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Superior radiation tolerant materials: Amorphous silicon oxycarbide

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ABSTRACT

We studied the radiation tolerance of amorphous silicon oxycarbide (SiOC) alloys by combining ion irradiation, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The amorphous SiOC alloys thin films were grown via co-sputtering from SiO_2 and SiC (amorphous phase) targets either on a surface oxidized Si (100) substrate or on a sodium chloride substrate. By controlling the sputtering rate of each target, SiOC alloys with different compositions (1:2, 1:1, 2:1 ratios) were obtained. These alloys were irradiated by 100 keV He^+ ions at both room temperature and 600 °C with damage levels ranging from 1 to 20 displacements per atom (dpa). TEM characterization shows no sign of crystallization, void formation or segregation in all irradiated samples. Our findings suggest that SiOC alloys are a class of promising radiation-tolerant materials.

1. Introduction

To extend the lifetime of current nuclear power plants and to meet the needs of advanced reactor designs, it is necessary to develop radiation tolerant alloys without significant structural changes and serious thermal/mechanical degradation under harsh environments [1–5]. Different strategies have been explored to improve radiation tolerance of structural materials. In particular, efforts have been made to introduce interfaces as point-defect sinks to remove radiation damage and suppress swelling. For example, oxide dispersion strengthened (ODS) steels with a large amount of interfaces between the matrix and nanoscale oxide precipitates have proven to have good swelling resistance and good creep resistance [6,7]. Nanoscale metallic interfaces, e.g. interfaces of face-centered cubic and body-centered cubic alloys, have displayed strong sink strength and suppressed He bubble formation [8,9]. Nanocrystalline metals, although facing challenges of grain stability under irradiation, have shown enhanced radiation resistance due to grain boundary assisted defect annihilation [10,11].

Unlike crystalline solids, whose radiation responses have been studied for decades [12,13], radiation effects in amorphous alloys have received much less attention [14] and were therefore still largely unknown. Molecular dynamics (MD) simulations of damage cascade development in ion irradiated amorphous materials did not reveal partial crystallization. Instead, radiation was found to create excessive free volume in localized region and these "defects" can anneal out on a time scale of about 100 ps at room temperature, and thus sustaining their glassy states [15]. Because amorphous materials possess no long range order, they do not contain conventional crystal defects such as vacancies, interstitials, or dislocations [16]. Therefore they offer the possibility of eliminating the root cause responsible for radiation damage in crystalline solids—namely the production of point defects and defect clusters—and may serve as the basis for developing a new class of radiation tolerant structural materials. Fig. 1 shows two possible consequences of amorphous alloy structural evolutions after radiation. One is irradiation-induced crystallization. Since collision cascades caused by ion bombardments will lead to high density atomic displacements and possibly correlated atomic re-arrangements, the nucleation of a crystalline phase may be possible under irradiation [17]. The second possible consequence of amorphous alloys under irradiation is that they maintain their amorphous structure. Although glassy states are generally metastable, some glasses may possess large kinetic barriers to the nucleation of a crystalline phase. Several studies on metallic glasses have shown that a direct crystallization in the damage cascade core is unlikely considering because the cooling rates during the thermal spike quenching stages are typically a few orders of magnitudes higher than the critical cooling rates required for crystallization [18].

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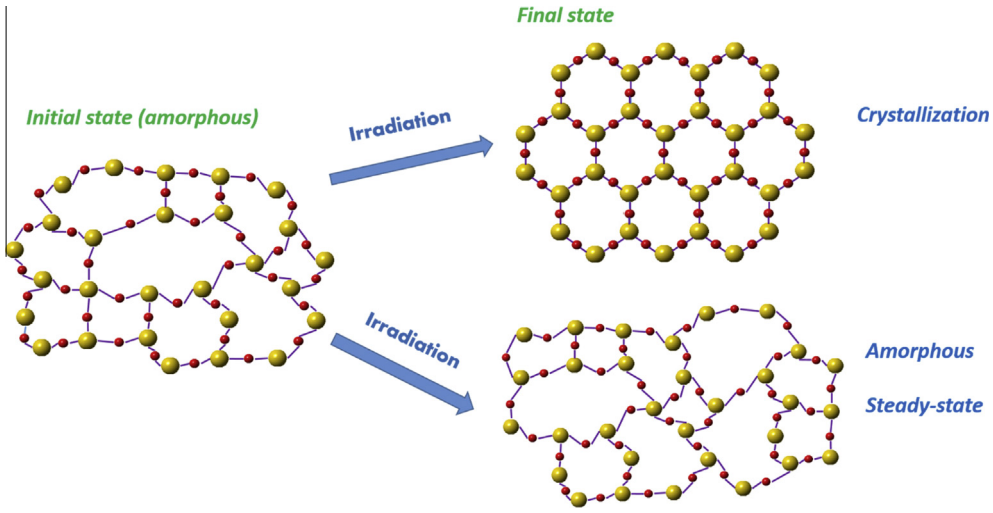

Fig. 1. The schematic illustration of two possible irradiation-induced structure for initial amorphous material: one is to become crystalline and the other is to remain amorphous.

Therefore, the local molten zone formed in the damage cascade core maintains a glassy state upon thermal spike quenching and subsequent cooling at longer time scales.

In the present study, silicon oxycarbide (SiOC) was selected due to several reasons. First, this class of amorphous ceramics has been shown to have crystallization temperatures in excess of 1300 °C and good oxidation and creep resistance [19–22]. Second, it is convenient to fabricate amorphous SiOC alloy thin films with controlled composition by the magnetron sputtering method [23]. The high crystallization temperature indicates that the amorphous state is highly stable. In addition, good mechanical properties make it a promising candidate for a structural material. Third, the irradiation resistance of an amorphous alloy is believed to be closely coupled to its crystallization temperature. Therefore, SiOC has an extremely high crystallization temperature which suggests that service operating temperatures of this material should be well above 500 °C.

2. Experimental

There were three types of SiOC film systems used in the present study. The first type SiOC films was deposited on a sodium chloride substrate. After dissolving the substrate in deionized water, SiOC films were self-suspended on TEM grids. These TEM specimens were subject to a series of repeated He ion irradiations followed by TEM characterization after each He ion fluence. Such self-supported membrane films, however, were not suitable for irradiation at elevated temperatures. To alleviate this issues, the second type of SiOC films were deposited on surface oxidize Si substrates with their top SiO_2 layer thickness of 300 nm. After ion irradiation at elevated temperature, either a focused ion beam technique or a conventional dimple and grinding followed by ion-milling technique were used to prepare specimens for cross-section TEM characterization. The third type of SiOC films were deposited on carbon substrates. The low Z substrate allows for Rutherford backscattering spectrometry (RBS) composition analysis of the deposited SiOC films.

Amorphous SiOC films were grown via radio frequency (RF) co-sputtering from SiO_2 and SiC targets at room temperature. Three different compositions of SiOC alloys were obtained by varying the sputtering rates of the SiO_2 and SiC targets. The SiO_2 to SiC sputtering ratios in three alloys were 1:1, 1:2 and 2:1. Both the SiC (purity 99.5%) and SiO_2 (purity 99.995%) targets were

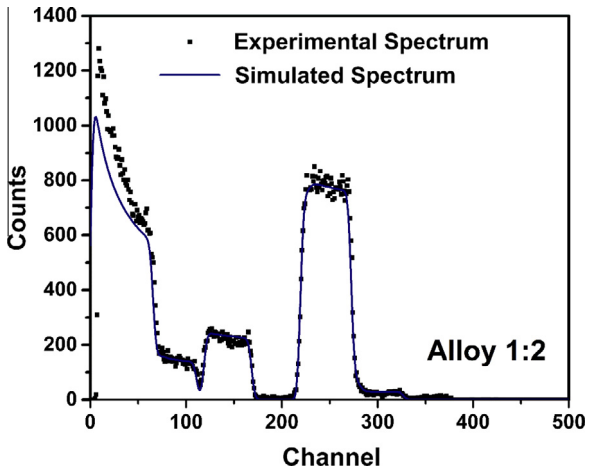

Fig. 2. The typical experimental (scattered point) and simulated (solid line) RBS spectrum for SiOC alloy (1:2). The composition of SiOC alloy is obtained by properly fitting of experimental RBS data.

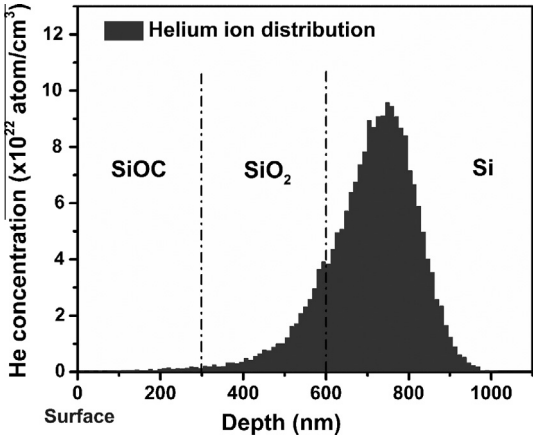

Fig. 3. The helium concentration as function of penetrating depth simulated by TRIM (20 dpa, dose of 2.3E18 ion/cm^2). According to the simulation, most of helium ions penetrate through the SiOC layer and rest in Si and SiO_2 layer. It results in pure atomic displacement in SiOC layer.