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Feature article

Microstructure and mechanical properties of titanium aluminum carbides neutron irradiated at 400–700 °C☆

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ABSTRACT

This work reports the first mechanical properties of Ti_3AlC_2-$Ti_5Al_2C_3$ materials neutron irradiated at ~400, 630 and 700 °C at a fluence of 2×10^{25} n m^{-2} (E > 0.1 MeV) or a displacement dose of ~2 dpa. After irradiation at ~400 °C, anisotropic swelling and loss of 90% flexural strength was observed. After irradiation at ~630–700 °C, properties were unchanged. Microcracking and kinking-delamination had occurred during irradiation at ~630–700 °C. Further examination showed no cavities in Ti_3AlC_2 after irradiation at ~630 °C, and MX and A lamellae were preserved. However, disturbance of (0004) reflections corresponding to M-A layers was observed, and the number density of line/planar defects was ~10^{23} m^{-3} of size 5–10 nm. HAADF identified these defects as antisite Ti_{Al} atoms. Ti_3AlC_2-$Ti_5Al_2C_3$ shows abrupt dynamic recovery of A-layers from ~630 °C, but a higher temperature appears necessary for full recovery.

1. Introduction

Ti_3AlC_2 is a material known as a $M_{n+1}AX_n$ (MAX) phase, where M is an early transition metal, A is an A-group element (e.g., Al, Si) and X is either C or N [1]. The combination of metallic and ceramic properties is associated with the nanolamellar structure of M-X and M-A layers. The high fracture toughness values (of up 10 MPa m^{½} compared to values of ~4 MPa m^{½} in monolithic SiC, for example) [2] are the result of delamination from the M-A layers within grains, coupled with diffuse intragranular microcracking, high-aspect ratio grain interlocking and push/pull-out mechanisms [3–5]. The key properties of interest for fission and fusion applications are the A-layer derived electronic thermal conductivity, high monolithic fracture toughness, and potential radiation resistance [6–8].

As a result, extensive ion irradiations of Ti_3AlC_2 and Ti_3SiC_2 have been supplemented by recent neutron irradiations. The results have been broadly consistent. *Ab initio* studies predicted that defect accumulation would occur in M-A layers [9], and this is confirmed by a ~20% decrease in electrical conductivity attributed to A-layer damage even at 0.1 displacements per atom (dpa) at ~360(20) °C [10]. The defect accumulation caused anisotropic lattice parameter (LP) expansion in Ti_3SiC_2 [11]. For Ti_3AlC_2 anisotropic LP expansion is 50% higher at room temperature ion irradiations, and neutron irradiations at 400 °C, and unlike Ti_3SiC_2, large values of a-axis shrinkage is also observed [10,12–14]. Mechanical properties are highly influenced by defect induced swelling. Ti_3AlC_2 and Ti_2AlC after neutron irradiation at ~400 °C at 2 dpa and 0.1 dpa respectively report microcracking, and irradiated Ti_3AlC_2-$Ti_5Al_2C_3$ reported low fracture strengths of ~30 MPa [15,16]. Additional mechanical data is lacking due to the small size of ion-irradiated samples (<10 × 10 mm) [17,18].

After neutron irradiation at ~695(20) °C, Ti_3AlC_2 and Ti_2AlC showed no lattice parameter changes, and electrical properties appeared unchanged [10]. This manuscript focuses on Ti_3AlC_2,–$Ti_5Al_2C_3$ irradiated at the dynamic recovery range of 400–700 °C, and discusses the effect of neutron irradiation to a higher displacement dose of ~2 dpa on elastic modulus, fracture strength, swelling, density and phase stability. In particular, the effect of A-atom displacement on fracture strength, macroscopic swelling and the early "recovery" microstructure is discussed.

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2. Experimental

The experimental details have been previously published [11,16], and the materials characterization is included in the results. Materials were machined into beams (25 × 2 × 1.5 mm) for dimensional swelling, density and elastic modulus measurements. Square discs (6 × 6 × 0.5 mm) were used for X-Ray Diffraction (XRD), equibiaxial fracture, density measurements and electron microscopy. Samples were inserted into previously described irradiation capsules; due to non-symmetry, the beams may have experienced a higher temperature (+25 °C). Samples were exposed to a neutron fluence of 2×10^{25} n m^{-2} (E > 0.1 MeV) or ~2 dpa at ~400 °C, ~630 °C and 700 °C at a damage rate of 4.5–6 × 10^{-7} dpa s^{-1} based on the conversion for SiC [19].

Volumetric swelling was measured using beams. Length was measured from vertexes and the average value taken to be equal to the length of the specimen. Four measurements were also taken of the height and width, and the lowest standard deviation (usually not the length value) was ± 3 μm. Dynamic Young's modulus was determined using the impulse excitation and vibration method (by ASTM C1259) on beam specimens. Poisson's ratio is typically 0.2 (c.f. Tzenov and Barsoum) but their material was >95% Ti_3AlC_2 with Al_2O_3 impurities [20]. Due to the presence of softer intermetallics, a value of 0.21 was used.

XRD patterns were acquired using Cu Kα (40 kV, 40 mA) radiation with a Scintag Pad V system on square discs placed on a zero-background (SiO_2 Optical Grade from MTIXTI) mount. Due to substantial difficulties in characterization, a Bruker D2 Phaser and a Phillips X'pert Diffractometer were also used in conjunction with three software suites: PANalytical HighScore Plus (HS+), Bruker TOPAS 4.2 and GSAS [21]. Independent lattice parameters (without structure) were obtained using TOPAS 4.2 using a Le Bail et al. fit for all phases [22]. Samples used an internal Si SRM640b for lattice parameter refinements. Microstrain and crystallite size for Ti_3AlC_2 and $TiC_{(1-x)}$ were determined by Williamson-Hall method from GSAS data [23].

Archimedes density (by ASTM B962) used 3M Fluorinet Liquid FC-43 as the suspension and immersion medium. Room temperature equibiaxial flexural strength (by ASTM C1499) was conducted to obtain Weibull statistics on 32 unirradiated specimens. The probability of failure due to flaws in processing is given by;

$$P = 1 - \exp\left(\frac{-1}{V}\int_V^1 \left(\frac{\sigma}{\sigma_0}\right)^m dV\right)$$

where V is the characteristic volume, m is the Weibull shape parameter, σ_0 is the characteristic strength or scale parameter. In order to obtain *m*, a population of 32 unirradiated specimens was plotted to:

$$\ln\left(\ln\frac{1}{(1-P(f))}\right) = m\ln(\sigma_i)$$

where P_f is the probability of failure (using the median (i – 0.3)/(n + 0.4) i^{th} ordered failure specimen and n is the population), and σ_i is the failure stress of the i^{th} specimen [24]. After irradiation, the equibiaxial strength was conducted on a minimum of 3 specimens. The crosshead speed was 0.1 mm min^{-1}, with slack (minimum) load of 5 N. Tests were validated as per Kondo et al.; as biaxial testing removes edge effects from relatively small specimens, avoidance of tensile stress magnification in the region between load ring and outer support ring is necessary [24]. Prevention of outer overhang of the sample from moving toward the center causes lower failure stresses with cracks initiating from the overhang, and thus validation of the test should be demonstrated by fractures initiating in the central load area [24]. Scanning Electron Microscopy (SEM) was conducted on polished and fracture surfaces with a JEOL 6500F [24,25].

Unirradiated materials were analyzed in high-angle annular dark-field (HAADF) mode on the FEI Titan G2 aberration-corrected STEM at North Carolina State University, Analytical Instrumentation Facility. The instrument was operated at 200 kV accelerating voltage. On irradiated samples, STEM was conducted using an FEI Talos F200X S/TEM at 300 kV, equipped with four detectors ((HAADF), medium-angle annular dark field, low angle annular dark field, and bright field). The annular detectors are collectively referred to as HAADF. Foil thickness was derived using "Absolute Thickness" method by Egerton et al. [26,27] Number densities (N_d) were counted using a 50 × 50 nm region. All images were captured using a high-speed, high-resolution (4096 × 4096 pixel) TEM camera system.

3. Results

3.1. Density and swelling

Table 1 shows density and dimensional data for all three irradiation temperatures. Dimensional swelling is (L)ength, (W)idth and (H)eight components and the multiple represents the (V)olumetric swelling. Archimedes density decreased after irradiation at ~400 °C and was relatively unchanged after irradiation at ~630 and ~700 °C based on two samples per irradiation condition.

It can be observed from Table 1 that:

- Density and swelling have the correct negative relationship as expected, but there are significant margins; at ~400, 630 and 700 °C, there are differences of +1.1%, −0.6% and +1.2% respectively when comparing the volumetric swelling to Archimedes density.
- These differences can be caused by porosity, densification and phase changes, but are difficult to verify due to limited pattern fitting in the XRD data.
- All materials are polycrystalline without preferred orientation since they were pressurelessly sintered, so the L, W, H and V components of the 25 × 2 × 1 ½ mm beams show the same trend.

After irradiation at ~400 °C, density decreased and volumetric swelling increased, consistent with open pore volume from swelling and microcracking [16]. From irradiations at 630–700 °C densification of the intermetallic could be responsible for the changes in density and swelling and are interpreted as a 0.5–1% macroscopic swelling for the higher irradiation temperatures.

3.2. Morphology

Fig. 1(a) shows the morphology of the Ti_3AlC_2-$Ti_5Al_2C_3$ as-machined and polished. Back-Scattered Electron (BSE) images are provided for phase differentiation. The MAX phase is the high-aspect ratio grains up to ~50 μm in length. A slight change in channeling contrast in MAX grains reveals the c-axis contrast. Channeling contrast is indicative of a chemistry and stacking change, such as Ti_3AlC_2 to $Ti_5Al_2C_3$. The intermetallic phase is the darker intergranular regions.

Fig. 1(b) shows transgranular microcracking after irradiation at ~400 °C as previously reported [16]. Fig. 1(c) shows the material after irradiation at ~630 °C. Microcracking was confined within grains, and the major difference in morphology to the unirradiated material was delaminations indicated by the white arrows. The delamination and microcracks increased in density after irradiation at ~700 °C (Fig. 1(d)).