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Effects of ion irradiation on structural and mechanical properties of crystalline Fe/amorphous SiOC nanolaminates

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Irradiation-induced changes in the structural and mechanical properties of nanocrystalline Fe, amorphous silicon oxycarbide (SiOC), and Fe/SiOC nanolaminate films were studied using X-ray diffraction, atomic force microscopy, scanning/transmission electron microscopy, and micro/nanoindentation. The films were fabricated by magnetron sputtering and then irradiated at room temperature with 3.5 MeV Fe ions to damage levels of 10, 20, or 50 displacements per atom (dpa). Irradiation of the Fe films was found to increase the compressive residual stress and hardness. For the SiOC films, irradiation led to densification and a subsequent increase in elastic modulus and hardness. The as-deposited Fe/SiOC nanolaminate with individual layer thicknesses of 72 $\pm$ 10 nm exhibited a higher hardness compared to the Fe and SiOC films. Furthermore, cross-sectional scanning/transmission electron microscopy of the Fe/SiOC nanolaminate after indentation showed a reduction in the thickness of both the Fe and SiOC layers with no evidence of cracks, shear bands or interface delamination. The combination of increased hardness and deformability of the Fe/SiOC nanolaminate is the result of homogenous plastic co-deformation in the Fe and SiOC layers through the constraint of localized shear flow in the SiOC. Although irradiation of the Fe/SiOC nanolaminate led to recoil mixing of Fe into the SiOC layers, the nanolayered structure remained intact. Increasing the irradiation damage level from 10 to 50 dpa led to more recoil mixing and also a reduction in elastic modulus and hardness of the Fe/SiOC nanolaminate. The study suggests Fe/SiOC nanolaminates are a promising class of irradiation tolerant materials.

1. Introduction

Nanolaminate composites have received considerable attention over the past few decades due to their exceptional mechanical, electrical, and magnetic properties [1–3]. The mechanical behavior of nanolaminates depends on the crystallinity of the constituent phases, geometrical design parameters (e.g., the thickness of individual layers), and the nature of the interfaces (e.g., coherent or semi-coherent interfaces in crystalline/crystalline nanolaminates or crystalline/amorphous interfaces). As an example, the maximum strength achievable for crystalline metal/crystalline metal nanolaminates is typically higher than the strength of both constituent phases. On the other hand, crystalline metal/amorphous metal or ceramic nanolaminates typically demonstrate strengths lower or comparable to the strength of the amorphous phase [4]. Other examples include the effect of layer thickness on the predominant deformation mechanism [4–7] or the interaction of the interfaces with defects or instabilities [4]. Therefore, nanolaminates with an appropriate choice of constituent phases and optimum geometrical design can demonstrate properties desirable for a wide range of applications in aerospace, micro-electro-mechanical systems, and energy fields [4,8–10].

Our previous studies, and those of others, have demonstrated that nanolaminates with a large ratio of interface area to volume have desirable irradiation stability [1,8–15]. The interfaces act as effective sinks for point defects and promote the recombination of vacancies and interstitials. As a result, the interfaces can play a dominant role in reducing damage caused by ion irradiation and

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suppress the irradiation-induced changes in material properties and microstructure. Nanolaminates consisting of such interfaces experience minimum structural changes under irradiation and are promising candidates for developing irradiation tolerant materials with longer life times for reactor applications.

In our previous studies, we investigated the irradiation stability of crystalline Fe/amorphous silicon oxycarbide (SiOC) nanolaminates subjected to ion irradiation with different ion species and energies at different temperatures [8,9,13]. Nanocrystalline α-Fe was chosen as a model for steel used in reactors, and SiOC because of its high crystallization temperature and irradiation tolerance [16,17]. Our findings indicated that Fe/SiOC nanolaminates with individual Fe and SiOC layer thicknesses of 60 and 80 nm, respectively remain structurally and thermodynamically stable after ion irradiation up to 30 displacements per atom (dpa) at room temperature and also at temperatures as high as 573 K [8,9,13]. Irradiation-induced changes in the mechanical properties of these Fe/SiOC nanolaminates were not addressed. The degradation of mechanical properties can affect the successful application of these materials under long-term irradiation conditions [12]. Studies of the effects of He irradiation on the mechanical response of crystalline/crystalline Cu/Fe [18], Fe/W [11], Al/Nb [14], and Cu/Nb [12] nanolaminates revealed the role of interfaces on changes in mechanical properties. However, the mechanical response of crystalline/amorphous nanolaminates subjected to ion irradiation has not been addressed. Therefore, the objective of the present study was to examine the effects of ion irradiation on the mechanical response of Fe/SiOC nanolaminates and to relate the observed changes in mechanical properties with structural alterations induced by irradiation. The role of the interfaces was also examined by comparing the irradiation-induced changes of the Fe/SiOC nanolaminates with Fe and SiOC films.

2. Experimental details

Films consisting of only Fe, only SiOC, and a Fe/SiOC nanolaminate were fabricated by magnetron sputtering using a base pressure of 9.6×10^{-6} Pa or less. The nominal composition of the SiOC film was 30% Si, 40% O, and 30% C (at. %). All films had a total thickness of ~1 μm and were deposited on a 300 nm thick SiO_2 layer on a Si wafer. The Fe/SiOC nanolaminate consisted of 72 ± 10 nm thick alternating layers of Fe and SiOC with the outermost layer being SiOC. The as-deposited films were irradiated with 3.5 MeV Fe ions at room temperature. For each film, the irradiation fluences were selected such that a damage level of 10, 20, or 50 dpa was obtained at a depth of 500 nm. For example, to obtain a damage level of 10 dpa at a depth of 500 nm in the Fe, SiOC, and Fe/SiOC films, fluences of 1.18×10^{16}, 3.90×10^{16}, and 1.95×10^{16} ions/cm^2 were used, respectively. The fluences were increased accordingly to reach damage levels of 20 and 50 dpa at a depth of 500 nm.

The simulated depth profiles of implanted ion concentration and irradiation damage were calculated with the Stopping and Range of Ions in Matter (SRIM)-2008 software using the ion distribution and quick calculation of damage option [19]. The Fe/SiOC nanolaminate was treated as a uniformly distributed amorphous target material for the purpose of the simulations. To obtain the density of SiOC, required for SRIM simulations, X-ray reflectivity (XRR) experiments were performed on the as-deposited SiOC film using the 4-ID-D beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. The incident photon energy of the XRR measurements was 14 keV (0.08856 nm wavelength) [20].

The crystallographic structure of the as-deposited and irradiated films was characterized by a Bruker-D8 Discover X-ray diffractometer with Cu Kα radiation (λ = 0.15402 nm). While the XRD patterns of the Fe films were collected using the conventional θ/2θ scanning method, a grazing incident configuration with an incident X-ray angle of 7.5° was used for the SiOC and Fe/SiOC films to minimize the substrate signal and enhance any possible features from the SiOC. The microstructure of the films before and after irradiation was examined by transmission electron microscopy (TEM). The cross-sectional TEM specimens were prepared by a conventional grinding, polishing and ion milling method.

The mechanical response of the as-deposited and irradiated films was studied by nanoindentation experiments performed with a force-controlled Hysitron Triboindenter. A diamond Berkovich indenter was used for indentations. Prior to performing each experiment, the instrument and the film were allowed to thermally equilibrate for 10–12 h inside a thermal enclosure. The compliance of the instrument and the area function of the indenter were calibrated by performing indentations in fused silica and tungsten according to the procedure of Oliver and Pharr [21] and consistent with ISO 14577-4 [22]. The loading sequence used to obtain the modulus and hardness profiles of the as-deposited films consisted of loading at 0.2 mN/s to a maximum force of 4, 2, 1, and 0.5 mN, a 60 s hold at the maximum force to allow any time dependent plastic effects to diminish, 10 s unloading to 10% of the maximum force, a 60 s hold at 10% of the maximum force to measure thermal drift and a 2 s final unloading. Additional nanoindentation experiments at a maximum force of 2 mN were also performed on the irradiated films to quantify the irradiation-induced changes in elastic modulus and hardness. The loading cycle used for these experiments was similar to the one described above. To better understand the deformation mechanism of the Fe/SiOC films, the area around the impressions made by nanoindentation was studied by a commercial Bruker atomic force microscope (AFM) used in tapping mode. In addition, focused ion beam (FIB) milling was used to create cross-sections of the Berkovich impressions, which were subsequently studied by scanning electron microscopy (SEM). For larger deformations, a Clarke CM 700 microindenter was used to perform microindentation on the as-deposited Fe/SiOC film with a Vickers indenter at a maximum force of 245.6 mN (25 g) and a displacement rate of 50 μm/s. The cross-sections of the Vickers impressions were prepared by FIB and examined by TEM.

3. Results

Fig. 1 shows the depth profiles of implanted Fe ion concentration and irradiation damage measured in dpa for the Fe, SiOC and Fe/SiOC films irradiated with fluences of 1.18×10^{16}, 3.90×10^{16}, and 1.95×10^{16} ions/cm^2, respectively, calculated using SRIM [19]. The displacement energies used for Fe, Si, O and C were 40, 15, 28, 28 eV, respectively [23]. The density of SiOC used for the simulation was 2.2 g/cm^3. This value was measured from XRR experiments performed on the as-deposited SiOC film. The simulation predicts a monotonic increase in the implanted Fe concentration for the Fe and Fe/SiOC films. For the SiOC film, the implanted Fe concentration is low throughout the film indicating that the majority of the ions come to rest in the substrate. Based on the simulations shown in Fig. 1, the damage level varies with depth and reaches 10 dpa at a depth of 500 nm for all the films. Simulations were also performed for the rest of the irradiation fluences used in this study (not shown here) where damage levels of 20 or 50 dpa were obtained a depth of 500 nm. The magnitude of damage level at a depth of 500 nm (10, 20, or 50 dpa) is used as a nominal damage level to identify the irradiated films throughout. Where the presented results correspond to a damage level different from the nominal values, both nominal and calculated damage levels are reported.

XRD was used to examine the irradiation-induced changes in crystal structure. Fig. 2 shows the XRD patterns of the Fe, SiOC, and Fe/SiOC films before and after irradiation with different ion fluences