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High temperature ion irradiation effects in MAX phase ceramics

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ABSTRACT

The family of layered carbides and nitrides known as MAX phase ceramics combine many attractive properties of both ceramics and metals due to their nanolaminate crystal structure and are promising potential candidates for application in future nuclear reactors. This investigation examines the effects of energetic heavy ion (5.8 MeV Ni) irradiations on polycrystalline samples of Ti_3SiC_2, Ti_3AlC_2, and Ti_2AlC. The irradiation conditions consisted of midrange ion doses between 10 and 30 displacements per atom at temperatures of 400 and 700 °C, conditions relevant to application in future nuclear reactors and a relatively un-explored regime for this new class of materials. Following irradiation, a comprehensive analysis of radiation response properties was compiled using grazing incidence X-ray diffraction (XRD), nanoindentation, scanning electron microcopy (SEM), and transmission electron microscopy (TEM). In all cases, XRD and TEM analyses confirm the materials remain fully crystalline although the intense atomic collisions induce significant damage and disorder into the layered crystalline lattice. X-ray diffraction and nanoindentation show this damage is manifest in anisotropic swelling and hardening at all conditions and in all materials, with the aluminum based MAX phase exhibiting significantly more damage than their silicon counterpart. In all three materials there is little damage dependence on dose, suggesting saturation of radiation damage at levels below 10 displacements per atom, and significantly less retained damage at higher temperatures, suggesting radiation defect annealing. SEM surface analysis showed significant grain boundary cracking and loss of damage tolerance properties in the aluminum-based MAX phase irradiated at 400 °C, but not in the silicon counterpart. TEM analysis of select samples suggest that interstitials are highly mobile while vacancies are immobile and that all three materials are in the so-called point defect swelling regime between 400 and 700 °C. All results are consistent with previous work involving traditional and MAX phase ceramics. Results show the aluminum MAX phases are not fit for application near 400 °C and that the silicon MAX phase is more damage tolerant at 400–700 °C.

1. Introduction

Currently, one of the largest technical challenges in the nuclear energy industry is with respect to neutron radiation-induced degradation of materials properties. The materials used in existing nuclear reactors provide the basis for and greatly influence the reliability, safety, and economics of these reactors. Power up-rates, reactor lifetime extensions, and fuel integrity are but a few specific examples that are directly affected by material concerns. Material challenges are also expected to be major roadblocks to the development of future fission (Generation IV) reactors and fusion reactors, which generally require materials to reliably operate at higher temperatures and/or radiation damage levels compared to existing water-cooled commercial power reactors. Due to this, there is a renewed interest in advanced and innovative nuclear materials research [1,2].

A promising but as yet unproven class of material known as MAX Phase Ceramics (or simply MAX Phases) represents a relatively new class of solids best described as *thermodynamically stable nanolaminates*. MAX Phases are a family of layered compounds with chemical formula $M_{n+1}AX_n$, where M is an early transition metal, A is an element from the IIIA or IVA groups, X is carbon or nitrogen, and $n = 1, 2$, or 3 [3–7]. The atomic stacking is based on a layered hexagonal close packed (HCP) crystal structure with alternating layers of close-packed M-atoms and X-atoms filling octahedral sites (comprising a formula identical to those found in the rock salt structure of MX binaries), and layers of pure A-group elements. Due

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to their unique crystal structure, MAX phases combine many attractive properties of both ceramics and metals. These properties include high temperature stability, high stiffness, good electrical and thermal conductivity, fracture toughness, thermal shock resistance, and machinability [3–7]. Certain MAX phases also promise good oxidation resistance and chemical compatibility [8]. Due the MAX phases' unique combination of high temperature stability, stiffness, conductivity, corrosion resistance, machinability, and possible radiation tolerance, they are currently being considered as a possible advanced nuclear material for a variety of applications, including current generation fission light water reactors (LWRs), future generation (Gen. IV) fission, and proposed fusion reactors. Proposed applications include: oxidation-resistant spray-on coating for cladding, piping, and steam generator tubes in current LWR systems, structural material piping and core internals in advanced fission reactors due to high chemical compatibility with select coolants such as molten lead and sodium, high temperature, high dose cladding material for future generation fission reactors, and high temperature, high dose structural materials for future generation fission and fusion reactor systems [9,10].

Due to their relatively recent discovery, the radiation response mechanisms of the MAX phase ceramics are still largely unexplored, with studies only emerging in publication within the last half decade. Though the majority of studies to date have only focused on the low dose, low temperature irradiation regime, some basic conclusions regarding their radiation response can still be drawn. The first and most basic conclusion is that the MAX phases are expected to follow physical and mechanical property radiation-induced change trends similar to those seen in traditional HCP ceramics. Secondly, previous experiments suggest that the MAX phases are generally resistant to amorphization up to doses of ~25 displacements per atom (dpa) following irradiation between 25 and 500 °C. This has been confirmed using selected area electron diffraction (SAED) and transmission electron microscopy (TEM) imaging techniques in Ti_3SiC_2 and Ti_3AlC_2 at ~25 dpa [11] and using SAED, TEM, x-ray diffraction (XRD), and nanoindentation for Ti_3SiC_2 at lower damage levels (~5 dpa) for multiple irradiation conditions between RT and 500 °C. Since radiation-induced amorphization typically only occurs at relatively low temperatures where interstitial point defects are immobile [12], amorphization is not expected to be an issue at fission and fusion reactor-relevant temperatures of ~300–1000 °C [3,10,11,13–18]. Additionally, there is no evidence of void formation in Ti_3SiC_2 and Ti_3AlC_2 up to 500 °C and ~25 dpa [11], suggesting that vacancies are immobile below 500 °C (or else void nucleation and growth is strongly suppressed). These two factors hint that 25 and 500 °C in MAX phases correspond to temperatures above recovery Stage I (onset temperature for interstitial motion) and below recovery Stage III (onset temperature for vacancy motion), respectively [12,19]. Finally, XRD, TEM and nanoindentation results suggest that the MAX phases have a positive correlation between temperature and radiation damage recovery. This is manifest in a progressive decrease in crystalline lattice disorder and defect cluster density with increasing irradiation temperature by XRD and TEM [13–16,20], as well as a pronounced decrease in nanoindentation hardness at higher irradiation temperatures [10,18]. Collectively, these observations are consistent with mobile interstitials and immobile vacancies ("point defect swelling" regime). One of the characteristics of the point defect swelling regime is that damage accumulation approaches a saturation level at doses above 0.1–1 dpa due to the high concentration of immobile vacancies that serve as recombination centers for the migrating interstitials [12]. Hence, it is hypothesized that the MAX phases may have substantial radiation resistance up to relatively high damage levels between 25 and 500 °C or higher.

2. Experimental procedure

2.1. Material

The MAX phase bulk samples used in this experiment were synthesized at Drexel University; a detailed explanation of the synthesis and processing conditions is discussed elsewhere [21,22], but an abbreviated description is as follows. The Ti_2AlC samples were prepared by pouring pre-reacted Ti_2AlC powders (Kanthal, Hallstahammar, Sweden) into graphite dies, which were loaded into a vacuum hot press and hot pressed for 4 h under a load corresponding to a stress of ~40 MPa and a vacuum pressure of 10–1 Pa at a temperature of 1300 °C. The Ti_3AlC_2 samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti_2AlC and TiC powders (Alfa Aeser, Ward Hill, MA, USA) for 24 h and in turn, hot pressed at 1400 °C for 4 h. Finally, the Ti_3SiC_2 samples were prepared by ball milling stoichiometric mixtures of Ti, Si, and C powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h, which were then hot pressed at 1450 °C for 4 h [20].

In preparation for the experiment, the bulk samples received from Drexel were subsequently sectioned with a low speed diamond saw, cut into ~3 mm diameter disks, ground to ~0.6 mm thickness, and polished using diamond lapping film and colloidal silica suspension on polishing cloth. After the final polishing, the 3 mm diameter disk samples had a nominal final thickness of 0.55 mm.

2.2. Irradiations

The samples were irradiated to midrange doses of 10 and 30 dpa, at temperatures of 400 and 700 °C, at the Texas A&M Accelerator Laboratory using 5.8 MeV Ni^{4+} ions at a particle flux of ~3×10^{11}/cm^2-s (~1.4×10^{-4} dpa/s at a midrange depth of ~1.4 μm). The correlation between ion fluence and dpa was determined using SRIM 2013 with recommendations from Stoller et al. [23], and an assumed threshold displacement energy of 30 eV. A graphic of normalized dpa vs. ion penetration depth for all three materials can be seen in Fig. 1, with the selected area for post-irradiation analysis defined by the red box. Irradiated regions associated with the peak damage region (~3 μm depth) were avoided in the post irradiation analysis due to potential complications associated with implanted Ni ions. Similarly, regions near the surface were avoided due to potential artifacts. A list of irradiation conditions and corresponding ion fluences for the four dose-temperature conditions can be seen in Table 1.

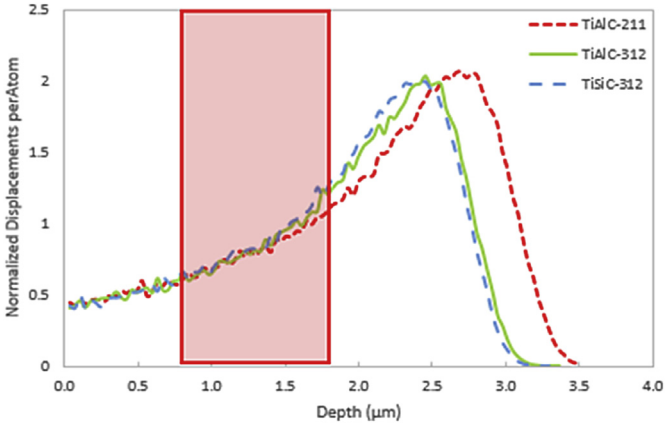

Fig. 1. Normalized damage versus depth profiles for 5.8 MeV Ni^{4+} ion irradiated MAX phase ceramics.