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Letter to the Editors

Helium-bubble formation behavior of SiCf/SiC composites after helium implantation

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Abstract

Helium-bubble formation behavior in SiC-fiber-reinforced SiC-matrix (SiCf/SiC) composites was studied using helium implantation. Microstructural observation of the He-implanted specimens was carried out after post-implantation annealing at 1673 K for 1 h. Microstructural observation revealed small cavities in the SiC matrix only. No cavities were observed in the SiC fibers or in the carbon coating layers or their interfaces.

1. Introduction

Silicon carbide (SiC) has been proposed for use in fusion-reactor structural materials due to its low activity after neutron irradiation and its strength under high temperature. Since monolithic SiC is very brittle, SiC-fiber-reinforced SiC-matrix composites (SiCf/SiC) have been developed to increase its toughness for application to structural materials of fusion reactors. The recent status of the SiCf/SiC composites for fusion has been reviewed by Snead et al. [1].

In fusion reactor environments, helium is produced in SiC in the first wall region at a rate of about 1500–2000 appm He/(MW a m^2) by transmutation reactions, with a displacement damage of 10–15 dpa/(MW a m^2), depending on the details of the blanket structure and on the neutron spectrum [1,2]. The He/dpa ratio of SiC is higher than that of other candidate alloys, such as vanadium and ferritic steels [1]. Because the presence of helium in irradiated materials accelerates swelling and creep, and since helium bubbles precipitate at interfaces such as the grain-boundary and fiber/matrix interfaces, mis matching and interface debonding between fibers and matrices may occur in SiC/SiC composites under fusion reactor conditions. On the other hand, the strength of the fiber/matrix interface will influence the fracture strength and toughness of the fiber-reinforced composites. Therefore, an understanding of the behavior of helium gas atoms and bubbles of the SiC/SiC composite is important for its application to structural materials of fusion reactors. The behavior of helium gas atoms in monolithic SiC and graphite has been studied by several researchers [3–6] using helium-release measurements and TEM observation, but the behavior of these atoms in SiCf/SiC composites has not been investigated. The purpose of this work is to study helium-bubble formation in SiCf/SiC composites that are reinforced with SiC weaves

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made of Hi-Nicalon fibers using helium implantation methods by accelerators.

2. Experimental

In this work, we studied helium effects on a 2D-SiCf/SiC composite reinforced by SiC weaves made of Hi-Nicalon fibers. The composite was fabricated by Dupont in USA. The CVI process was used to coat the fibers with carbon, and the SiC matrix was also deposited by CVI. The resulting carbon coating was approximately 1.2 μm thick. The composite was manufactured in the form of plate and bend bars of width 4 mm, length 25 mm and thickness 2 mm were cut from the plate. Implanted specimens were cut from the bar as thin plates of the composites, and the implanted surface was a cross sectional surface of the bend bar. The specimens were 2 mm in width, 3 mm in length and 0.3 mm in thickness. Finally, the specimen surface was polished using a diamond paste.

Helium implantation was carried out using a dynamitron accelerator at Tohoku University. The accelerated energy of the helium ions was 3.00 and 2.95 MeV. The projected range in SiC was approximately 9 μm and was calculated using the TRIM code [7]. To obtain uniform helium depth distribution, a degrader wheel consisting of 11-step thickness aluminum foils was used. To obtain a smooth depth distribution of helium, implantation was conducted twice for each specimen using accelerating voltages of 3.00 and 2.95 MeV. Fig. 1 shows the calculated depth distribution of helium and the displacement damage in SiC fibers (density: 2.7 g/cm^3). The total amount of implanted helium concentration calculated from the irradiation fluence was 10 000 appm in the range from 1 to 5.5 μm depth. Displacement damage in the helium-implanted area was approximately 0.5 dpa using $E_d = 45$ eV. The implantation temperature, was as measured by an infrared pyrometer during irradiation, was about 100°C. After implantation, annealing at 1667 K for 1 h was carried out to emphasize helium-bubble formation in the composite.

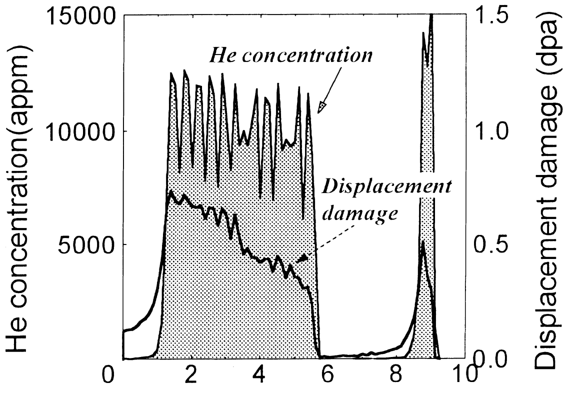

Fig. 1. Calculated depth distribution of implanted helium and displacement damage by TRIM code [7].

The TEM specimen was prepared by a Focused Ion Beam (FIB) machine using a 40 keV gallium ion beam at CARET of Hokkaido University. The area from the implanted surface to 3 μm depth was sputtered and back thinning was carried out using the FIB machine. The microstructural observation was conducted using a transmission electron microscope (JEOL-2010) at 200 kV.

3. Results and discussion

The microstructural observation results are shown in Fig. 2 for the following observation areas: (a) SiC fiber and carbon coating; (b) carbon coating and SiC matrix; and (c) SiC matrix. As shown in Fig. 2(c), cavity was observed only in the SiC matrix. Cavities were not observed in unimplanted specimens. The cavities in the SiC matrix may be helium bubbles. The helium bubbles are located at the grain-boundaries of β-SiC. There are large cavities at the growth-boundaries in the SiC matrix, such as the large hole in the center of Fig. 2(c). A large cavity at the growth-boundary is sometimes observed in unimplanted specimens but its number density is generally much less than that of the small bubbles of implanted specimens. The large cavity may be a defect induced during the CVI process. The small, dense bubbles are not observed in the SiC matrix of the unimplanted specimens.

A bubble-denuded zone of the SiC matrix in the vicinity of the interface of the carbon coating layer is indicated by an arrow in Fig. 2(b). The width of the denuded zone is about 100 nm. Bubbles are not observed at the matrix/carbon coating interface, in the carbon coating layer, or in the SiC fibers. Sasaki reported helium bubble formation in B-doped sintered β-SiC after neutron irradiation above 1473 K [5], which finding agrees with the helium-bubble formation in the SiC matrix seen here. Atsumi reported a termination of helium release from graphite at lower temperature (<1200 K) [6]. Jung reported the helium diffusion coefficient of pyrolytic graphite and reaction sintered SiC using 5–28 MeV He ion implantation [4]. From his results, the present magnitude of the diffusion coefficient of helium in graphite was about 30 times larger than that in SiC in the temperature range of 800–1050 K. Based on these previous works, helium atoms in the carbon coating layer appear to have been released during annealing and helium atoms in the SiC matrix near the carbon layer also would seem to have been released from the SiC. The

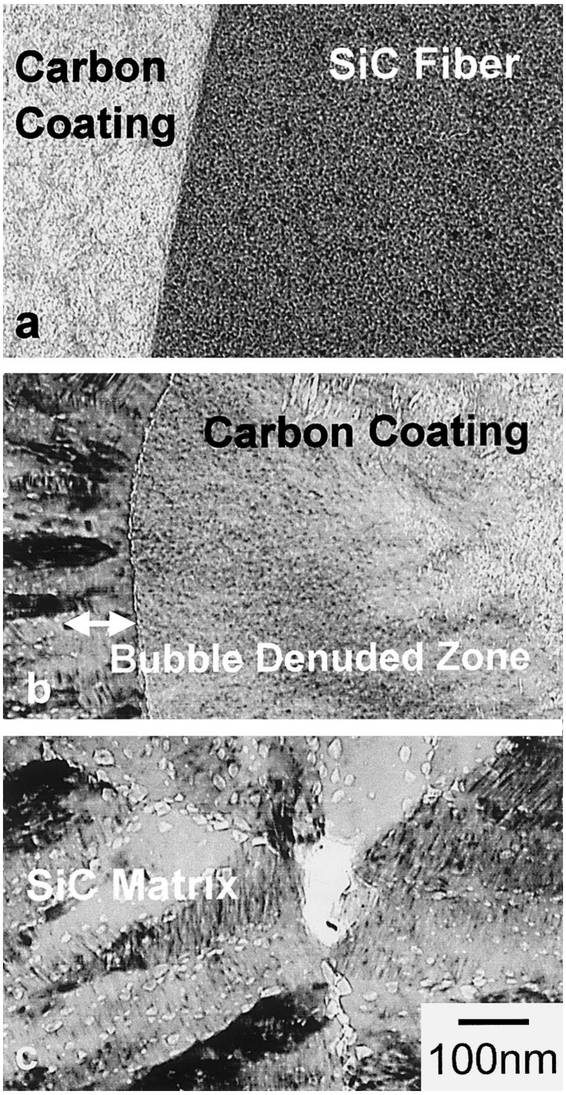

Fig. 2. TEM micrographs of SiCf/SiC composites after helium implantation and annealing at 1673 K for 1 h: (a) SiC fiber/Carbon coating; (b) Carbon coating/SiC matrix; (c) SiC matrix.

driving force of helium release from SiC was the gradient of concentration of helium near the interface area. The formation of a bubble-denuded zone in the SiC matrix may be attributable to the non-uniform remaining helium atom distribution in the vicinity of the interface area.

The same material pair of SiC and graphite exists in the SiC fiber. The SiC fiber consists of small SiC grains (grain size, about 10 nm) and extra carbon atoms located between the SiC grains as graphite [8,9]. In the case of the Hi-Nicalon fiber, there is a large amount of extra carbon; for example, the C/Si atomic ratio of Hi-Nicalon is 1.39 [10]. Bubbles are not observed under these experimental conditions in the SiC fiber or the carbon layer. Helium in the SiC grains may move at 1673 K and be removed from SiC grains through an extra carbon layers in the fiber, because the grain size of SiC in the fiber is smaller than the width of the helium-bubble-denuded zone in the SiC matrix, which reflects the diffusion distance of helium in SiC at 1673 K. In the experimental configuration of this work, the distance from the helium-implanted area to the free surface (implanted surface) is smaller (1–5.5 μm) than the diameter of the SiC fiber (about 14 μm), and therefore, a large percentage of the helium atoms in SiC fiber might be released from the fiber's implanted area directly to the surface during annealing at 1673 K.

Recent works revealed that neutron irradiation induced degradation and creep resistance of SiC fibers at high temperature depended on their oxygen contents [11,12] and degree of crystallization [13]. Densification and grain growth occurred in the irradiated conventional SiC fiber such as Nicalon$^{\text{TM}}$ [11,14], therefore highly crystalline and nearly stoichiometric composition SiC fibers, such as Hi-Nicalon type-S$^{\text{TM}}$ [10] and Sylamic$^{\text{TM}}$, are expected to have resistance to displacement damage and creep. On the other hand, the result of this work suggest that helium atoms may remain and form bubbles in highly crystalline SiC and these remaining helium atoms may induce helium bubble swelling and degrade the mechanical properties of the composites at fusion-reactor operating temperatures (1000–1200 K). The results of this work also suggest that helium bubbles may not precipitate at the interface in the SiCf/SiC composite because of the high diffusivity of helium in graphite. For this reason, optimization of the carbon contents of fibers is required, as well as microstructural observation of the bulk composite and its helium atom release in order to confirm the behavior of helium. To generalize and confirm the results on bulk composites, higher energy (ex. 28–36 MeV [4,15]) He implantation experiments will be required.

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