density is ~ 1.5 orders of magnitude *greater* than that observed in FG-312 exposed to the same conditions.

Figure 8. TEM micrograph of Ti_2AlC lift-out irradiated to LD-HT, a) in brightfield and, b) in darkfield condition using $g = 11\bar{0}3$ near the $[11\bar{2}0]$ zone showing dislocation loops within the basal planes. Yellow circles in the inset SAED patterns denote location of objective aperture used for darkfield imaging. The dislocation loops appear as strong white contrast in

(b);c) near the $[\bar{3}301]$ zone axis, showing the dislocation loops as open ellipses; d) near the $[11\bar{2}0]$ zone axis showing edge on loops with an average diameter of 10 ± 5 nm and a defect density of 1×10^{23} loops/m³. Bold dark lines in (d) are SFs denoted by black arrows.

iv) Stacking Faults, SF

When imaged down the $[11\bar{2}0]$ zone axis, one area of the LD-HT FG-312 sample showed significantly more damaged regions near SFs (Fig. 9a). A high density of loops in, and around, these SFs was observed, as opposed to the relatively clear areas in the surrounding MAX phase matrix (Fig. 9a). This same region tilted to excite $g = 11\bar{2}0$ to render the basal plane defects invisible, is seen to have a high density of loops and spots within the wider stacking faults, (see region A in Fig. 9b). In comparison, the LD-HT Ti_2AlC sample had a higher number of stacking faults, which spanned entire grain lengths (Fig. 9c). HRTEM within the FG-312 SFs reveals the presence of cubic (i.e. rock salt) TiC layers within the band (Fig. 9d). STEM EDS line scans across stacking fault A in Fig. 8a confirmed the absence of Si within the fault (Fig. 9e). Analysis of the stacking faults imaged edge on, in both Ti_3SiC_2 and Ti_2AlC samples revealed a broader distribution of widths in the former, with most SF in Ti_2AlC being < 7 nm wide (Fig. 9f). Several SF in Ti_3SiC_2 were > 15 nm wide, all of which show a high concentration of defects within them (Fig. 9b). As discussed in more detail below, at this time it is not clear if the SFs were pre-existing or irradiation induced.

Figure 9. a) Brightfield TEM micrograph taken on the $[11\bar{2}0]$ zone shows extensive damage around and within stacking faults in FG-312 sample irradiated to LD-HT. Dislocation loops and black spots are clustered around the wider SFs. b) In a 2 beam condition with $g = 1\bar{1}00$, the basal loops in FG-312 reach the $b \cdot g = 0$ criterion for weak diffraction contrast, and are thus invisible. c) Brightfield TEM micrograph taken near the $[11\bar{2}0]$ zone in the Ti₂AlC sample irradiated to LD-HT shows a high number of stacking faults spanning the grain. d) HRTEM micrograph of a wider SF in (b) reveals de-twinned TiC layers within the band. e) Drift corrected STEM EDS composition profile across the SFs (dotted line in b) confirms the absence of Si. f) Statistical distribution of SFs widths in FG-312 and Ti₂AlC after irradiation to LD-HT. The wider, de-twinned stacking faults are seen to have black spots and defect clusters within the TiC phase (region A).

v) Grain Boundaries and Impurity Phases

A grain boundary in the LD-HT FG-312 sample appears to have grown - along the *a*-direction – into a neighboring grain (Fig. 10a). Such stepped and jagged grain boundaries were not observed in the as-received samples. Anisotropic grain growth is common in the MAX phases, and occurs in a more rapidly in the *a*- than the *c*-direction, which ultimately results in the typical plate-like grains observed in the literature (e.g. [47], [48]). While *c*-direction growth is not prohibited, it occurs at a much slower rate than in the *a*-direction presumably due to the difficulties in nucleating new basal planes that are atomically smoother than the prismatic planes.

TEM micrographs of TiC impurity particles in the FG-312 samples exposed to LD-LT show a high density of defect clusters (Fig. 10b). Similarly, impurity Al₂O₃ particles in the Ti₂AlC sample were also highly damaged after irradiation at LD-LT (Figs. 10c) and MD-LT (Fig. 10d), with larger defect clusters in the latter condition. In both cases the surrounding MAX grains were relatively defect free. These micrographs, more than any others, confirm the importance of the A-layers in mitigating neutron irradiation damage.

Figure 10. Brightfield TEM micrograph of a, a) grain boundary found in the FG-312 LD-HT sample. The jagged features imply irradiation induced growth has occurred along the a-direction. b) of preexisting TiC particle found in the FG-312 sample irradiated to LD-LT showing extensive microstructural damage compared to the relatively clean surrounding Ti₃SiC₂ matrix. Al₂O₃ impurity particle observed in Ti₂AlC of a LD-LT sample and, d) Al₂O₃ particle in a MD-LT sample. Density of irradiation-induced defects is larger in (d) than in (c) and in both cases, significantly higher than the defects in the surrounding Ti₂AlC.

As reported in our previous study [39], the room temperature electrical resistivity, ρ_{RT} , increases as a function of neutron dose. This trend continued here (see Fig. 11). At 8.3 ± 0.1 and $8 \pm 2 \mu\Omega\cdot m$, the Ti₂AlC and Ti₃AlC₂ samples, respectively, showed the highest increases in ρ_{RT} after the MD-LT irradiation. At

$3.34 \pm 0.01 \mu\Omega\text{-m}$, the ρ_{RT} values for the Ti_2AlN sample, did not increase as much as its carbide counterpart. Interestingly, ρ_{RT} of both the FG-312 and CG-312 samples appear to approach a saturation point after the MD-LT irradiation. Interestingly at $2.82 \pm 0.01 \mu\Omega\text{-m}$, ρ_{RT} for the CG-312 was double that of its fine-grained counterpart, at $1.43 \pm 0.01 \mu\Omega\text{-m}$.

Figure 11. Effect of neutron irradiation dose on room temperature resistivity for various MAX phase samples irradiated at LT, including results up to 0.1 dpa replotted from [39]. In all cases the resistivities increased with increasing dose. Note that the resistivity increases for both FG-312 and CG-312 compositions appear to reach a near saturation level.

IV. Discussion

Rietveld refinement results shown in Table 1, of the XRD patterns of the FG-312 (Fig. 1b) and Ti_2AlC (Fig. 1d) samples after the MD-LT exposure revealed that neither dissociated into TiC as observed for some other MAX phases, notably Ti_3AlC_2 [39]. The increased irradiation dose also increased the microstrains in both materials (Table 1), above the values reported for LD-LT and pristine samples [39]. The increase in point defects and defect clusters likely contribute to the microstrains and lattice parameters' distortions.

Cascade events caused by neutron irradiation result in the formation of Frenkel pairs, FPs, most of which annihilate rapidly after formation. During prolonged irradiation exposure, however, defects can accumulate within the lattice, forming black spots and defect clusters observable in a TEM. The latter were readily observed in the Ti_2AlC sample after LD-LT exposure (Fig. 4b). With increased irradiation dose to 0.4 dpa, at a comparable temperature, an increase in defect size and density was observed (Figs. 4d). Similar defect clusters were only observed in the Ti_3SiC_2 samples after MD-LT irradiation (Fig. 3d).

Several recent first principles studies [49-53] have concluded that the presence of the A-layer could provide significant irradiation tolerance for the MAX phases. The general trends showed that FPs of Ti, A (either Si or Al), and C readily form as interstitials within the A-layer and/or in the space between the A and Ti layers. While varying in values due to differences in calculation methods, the energies of formation, E_f , for point defects in the A-layers were consistently much lower, around $\sim 1\text{-}3\text{ eV}$, compared to defects within the TiC blocks, $>9\text{ eV}$ [49-52]. Antisite defects, e.g. Ti_{Al} , were also shown to have quite low E_f 's comparable to A-layer FPs. These low E_f 's within the A-layer suggest that these layers – as shown here – can act as potent defect sinks.

In comparing various A-elements, Wang *et al.* [50] showed that C_{FP} and Si_{FP} with $E_f = 1.5$ and 2.1 eV , respectively, were the lowest energy defects in Ti_3SiC_2 . In contrast, $\text{Ti}_{\text{Al}} + \text{Al}_{\text{Ti}}$ antisite defects, requiring only 1.6 eV to form, were the lowest E_f defects in Ti_3AlC_2 . Interestingly, at 2.96 eV , the same antisite defect was also the lowest energy defect in Ti_2AlC [49]. Xiao *et al.* [49] concluded that the more ionic character of the Ti-Al bonds found in Ti_3AlC_2 and Ti_2AlC as compared to the Ti-Si bonds in Ti_3SiC_2 would lead to enhanced irradiation tolerance of the former by allowing for easier lattice damage recovery. They also predicted that the higher Al:Ti ratio in Ti_2AlC than in Ti_3AlC_2 would result in a larger volume of point defect sinks, rendering the former more irradiation tolerant than the latter [49]. It was then theorized that the Al-containing phases would have better irradiation tolerance, due to the ease of forming stable antisite defects over FPs, which in principle should recover irradiation damage more easily.

In contrast to these predictions it is evident from the results shown herein that the irradiation tolerance of Ti_3SiC_2 is greater than that of Ti_2AlC . For example, after the LD-HT irradiation, the loop density in Ti_2AlC was 1.5 orders of magnitude higher than that observed in Ti_3SiC_2 . While FPs can readily recombine via migration of interstitials and vacancies, the low cost antisite defects predicted to

form more prominently in the Al-containing phases would not as easily return to their normal lattice positions. As seen herein in Ti_2AlC (Fig. 8d), this would result in increased structural disorder and greater dislocation -or antisite- loop density formation. The Ti_2AlC samples were also found to microcrack significantly more compared to their Ti_3SiC_2 counterparts (compare Figs. 5d and 5h) indicating that the latter are more resistant to neutron irradiation.

Evidence of a defect-free denuded zone was also observed in Ti_3SiC_2 (Fig. 7a). At this time why, or how, the grain boundary leadsto these denuded zones is unclear. However, given the relatively large denuded zone and the relatively low irradiation temperatures, here again it is reasonable to assume that enhanced diffusion along the A-layers [52]are somehow implicit. The fact that such zones were absent in the TiC grains is in accord with this postulate. Another feature attributed to the increased mobility along the a-direction is the anisotropic grain growth observed in Ti_3SiC_2 after irradiation (Fig. 10a). Further work is required to fully understand the relationship of bonding and defect formation in this family of materials. This is especially true given that the microstructures observed herein are unlike any reported by ion irradiation[21-22, 26-33, 36, 38].

In concurrence with theoretical studies [49-51, 53], the irradiation tolerance of Ti_3SiC_2 is unequivocally greater than that of its binary counterpart TiC. The TiC impurity particles (Fig 10b) and de-twinned TiC platelets within SFs (Fig. 9a) form dislocation loops and defect clusters, a response similar to a recent proton irradiation study [54]. The same is the Al_2O_3 impurity particles in Ti_2AlC (see Figs. 10c and d). The presence of the A-layer, and the low energy of formation of defects within the layer, clearly provides a defect sink at the nanoscale level. SFs in Ti_3SiC_2 appear to promote dislocation loop formation, as loops are seen to accumulate nearby (Figs. 7a and 9a). At this point, it is fairly well established that when the A-group element from the MAX phases diffuses out of the basal planes, the resulting highly twinned TiC blocks can de-twin, aligning the (111) TiC planes with the (0001) basal planes of the MAX structure[55-56]. SFs – defined in the MAX phases as regions where the A-layers are absent - also form during synthesis due to inhomogeneous mixing of constituent elements[57]. The loss of the A-element also results in a $\sim 15\%$ volume shrinkage[55-56]. Irradiation of presumably preexisting SFs resulted in varied defect microstructures (Fig. 9). Above a certain width, the SFs apparently behave like bulk TiC platelets, in that a high density of black spots and small loops after irradiation are observed (Fig. 9b). Not surprisingly, the morphology of these spots is similar to the ones seen in the TiC impurity particles (Fig. 10b). While it is unclear at this time whether the increase in

stacking fault widths was induced by irradiation, the density of stacking faults observed appear to be quite high, notably in one grain of the LD-HT TAC sample (Fig. 9c). However, the high number of faults were not observed uniformly in all grains, and we thus propose that they are growth SFs. Future studies at higher irradiation doses are needed to determine whether these SFs are irradiation induced - where one would expect to see an even further increase in SF density - or not.

This difference in irradiation behavior is fully attributed to the presence of the A-layer. As defects accumulate and interact during irradiation in Ti_3SiC_2 , interstitials are able to migrate rapidly along the basal plane, finding annihilation sites with more ease compared to TiC. When defects agglomerate, they are seen to form dislocation loops contained within the basal planes, most probably between the M and A layers. This differs from the TiC behavior, which shows more widespread defect generation, and various loop habit planes.

DFT calculations of point defects in the MAX phases predict interstitials favor the A-layer, most favorably residing in a hexagonal bi-pyramidal configuration in-plane between 3 A atoms and 2 M atoms [49]. This, however, would lead to an increase in the bond lengths between neighboring A atoms, resulting in, if any distortion, an *increase* in the a-LP. As reported previously by Tallman et al. [39], and confirmed herein, the XRD results, at least for the LT, samples show a decrease in the a-LP with an increase in c-LP. It follows that after neutron irradiation some other defect configuration was stabilized.

Based on our results, we propose two preliminary defect models that transform the unirradiated lattice (Fig. 12a); one that occurs after neutron irradiation at relatively lower temperatures, e.g. $\sim 350^\circ\text{C}$ (Fig. 12b), and one after irradiation to higher temperatures, $\sim 700^\circ\text{C}$ (Fig. 12c) to describe the lattice parameter distortions observed.

DFT calculations have shown that $\text{Ti}_2\text{Al}_{1-y}\text{C}$ can exist over a y that ranges from 0 to 0.5 [58]. This deficiency in Al content, however, results in a decrease in c-LP. In this case, the loss of Ti-Al bonds between layers resulted in shrinkage of the c-LP. The a-LP was determined to depend on the $\text{Ti}_{n+1}\text{C}_n$ block structure, and remained more or less constant [58]. It follows that Al loss alone cannot explain the expansion in c-LPs observed after neutron irradiation at lower temperatures. For the binary, rock salt, TiC_{1-x} structure, on the other hand, it is well established that a-LP shrinks with increasing C-vacancies, V_c . [59]. Therefore, it is reasonable to assume that neutron irradiation introduces carbon vacancies in the TiC blocks. This is not unexpected, since at $\sim 2-3$ eV, the formation energies, E_f , of V_c are relatively low,

in both Ti_3SiC_2 and Ti_3AlC_2 [49-52]. The accumulation of C, M and/or A-atoms in the basal planes, on either side of the A-layers [49] as shown schematically in Fig. 12b, would explain the c-LP expansion observed.

Figure 12. $(10\bar{1}0)$ view of M_3AX_2 structure a) pristine, b) after irradiation at low temperatures (350 °C), and c) after irradiation at higher (700 °C) temperatures. Region I shows coherent interstitial loops; region II shows M atom antisite layers. Combinations of the two types of defects in a single layer are also possible. The unit cell is shown by the dotted line in a.

At low irradiation temperatures, where defect mobility is limited, interstitials that become separated from their respective vacancies by the impenetrable M_{n+1}X_n blocks are more likely than not to form complex defect structures adjacent to the A-layers, resulting in an overall c-LP expansion (Figure 12b). It follows that the combination of V_c in the MX blocks, along with the presence of interstitial atoms adjacent to the A-layers, would explain the LP distortions observed in the XRD results (Table 1). As importantly, these complex defect structures are most probably the dark defect spots observed in the TEM micrographs after low temperature irradiation (see Figs. 3d and 4)

At higher irradiation temperatures, where defect mobility is higher, localized regions of defect clusters could collapse into lattice-coherent dislocation loops- as observed herein (see Figs. 7 and 8). Interstitial atoms, likely A or M, could agglomerate into a platelet within, again, the free volume between the A and M layer. Such a configuration is shown schematically in Fig. 12c and labeled I. Alternatively, or in addition, substitutional antisite defects -likely M atoms on the A-sublattice positions- could also form into platelets within the A-layer as shown schematically as region II in Fig. 12c. As point

defect clusters transition into loops of this nature, the result would be an overall relaxation of the crystal lattices, as reported previously [39], with dislocation loops throughout. This hypothesis also explains the disappearance of the dark defect spots when the dislocation loops are formed.

The fate of the C-interstitials is unclear at this time, but given the almost full recovery in electrical resistivity after the high temperature irradiations, it is not unlikely that the C-atoms start filling in the C-vacancies in the MX-blocks. This model and comments notwithstanding, it is hereby acknowledged that much more work, both theoretical and experimental, is needed before a clear picture of the nature of neutron irradiation defects in the MAX phases comes into focus.

SEM micrographs of post-irradiated FG-312 and Ti_2AlC samples reveal increased grain pullouts after polishing and microcracking (Fig. 5). However, the higher temperature of the LD-HT irradiation condition appears to somewhat mitigate the effects (Figs. 5c and g). After the MD-LT irradiation, the Ti_2AlC sample was found to be significantly microcracked (Fig. 5h), and showed increased friability during decontamination. The increased pullout is believed to be due to microcracking and the presence of residual microstrain. Based on this work, the microstrain increases documented by Tallman *et al.* [39] could be caused by several reasons. They include irradiation induced defects, increased lattice disorder, highly damaged impurity grains and possibly anisotropic grain growth. At higher irradiation temperatures, some of the point defects presumably anneal out or agglomerate into larger coherent structures (Figs. 7 and 8), reducing lattice strain and distortion, and relieving microstrain within the material.

As the defect density, particularly point defects, increases the resistivity increases because these defects are potent scatterers of conduction electrons [60]. This is particularly true of the binary early transition carbides [61-62] and the MAX phases [5]. Point defect formation also increases as a function of irradiation dose. Post-irradiation ρ_{RT} values of irradiated MD-LT samples increased by a factor of 30 compared to unirradiated samples, and were greater than those reported for the 0.1 dpa samples at a similar temperature (Fig. 11) [39].

However, both the FG- and CG- Ti_3SiC_2 samples appeared to approach a saturation in ρ_{RT} after the MD-LT irradiation. At $1.43 \pm 0.01 \mu\Omega\cdot\text{m}$, ρ_{RT} for the FG-312 sample is roughly half that of the CG-312 sample, at $2.82 \pm 0.01 \mu\Omega\cdot\text{m}$. This is an important result because it suggests that the increased grain boundary area in the FG-312 sample provides a potent defect sink compared to its CG-312 counterpart.

At $\sim 8 \mu\Omega\text{m}$, ρ_{RT} for both Ti_2AlC and Ti_3AlC_2 increased to comparable values. The latter values are 2 to 3 times those of Ti_3SiC_2 . This large increase in ρ_{RT} can also be partially ascribed to the extensive microcracking (Fig. 5) that was not revealed in our previous work. At $3.34 \pm 0.01 \mu\Omega\text{-m}$, ρ_{RT} of Ti_2AlN after MD-LT irradiation increased linearly as a function of dose.

We have shown that in most MAX phases, a majority ($> 90\%$ in Ti_3SiC_2) of the thermal conductivity is due to electron transport [5]. Said otherwise, electrical resistivity is a good measure of the magnitude of the thermal conductivity. It follows that the possible saturation in electrical resistivity for the Ti_3SiC_2 with dose (Fig. 11) bodes well for its use in any nuclear application where thermal transport is important. This is in sharp contrast to SiC, for e.g. wherein the thermal conductivity is sharply reduced with small irradiation doses [60]

V. Summary and Conclusions

XRD diffraction and TEM analysis of Ti_3SiC_2 and Ti_2AlC showed them to remain crystalline after neutron irradiation up to 0.4 dpa at $350 \pm 40^\circ\text{C}$.

Neutron irradiation resulted in the formation of black spots and defect clusters in Ti_2AlC after irradiation at 0.1 dpa at $350 \pm 40^\circ\text{C}$, and in both Ti_2AlC and Ti_3SiC_2 after 0.4 dpa at $350 \pm 40^\circ\text{C}$. The size and density of spots increased with irradiation dose. Dislocation loops were observed in Ti_3SiC_2 and Ti_2AlC after irradiation to 0.1 dpa at $695 \pm 25^\circ\text{C}$. At 1×10^{23} loops/ m^3 , the loop density in Ti_2AlC is 1.5 orders of magnitude greater than that observed in Ti_3SiC_2 , at 3×10^{21} loops/ m^3 . The dislocation loops were found to have a Burgers vector $\mathbf{b} = 1/2[0001]$, and lie in basal planes, with diameters of 9 ± 3 nm and 10 ± 5 nm, for FG-312 and Ti_2AlC samples, respectively. As predicted by first principles, all dislocation loops observed were restricted to the basal planes.

Impurity particles, such as TiC and Al_2O_3 , were found to be significantly more damaged than their surrounding MAX phase matrices, indirectly confirming an important conclusion of this work, which is that the presence of the A-layers provides a powerful mitigator of neutron radiation damage. In Ti_3SiC_2 , wide TiC stacking faults, showed extensive defect and dislocation loop formation. It is unclear at this time if the apparent increases in stacking fault width and density were induced by neutron irradiation or were preexisting. Further work is needed and is ongoing.

Evidence of irradiation induced grain growth along the a-direction was found.

Post-irradiation ρ_{RT} measurements of Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , and Ti_2AlN increased significantly after irradiation to 0.4 dpa at 350 ± 40 °C, compared to unirradiated samples. This increase can be attributed to increased defect concentrations and/or microcracking. Extensive microcracking was observed in Ti_2AlC , likely further contributing to its increased ρ_{RT} . Notably, ρ_{RT} of both FG- and CG-312 samples appeared to approach a saturation point after irradiation to 0.4 dpa 350 ± 40 °C, deviating from the, more or less, linear trend, of the Al-containing samples. At 2.82 ± 0.01 $\mu\Omega\cdot m$, ρ_{RT} of CG- Ti_3SiC_2 was twice that of FG- Ti_3SiC_2 at 1.43 ± 0.01 $\mu\Omega\cdot m$.

These results suggest that Ti_3SiC_2 remains a potential candidate for future nuclear materials applications, though more work is needed to fully understand the role of the A-layer in providing irradiation resistance. Commercially available Ti_2AlC has shown significant damage after irradiation to relatively low neutron doses, both in defect morphology and microstructure. More work is required to explore the role that antisite defects play in the irradiation tolerance of this material, and if it should be considered for nuclear applications. While the presence of the A-layer in the MAX phases clearly mitigates neutron damage compared to their binary MX compounds, the antisite criterion proposed by Wang *et al.*[50] alone does not sufficiently predict irradiation tolerance between different members of the MAX phase family. Furthermore, a recent study has shown that some fission products may diffuse through Ti_3SiC_2 at temperatures as low as 600 °C[63]. While the results herein are promising, a more thorough investigation to higher irradiation doses and temperatures is necessary, including an assessment of post-irradiation mechanical properties.

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Table 1. Irradiation induced structural and compositional changes in FG-312 and Ti₂AlC irradiated at MD-LT conditions.

Condition	χ^2	a-LP (Å)	c-LP (Å)	Ti _L _z position	C_z position	TiC content wt. %	TiC a-LP (Å)	FWHM Parameter, U	με%	Ref.
FG-312-Pristine	2.10	3.0685(6)	17.680(5)	0.3658(3)	0.573(1)	23(1)	4.3200(2)	0.0174(2)	0.19	[39]*
FG-312-MD-LT	2.43	3.0637(1)	17.887(1)	0.3657(3)	0.5578(2)	22(1)	4.3217(1)	0.0569(1)	0.36	This work
				Ti _L _z position						
Ti ₂ AlC-Pristine	1.95	3.0614(2)	13.650(2)	0.589(1)	-‡	8(1)	4.3068(9)	0.00602	-	[39]*
Ti ₂ AlC-MD-LT	1.9	3.0206(3)	14.056(3)	0.586(2)	-‡	2(1)	4.264(1)	0.438(4)	1.14	This work

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

*Corrected values from additional refinement of data in Ref. [39]

‡ In the M₂AX compounds, the C-atom z position is fixed at the origin.