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Full Length Article

Structural evolution of oxidized surface of zirconium-silicide under ion irradiationm

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ABSTRACT

Irradiation-induced structural evolution and compositional alterations on nanometer length scales of ZrO_2-SiO_2 nanocomposite and crystalline $ZrSiO_4$, produced by oxidation of $ZrSi_2$ at 1000 °C and 1400 °C, respectively, have been investigated. Irradiations were performed with 3.9 MeV Si^{2+} at 305 °C up to damage levels of 60 displacements per atom (dpa), and post-irradiation characterization was conducted by cross-sectional scanning- and transmission electron microscopy (STEM and TEM) in conjunction with energy dispersive spectroscopy (EDS), as well as glancing-angle X-ray diffraction (XRD). The multilayered nanocomposite oxide showed extensive phase mixing so that the originally distinct interfaces between ZrO_2 and SiO_2 phases were obliterated resulting in the formation of a single amorphous Zr-Si-O phase. Crystalline $ZrSiO_4$ grains were completely amorphized at damage levels of 5–15 dpa, as evidenced by disappearance of grain boundaries and as confirmed by electron diffraction. The irradiation-induced phase transformation for both types of oxide structures has the potential to dramatically enhance corrosion resistance in high temperature aqueous and steam environments.

1. Introduction

Zirconium-silicide compounds have been considered as promising functional and structural materials in future nuclear reactor systems such as neutron reflectors in gas-cooled fast reactors (HTGR) [1,2] and protective coating materials for Zr-alloy cladding in light water reactors (LWR) [3]. The materials are attractive as the neutron reflector in the light of their high melting points (e.g. ZrSi and $ZrSi_2$ melt at 2215 °C and 1620 °C, respectively [4]), excellent mechanical properties at high temperatures (e.g. compressive yield stress of $ZrSi_2$ was 900 MPa at 800 °C [5]), and highly compatible elastic scattering cross-section with fast neutron spectrum [2]. The reflector can improve neutron economy in nuclear reactors and mitigate irradiation damage to other structural materials by scattering back escaped neutrons to the core. Computational simulation of fuel-cycle analysis concluded that performance and safety advantage of zirconium-silicide reflector was superior to other candidate materials such as ZrC and 316 stainless steel [6]. Furthermore, zirconium-silicides are robust under oxidative high temperature environment due to the formation of oxidation-resistant passive oxide layers of SiO_2 and $ZrSiO_4$ (zircon). For HTGR applications, it is strongly desirable for structural materials to resist corrosion effects arising from the interaction with reactive impurities H_2O, O_2, and CH_4 in helium cooling gas at temperatures between 800 °C and 1000 °C. Previous studies have reported that oxidation of $ZrSi_2$ at 700 °C, 1000 °C, and 1200 °C in ambient air showed a diffusion limited parabolic-cubic oxidation kinetics [7]. Oxidation of $ZrSi_2$ sputter coating on Zr-alloy substrates formed tenacious surface oxide films consisting of nanocrystalline/amorphous $ZrSiO_4$ and SiO_2 at 700 °C and multilayered ZrO_2 and SiO_2 at 1000 °C, respectively. The oxidation resistance improvement factor of the $ZrSi_2$ coating was more than eighty-five compared to uncoated Zr-alloy at 700 °C in ambient air [8]. Finally, the highly corrosion resistant zircon phase ($ZrSiO_4$), has been observed to form during post-heat treatment of a thin $ZrSi_2$ coating on SiC substrate at 1400 °C for 5 h in ambient air [3].

One major challenge for the application of structural materials in nuclear reactors is radiation damage particularly in high dose environments. The radiation damage for ceramics include irreversible property change such as radiation-induced phase ordering/disordering [9], swelling, decrease in thermal conductivity due to the formation of a high-density of radiation-induced defects. However, until now published information for radiation response of zirconium-silicide under oxidative environments is very limited. Examination of the fine-scale oxide nanostructure and thermodynamic stabilities provide the potential of self-healing corrosion qualities under high doses radiation due to mixing of interphase boundaries, atomic disordering, and the formation of the highly corrosion-resistant zircon phase.

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The present study is aimed at examining microstructural and compositional stability of oxide layers of $ZrSi_2$ (a common zirconium-silicide intermetallic compound) under 3.9 MeV Si^{2+} ions at 305 °C. The oxidation of the bulk $ZrSi_2$ was performed at 1000 °C and 1400 °C in ambient air prior to the irradiation experiment. The oxidation of the material simulates material degradation in elevated temperature oxidative environments with the formation of surface oxide layers on zirconium-silicide structural components. Ion irradiation provided data on the radiation stability of these surface oxide layers. In this paper, evolution of oxide phases of $ZrSi_2$ during the heat treatments is first introduced followed by a discussion of radiation-induced phase alterations of these oxide layers. This study provides initial experimental data and serve a better understanding of radiation response of zirconium-silicide in high temperature oxidative conditions.

2. Experimental procedures

Polycrystalline and dense $ZrSi_2$ (American Elements Inc., Los Angeles, CA) with a reported purity of 99.5% was used in this study. The material was sectioned into samples of dimensions of approximately 5 mm × 10 mm, 6.4 mm thick square coupons. The samples were progressively polished with 400 grit, 600 grit, and 1200 grit SiC abrasive papers and then cleaned ultrasonically in acetone and ethanol baths. Phase identification of the specimens using X-ray diffraction (XRD) and scanning electron microscopy in conjunction with energy dispersive spectroscopy (SEM-EDS) was reported in previous study by the authors [7]. Isothermal heat treatments of the as-polished specimens were performed at high temperatures using a commercial furnace (MTI Corp. Model GSL1600X). Different microstructures of oxide scale of $ZrSi_2$ specimens were prepared by oxidation at 1000 °C for 15 h and 1400 °C for 5 h in ambient air, respectively. Furnace ramp rate to exposure temperatures was maintained at 5 °C/min.

Silicon irradiation for the oxidized $ZrSi_2$ samples was performed using the 1.7 MV tandem accelerator located at University of Wisconsin-Madison. 3.9 MeV Si^{2+} ions with 1.8×10^{17} ions/cm^2 dose was irradiated to obtain a high level of displacement damage. Sample temperature during the irradiation was 305 °C measured by two K-type thermocouples attached to a sample holder. The base pressure during the radiation was 3×10^{-7} torr. Fig. 1 shows estimated displacements per atom (dpa) and concentration of implanted Si as a function of depth using the Monte Carlo simulation code SRIM-2013 [10] and the procedure described by Stoller et al. [11]. For the damage simulation, in oxide layer structure formed at 1000 °C, was assumed to be a homogeneous mixture of ZrO_2 and SiO_2 with a molar ratio of one to two (based on the oxide products in Eq. (1), Fig. 1a). For samples oxidized at 1400 °C, a dual-layered microstructure consisting of continuous $ZrSiO_4$ layer and SiO_2 was assumed for simulation based on previous experimental observations (Eq. (2), Fig. 1b) [3].

$$ZrSi_2 + O_2 \rightarrow ZrO_2 + 2SiO_2 \quad (1)$$

$$ZrSi_2 + O_2 \rightarrow ZrSiO_4 + SiO_2 \quad (2)$$

Threshold displacement energies for Zr [12], Si [13], and O [14] were assumed to be 40 eV, 35 eV, and 23 eV, respectively. As shown in Fig. 1, the maximum damage in the oxide scale at 1000 °C and the oxide layer at 1400 °C was 61.7 dpa (at 2.16 μm depth) and 64.5 dpa (at 2.31 μm depth), respectively. The overall composition of the oxide layer is not expected to be altered due to irradiation because of the low concentration of implanted Si in both cases.

The effect of irradiation on surface morphology of the oxides was investigated by Zeiss LEO Scanning Electron Microscope in conjunction with Energy Dispersive Spectroscopy (SEM-EDS). Glancing-incidence XRD (Bruker D8 Discovery) was utilized for phase identification of the samples. Diffraction peaks from Cu Kα radiation were acquired from 30° to 50° in 2θ with a 2° grazing incident beam. Detailed cross-sectional examination of the as-oxidized samples, as-oxidized, and irradiated samples was performed with transmission electron microscopy (TEM). For preparation of TEM sample, a thin lamella was fabricated from the irradiated and unirradiated sample surfaces using the Focused Ion Beam (FIB) technique. A thin Pt layer was deposited on the sample surface to protect the microstructure underneath the surfaces prior to the FIB sectioning. The structural analysis and compositional characterization of the was performed using Tecnai TF30 TEM operating at 300 kV and FEI Titan Scanning transmission electron microscope equipped with EDS (STEM-EDS) working at 200 kV. Table 1 summarizes experimental conditions of the samples investigated in this study.

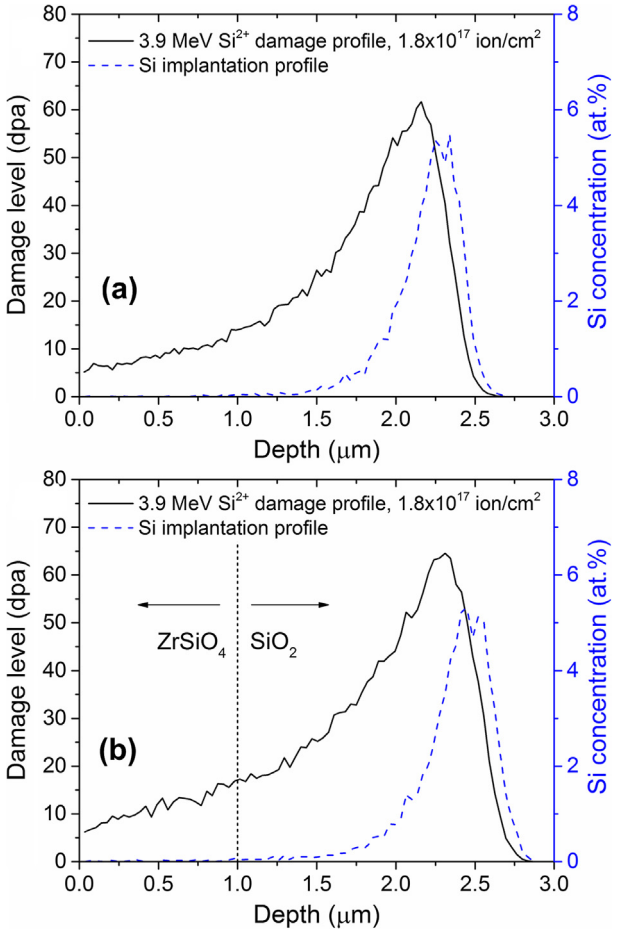

Fig. 1. Depth profile of damage level (dpa) and implanted Si atoms in irradiated oxide scales on $ZrSi_2$ (a) homogeneous mixture of ZrO_2 and $2SiO_2$ formed at 1000 °C and (b) dual-layer of $ZrSiO_4$ and SiO_2 formed at 1400 °C with 3.9 MeV Si ions. Calculations were performed using SRIM-2013 code.

3. Results and discussion

3.1. Oxide structures of $ZrSi_2$ formed at 1000 °C and 1400 °C

Oxidation products of $ZrSi_2$ at 1000 °C and 1400 °C were identified by grazing incidence XRD analysis as shown in Fig. 2. The XRD peaks

Table 1
Summary of $ZrSi_2$ samples investigated in this study.

Sample ID	Experimental conditions
Sample A	Oxidized at 1000 °C for 15 h in ambient air
Sample B	Oxidized at 1400 °C for 5 h in ambient air
Sample AR	Ion irradiated surface of Sample A
Sample BR	Ion irradiated surface of Sample B