7.4 Effects of Neutron Irradiation on Ti-Si-C MAX-Phase Ceramic Microstructures —

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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 applications.

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 the MAX phase ceramic Ti_3SiC_2 after neutron irradiation to 3.4 dpa and 5.0 dpa at temperatures of 500 and 800°C, respectively. Initial results showed large amounts of atomic-scale radiation damage in the material, but minimal loss of strength in selected Ti_3SiC_2/Ti_5Si_3 samples.

PROGRESS AND STATUS

Introduction

MAX phase ceramics are defined as 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. They have a have hexagonal crystal structure with the primary lattice consisting of M and A atoms and the sublattice consisting of X atoms in the interstitial spots (Figure 1). Though these unique carbide and nitride ceramics were first discovered in the 1960s [1], 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 and elucidated upon some of the material's unique mixture of metallic and ceramic properties [2]. Since then, interest in MAX phase materials has magnified greatly, with various MAX phase ceramics being reported to exhibit high modulus, low specific gravity, adequate machinability (as comparable to graphite), 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]. For potential fusion applications, it is also important to note that many of the compositions for MAX phase ceramics qualify as low activation materials [7].

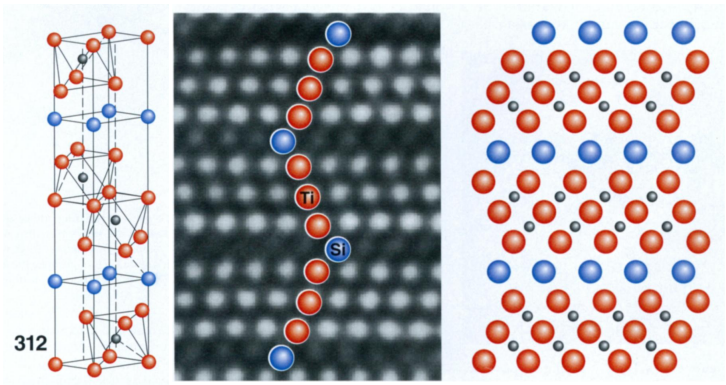

Figure 1. Crystal structure of a 312 MAX phase material (left), along with a HRTEM image of Ti_3SiC_2 (middle) and a diagram showing atomic configurations (right). Ti atoms are red, Si atoms blue, and C atoms grey [5].

By far, the most extensively studied MAX phase ceramic thus far has been Ti_3SiC_2, a member of the 312 family of MAX phases. Ti_3SiC_2 has been shown to exhibit high compressive strength (560-1000 MPa at room temperature, 200-260 MPa at 1200-1300°C) and tensile strength (200 to 300 MPa at room temperature), which is better than most monolithic ceramics, as well as fracture toughness comparable to or slightly higher than most ceramics (5 to 16 MPa-m$^{1/2}$ at room temperature) [3,4,8]. Ti_3SiC_2 also happens to possess a thermal conductivity comparable or superior to many engineering structural alloys (37 to 32 W/m-K as temperature is increased from room temperature to 1200°C), with the conductivity predominantly due to electronic conduction [9].

Perhaps the most promising aspect among the anticipated irradiation resistance of MAX phase ceramics, such as Ti_3SiC_2, is their potential to retain adequate thermal conductivity. Silicon carbide (SiC), which is otherwise a nearly perfectly irradiation resistant ceramic material, suffers a large decrease in thermal conductivity during irradiation due to the production of a very high density of radiation defects in the matrix, which are very effective in scattering the phonons that are predominantly responsible for heat conduction in silicon carbide [10,11]. Conversely, the thermal conductivity of MAX phase ceramics such as Ti_3SiC_2 is predominantly due to electronic conduction [8], which is only weakly affected by the presence of radiation defects [12,13].

Over the past several years, a number of new ion irradiation studies have been performed on Ti_3SiC_2 and Ti_3AlC_2, investigating damage tolerance, microstructural changes, mechanical properties, and thermal stability, among other properties [14-24]. Here, we investigate the effects of neutron irradiation upon the MAX phase ceramic 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) were used. Two hundred µm thick calendered 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 [25]. 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

The failure modes of primary interest in ceramic joints are shear and tension, and of these, shear is the more common mode of failure. While numerous methods can be used for shear strength determination of ceramic composite joints, only torsional tests are capable of producing true shear loading and are appropriate for testing lap-joined small specimens.

Therefore, torsional tests were chosen for determining joint shear strength in this study. In this document, nominal shear strength values (t_{th}) are reported as $t_{th} = 16T/\pi d^3$, where T = applied torque and d = specimen (fillet) diameter at the joint plane. Overall, Ti_3SiC_2/Ti_5Si_3 joints retained full strength after neutron irradiation, while Ti_3SiC_2/SiC joints saw a 16% drop in strength and a shift from basal failure to failure in the joint following irradiation. Full results are shown 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

SEM analysis of the unirradiated material revealed some major cracking through the thickness of the bonding layer as well as some porosity at the bond interface in the Ti_3SiC_2/Ti_5Si_3 sample. In the unirradiated Ti_3SiC_2/SiC sample, no cracking or porosity was observed. After irradiation, both samples exhibited increased microcracking throughout. A much more extensive

microstructural analysis than that provided here, including figures of the samples in question, has recently been published and is available in reference [26].

TEM analysis is currently in progress and has been partially completed on the Ti_3SiC_2/Ti_5Si_3 sample irradiated to 3.4 dpa at 500°C. Microcracking seen in initial SEM analyses was found to be primarily transgranular, though some cracking along Ti_5Si_3 grain boundaries was observed. No cracking was found along Ti_3SiC_2/Ti_5Si_3 grain boundaries, but due to the nature of the FIB sample, the sample size of observable Ti_3SiC_2 grains was very small. A composite image of the microcracks is shown in Figure 1.

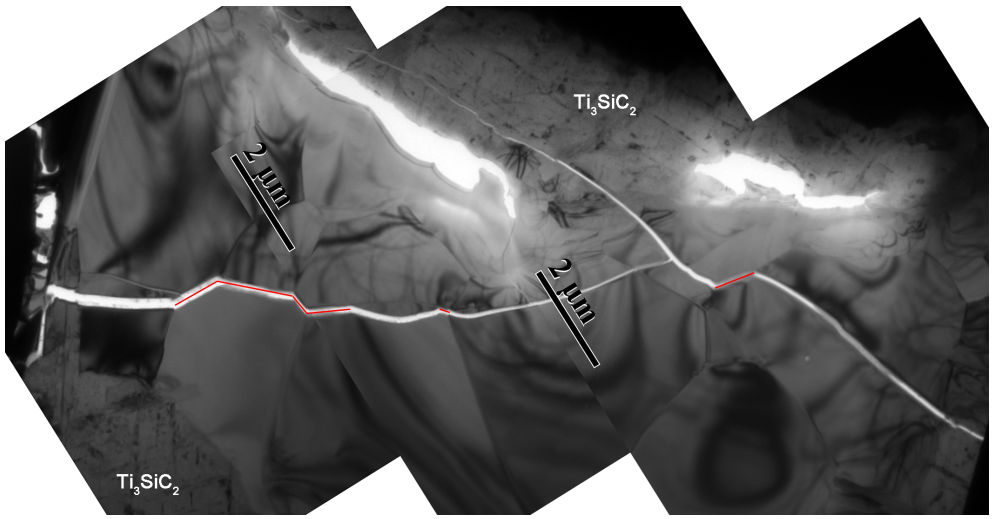

Figure 1. Microcracks in the Ti_3SiC_2/Ti_5Si_3 sample irradiated to 3.4 dpa at 500°C. Cracking along grain boundaries is marked in red. Ti_3SiC_2 grains are labeled. All other grains are Ti_5Si_3.

TEM also revealed extensive radiation-induced defect formation in the Ti_3SiC_2 MAX phase grains following irradiation, as shown in Figure 2. Figure 2a displays an unirradiated Ti_3SiC_2 grain that exhibits thickness fringes due to variations in sample thickness but exhibits no visible microstructural damage or defects. Figure 2b shows a Ti_3SiC_2 grain after irradiation, displaying numerous planar defects that are suspected to be stacking faults. Figure 3b then shows the same area as Figure 2b but at a diffraction condition where irradiation-induced dislocations and black spot damage are visible, and the damage is so dense as to turn the image of the sample nearly black. Surprisingly, the Ti_5Si_3 grains did not show any evidence of irradiation-induced defects of any kind, merely displaying thickness fringes as shown in Figure 1. Continued analysis of the Ti_3SiC_2 grains is ongoing, with compositional analysis and detailed analysis of defect structures upcoming.

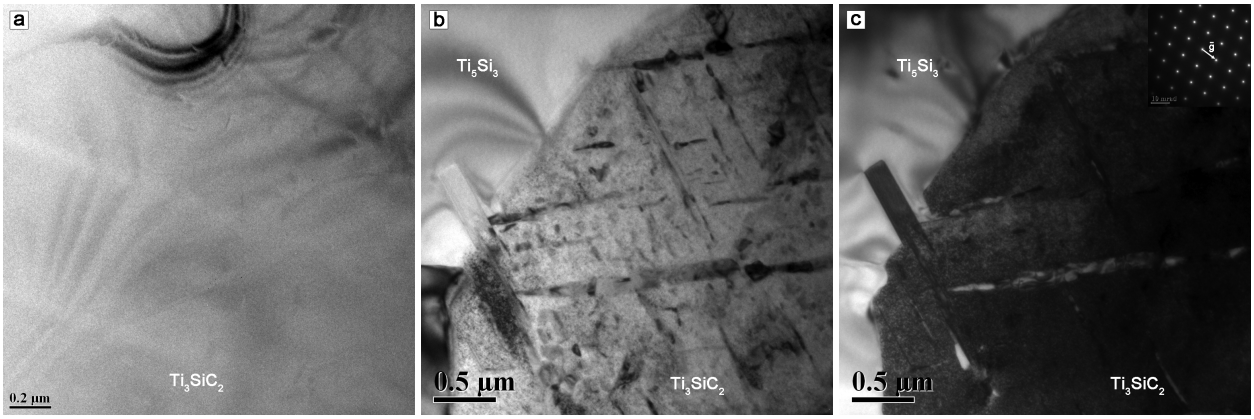

Figure 2. Bright field TEM images of a) unirradiated Ti_3SiC_2 and b,c) Ti_3SiC_2 irradiated to 3.4 dpa at 500°C. b) Numerous planar defects are visible at an arbitrary diffraction condition. c) Heavy dislocation damage is visible under 2-beam conditions.

Conclusions and Future Work

Mechanical property evaluations showed loss of strength in Ti_3SiC_2/SiC joints after neutron irradiation but not in Ti_3SiC_2/Ti_5Si_3 joints. Ti_3SiC_2/Ti_5Si_3 joints showed greater strength overall, both before and after irradiation. From a microstructural standpoint, extensive radiation damage was visible in Ti_3SiC_2 grains following neutron irradiation to 3.4 dpa at 500°C. Ti_5Si_3 grains, however, showed no evidence of irradiation damage.

While the sheer magnitude of irradiation-induced defects in the irradiated Ti_3SiC_2 grains is visually striking, density of defects is not necessarily indicative of poor radiation performance. As such, further microstructural analysis of Ti_3SiC_2, both in Ti_3SiC_2/Ti_5Si_3 and Ti_3SiC_2/SiC joints, is needed before the viability of Ti_3SiC_2 as a fusion material can be assessed.

Future work for this project includes additional TEM analysis, specifically on the Ti_3SiC_2/SiC joined specimen, as well as analysis of bulk Ti_3SiC_2 and Ti_2AlC currently being neutron irradiated to 2-10 dpa at 400-1000°C in HFIR.

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] E. N. Hoffman, D. W. Vinson, R. L. Sindelar, D. J. Tallman, G. Kohse, and M. W. Barsoum, *Nucl. Eng. Des.* **244** (2012) 17-24.
[8] M. W. Barsoum and M. Radovic, *Annu. Rev. Mater. Res.* **41** (2011) 195-227.
[9] M. W. Barsoum, T. El-Raghy, C. J. Rawn, W. D. Porter, H. Wang, E. A. Payzant, and C. R. Hubbard, *J. Phys. Chem. Sol.* **60** (1999) 429-439.
[10] L. L. Snead, *J. Nucl. Mater.* **329-333** (2004) 524-529.

[11] L. L. Snead, S. J. Zinkle, and D. P. White, *J. Nucl. Mater.* **340** (2005) 187-202.
[12] S. J. Zinkle, *J. Phys. F: Met. Phys.* **18** (1988) 377-391.
[13] S. J. Zinkle and S. A. Fabritsiev, *At. Plasma-Mater. Interact. Data Fusion* **5** (1994) 163-192.
[14] J. C. Nappe, Ph. Grosseau, F. Audubert, B. Guilhot, M. Beauvy, M. Benabdesselam, and I. Monnet, *J. Nucl. Mater.* **385** (2009) 304-307.
[15] M. Le Flem, X. Liu, S. Doriot, T. Cozzika, and I. Monnet, *Int. J. Appl. Ceram. Technol.* **7** (2010) 766-775.
[16] X. Liu, M. Le Flem, J.-L. Bechade, F. Onimus, T. Cozzika, and I. Monnet, *Nucl. Instrum. Methods Phys. Res. B* **268** (2010) 506-512.
[17] X. M. Liu, M. Le Flem, J. L. Bechade, and I Monnet, *J. Nucl. Mater.* **401** (2010) 149-153.
[18] K. R. Whittle, M. G. Blackford, R. D. Aughterson, S. Moricca, G. R. Lumpkin, D. P. Riley, and N. J. Zaluzec, *Acta Mater.* **58** (2010) 4362-4368.
[19] J. C. Nappe, C. Maurice, Ph. Grosseau, F. Audubert, L. Thome, B. Guilhot, M. Beauvy, and M. Benabdesselam, *J. Eur. Ceram. Soc.* **31** (2011) 1503-1511.
[20] J. C. Nappe, I. Monnet, Ph. Grosseau, F. Audubert, B. Guilhot, M. Beauvy, M. Benabdesselam, and L. Thome, *J. Nucl. Mater.* **409** (2011) 53-61.
[21] L. Zhang, Q. Qi, L. Q. Shi, D. J. O'Conner, B. V. King, E. H. Kisi, and D. K. Venkatachalam, *Appl. Surf. Sci.* **258** (2012) 6281-6287.
[22] L. F. Marion and I. Monnet, *J. Nucl. Mater.* **433** (2013) 534-537.
[23] C. Liu, L. Shi, Q. Qi, D .J. O'Conner, B. V. King, E. H. Kisi, X. B. Qing, and B. Y. Wang, *Nucl. Instrum. Methods Phys. Res. B* **307** (2013) 536-540.
[24] C. Wang, T. Yang, S. Kong, J. Xiao, J. Xue, Q. Wang, C. hu, Q. Huang, and Y. Wang, *J. Nucl. Mater.* **440** (2013) 606-611.
[25] M. Ferraris, M. Salvo, V. Casalegno, A. Ventrella, and M. Avalle, *Int. J. Ceram. Appl. Technol.* **9** (2012) 795-807.
[26] Y. Katoh, L. L. Snead, T. Cheng, C. Shih, W. D. Lewis, T. Koyanagi, T. Hinoki, C. H. Henager, and M. Ferraris, *J. Nucl. Mater.* (in press), http://dx.doi.org/10.1016/j.jnucmat.2013.10.002.