7.1 QUALITATIVE ANALYSIS OF COMMERCIAL $M_{n+1}AX_n$ PHASES UNDER NEUTRON IRRADIATION—

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OBJECTIVE

$M_{n+1}AX_n$ (MAX) phases are candidate ceramics for future nuclear applications, due to their potentially unique radiation tolerance and high fracture toughness. The report summarizes the data since DOE/ER-0313/58 and in particular, the data on mechanical feasibility, which has been the focus of the publications released in 2016.

SUMMARY

$M_{n+1}AX_n$ (MAX) phases are ternary nitrides and carbides. The materials studied were purchased from 3-ONE-2, LLC, and were previously characterized (see DOE/ER-0313/58). These were nominally "Ti_3SiC_2" and "Ti_2AlC" compositions irradiated to 2 x 10^{25} n/m^2 (E > 0.1 MeV) or ~ 2 dpa (based on the SiC displacement cross-section). After extensive characterization, weighted compositions were determined to be ~80% MAX phase. Irradiation temperatures were determined by passive dilatometry to have reached ~400, 630 and 700°C. After irradiation at ~400°C, swelling of Ti_3AlC_2-$Ti_5Al_2C_3$ material was 50% higher than Ti_3SiC_2, and this was reflected in the loss of room temperature equibiaxial fracture strength. The Si-containing MAX phase was more radiation resistant than the Al-containing material at lower temperatures. After irradiation at 630°C, electrical, thermal, and mechanical properties were unaffected. Lattice parameter swelling was mitigated at high temperature, but ~0.5-1% volumetric swelling was observed.

PROGRESS AND STATUS

Introduction

The attraction of $M_{n+1}AX_n$ (MAX) phases as engineering ceramics is due to their reversible slip-based deformation mechanism including kinking and delamination.[1] This mitigates catastrophic failure associated with brittle fracture. In these materials, the "A-layer" metal (Al or Si atoms) alternating between crystalline "MX" ceramic (TiC) unit cells results in good machinability, thermal and electrical conductivity. For radiation tolerance, the alternating layers represent a density of nanoscale interfaces that may function as natural sinks for mitigating defect accumulation that is responsible for degradation of materials under irradiation.[2] This seems to be verified by low activation energies for migration for interstitial defects and A-atom vacancies, modeled antisite accommodation of defects and the high energy barrier of migration through MX.[3,4] These layers should prevent growth in the c-axis. Specimens were irradiated at the High Flux Isotope Reactor (HFIR) in 2013 to 2, 6 and 10 dpa. After a delay of 12 months due neutron activation of Ti, investigation of mechanical properties (swelling, elastic modulus, fracture strength), morphology (microcracking, changes in interfaces) and microstructure (irradiation-induced defects, lattice expansion, phase changes) commenced on the ~2 dpa specimens in early 2015. The acquired materials were sufficient for screening of suitable MAX phases.

Experimental Procedures

Details on these experiments have been reported in DOE/ER-0313/55 and /58.

<u>X-ray analysis</u>
X-ray characterization of the compositions included Rietveld analysis of XRD data by GSAS™, TOPAS™ v4.2 and use of CrystalDiffract™ Suite. Crystallite size and strain were calculated by Williamson-Hall method. Both MAX phases have a HCP crystal structure. The Ti_3SiC_2 material was a ceramic composite of Ti_3SiC_2-20TiC-6$TiSi_2$. The morphology of the phases was high-aspect ratio Ti_3SiC_2 and equiaxed TiC grains, with remaining intermetallics wetting the surfaces of the grains, which indicated an excess of C

and/or insufficient reaction kinetics (since the residual is ~3:Ti:Si:3C). Nappe et al used material from the same vendor, but a different batch, which suggested a systematic issue.[5-8] The Al-containing MAX phase was carbon depleted and had several other stable phases after sintering, and was calculated to be Ti_3AlC_2-$Ti_5Al_2C_3$ with ~6 wt% Ti_5Al_{11}. Irradiation temperatures were designed for 400, 700 and 1000°C but the latter capsule appeared to undergo axial heat loss, and monitors showed that it did not reach the target temperatures. Dilatometer measurement of CVD SiC passive temperature monitors yielded CTE inflections of defect annealing at ~400, 630 and 700°C for end of cycle temperatures. This mid-value of 630°C was actually serendipitous as it appeared that recovery of lattice parameter swelling occurred between these temperatures.

Swelling

As a previous paper reported, after irradiation at ~400°C the swelling of Ti_3AlC_2-$Ti_5Al_2C_3$ was anisotropic with a change in the c-axis (Δc/c) of 3% and a change in the a-axis (Δa/a) of 1% for both Al-phases.[9] Ceramics have low strain to failure, and these values are sufficient to introduce cracks in a ceramic. The volumetric swelling of larger (25 x 1.5 x 2 mm) coupons indicated a 4% increase in volume. Due to this cracking, post-irradiation fracture strength was ~10% of as-received values. At the same irradiation temperature of ~400°C, retained room temperature strength of Ti_3SiC_2 was 66% of as-received values. Figure 1 shows a photograph of the fractured materials; note that the peening depression in (a) indicates almost no compression-tension flexure took place on the outer-ring fulcrums compared to the (b) Ti_3SiC_2 material.

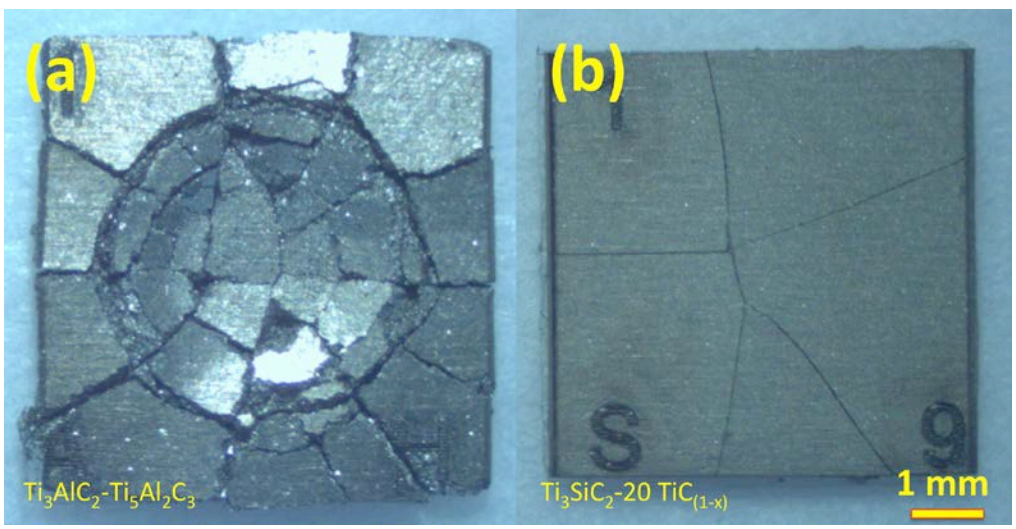

Figure 1. Low temperature irradiated (a) Ti_3AlC_2-$Ti_5Al_2C_3$ and (b) Ti_3SiC_2-20TiC after equibiaxial fracture. The measured strength in (a) was 30 MPa, or less than ~20 N applied force.

The fracture surfaces also indicated that something had occurred to negate the kinking-delamination mechanism. A smaller value of Δc/c of 1.5% was observed for Ti_3SiC_2, and minimal a-axis shrinkage. Compared to the Al-containing MAX phase, this showed that defect accumulation was different in either microstructure or physical siting of displaced defects. The measured swelling of only ~0.7% would seem to indicate the absence of swelling from other phases. As expected, lattice parameter swelling was mitigated at high temperature, but volumetric swelling was still observed at ~0.5-1% in both materials.

Properties after irradiation

Electrical resistivity increased by 15x in Ti_3AlC_2-$Ti_5Al_2C_3$ and less than 4x in Ti_3SiC_2, which also suggested Al and Si-layer disruption, and further showed the difference between the two material compositions. Above irradiation temperatures of ~630°C, in both materials, electrical, thermal, elastic modulus and strength were unchanged compared to as-received values. Thermal diffusivity data showed that recovery of the defects responsible for thermal conduction returned more abruptly for Al- than the Si-

MAX phase. In summary, it appeared that displacement of A-layer atoms resulted in anisotropic swelling and significant detrimental effects on all desirable properties.

Equibiaxial strength and fracture surfaces

The analysis indicates an abrupt change in fracture strength and fracture surface appearance between ~400 and 630°C. The equibiaxial ring-on-ring fracture strength testing was conducted using multipurpose square coupons (Figure 1) at room temperature according to ASTM C1499. Figure 2 shows the fracture strength from three coupons at each irradiation temperature for Ti_3AlC_2-$Ti_5Al_2C_3$, and it shows an obvious difference caused by temperature. Note that the materials irradiated at ~630-700°C show minor variations, indicating that the phenomenon that affects mechanical properties changes between 400-630°C. The dotted line shows the swelling value at each irradiation temperature.

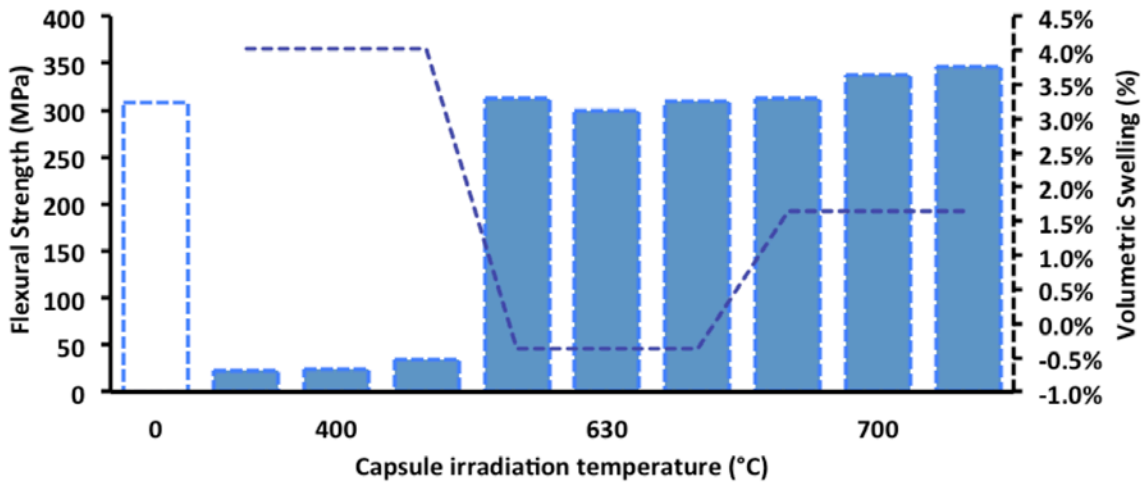

Figure 2. Equibiaxial fracture strength values of Ti_3AlC_2-$Ti_5Al_2C_3$ materials at their respective initial condition and after irradiation at selected temperatures. Swelling is shown by the dotted line from multipurpose bars irradiated in the same capsule.

Figure 3(a) shows a fracture in the unirradiated material, exhibiting a combination of delamination of kink-bands and microcracking. The kink-bands are the parallel striations in the long axis of the grain, which are observed when delamination occurs between these parallel regions. Figures 3(b) and (c) show the difference in the fracture surfaces of the samples irradiated at ~400°C and ~700°C respectively for Ti_3AlC_2-$Ti_5Al_2C_3$ material. In Figure 3(b), flat facets and transgranular cracking progressed through the morphology and explains the low strength values seen in Figure 2(a). Most of the microstructure is dominated by microcracking, shown at lower magnification than the unirradiated case of Figure 3(a). This explains why the depression in the optical micrograph in Figure 1(a) shows the morphology of a powder compact. The microcracks are so large that the samples irradiated at ~400°C had effectively no cohesion.

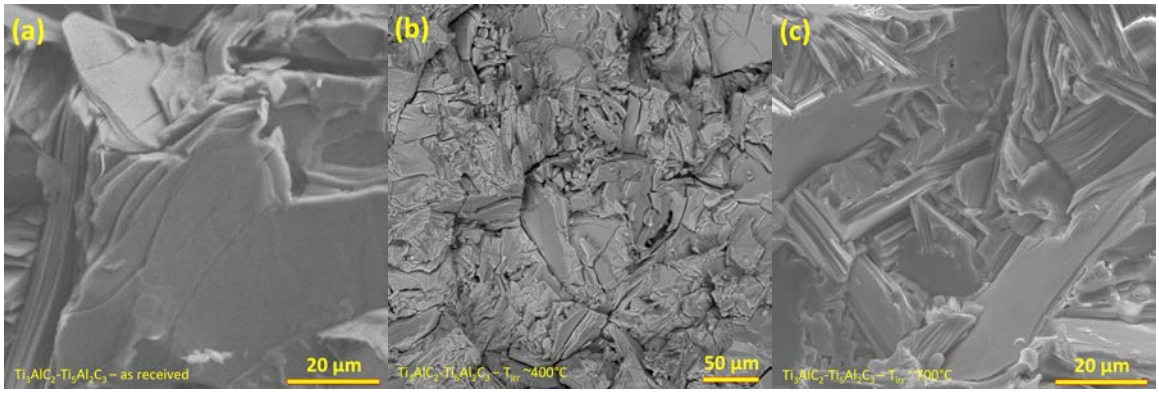

Figure 3. Ti_3AlC_2-$Ti_5Al_2C_3$ fracture surfaces (a) as-received and after being irradiated at (b) ~400°C and (c) ~700°C followed by equibiaxial test.

In Figure 3(c), the kink-bands and smaller facets are clearly obvious and appear to show a normal fracture pattern similar to Figure 3(a). As before, the facets are sub-grain size, show parallel striations with identical morphology to the kink-bands in Figure 3(a). Fracture after irradiation at ~700°C thus expends a significant amount of energy in making kinks unstable. This indicates that there is no change in fracture mechanism, which has been emphasized in recent publications.[10,11]

Results

MAX phases appear to respond under irradiation consistent with behavior of other HCP ceramics, accumulating defects that expand the c-axis. The recovery of the A-atom displacement damage appears to occur at a relatively low temperature of ~500-600°C and is thus responsible for unchanged properties. Fracture surfaces indicate that the kinking-delamination is not operational after irradiation temperatures of ~400°C. Ti_3SiC_2 performs slightly better at these temperatures. Coupled with the substantial lattice parameter and volumetric swelling, this indicates MAX phases are suitable for the higher temperature systems, and is more suitable as a fusion system material rather than for the “lower temperature” fission reactors.. Further data is required. Since the original FOA included ~6 and ~10 dpa specimens, a tentative plan exists to examine these (6 x 6 x 0.5 mm) coupons for (XRD) lattice parameter swelling to confirm saturation, morphology (SEM) and volumetric swelling. Further investigation will continue as resources are available.

Acknowledgements

The authors would like to thank Patricia Tedder, Brian Eckhart, Bill Comings, Ashli Clark, Jordan Couch, Michael McAllister and Felipe Mora for sample preparation and technical support. Particular thanks to Kenny Curtis, Jeremy McKinney and Becky Johnson for contamination control and activated materials handling. This research used equipment at the Low Activation Materials Development and Analysis (LAMDA) and the High Temperature Materials Laboratory (HTML) facility. Research was sponsored by the Office of Fusion Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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