7.2 EFFECTS OF NEUTRON IRRADIATION ON Ti-Si-C MAX-PHASE CERAMIC MICROSTRUCTURES – A. G. Perez-Bergquist[1,2], Y. Katoh[1], C. Shih[1], and S. J. Zinkle[1,2] (*[1]Oak Ridge National Laboratory, [2]University of Tennessee)*

OBJECTIVE

The goal of this study is to investigate the neutron irradiation behavior of the MAX-phase ceramic Ti_3SiC_2 and to determine if it is a viable candidate for high-radiation structural applications in fusion systems.

SUMMARY

MAX phase ceramics are intriguing candidates for structural applications in nuclear environments due to their unique mixture of metallic and ceramic properties. Specifically, their potential to retain adequate thermal conductivity after high levels of irradiation damage may make them an attractive alternative to SiC in fusion environments. In this study, we investigate samples containing MAX phase Ti_3SiC_2 after neutron irradiation to 3.4 and 5.0 dpa at temperatures of 500 and 800°C. Ti_3SiC_2 in the 500°C sample appeared to decompose into TiC under irradiation, whereas the Ti_3SiC_2 in the 800°C sample did not. Limited radiation damage was visible in the 800°C sample.

PROGRESS AND STATUS

Introduction

MAX phase ceramics are a family of ternary compounds with the general composition of $M_{n+1}AX_n$ where n = 1, 2, or 3, M is early transition metal, A is a Group A element, and X is carbon, nitrogen, or both. These unique carbide and nitride ceramics were first discovered in the 1960s [1], but interest in them was minor until the mid 1990's when Barsoum and El-Raghy first synthesized relatively phase-pure samples of Ti_3SiC_2 [2]. Work in MAX phase materials has since intensified greatly, with MAX phase ceramics being reported to exhibit high modulus, low specific gravity, adequate machinability, outstanding tolerance against oxidation and thermal shock, good thermal conductivity, moderate ductility, and the capacity to maintain strength up to about 1300°C [2-6]. Recently numerous ion irradiation studies have been performed on Ti_3SiC_2 and Ti_3AlC_2. A more thorough review of MAX phase Ti_3SiC_2 and ion irradiation studies in this material are available in the previous semi-annual report (for period ending December 31, 2013).

In this work, we investigate the effects of neutron irradiation on both phase-pure and phase-impure Ti_3SiC_2.

Experimental Procedures

MAX phase Ti_3SiC_2 was fabricated in the seams of joined SiC plates via two different methods. In one set of samples, a 20 µm pure titanium foil was used to diffusion bond the SiC plates. The bond was formed by inserting the foil between the plates and hot pressing at 1170°C at 20 MPa for 3 hours in an argon atmosphere, producing Ti_3SiC_2/Ti_5Si_3 in the joints. In the second set of samples, a tape calendaring process using organic binders and a mixture of TiC and Si powders (99.99% purity, TiC:Si ratio of 3:2) was used. 200 µm thick calendared tapes were pressed and heated between two SiC plates at 1425°C at 30 to 40 MPa applied pressure for 2 hours, producing Ti_3SiC_2/SiC in the joints. Samples were then neutron irradiated at the Flux Trap Facility in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory to 3.4 dpa and 5.0 dpa at temperatures of 500 and 800°C, respectively.

Post-irradiation examination was carried out in the Low Activation Materials Development and Analysis (LAMDA) laboratory at ORNL. Detailed examination in LAMDA included torsional shear strength evaluation and cross-sectional microstructural and micro-chemical analyses. Details of the shear strength

test procedure are given in reference [7]. Scanning electron microscope (SEM) examinations and analyses were performed using field-emission-gun SEM Hitachi Models S4700 and S4800 equipped with energy dispersive X-ray spectroscopy (EDS) systems. Transmission electron microscopy (TEM) foils were fabricated using an FEI Quanta Dual-beam focused ion beam (FIB)/SEM with a final thinning step of 2kV Ga^+ ions at a glancing angle of about 4° in order to minimize ion beam milling damage. Samples were then analyzed in a Phillips CM 200 TEM operating at 200 kV using the techniques of bright field (BF) imaging, selected area electron diffraction (SAED), high resolution TEM (HRTEM), and EDS performed in scanning TEM (STEM) mode.

Mechanical Properties

Torsional tests to determine joint shear strength of the irradiated samples was performed and recorded in the previous semi-annual report. Results are shown here as a reminder in Table 1.

Table 1. Torsional test (shear strength) results.

Joint	Strength, Unirradiated (MPa)	Failure Location, Unirradiated	Irradiation Condition	Strength, Irradiated (MPa)	Failure Location, Irradiated
Ti_3SiC_2/Ti_5Si_3	124 (23)	Joint (Full/Partial)	500°C, 3.4 dpa	125 (36)	Joint (Full/Partial)
Ti_3SiC_2/SiC	117 (10)	Basal Plane	800°C, 5.0 dpa	98 (22)	Joint (Full)

Microstructure

In the previous semi-annual report, we reported on microcracking and radiation-induced defect formation in the Ti_3SiC_2/Ti_5Si_3 sample. At that point, TEM analysis had yet to be performed upon the Ti_3SiC_2/SiC sample. That work will be discussed shortly, but some incongruous results between the two samples forced us to reconsider the work that had already been done.

Shown in Figure 1 is the sample irradiated at 500°C to 3.4 dpa that was ostensibly comprised of Ti_3SiC_2/Ti_5Si_3. The image shows a portion of a Ti_5Si_3 grain, which shows no irradiation defects at any diffraction or tilt conditions, and the presumed Ti_3SiC_2 grain, which exhibited a number of planar defects oriented along certain crystallographic directions in the material. However, the diffraction patterns taken did not correspond to an HCP material, the known crystal structure of Ti_3SiC_2 is, but rather an FCC material. Figure 1b was taken at a [110] FCC zone axis. Figure 2 shows the same diffraction pattern indexed with proper orientations, as well as the diffraction pattern taken from the same grain after orientation to the FCC [112] zone axis. Given the crystal type, the grains which had been presumed to be Ti_3SiC_2 were clearly not, instead they were likely FCC TiC.

EDS performed on the grains had initially been inconclusive, in part possibly due to inaccuracies in the estimated carbon concentration due to carbon being at the tail end of the EDS detector's range of detectability. EDS performed on unirradiated Ti_3SiC_2 had thus shown slightly higher than expected Ti and Si concentrations. Ti concentrations were measured at 60 at% versus 50 at% expected and Si was measured at 25 at% versus 17 at% expected, while C measured at just 16 at% versus 33% expected. Initial EDS measurements on the irradiated, presumed Ti_3SiC_2 grains had instead shown even higher than expected Ti concentrations, high C concentrations, and low Si concentrations. Reanalysis using a tighter beam area with a strict distinction between data points gathered in the bulk of the crystal versus in the planar defect areas resulted in the measurements shown in Table 2. Points noted in Table 2 refer to distinct spots shown in the HAADF image in Figure 3. EDS results showed the bulk of the grain to contain less than 5 at% Si, while the planar defects regions contained no carbon at all, instead appearing to be fully Ti and Si in a concentration that would indicate perhaps Ti_3Si_2.

Overall, this is a very interesting result because pre-irradiation characterization of the joint indicated combined concentrations of Ti_3SiC_2 and Ti_5Si_3 of greater than 99% in the joint. To find TiC with a form of titanium silicide inclusions indicates phase decomposition of the MAX phase during neutron irradiation. Further investigation is currently underway to confirm the TEM results via other experimental methods and to determine the reason for the transformation.

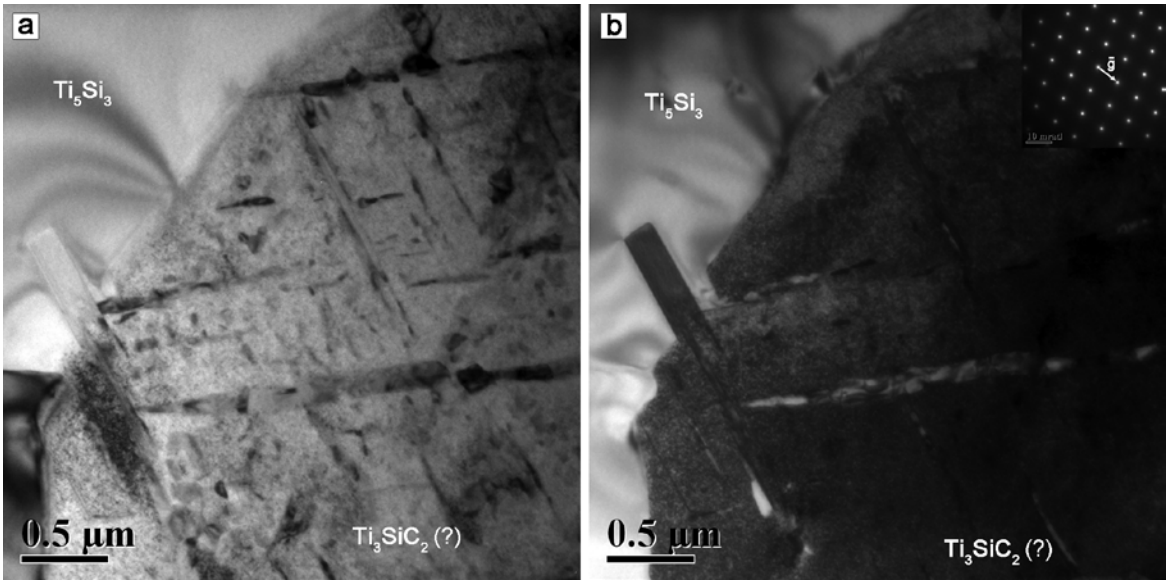

Figure 1. BF TEM images from the 'Ti_3SiC_2/Ti_5Si_3' sample irradiated to 3.4 dpa at 500°C. a) Both types of grains at an aribitrary diffraction condition. b) The same area tilted on zone with diffraction pattern inset.

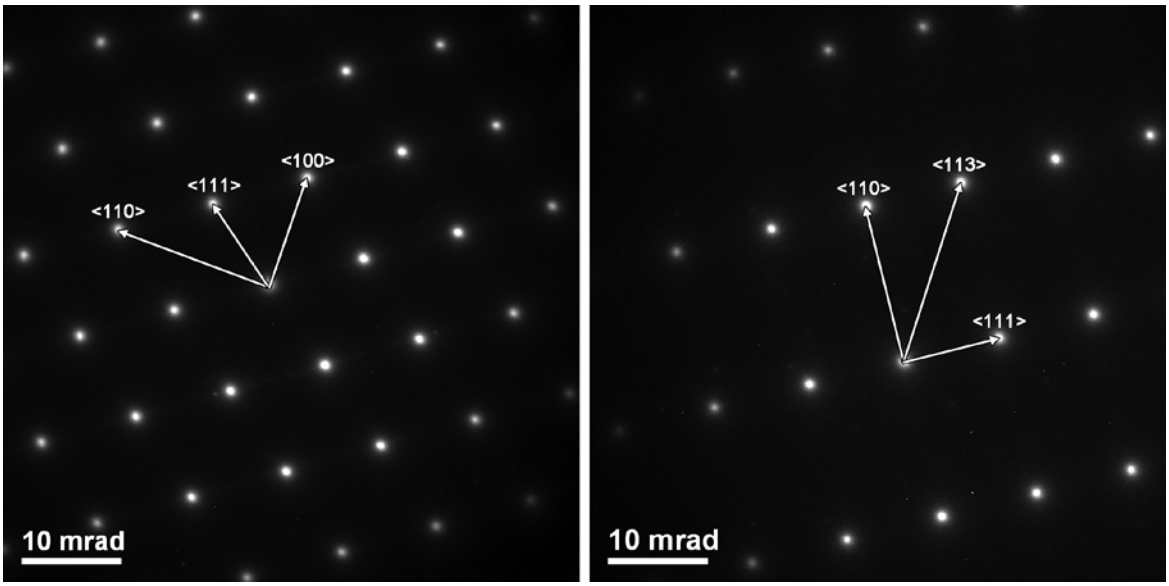

Figure 2. Diffraction patterns from the TiC grain – previously thought to be Ti_3SiC_2. At left, the FCC [110] zone axis. At right, the FCC [112] zone axis.

Table 2. Concentrations of elements measured by EDS in STEM mode from selected spots in Figure 3.

		Weight %:	Atomic %:			Weight %:	Atomic %:
1	Ti	92.1	76.3	3	Ti	69.6	57.4
	Si	1.3	1.8		Si	30.4	42.6
	C	6.6	21.9		C	-	-
2	Ti	89	71.2	4	Ti	69.8	57.5
	Si	3.4	4.6		Si	30.2	42.5
	C	7.6	24.2		C	-	-

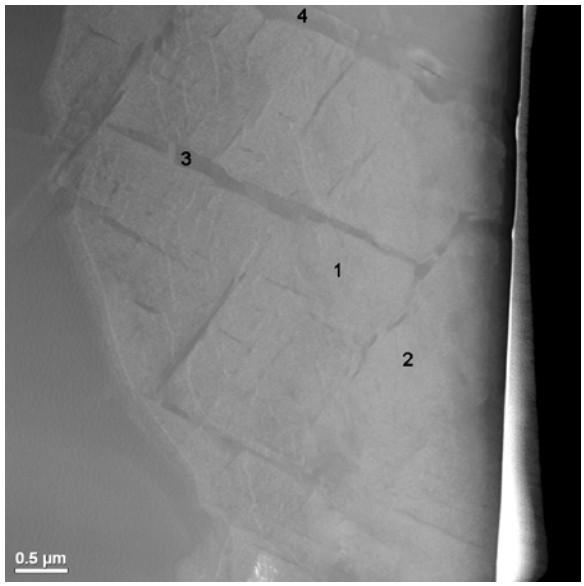

Figure 3. High angle annular dark field (HAADF) of the TiC grain showing spots chosen for EDS analysis, shown in Table 2.

The behavior of the Ti_3SiC_2 irradiated to 3.4 dpa at 500°C is more interesting when viewed in contrast to the sample irradiated to 5.0 dpa at 800°C. In this latter sample, EDS confirmed the presence of Ti_3SiC_2, with MAX phase grains containing concentrations of Ti, Si, and C all within a couple % points of the readings measured from the unirradiated MAX phase material. Due to the smaller size of the grains in this sample, individual diffraction patterns could not be taken and indexed, but grains were not so small as to produce quality ring patterns. Therefore, we have thus far not been able to confirm the phase of the grains via diffraction.

Overall, the 5.0 dpa sample was fairly unremarkable throughout. Microcracking was less significant in this sample than in the one irradiated to 3.4 dpa at 500°C with no cracks observed to propagate throughout the entire TEM sample. Numerous dispersed and disconnected cracks ranging from ~70 nm to several microns in length were noticed with a maximum observed transverse crack width of ~40 nm. Similar to the Ti_3SiC_2/Ti_5Si_3 sample, cracking was primarily transgranular, though a limited sample set of cracks made quantification of the precise amount difficult. While some radiation-induced defects were spotted both in the Ti_3SiC_2 and SiC portions of the sample, the density of the defects was fairly low, with black spot damage and stacking faults the primary defects spotted (Figure 4). The overall density of defects was much lower that seen in the TiC grain in the other sample.

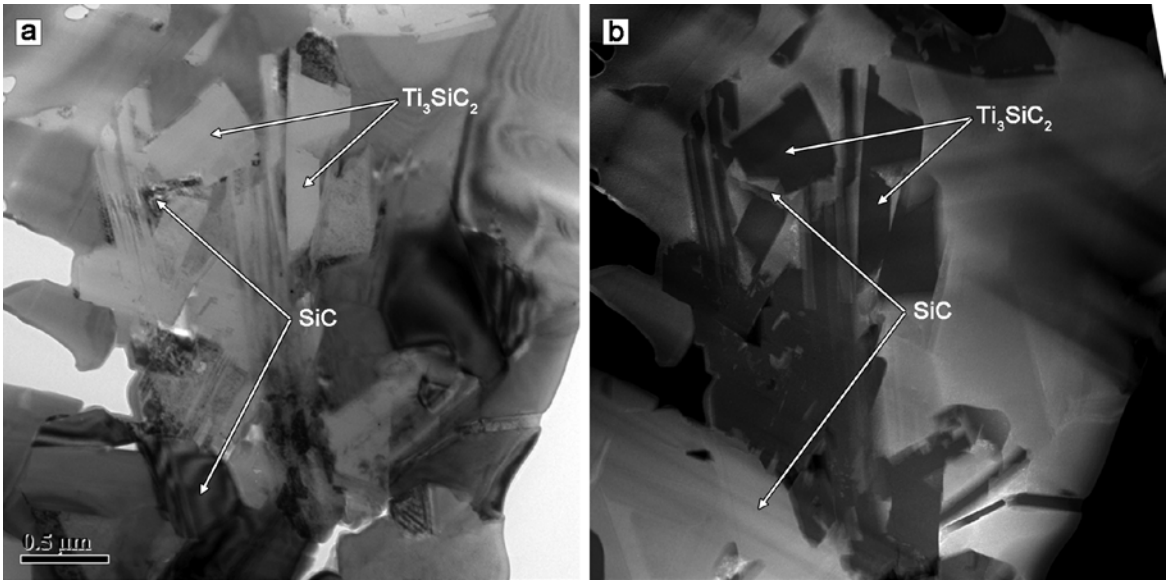

Figure 4. TEM images of the samples irradiated to 5.0 dpa at 800°C. a) BF and b) HAADF images. There was limited visible irradiation damage in the Ti_3SiC_2 grains, though some black spot damage and stacking faults were observed.

CONCLUSIONS

Microstructural evaluations showed a phase change in the Ti_3SiC_2/Ti_5Si_3 sample to TiC/Ti_5Si_3. This is an interesting development that merits further research and thought, especially given that Ti_3SiC_2 in the Ti_3SiC_2/SiC sample retained its phase following irradiation. Further work may be needed to determine the role of temperature in the irradiation-induced phase instability of Ti_3SiC_2.

REFERENCES

[1] W. Jeitschk and H. Nowotny, Monatsh. Chem. **98** (1967) 329-337.
[2] M.W. Barsoum and T. El-Raghy, J. Am. Ceram. Soc. **79** (1996) 1953-1956.
[3] M.W. Barsoum, Prog. Soild State. Chem. **28** (2000) 201-281.
[4] N. Tzenov and M.W. Barsoum, J. Am. Ceram. Soc. **83** (2000) 825-832.
[5] M.W. Barsoum and T. El-Raghy, American Scientist **89** (2001) 334-343.
[6] P. Eklund, M. Beckers, U. Jansson, H. Hogberg, and L. Hultman, Thin Solid Films **518** (2010) 1851-1878.
[7] M. Ferraris, M. Salvo, V. Casalegno, A. Ventrella, and M. Avalle, Int. J. Ceram. Appl. Technol. **9** (2012) 795-807.