In-situ Observation of Radiation Damage in Nano-structured Amorphous SiOC/Crystalline Fe Composite

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Abstract

The radiation tolerance property of amorphous silicon oxycarbide (SiOC) and crystalline Fe nanocomposites were examined by in-situ transmission electron microscope at 50 Kelvin (K), room temperature and 573 K. Results showed that intermixing between Fe and SiOC was most severe for irradiation at 50 K. However, for irradiations at 573 K, a demixing process was observed. The results indicated thermodynamic stability and radiation tolerance of Fe/SiOC nanocomposite at elevated temperature. Compared with thin Fe/SiOC multilayers, thick Fe/SiOC multilayer exhibited better irradiation stability. Discussion covers two possible reasons for these observations including the role of composite interface energy and collision cascade size.

Keyword: Radiation tolerant materials, amorphous SiOC, nanocrystalline Fe, interface.

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1. Introduction

Next-generation nuclear energy technology requires the development of radiation tolerant materials which experience minor structural changes and minimum thermal/mechanical degradation under harsh environments to ensure longer and safer life cycles.[1, 2] One of the emerging approaches of removing radiation damage and suppressing radiation induced dimensional and property changes is to develop materials with engineered grain boundaries and interfaces that serve as defect sinks.[3] For example, grain boundaries of nanocrystalline metals have been demonstrated to assist defect annihilation and enhance radiation resistance.[4, 5] Interfaces between nanoscale oxide particles and the metal matrix have been proven to enhance swelling resistance and creep resistance in oxide dispersion strengthened (ODS) steels systems.[6, 7] In addition, several incoherent interfaces including Cu/Nb,[8] Cu/V,[9] Fe/W[10] interfaces have been shown as strong defect sinks to promote vacancies and interstitials recombination. Rather than preventing microstructure changes in polycrystalline aggregates, a new kind of irradiation tolerant material, amorphous silicon oxycarbide (SiOC), has been developed recently whose amorphous microstructure remains unchanged after irradiation. Studies have shown that SiOC alloys remain amorphous at both room temperature and 600 °C irradiation with damage levels up to 20 displacements per atom (dpa).[11, 12] To possess good mechanical properties, be capable of operation at temperatures greater than 500°C, and have extreme radiation tolerance, an amorphous SiOC/crystalline Fe composite has been developed. α -Fe, in the composite, was chosen to serve as a model material for steel.[13] From a preliminary study, the α -Fe/amorphous SiOC composite showed radiation stability after He irradiation to ~1.3 dpa at room temperature and the crystalline/amorphous interface was shown to be effective at annihilating point defects and enhancing radiation tolerant properties.[14]

Compared with ex-situ transmission electron microscope (TEM) experiments, which only observe the initial and final stage of irradiated specimen, in-situ irradiations inside a TEM provides real-time observation of microstructural evolution in irradiated composite materials. Therefore, in-situ irradiations offer a unique way to examine the dynamics of defect-defect and defect-interface interactions. Many phenomena have been observed via TEM in-situ irradiation studies, such as irradiation-induced grain growth in Zr and Fe,[15] defect removal by twin boundaries,[16] and defect migration kinetics in nanoporous metals.[17]

In extension to our previous work on light ion (He) irradiation which produces dilute and small collision cascades, this in-situ study examined the heavy ion (Kr) irradiation response of Fe/SiOC nanocomposites at 50 K, RT and 573 K. Heavy ion (Kr) irradiation results in dense and large collision cascades which is vital to the examination of our nanocomposite radiation stability. Besides collision cascade size and density the, irradiation temperature is another key factor affecting stability through the kinetics of defect–defect and defect–interface interactions. For example, irradiation at 50 K results in low defect mobility and a high density of retained Frenkel pairs, while irradiation at elevated temperature leads to high defect mobility and formation of vacancy and interstitial clusters.[18] The aim of this work is to investigate irradiation response of Fe/SiOC nanocomposite with crystalline/amorphous interfaces at these three temperature points.

2. Experimental

In this work, magnetron sputtering was used to fabricate nano-structured Fe/SiOC multilayer films with controlled individual layer thicknesses. Prior to depositions, the base pressure was 9.8×10^{-6} Pa or lower. The Ar partial pressure used for film deposition was ~ 0.65 Pa. DC magnetron sputtering was used to prepare nanocrystalline α -Fe layers while radio frequency (RF) co-sputtering was used to synthesize amorphous SiOC layers from SiO₂ and SiC targets at room temperature. The total thickness of all films was ~ 420 nm and the individual layer thicknesses was controlled by deposition time. In thick Fe/SiOC multilayer films, Fe and SiOC layers were 60, 80 nm in thickness, respectively. The individual layer thickness for thin Fe/SiOC multilayer films was 14 nm. The detailed microstructure characterization of as-deposited Fe/SiOC multilayers can be found in reference.[19]

All cross-sectional transmission electron microscopy (TEM) specimens were prepared by grinding, polishing and ion milling. During TEM sample preparation, low energy (3.5 keV) and low angle (5°) were selected to reduce the ion milling-induced damage. The cross-sectional microstructure of Fe/SiOC multilayers before and after irradiation was investigated by an FEI Tecnai G2 F20 microscope operated at 200 keV. A set of Fe/SiOC multilayer specimens were in-situ irradiated with 1 MeV Kr ions at the IVEM-TANDEM facility at Argonne National Laboratory, where an ion accelerator is attached to a HITACHI H-9000NAR microscope with an operation voltage of 200 keV. Irradiation temperatures were 50 K, RT and 573 K. The ion beam

size was 1.5 mm (without rastering) which was able to cover the whole TEM specimen. Depth-dependent damage and defect concentration profiles were calculated by the Stopping and Range of Ions in Matter (SRIM)-2008 using the ion distribution and quick calculation of damage option in the SRIM software.[20]

3. Results and discussion

1 MeV Kr ions were selected for the irradiation of Fe/SiOC multilayer films. The SRIM calculated projected range for 1 MeV Kr in Fe and SiOC is 241.3 nm and 700.2 nm, respectively. Because both ranges far exceeded the thickness of the TEM specimens (~100 nm), the majority of Kr ions penetrate through the thin Fe/SiOC specimen. Fig. 1a presents the experimental set-up for irradiation of TEM specimens. The accelerated Kr ions bombard the TEM specimen with an incident angle of $\sim 15^\circ$. Since the Kr^{++} ion beam direction is almost parallel with the Fe/SiOC interface, damage simulations were carried out for the Fe and SiOC layers separately. Fig. 1b and 1c show the SRIM dpa profiles in the Fe and SiOC films respectively with a fluence of 4×10^{14} ions/cm². These data show that the Kr^{++} irradiation damage with a dose of 4×10^{14} ions/cm² is ~ 1.1 dpa in the Fe layers and ~ 0.42 dpa in the SiOC layers.

Fig. 2a shows typical cross-sectional bright-field TEM micrographs of thin Fe/SiOC multilayer films before Kr irradiation where there are alternating Fe and SiOC nanolayers with clear interfaces. The as-deposited Fe layers exhibit a typical columnar growth with average grain size of ~ 20 nm while all SiOC layers show uniform contrast. The corresponding selective area diffraction (SAD) patterns shown as insets of Fig. 2a exhibit a diffuse halo around the central beam and ring diffraction patterns with similar interval spacing, suggesting the amorphous nature of the SiOC layers and body-centered cubic (BCC) structure of Fe, respectively. To further examine the radiation stability in Fe/SiOC nanocomposite as a function of temperature, in-situ irradiation were performed at 50 K, RT and 573 K. Fig. 2b presents the microstructure of thin Fe/SiOC multilayer after irradiation at 50 K with dose of 4×10^{14} ions/cm². The nanolayer structure has been completely destroyed and severe irradiation induced intermixing between Fe layers and SiOC layers is observed. However, the corresponding SAD pattern shows that this ion mixed Fe/SiOC film is still composed of nanocrystalline α -Fe and an amorphous phase. In comparison, the thin Fe/SiOC sample irradiated at room temperature exhibits less intermixing. Several un-mixed areas with bright contrast are observed in Fig. 2c. Also, the nanocrystalline α -

Fe and amorphous phases coexist in Fe/SiOC film after RT irradiation, which is confirmed by the corresponding SAD pattern (shown as inset of Fig. 2c). In contrast to the intermixing observed at 50 K and RT, no Fe and SiOC intermixing is observed in the sample irradiated at 573 K with a doubled dose of 8×10^{14} ions/cm² (Fig. 2d). The results suggest that a demixing process takes place within the thin Fe/SiOC multilayer during 573 K irradiation to maintain phase separation and a layered structure.

Fig. 3a presents the cross-sectional bright-field TEM micrograph of as-deposited thick Fe/SiOC multilayer films. It exhibits similar Fe grain size and same crystal structure with that of thin Fe/SiOC multilayer films shown in Fig. 2a. Compared with the thin multilayer films, the thick Fe/SiOC multilayers exhibit better radiation stability after irradiation at 50 K with dose of 4×10^{14} ions/cm², (Fig. 2b). The Fe/SiOC interfaces are all clearly observed after the 50 K irradiations, indicating no irradiation-induced mixing or secondary phase formation between the Fe layers and the amorphous SiOC layers. As the dose increases to 1×10^{15} ions/cm², an intermixed layer with thickness of ~10 nm is observed between Fe layer and SiOC layer as seen in Fig. 3c. To further examine the composition profile of the multilayers irradiated with 1×10^{15} ions/cm², scanning transmission electron microscopy (STEM) was conducted under a high-angle annular dark field (HAADF) condition. The STEM images of Fig. 3d show that a light contrast layer is observed between the bright contrast Fe layer and dark contrast SiOC layer. Element mapping (not shown here) reveals the formation of a Fe_xSi_yO_z interlayer. Cross-sectional TEM images of thick Fe/SiOC multilayer after RT and 573 K irradiation with dose of 1×10^{15} ions/cm² are shown as Fig. 3e and 3f, respectively. Thick Fe/SiOC multilayer films exhibit clear interfaces after RT and 573 K irradiation without the formation of a Fe_xSi_yO_z layer. The insets of Fig. 3e and 3f are the corresponding SAD patterns showing BCC Fe and amorphous SiOC diffraction patterns.

Two most important features observed during in-situ Kr irradiation at 50 K, RT and 573 K are as follows:

- (i) Fe/SiOC layered structures are more radiation tolerant at elevated temperature (573 K) than that at low temperature (50 K).
- (ii) Fe/SiOC multilayer films with larger length scale are more radiation stable than films with smaller length scale.

Perhaps the most significant feature of the Fe/SiOC multilayers after Kr irradiation after different temperatures is the higher radiation stability at elevated temperatures. The results suggest that the breakdown mechanism for thin Fe/SiOC multilayer films is ballistic mixing. When Kr ions interact with Fe/SiOC multilayers, the interaction results in numerous collision cascades and sub-cascades which force Fe and SiOC atoms to intermix with each other. At low temperature (50 K), there is negligible thermal energy for mixed atoms to diffuse. Therefore, the movement of these atoms is restricted within the cascade (estimated 0.7 nm diffusion length at 1 dpa Kr irradiation)[21] and leads to intermixing between Fe and SiOC atoms. As the dose increases, the collision cascades overlap, leading to the observed layer breakdown. At elevated temperature (573 K), thermal energy enables atomic movement after cascades- intermixing. Both thin and thick Fe/SiOC multilayers after Kr irradiation at 573 K clearly show stable layered structures, indicating that intermixed Fe and SiOC atoms de-mix and suggesting that there is a positive heat of mixing between those two materials. As long as kinetics permit, Fe layers and SiOC layers prefer to stay with their original form. Moreover, irradiation induced point defects are more mobile at elevated temperature, which allow them to migrate to defect sinks (Fe/SiOC crystalline/amorphous interface or Fe grain boundaries in this system) to recombine, enhancing the stability of Fe/SiOC nanocomposite system.

Fe and SiOC nanocomposites appear to be thermodynamically stable and tend to a layered structure during irradiation at elevated temperature. However, at this point it is unclear why intermixing and layer breakdown is observed in the thin Fe/SiOC multilayers. One possibility is that the greater number of interfaces adds additional positive enthalpy to the system, as suggested by Liu *et al.*[22, 23] Liu *et al.* have shown that interfaces can assist ion-beam mixing in several immiscible metallic systems even with a large positive heat of mixing. For low temperature irradiation where radiation induced point defects cannot migrate, the Fe/SiOC nanocomposite systems with a greater interfacial area per unit volume are more vulnerable to mixing. This hypothesis is supported by the observations that show that there is less intermixing for thick Fe/SiOC multilayer films compared to that of thin multilayer films at the same doses and temperatures. Another possibility is that the layered structure is damaged by one collision cascade. To estimate the cascade size of 1 MeV Kr irradiation, a SRIM simulation was performed to examine the 3-D vacancy distribution inside the Fe layers. Fig. 4a presents the 3D-vacancy depth profile where the lateral and longitudinal concentrations increase with projectile depth. An

estimate of the cascade width can be made by determining the lateral straggling in the vacancy concentration. The lateral vacancy distribution at 50 nm, fitted with a Gaussian distribution, is shown in Fig 2b, which renders a variance of ~ 3.2 nm. Relating the variance to a cascade width requires multiplying the Monte Carlo value obtained from TRIM by a correction factor of 0.77.[24, 25] This gives the approximate radius of a Kr cascade in the TEM specimen of ~ 2.5 nm. Thus, the collision cascade diameter is ~ 5 nm which is less than the thickness of SiOC layer (14 nm). Because the collision cascade size does not exceed the thickness of individual layer, it is expected that only overlapped collision cascade can result in layer breakdown in this case. However, once the average size of collision cascade is bigger than the layer length scale, one cascade may damage the layered structure within this cascade regime during low temperature irradiation.

4. Conclusions

We examined the temperature dependent Kr radiation stability of the Fe/SiOC composite system. Fe/SiOC nanocomposite systems exhibit better Kr radiation stability at elevated temperature (573 K) than that at low temperature (50 K). The results suggest that the layered structure is damaged by ballistic ion mixing. Also, Fe and SiOC tend to de-mix during irradiation at elevated temperatures and Fe/SiOC crystalline/amorphous interface acts as efficient defect sinks. Compared with thin Fe/SiOC multilayers, thick Fe/SiOC multilayer films possess better radiation tolerance properties for all doses and temperatures studied. This suggests that the greater number of interfaces adds additional mixing enthalpy to the system. By estimation of the radius of the Kr collision cascade, layer breakdown appears to require overlapping collision cascades.

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Figure Captions

Figure 1. (a) Schematic illustration of in-situ irradiation. The depth profile of radiation damage on (b) Fe layers and (c) SiOC layers which is simulated by TRIM (a fluence of 4×10^{14} ions/cm²).

Figure 2. The typical cross-sectional bright-field TEM micrographs of thin Fe/SiOC multilayer films (a) before, and after (b) 50 K, (c) RT, (d) 573 K irradiation. The inset is the corresponding SAD pattern of each micrograph.

Figure 3. (a) The typical cross-sectional bright-field TEM micrographs of as-deposited thick Fe/SiOC multilayer films. The microstructure evolution of films and after 50 K irradiation with a dose of (b) 4×10^{14} ions/cm², (c) 1×10^{15} ions/cm². (d) The scanning transmission electron microscope (STEM) images of thick Fe/SiOC multilayer films after 50 K irradiation with a dose of 1×10^{15} ions/cm². The cross-sectional bright-field TEM images of thick Fe/SiOC multilayer films after (e) RT, (f) 573 K irradiation (a dose of 1×10^{15} ions/cm²).

Figure 4. (a) The simulated 3-D vacancy distribution inside the Fe layers. (b) The vacancy profile of Fe layer at the depth of 50 nm. The data is fitted by Gaussian equation shown as red line.

Figure 1

(a)

(b)

(c)

Figure 2

(a) Virgin

(b) 50K, 4×10^{14} ions/cm²

(c) RT, 4×10^{14} ions/cm²

(d) 573 K, 8×10^{14} ions/cm²

Figure 3

(a) Virgin

(b) 50 K, 4×10^{14} ions/cm²

(c) 50 K, 1×10^{15} ions/cm²

(d) 50 K, 1×10^{15} ions/cm²

(e) RT, 1×10^{15} ions/cm²

(f) 573 K, 1×10^{15} ions/cm²

Figure 4

(a)

(b)

Graphical abstract

In-situ Observation of Radiation Damage in Nano-structured Amorphous SiOC/Crystalline Fe Composite

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Fig. 1. (a) Schematic illustration of in-situ irradiation. The typical cross-sectional bright-field TEM micrographs of thin Fe/SiOC multilayer films after (b) 50 K and (c) 573 K irradiation with a dose of $1 \times 10^{15} \text{ ions/cm}^2$. Results clearly show that intermixing between Fe and SiOC is most severe for irradiation at 50 K and a demixing process is observed for thin multilayer sample after irradiations at 573 K. The cross-sectional bright-field TEM images of thick Fe/SiOC multilayer films after (d) 50 K, (e) 573 K irradiation (a dose of $1 \times 10^{15} \text{ ions/cm}^2$). The results show a formation of intermixed layer after 50 K irradiation but no observed change after 573 K irradiation in thick Fe/SiOC multilayer sample.