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# Microstructural evolution analysis of NITE SiC/SiC composite using TEM examination and dual-ion irradiation

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**Abstract**

Irradiation effects in a SiC/SiC composite reinforced by Tyranno-SA fibers and produced by an innovative processing method, nano-powder infiltration and transient eutectic phase (NITE) processing, were investigated. Dual-beam ion irradiation methods and energy-filtered transmission electron microscopy were used in the investigation. The NITE SiC matrix had dense, isotropic grains several hundreds nm in diameter. A small amount of secondary phases from residual additives were found within the SiC fiber bundles. Dual-ion irradiations achieved a dose of 60 dpa at 1200 °C. TEM investigation showed no significant modification by irradiation in either the Tyranno-SA fibers or the NITE SiC matrix, except for a small amount of micro-cavity formation. The synergistic effects of heavy irradiation and helium atoms in NITE SiC/SiC composites at elevated temperature are discussed.
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## 1. Introduction

The nano-powder infiltration and transient eutectic phase (NITE) process is expected to be appropriate for the mass production of SiC/SiC composites having the properties needed for use as a fusion material [1]. Previous research on SiC/SiC composites produced by the chemical vapor infiltration (CVI) and the polymer infiltration and pyrolysis (PIP) methods have shown that high purity SiC fibers and matrix provide adequate microstructural stability during irradiation [2,3]. Earlier grades of Si–C–O fibers included amorphous SiC phases which resulted in a significant shrinkage in irradiation environments and caused the debond of interface between matrix and fibers. This resulted in the degradation of mechanical properties [4]. The normal behavior of SiC in irradiation environments is swelling; shrinkage is a special phenomenon seen in amorphous SiC. The use of crystallized SiC fibers, such as Hi-Nicalon Type-S and Tyranno-SA [5], solved the problem of degradation of mechanical properties of SiC/SiC composites in irradiation environments. The displacement damage accumulation and dimensional stability of SiC were also studied in the previous research [6]. The swelling produced by irradiation trends to decrease with increase of temperature up to 1400 °C. Dual-ion irradiation research showed that helium in SiC enhanced the cavity formation at temperature over 1000 °C. Because of the low rate of defect clustering, helium cavity formation was slow. The diameter of grains

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in SiC affected the size and number density of helium cavities. For example, 0.3% swelling by helium cavities were found in CVI-SiC after dual-ion irradiation at 1000 °C to 100 dpa, but only a very small amount of micro-cavities were observed in Tyranno-SA fibers under the same condition [3]. There may be difficulties adapting the CVI method for the mass production of SiC/SiC composites, so the NITE processing method is being developed as an alternative production technique [7]. The NITE process is able to produce high-quality SiC/SiC composites having the following characteristics: (1) dense and robust, (2) fairly high thermal conductivity, (3) chemically stable and (4) low production cost. These characteristics are appropriate for the blanket materials in fusion reactor. The present research examines the chemical feature of microstructures of the NITE SiC/SiC composites using energy filtered TEM and evaluates the microstructural and dimensional stability of the composites under irradiation environments using ion irradiation methods.

## 2. Experiments

The reinforcement used was Tyranno™-SA grade-3 polycrystalline fiber (UBE Industry, Ltd., Yamaguchi, Japan). These fibers were coated with pyrolytic carbon (PyC) by chemical vapor deposition, with the coating thickness about 0.5–1 μm. The NITE SiC/SiC composites were fabricated at Ube Co. Ltd using β-SiC nano-powder (Marketech International Inc., USA). This NITE SiC/SiC composite grade is named Pilot grade-2 [8]. The particle size of β-SiC nano-powder was below 30 nm. The powders and fibers were compacted at 1800 °C and 20 MPa by hot pressing. $Al_2O_3$–$Y_2O_3$–$SiO_2$ ternary system additives were used for the fabrication of composites. The composites were cut to square shapes and their surfaces were polished by diamond particles. The dimension of specimens was $4 \times 2 \times 2$ mm. The surface for ion irradiation was selected to be normal to the fiber direction.

The irradiation experiments were performed at the dual-beam material irradiation facility for energy technology (DuET) in the Institute of Advanced Energy, Kyoto University, using 1.7 MeV tandem and 1 MeV single end accelerators [9]. Simultaneous ion irradiation of 5.1 MeV Si and 1 MeV He ions were used. A single-ion irradiation means that only 5.1 MeV Si ions were used. The irradiation temperature was 1200 °C, for nominal dose and dose rate of 60 dpa and $1 \times 10^{-3}$ dpa/s, respectively. The helium to displacement damage ratio was set at 60 appm He/dpa [10]. A focused ion beam (FIB) process was used for the preparation of TEM specimens from the irradiated SiC/SiC composites. The thinned foils were cut from the materials and lifted using a micro pick-up system. The foils were put on a carbon film supported by copper grids. The microstructural investigation and chemical composition analysis was carried out with a JEOL JEM-2200FS energy-filtrated, high-resolution analysis TEM, EDX.

## 3. Results

Fig. 1 shows a backscattered electron image of the surface on a NITE SiC/SIC composite. Few pores and a very dense matrix are seen in this as-fabricated material. Some residual additives are also observed in the fiber bundle and matrix. The bright contrast in the back scattered image of Fig. 1 indicates that these additives contain high $Z$ elements. At this TEM scale, the NITE SiC matrix is dense and highly crystalline. Isotropic grains have a diameter of several hundred nanometer. There are also some carbon phases which peeled off from the carbon coating of the SiC fibers [11].

A TEM image of a cross-section of a dual-ion irradiated NITE SiC/SiC composite is shown in Fig. 2. The irradiation temperature and nominal dose were 1200 °C and 60 dpa, respectively. This shows a typical microstructure of the NITE SiC/SiC composite; significant dimensional changes and void formation were not observed in either

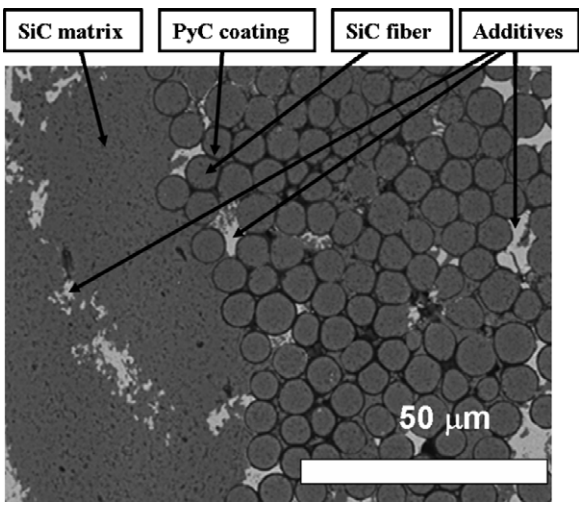


Fig. 1. Back scattered electron image of a NITE SiC/SiC composite.

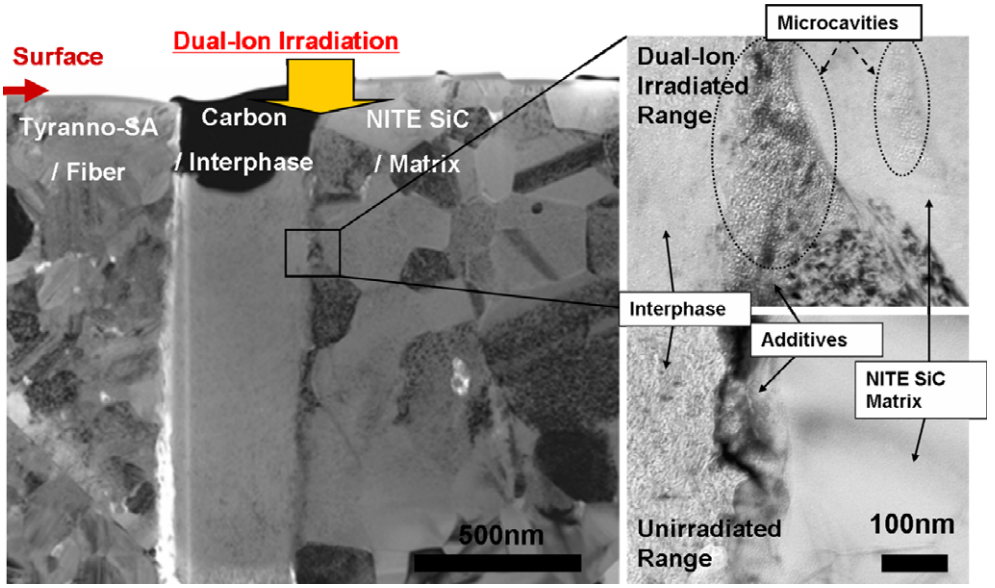


Fig. 2. Cross-sectional TEM image of typical microstructure and micro-cavity formation in a NITE SiC/SiC composite after dual-ion irradiation to 60 dpa at 1200 °C.

the matrix or fiber. Very fine cavities were observed in the matrix and the additive layer on the interface between matrix and carbon interphase. Fig. 3 shows an irregular microstructure including residual additives after a dual-ion irradiation to 60 dpa at 1200 °C. This thin foil was cut from the white contrast area surrounding a Tyranno-SA fiber in Fig. 1. Fig. 3 includes a bright field (BF) and a high-angle annular dark-field (HAADF) TEM images and EDX mapping images. The TEM–EDX data and XRD analysis showed that these were yttrium–aluminum oxides [12]. Because the ratio of aluminum and yttrium in yttrium–aluminum oxides was 1:2, the phase is speculated to be $Y_4Al_2O_9$ (YAM). The residual additives were not uniform, divided into two phases. The other phase found in the

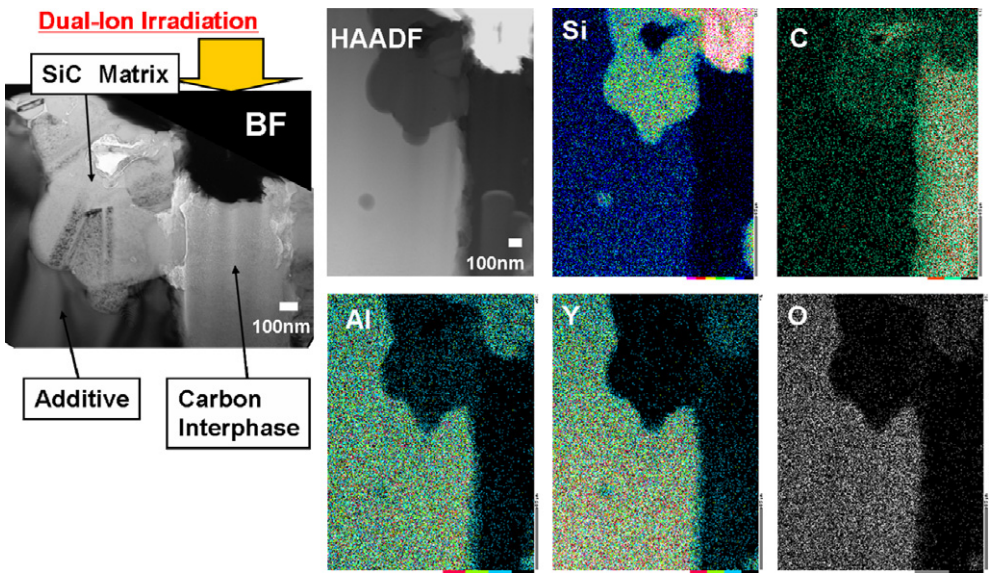


Fig. 3. Cross-sectional TEM images and EDX mappings of mixed phases of additives and NITE SiC matrix for dual -ion irradiation at 1200 °C and 60 dpa.

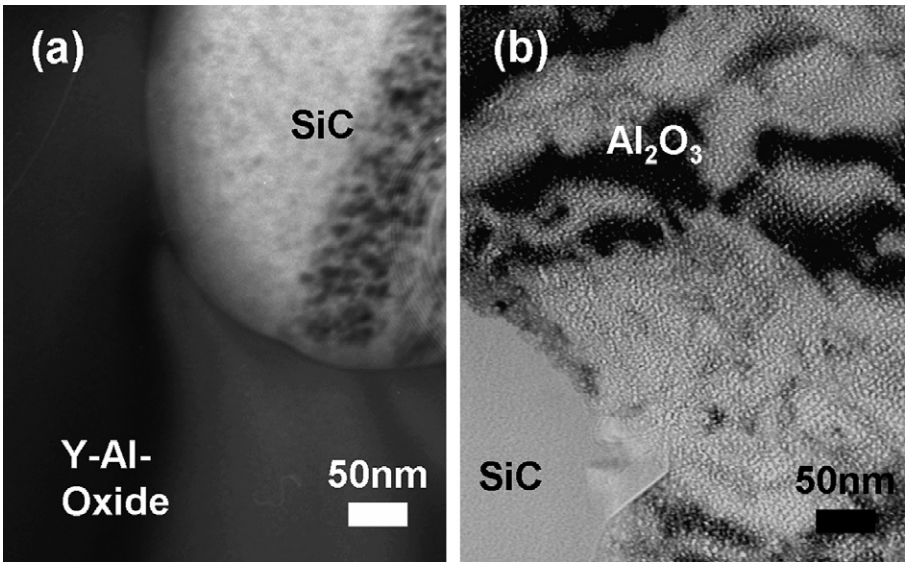


Fig. 4. TEM images of boundaries between SiC and additives after irradiation to 60 dpa at 1200 °C (a) dual-ion irradiated Y–Al oxide and NITE SiC matrix (b) single-ion irradiated $Al_2O_3$ and NITE SiC matrix.

additive was speculated to alumina ($Al_2O_3$). There is also the possibility that this phase included a small amount of silicon-oxides. A comparison of the stabilities of both additives during ion-irradiation is shown in Fig. 4(a) and (b); for irradiation temperature and dose of 1200 °C and 60 dpa, respectively. Fig. 4(a) is a TEM image containing a boundary between the yttrium–aluminum oxide and the NITE SiC matrix after the dual-ion irradiation. There is some irradiation damage in the NITE SiC matrix, but no helium cavity formation and little irradiation damage are observed in the yttrium–aluminum oxide. On the other hands, the void swelling occurred in the $Al_2O_3$ by after single-ion irradiation (without helium implantation), as shown in Fig. 4(b). Because this specimen had no implanted helium, this phenomenon suggests it is a result of only the accumulation of displacement damage.

## 4. Discussion

NITE processing is able to produce a high purity, crystalline SiC/SiC composite, so we have applied our knowledge from previous researches on CVD-SiC and SiC/SiC composites to the NITE SiC/SiC composites. The use of crystalline and stoichiometric SiC stabilizes the dimensional and mechanical properties of the composites in irradiation environments. Point defect swelling and void formation in SiC under fusion and fission condition have been studied for CVD-SiC and Tyranno-SA fibers using both neutron and ion irradiations [2,3]. Cavity formation in Tyranno-SA fibers is lower than that in CVI-SiC matrix under the dual-ion irradiation at 1000 °C and 100 dpa. This difference is believed to be caused by the difference in grain size. Because the helium is mainly absorbed at grain boundaries, the relatively smaller grains in Tyranno-SA compared with CVI-SiC provide a larger number of trapping sites for helium. This results in decreasing the helium cavity formation in grains. The typical microstructure of a NITE SiC matrix is very similar to that of Tyranno-SA fibers, thus most of irradiation effects on the NITE SiC may follow the trends observed in Tyranno-SA. In the case of the present research, the cavity formation by helium in the NITE SiC matrix during dual-ion irradiation at 1200 °C and 60 dpa is very similar to the results for Tyranno-SA fibers under dual-ion irradiation at 1000 °C and 100 dpa found in the previous research [3].

A large difference between NITE SiC/SiC and CVI SiC/SiC composites is the existence of residual additives. Instead of a fully dense and isotropic microstructure in the NITE SiC, a small amount of additives remains in the composite. This is unavoidable in the NITE process, developed as a potential engineering process for practical mass production. The investigation of the mixed microstructure of NITE SiC and additives shows that the

additives are not uniformly distributed in this composite. The yttrium–aluminum oxide which was speculated to be YAM includes a small amount of silicon, thus the real chemical formula might be $Y_4Al_{2(1-x)}Si_{2x}O_{9+x}$. The yttrium–aluminum oxide did not show significant microstructural modification, so this phase may be microstructurally stabile under ion-irradiation at 1200 °C. The detail of formation procedure of another additive phase, alumina ($Al_2O_3$) is not clear now. The fine cavities in $Al_2O_3$ are believed to be voids produced by vacancy clustering, since bulk $Al_2O_3$ shows void swelling in the temperature rang from 652 °C to 827 °C in neutron irradiation [13]. The irradiation temperature of the present experiment was much higher than 827 °C, and the high irradiation rate of ion-irradiation tends to shift the void swelling to a higher temperature range. Another possible explanation of the phenomenon is the gas production by chemical reactions between $Al_2O_3$ and SiC [14]. The experimental data on vaporization of $Al_2O_3$ and SiC mixtures in vacuum is very limited, so it is difficult to determine the cause of this phenomenon. The residual additives should be minimized because of the thermal and irradiation effects on them. However, it is not possible to remove the residual additives completely, so further investigation of the behavior of NITE SiC/SiC composites including additives is necessary.

## 5. Conclusion

The microstructural stability of NITE SiC/SiC composites under fusion environment conditions were studied using a dual-ion irradiation experiment method and TEM observation. Dual-ion irradiation to 60 dpa at 1200 °C did not modify the microstructure of the NITE SiC matrix except for limited micro-cavity formation. Residual additives in NITE SiC/SiC Pilot grade-2 consisted of yttrium aluminum oxide which was speculated to be $Y_4Al_2O_9$ (YAM) and $Al_2O_3$. The yttrium–aluminum oxide seemed to be stable under the dual-ion irradiation environment, but void swelling occurred in $Al_2O_3$. The development of optimized and stabilized additives in NITE SiC/SiC is believed to be important.

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