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Short communication

Effect of irradiation damage on corrosion of 4H-SiC in FLiNaK molten salt

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ABSTRACT

The corrosion behavior of 4H-SiC in the FLiNaK molten salt (650 °C), pre-irradiated with 70-keV Si ions to 2.5 dpa at 650 °C, was investigated in order to clarify the effect of irradiation on corrosion. The irradiated region of 4H-SiC is peeled off by the molten salt, and the corrosion depth is nearly consistent with the irradiation damage depth. Molten salt corrosion leads to the loss of Si element and the formation of carbon-rich phase in irradiated 4H-SiC surface. The broken of Si-C bonds induced by irradiation plays a key role in the irradiation-assisted corrosion of SiC.

1. Introduction

Due to the high temperature strength, chemical inertness and small neutron capture cross section, silicon carbide (SiC), in the form of SiC-fiber-reinforced SiC matrix composites, has been considered the most promising material for nuclear energy application [1–3]. It has been demonstrated that the high purity SiC ceramic and composite possess superior irradiation resistance to neutron irradiation up to the doses of 30–40 displacements per atom (dpa) in the temperature range of 300–800 °C [4]. Additionally, the corrosion resistance of the SiC materials is also very well in coolants of reactors, such as high-temperature water [5] and molten salt [6]. Nevertheless, SiC materials are subjected to both irradiation and high-temperature corrosion during the nuclear operation. Therefore, it is very important to clarify the synergistic effect of irradiation and corrosion for SiC materials in nuclear energy field. Recently, Kondo et al. investigated the hydrothermal corrosion behaviour of ion irradiated SiC, and found the corrosion rate increased with increasing irradiation fluence [7,8].

The SiC materials are also expected to be applied in the molten salt reactor (MSR), one of the six most promising Generation IV fission reactors. The corrosion behaviour of SiC materials has been widely investigated in high temperature FLiNaK molten salt, which is a mixture of 46.5 mol% LiF, 11.5 mol% NaF and 42 mol% KF [9]. The previous reports related to the corrosion of SiC in FLiNaK molten salt revealed oxygen impurities from SiC and salt could affect the corrosion, due to the corrosion of SiO_2 in FLiNaK molten salt [10]. In addition, it was found that a decrease of Si content in SiC and formation of a carbon-rich surface occurred after the corrosion [11]. However, the effect of irradiation damage on corrosion of SiC in the FLiNaK molten salt is rarely reported.

In the present work, the corrosion behaviour of the irradiated SiC in the FLiNaK molten salt was characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman spectroscopy and X-ray Photoemission (XPS). Energetic Si ions irradiation was performed on 4H-SiC at a selected dose. The samples before and after Si ion irradiation were corroded at 650 °C for 166 h in the FLiNaK molten salt. The corrosion behavior of SiC was investigated in response to irradiation, and the possible mechanism was also discussed.

2. Material and methods

The material used for this study was cut from a 4H–SiC (0001) bulk single crystal wafer (350 ± 25 μm thick, n-type, supplied by Cree Research Inc.). Ion irradiation experiment was carried out with 70 keV Si^+ ions at 650 °C using a 100 keV isotope separator at the Shanghai Institute of Applied Physics, Chinese Academy of Science (SINAP-CAS). The irradiation fluence of 4×10^{15} ions/cm^2 was adopted to obtain the peak damage dose of 2.5 dpa according to the calculation using the Stopping and Range of Ions in Matter (SRIM) [12], as shown in Fig. 1. The density of 3.21 g/cm^3 and the displacement energies for C and Si atoms of 20 and 35 eV were used in the calculation [13].

Corrosion testing of the unirradiated and irradiated samples was performed at 650 °C for 166 h in a 200 g FLiNaK salt contained glassy carbon crucible inside a 316 L stainless steel cell, as shown in Fig. 2. In

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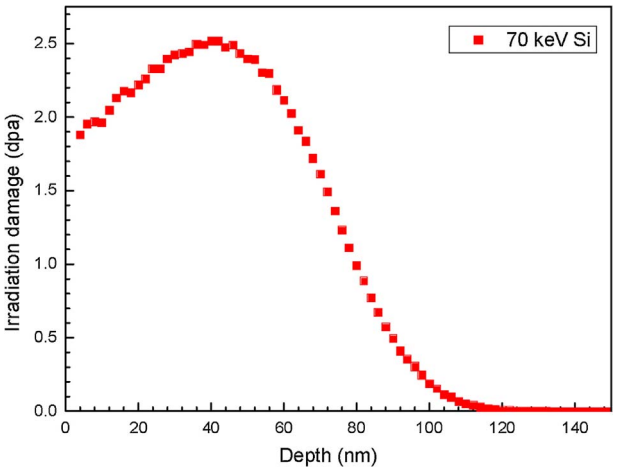

Fig. 1. Depth distributions of irradiation damage in SiC with the peak dose of 2.5 dpa by 70 keV Si^{+} ions (calculated using SRIM 2008).

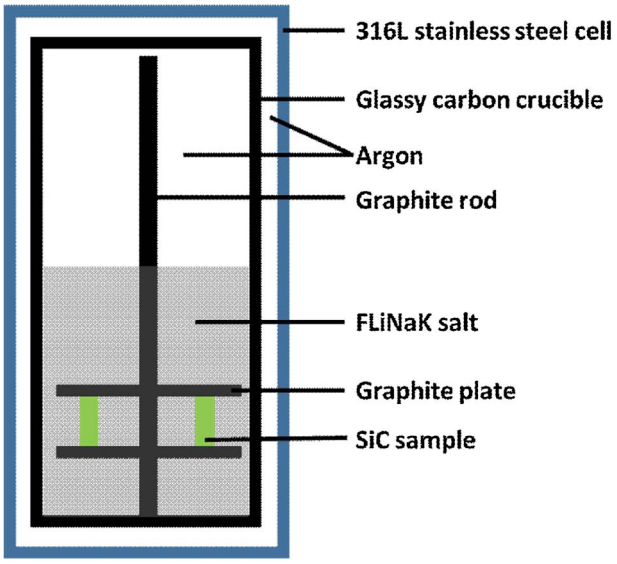

Fig. 2. Schematic diagram of corrosion experimental setup. The SiC samples were fixed by a graphite holder, which was made up of one graphite rod and two graphite plates.

this study, the irradiation and corrosion testing temperature keep the same to avoid the temperature effect on the evolution of irradiated defects. The FLiNaK salt was prepared and purified by Shanghai Institute of Organic Chemistry, Chinese Academy of Science (SIOC-CAS) [9]. The salt was stored and introduced into the glassy carbon crucible in a glove box (H_2O and O_2 < 5 ppm) filled with Ar gas before corrosion testing. Meanwhile, the samples were cleaned in deionized water, acetone and alcohol for 10 min and subsequently baked in a vacuum oven at 60 °C for 2 h. After the corrosion testing, the salt was washed from the corroded samples using aluminum nitrate aqueous solution, deionized water, acetone and alcohol subsequently.

The morphologies of the samples were analyzed by AFM (Bruker Nano Inc., Multimode-8) and SEM (Zeiss, LEO1530VP). In addition, the microstructal analyses were conducted by Raman spectrum (Bruker Senterra confocal Raman microscope with a 532 nm excitation laser) and XPS (a PHOIBOS 100 analyzer with a base pressure better than 2×10^{-10} mbar). In XPS measurement, C 1 s was measured using a monochromatic x-ray source (Al Kα: 1486.61 eV) with an instrumental energy resolution of 0.45 eV. All the spectra were collected at normal emission.

3. Results and discussion

The AFM surface morphologies of the corroded-only, irradiated-only and irradiated and corroded samples are shown in Fig. 3. It is obvious that the surface of the corroded-only sample remain nearly intact (Fig. 3a), meaning that defect-free high-purity single-crystal SiC has superior corrosion resistance to the FLiNaK molten salt. Meanwhile, the only irradiation has little effect on the surface morphology of the sample (Fig. 3b). As for the irradiated and corroded sample, the surfaces are heavily attacked by the high-temperature molten salt, and presented local denudation (Fig. 3c). The denudation depth is estimated about 40 ± 8 nm by AFM profiles (Fig. 3d), which is nearly consistent with the irradiation damage depth. AS for the samples half covered by a copper foil during irradiation, a 10 nm-deep step was clearly observed at the boundary area between unirradiated and irradiated regions (Fig. 3e). The boundary is also verified by SEM images (Fig. 3 f), which is believed to be due to the irradiation swelling [14]. It shows clearly that the denudation occurred on the irradiated region of the sample whereas just little change can be observed on the unirradiated region after the high-temperature FLiNaK molten salt corrosion, which suggests that the irradiation damage could enhance corrosion of SiC.

In order to elucidate the irradiation-assisted corrosion behavior of the SiC materials, the chemical state of C element was conducted by XPS. The C 1 s spectra (black spots) for the original, irradiated-only, corroded-only, irradiated & corroded samples are shown in Fig. 4. A careful inspection further indicates the spectra are asymmetric with extending tails or emerging sub-peaks at the high binding energy. It suggests that C 1 s should be more complex than a single component. A detailed curve fitting analysis in Fig. 4 indeed indicates that each spectrum consists of two different Gaussian peaks at binding energies of 283.2 and 284.2 eV, which represent individual contributions from C—Si and C—C components, respectively [15]. For irradiated-only and corroded-only samples, the stronger peaks of C—C bonds suggest that the chemical state of sample surface was actually affected by irradiation or corrosion. Moreover, a dominant peak of C—C bonds can be clearly observed in the irradiated and corroded sample, indicating the broken of C—Si bonds and formation of carbon-rich phase in the surface.

The formation of carbon-rich phase in the SiC surface is also demonstrated by Raman spectroscopy, as shown in Fig. 5. It should be noted that no new peaks were observed in both the irradiated-only and corroded-only samples as compared to the spectrum of original sample. However, two new broad peaks in the near 1340–1350 and 1580–1590 cm^{-1} are found in the irradiated and corroded sample, which are corresponding to the D (the disorder peak) and G (graphitic peak) vibration modes of graphite, respectively [16,17]. The evolution of Raman Spectrum confirms that the carbon-rich phase is formed and some Si atoms are lost in the SiC surface after irradiation and corrosion. Actually, the carbon-rich phase was also observed in chemical vapor deposition (CVD) SiC or SiC ceramics after the FLiNaK molten salt corrosion [10,18,19]. The loss of Si element and the formation of carbon-rich phase in the irradiated and corroded SiC indicate that the irradiation can accelerate the corrosion of SiC.

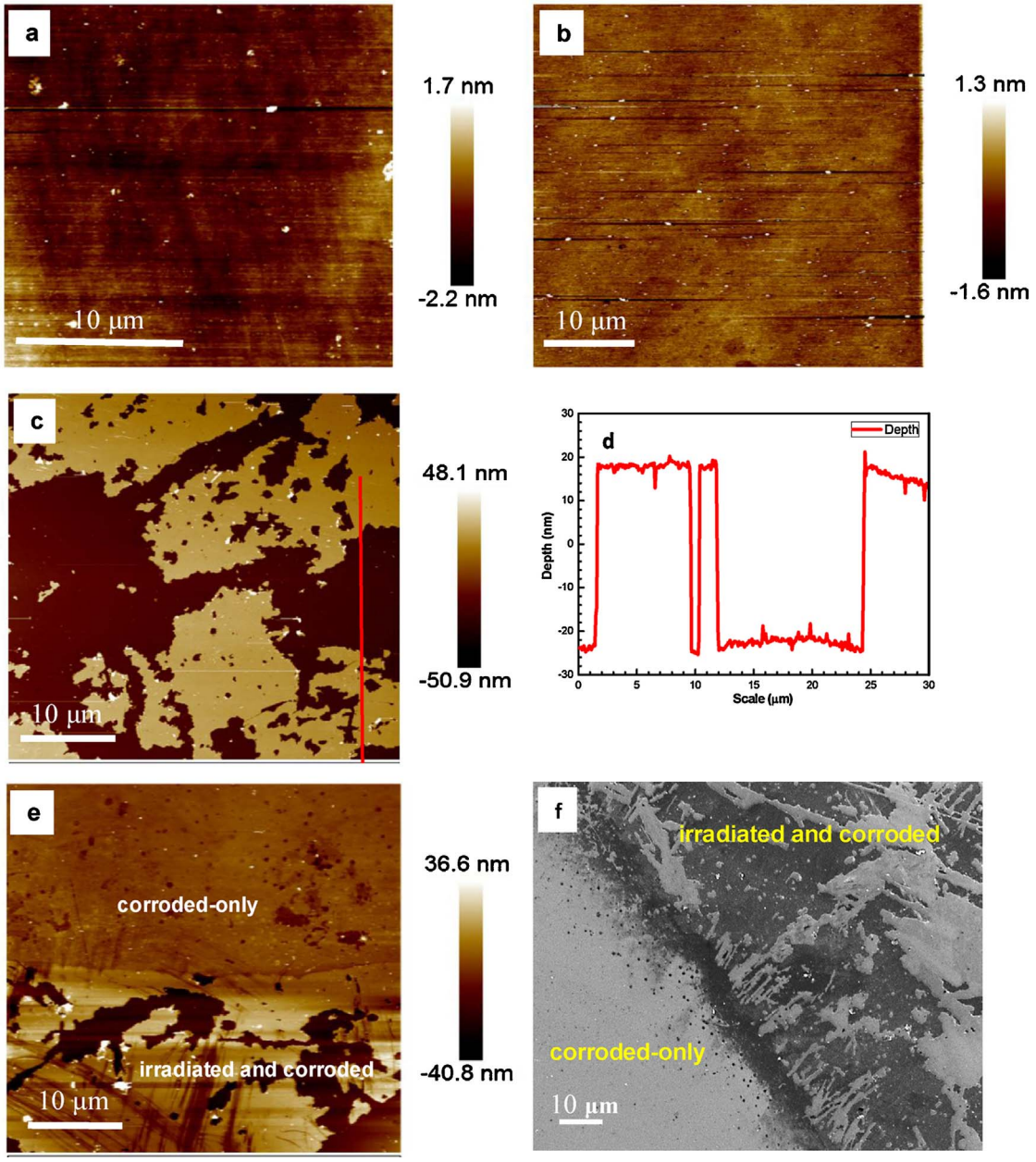

Fig. 3. AFM (a-e) and SEM (f) images for (a) the irradiated-only, (b) corroded-only and (c-f) irradiated & corroded samples. AFM line profile (d) was taken along the red line in images (c). Half of surface was covered with a copper foil to block ion beam during irradiation in the sample of (e, f). Corrosion testing of the unirradiated and irradiated samples (2.5 dpa) was performed at 650 °C for 166 h in the FLiNaK salt. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

In summary, the present study provides evidence for the effect of irradiation damage on corrosion of SiC in the FLiNaK molten salt at 650 °C. After irradiation and corrosion, the SiC surfaces are strongly attacked and denuded. It is worth noting that the denudation depth of 40 ± 8 nm is nearly consistent with the irradiation damage depth. Moreover, the loss of Si element and the formation of carbon-rich phase in irradiated and corroded SiC surface have been verified. Irradiation can accelerate the corrosion of SiC in FLiNaK molten salt.

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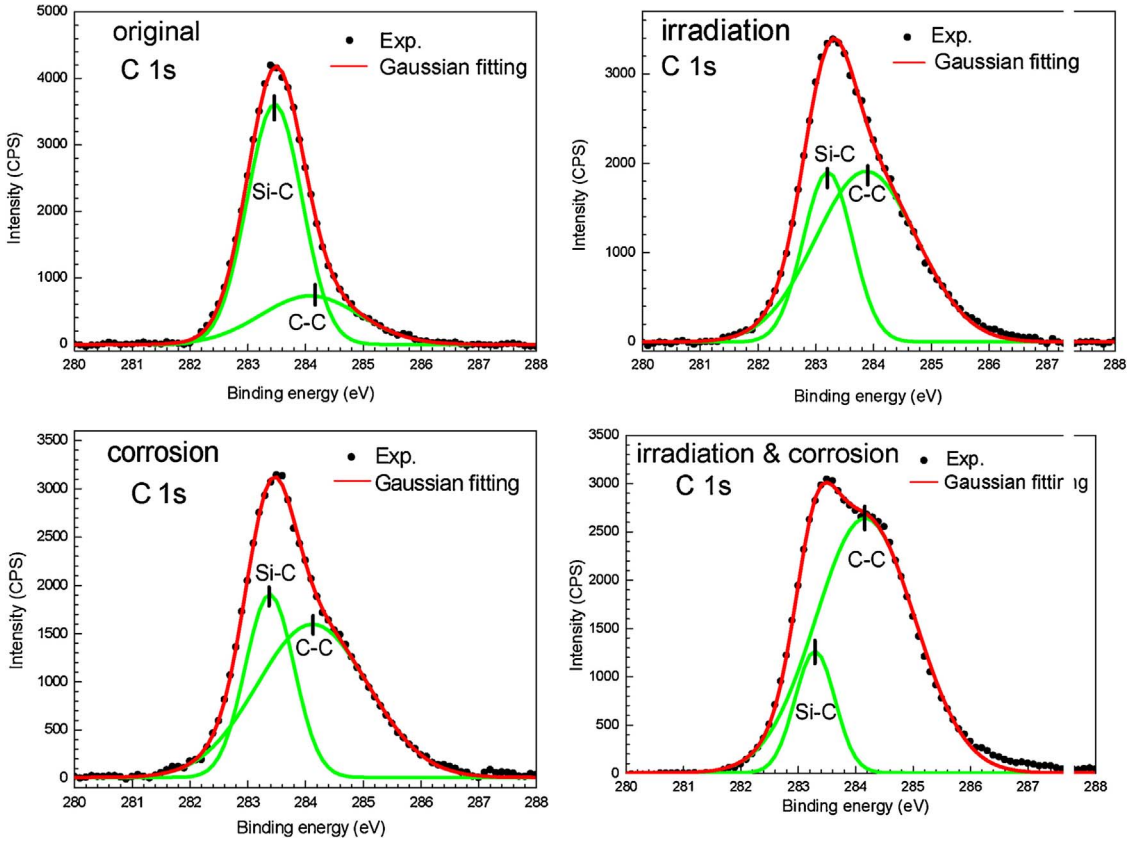

Fig. 4. XPS spectra (black dots) for C 1 s transitions in the original, irradiated-only, corroded-only and irradiated & corroded samples. The Gaussian fitting, representing different bonding components (C-Si and C-C) at the samples surface, with compared experiment data is also give in this figure. Corrosion testing of the unirradiated and irradiated samples (2.5 dpa) was performed at 650 °C for 166 h in the FLiNaK salt.

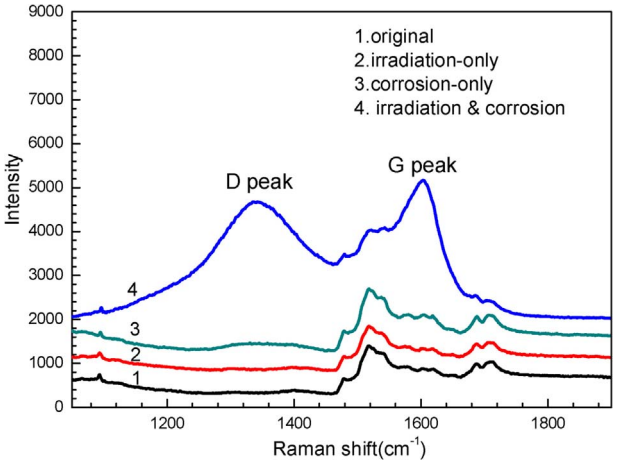

Fig. 5. Raman spectra of the original, irradiated-only, corroded-only and irradiated & corroded samples. Corrosion testing of the unirradiated and irradiated samples (2.5 dpa) was performed at 650 °C for 166 h in the FLiNaK salt.

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