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# Study of self-ion irradiated nanostructured ferritic alloy (NFA) and silicon carbide-nanostructured ferritic alloy (SiC-NFA) cladding materials

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ABSTRACT

Silicon carbide-nanostructured ferritic alloy (SiC-NFA) materials are expected to have the beneficial properties of each component for advanced nuclear claddings. Fabrication of pure NFA (0 vol% SiC-100 vol% NFA) and SiC-NFAs (2.5 vol% SiC-97.5 vol% NFA, 5 vol% SiC-95 vol% NFA) has been reported in our previous work. This paper is focused on the study of radiation damage in these materials under 5 MeV $Fe^{++}$ ion irradiation with a dose up to ~264 dpa. It is found that the material surfaces are damaged to high roughness with irregularly shaped ripples, which can be explained by the Bradley-Harper (B-H) model. The NFA matrix shows ion irradiation induced defect clusters and small dislocation loops, while the crystalline structure is maintained. Reaction products of $Fe_3Si$ and $Cr_{23}C_6$ are identified in the SiC-NFA materials, with the former having a partially crystalline structure but the latter having a fully amorphous structure upon irradiation. The different radiation damage behaviors of NFA, $Fe_3Si$, and $Cr_{23}C_6$ are explained using the defect reaction rate theory.

## 1. Introduction

Current light water nuclear reactors, which mainly use zirconium-based alloys as fuel cladding materials, have potential safety problems due to the rapid reaction between zirconium alloys and water coolant during severe accidents [1]. The release of hydrogen gas during zirconium corrosion can lead to explosions, such as what happened in the Fukushima Daiichi nuclear disaster [2]. As a result, development of more accident-tolerant cladding materials has become a top priority for the future design of nuclear reactors. Nanostructured ferritic alloy (NFA) [3–7] and silicon carbide (SiC) [8–12] are two promising accident-tolerant cladding materials due to their high thermal stability, good mechanical strength, and strong irradiation and corrosion resistance. Recently developed NFA materials, including Cr-based Fe alloys, such as Eurofer ODS (9Cr) [13], 9 YWTV (9Cr) [14], Eurofer 97 (9Cr) [15,16], 14YWT (14Cr) [17], 14Cr-ODS [18], ODS RAF (14Cr) [19], and European ODS (14Cr) [20], have achieved the hardness of 2–5 GPa. Recently, SiC-NFA materials have been fabricated using spark plasma sintering (SPS) and their microstructure and mechanical properties have been investigated in our previous work [21]. It is found that our pure NFA (0 vol% SiC-100 vol% NFA) and SiC-NFAs (2.5 vol% SiC-97.5 vol% NFA, 5 vol% SiC-95 vol% NFA) have comparable hardness values to the reported NFA steels and therefore are promising candidates for future nuclear cladding materials.

Irradiation resistance is one of the essential performance metrics for any cladding materials. The newly proposed Gen IV fission nuclear reactors require the irradiation tolerance up to 150 dpa at high temperatures [22,23]. Since irradiation induced damages vary from material to material due to the difference in materials properties, it is essential to understand the irradiation response of the SiC-NFA system, which has not been studied previously. In particular, SiC and the NFA matrix can react and form silicide and carbide phases [21]. The damage evolution in these regions may affect the overall performance of the system significantly. Ideally, nuclear irradiation experiments should be conducted in nuclear reactors. However, there is a worldwide paucity of accessible reactor capability, especially in the U.S., and the time to achieve the required damage levels is prohibitively time-consuming and expensive [24]. An alternative solution [25] is to use ion irradiation to emulate neutron irradiation. Ion irradiation can yield high damage rates with negligible or no residual radioactivity and at very low cost. The damage rates can be $10^4$ times faster than that of reactor irradiation [24]. High dose irradiation up to 200–500 dpa [26,27] has been demonstrated within days ($10^{-3}$–$10^{-1}$ dpa·$s^{-1}$) [28], whereas a neutron test reactor producing the same 500 dpa damage requires decades (typical ranges are $10^{-8}$–$10^{-6}$ dpa·$s^{-1}$) [28] and causes harmful radioactivity in the test samples at the same time. Because there is little or no activation, the samples are not radioactive upon ion irradiation, reducing the cost associated with post irradiation characterization. Above all, control of ion irradiation experiments (temperature, damage rate, and damage level) is much easier than that in a reactor. There is a

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growing body of evidence that the microstructural features (precipitates, voids, and radiation induced segregation) and properties (hardness, stress corrosion cracking susceptibility) from ion irradiation are in reasonably good agreement with those from neutron irradiation [29].

In this study, we focused on the ion irradiation study of pure NFA (0 vol% SiC-100 vol% NFA) and SiC-NFAs (2.5 vol% SiC-97.5 vol% NFA, 5 vol% SiC-95 vol% NFA), which were SPS sintered [21]. Their irradiation response was assessed using $Fe^{++}$ self-ion irradiation at room temperature. Particular attention was given to the damage evolution in the SiC-NFA reaction region, which is a unique microstructure of the SiC-NFA system. The surface morphology and irradiation-induced microstructures were characterized based on electron scanning/transmission microscopy (SEM/TEM). Complementary modeling studies with Bradley-Harper (B-H) model, SRIM calculations, and defect rate theory were utilized in order to reveal the irradiation response of different phases in the SiC-NFA materials.

## 2. Experimental

### 2.1. Ion irradiation

Pure NFA (0 vol% SiC-100 vol% NFA) and two SiC-NFA materials (2.5 vol% SiC-97.5 vol% NFA, 5 vol% SiC-95 vol% NFA) were made by SPS at 1000 °C [21]. In the materials, some reaction phases were produced during the sintering process. These reaction phases can be identified as iron silicide and chromium carbide from the electron diffraction characterization in the region without ion irradiation. The samples were polished to 1.3 mm thickness (final 1200 grit paper) before ion irradiation, which was carried out at the Michigan Ion Beam Laboratory (MIBL) of University of Michigan. These samples were exposed to 5 MeV $Fe^{++}$ ion irradiation with an ion fluence of $2.7 \times 10^{17}$ ions·cm$^{-2}$ for 21 h (flux of $3.6 \times 10^{12}$ ions·cm$^{-2}$·s$^{-1}$). The ion irradiation temperature was by default at 33 °C due to ion irradiation induced heat release. The sample layout on the stage and the samples with irradiation induced dark areas are shown in Fig. S1 of the Supplemental Materials. These dark areas resulted from the ion irradiation induced surface roughness as observed in Fig. 1a–c.

### 2.2. TEM sample preparation

A $Ga^{+}$ focused ion beam microscope (FIB, FEI Helios 600 Nano Lab, Hillsboro, OR) was used to prepare the transmission electron microscopy (TEM) sample. An area of 25 μm long and 2 μm wide on the ion irradiated 5 vol% SiC-95 vol% NFA sample surface was milled in the depth direction (Fig. S2a) and then lifted out at 4.5 μm height (Fig. S2b). The liftout foil in 25 μm × 2 μm × 4.5 μm size was further milled to 50–100 nm thickness (with the final voltage at 1 kV, current at 14 pA) for TEM observation.

### 2.3. Characterization

The surface morphology of the ion irradiated samples was examined by a scanning electron microscope (SEM, FEI FEG-ESEM Quanta600, FEI Company, Hillsboro, OR). The ion irradiation induced ripple wavelengths were measured manually from the SEM images. The thickness of the ion irradiation induced ripples was measured by SEM on FIB (FEI Helios 600 Nano Lab, Hillsboro, OR) milled cross sections. The microstructure and elemental distribution of the ion irradiated materials were observed by a transmission electron microscope (TEM, JEOL 2100, JEOL USA, Peabody, MA) and the attached energy-dispersive X-ray spectrometer (STEM-EDS).

### 2.4. Simulation by SRIM

SRIM calculations were conducted for the pure NFA and SiC-NFA materials using the SRIM (Stopping and Range of Ions in Matter) software 2013 [30] in order to predict the radiation damage profile. The ion source was $Fe^{++}$ with 5 MeV energy and the incident angle was 0°. The calculation of damage profiles was based on the quick Kinchin-Pease mode with all the displacement threshold energies at 40 eV and lattice binding energies at 0 eV [31]. The calculation for sputtering yield was based on Monolayer Collision mode with the target thickness at 30 Å and defaulted energies. A total incident ion number of 50,000 was used for the SRIM simulation. All the elements were included in the calculation with their equivalent atom percentages considered in a monolayer. The composition difference between the pure NFA and the SiC-NFA materials was that extra Si was dissolved into the NFA lattice for the SiC-NFAs due to reactions between SiC and NFA. The parameters used in the SRIM simulation for damage profile estimation are listed in Table 1. It should be noted that the creation of the actual composition distributions for the SiC-NFA system was not possible for the SRIM

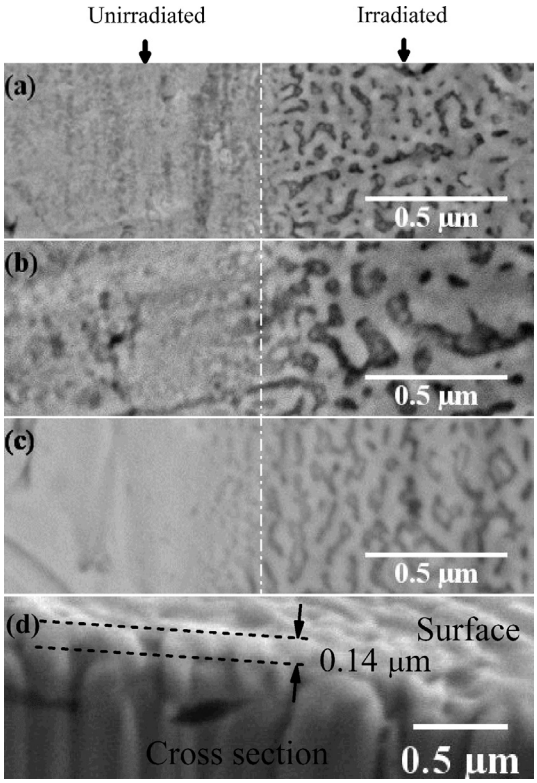


**Fig. 1.** Surface SEM images showing the ripples in the ion irradiated NFA and SiC-NFA materials, (a) pure NFA, (b) 2.5 vol% SiC-97.5 vol% NFA, (c) 5 vol% SiC-95 vol% NFA; cross section SEM image at 52° tilt showing the ripple thickness of the ion irradiated pure NFA (d).

**Table 1**
Parameters used in SRIM simulation for damage profile estimation.

| Element | Fe | Cr | W | Ti | V | C | Y | O | Si |
|---|---|---|---|---|---|---|---|---|---|
| NFA (at.%) | 85.8 | 9.5 | 0.6 | 0.2 | 0.2 | 0.5 | 0.1 | 3.1 | / |
| 2.5 vol% SiC-97.5 vol% NFA (at.%) | 81.6 | 9.1 | 0.6 | 0.2 | 0.2 | 2.9 | 0.1 | 2.9 | 2.4 |
| 5 vol% SiC-95 vol% NFA (at.%) | 77.6 | 8.6 | 0.5 | 0.2 | 0.2 | 5.2 | 0.1 | 2.8 | 4.8 |
| *$E_{disp}$ (eV) | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| *$E_{latt}$ (eV) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *$E_{surf}$ (eV) | 4.34 | 4.12 | 8.68 | 4.89 | 5.33 | 7.41 | 4.24 | 2 | 4.7 |

* $E_{disp}$ = Displacement Energy, the minimum energy required to knock a target atom away from its lattice site; $E_{latt}$ = Lattice Binding Energy, the minimum energy needed to remove an atom from a lattice site; $E_{surf}$ = Surface Binding Energy, the energy required to remove an atom from the surface.