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The effect of high dose/high temperature irradiation on high purity fibers and their silicon carbide composites

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Abstract

Silicon carbide composites were fabricated by chemical vapor infiltration method using high purity fiber, Hi-Nicalon Type-S and Tyranno SA, and non-high purity fiber Hi-Nicalon. Bare fibers, SiC/SiC composites and CVD SiC were irradiated at 7.7 dpa and 800 °C or 6.0 dpa and 300 °C. The density of fiber and CVD SiC was measured by gradient column technique. Mechanical properties of the composites were evaluated by four-point flexural tests. Fracture surfaces were observed by SEM. Tyranno SA fiber and CVD SiC showed similar swelling behavior following irradiation at 7.7 dpa and 800 °C. Mechanical properties of composites reinforced with Hi-Nicalon Type-S and Tyranno SA fibers were stable even following neutron irradiation at 7.7 dpa and 800 °C. Fracture surfaces of these composites following irradiation were similar to those of non-irradiated composites with relatively short fiber pull-out.

1. Introduction

The superior high temperature mechanical properties and low activation make SiC/SiC composites very attractive as fission and fusion reactor materials [1,2]. The higher thermal efficiency associated with self-cooled solid blanket [3,4] or gas-cooled solid blanket [5], where potential plant efficiency is 50%, can be available in the fusion blanket using SiC/SiC composites. In fusion reactor environment, nuclear collisions and reactions with high-energy neutrons and particles from fusion plasma have strong impacts on materials through the production of displacement damage and transmutation effects [6]. Degradation of material performance such as mechanical properties, thermal properties and so on has been recognized as the key issues and extensive efforts have been conducted [7].

Up to this point, interfacial properties between the fiber and matrix of neutron-irradiated SiC/SiC composites limited mechanical performance [8]. This limitation has been attributed primarily to shrinkage in the SiC-based fibers due to irradiation-induced grain growth of microcrystalline fibers [9,10], irradiation-assisted oxidation [11], and potentially large dimensional changes of the graphite [10,12] interphase applied to the fibers, while matrix swells a little by irradiation-induced point defect. Fiber shrinkage leads to fiber/matrix debonding as reported by Snead et al. [13] and a decrease in elastic modulus and fracture strength. Therefore, there is a critical need to optimize the microstructure of SiC/SiC composites (i.e. fiber, fiber/matrix interphase and matrix) to retain the interfacial shear strength between the fiber and matrix. To mitigate radiation effects, the recent

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trend in SiC fiber development is toward lower oxygen content, reduced free carbon and enhanced crystallinity. The development of more radiation-resistant SiC composites is based on the use of near stoichiometric SiC fibers with lower oxygen and SiC-based interphases. Recently, near stoichiometric SiC fibers have been developed including Hi-Nicalon™ Type-S [14], Sylramic™ [15] and Tyranno™ SA [16]. However the effect of high dose and high temperature irradiation on the SiC/SiC composites reinforced with highly crystalline fibers has not been revealed yet.

The objective of this work is characterization of neutron irradiation effects on high purity fibers and their silicon carbide composites for fusion application. For this purpose, the effects of high dose and high temperature neutron irradiation on mechanical properties of SiC/SiC composites reinforced with high purity fiber were evaluated.

2. Experimental procedure

The fibers used in this work were Tyranno™ SA (Ube Industries Ltd., Ube, Japan), Hi-Nicalon Type-S and Hi-Nicalon™ SiC fibers (Nippon Carbon Co., Tokyo, Japan). Both satin woven and plain woven fibers were used to fabricate composites with orientation of $0/90° \pm 30°$. Tyranno SA and Hi-Nicalon Type-S fibers contain a reduced amount of oxygen and a near-stoichiometric chemical composition and consist of β-SiC polycrystalline structures while another low oxygen fiber, Hi-Nicalon, has excess carbon and does not have highly crystalline structure compared with Tyranno SA and Type-S. Representative properties and chemical compositions of the fibers [14,17] reported by the manufactures are compiled in Table 1. Note Tyranno SA fiber used in this work was the first trial piece. Tyranno SA fiber has been improved and the mechanical properties of a current fiber are slightly different from those of the Tyranno SA fiber used in this work. The matrix of composite was formed by forced-flow thermal-gradient chemical vapor infiltration (FCVI) method [18] at Oak Ridge National Laboratory. A pyrolitic carbon interphase was applied to the fibers by CVI prior to the matrix processing. The nominal thickness of the interphase was 150 and 500 nm. The properties of material used in this work are summarized in Table 2.

Table 2
The properties of samples used in this work

Fiber	Woven type	C thickness (nm)	Irradiation temperature (°C)
Tyranno SA	Plain woven	150	800
Tyranno SA	Satin woven	150	300, 800
Hi-Nicalon Type-S	Plain woven	150	300, 800
Hi-Nicalon Type-S	Satin woven	150	300, 800
Hi-Nicalon Type-S	Satin woven	500	300
Hi-Nicalon	Plain woven	150	800

Neutron irradiation was carried out in the HFIR 14J capsule at Oak Ridge National Laboratory, USA. The fluence and temperature of the irradiation were 7.7×10^{25} nm^{-2} ($E > 0.1$ MeV) at 800 °C and 6.0×10^{25} nm^{-2} ($E > 0.1$ MeV) at 300 °C. The sample temperature was controlled by electric heaters.

Density was measured using density gradient column and chemicals were mixed to generate a column. The column with a density range between 2.90 and 3.10 g/cm^3 was mixed with bromoform and diiodomethane. Following a HF bath at room temperature to remove any surface silica, samples were dropped into the column. When the sample position was stable, accurate density was measured.

The composites were square-cut into 30 (long) × 6.0 (wide) × 2.2 (thick) mm^3 bar for the flexural tests. Four-point flexural tests were carried out at ambient temperature prior to and after the irradiations. The support span and the loading span were 20 and 5 mm, respectively. The crosshead speed was 0.51 mm/min. Fracture surfaces were observed by SEM following the flexural tests.

3. Results

Figs. 1–3 show the effect of neutron irradiation on strain–stress behavior of the four point flexural tests of

Table 1
The properties of fibers used in this work

SiC fiber	C/Si atomic ratio	Oxygen content (wt%)	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)	Density (Mg/m^3)	Diameter (μm)
Tyranno SA	1.07	<0.5	1.8	320	0.7	3.02	10
Hi-Nicalon Type-S	1.05	0.2	2.6	420	0.6	3.1	12
Hi-Nicalon	1.39	0.5	2.8	270	1.0	2.74	14

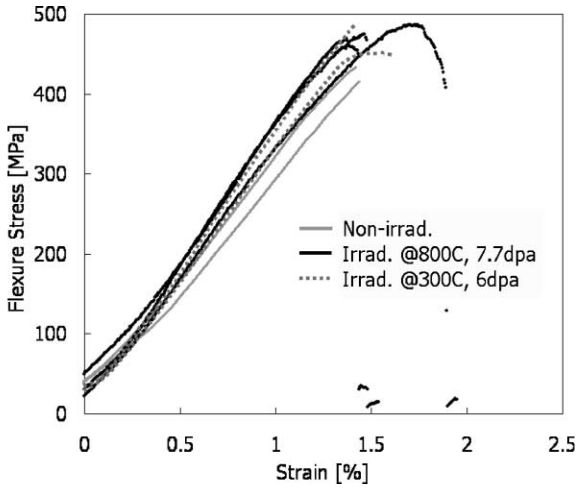

Fig. 1. Effect of irradiation on flexural behavior of Hi-Nicalon Type-S (P/W) samples.

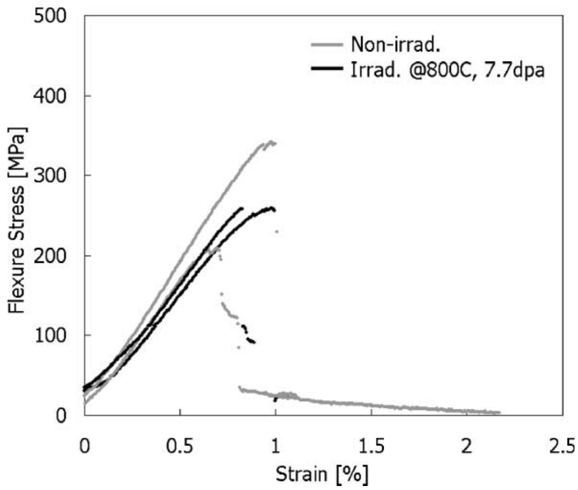

Fig. 2. Effect of irradiation on flexural behavior of Tyranno SA (P/W) samples.

SiC/SiC composites reinforced with plain woven fibers. Both composites reinforced with Hi-Nicalon Type-S fibers and Tyranno SA fibers were stable to neutron irradiations compared with composites reinforced with Hi-Nicalon fibers although the composites reinforced with Tyranno SA fibers had a large scatter in the non-irradiated composites. As mentioned in previous section the Tyranno SA fiber used in this work was the first trial piece, so there was scatter in grain size and mechanical properties. The non-irradiated strength of composites reinforced with Tyranno SA fibers used in this work was less than that of composites reinforced with the recent Tyranno SA fibers. However the average proportional limit stress (PLS) and average flexural strength of composites reinforced with Tyranno SA fibers were almost same between the non-irradiated composites and the irradiated composites. It was obvious that mechanical properties of composites reinforced with Hi-Nicalon fibers degraded following neutron irradiation and composites reinforced with Hi-Nicalon Type-S fibers were very stable to neutron irradiation.

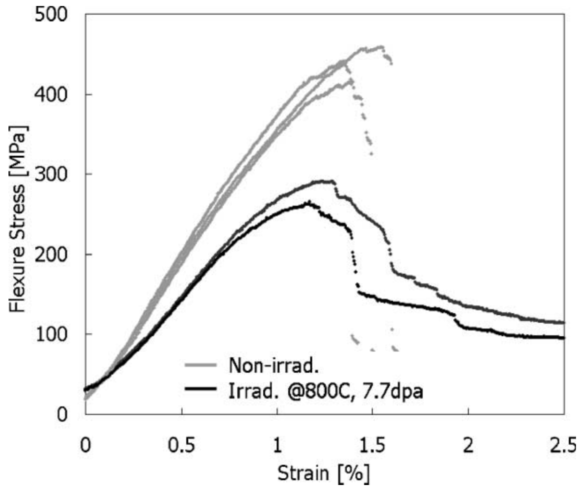

Fig. 3. Effect of irradiation on flexural behavior of Hi-Nicalon (P/W) samples.

Figs. 4 and 5 show the fracture surface of composites reinforced with Hi-Nicalon Type-S and Tyranno SA fibers following irradiation at 800 °C. In the previous

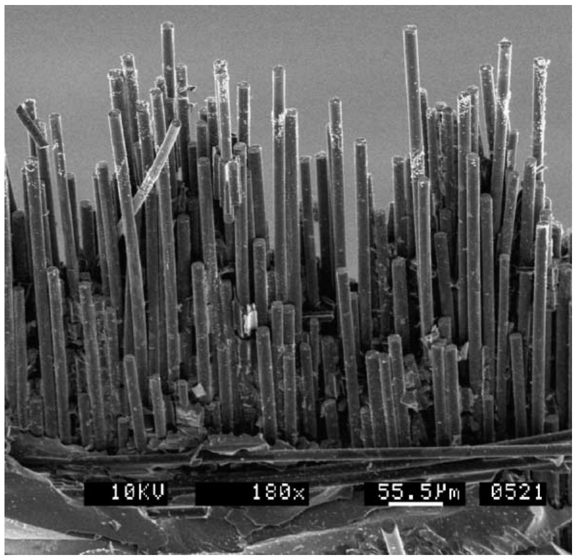

Fig. 4. Fracture surface of Hi-Nicalon Type-S sample following the irradiation at 800 °C.

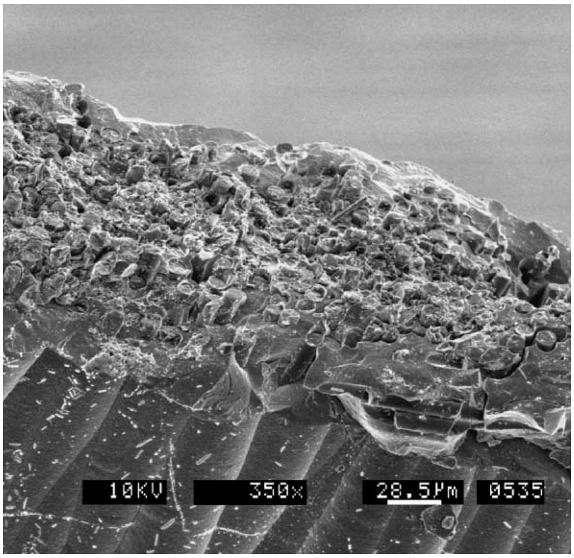

Fig. 5. Fracture surface of Tyranno SA sample following the irradiation at 800 °C.

composites containing off-stoichiometric SiC fibers such as Nicalon, Tyranno Lox M and Hi-Nicalon, significantly long fiber pull-out with more than several hundred μm length was seen following irradiation [8,19]. However in the composites reinforced with Hi-Nicalon Type-S fibers, fiber pull-out was relatively short and seemed almost same with non-irradiated composites even following 7.7 dpa irradiation. Composites reinforced with Tyranno SA fibers showed brittle fracture surface and seemed almost same with the non-irradiated composites, too.

Mechanical properties of SiC/SiC composites following irradiation at 800 and at 300 °C are compared with those prior to the irradiation in Figs. 6 and 7. The Figs. show the relative values, i.e. the value after irradiation/the value prior to irradiation, of modulus, PLS obtained from 0.01% strain offset and flexural strength. Error bars show maximum and minimum values. The composites reinforced with Type-S fibers and Tyranno SA fibers with plain weave fabric kept their flexural strength following irradiation, while the composites reinforced with Hi-Nicalon fibers decreased. Most of PLS decreased following the irradiation at 800 °C, while they increased following the irradiation at 300 °C. In all composites, the elastic modulus decreased following the irradiation with the exception of the composites reinforced with Hi-Nicalon Type-S plain weave fabric.

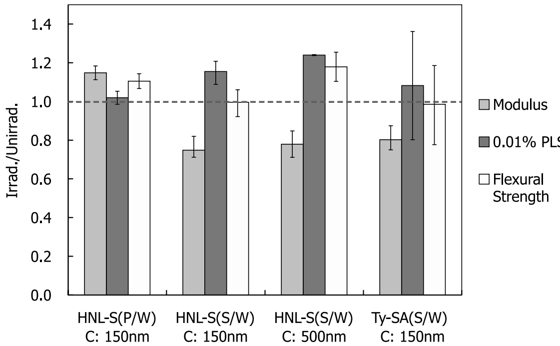

Fig. 7. Effect of irradiation at 6.0 dpa and 300 °C on mechanical properties.

Normalized density change of Tyranno SA fiber and CVD SiC irradiated at 7.7 dpa and 800 °C are shown in Fig. 8 with those of previous fibers, Nicalon and Hi-Nicalon and CVD SiC irradiated at 150°C. Tyranno SA fiber swelled slightly following irradiation, while the other fibers underwent radiation-induced densification. The normalized density change of Tyranno SA was very similar to that of CVD SiC irradiated at the same condition.

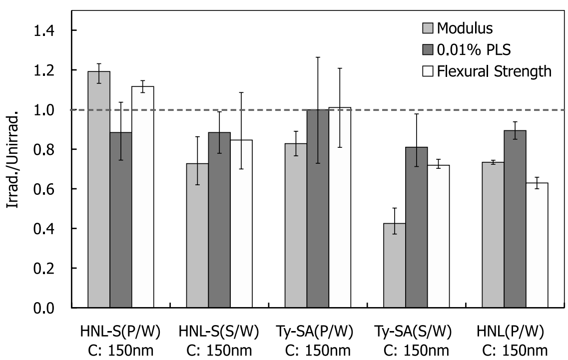

Fig. 6. Effect of irradiation at 7.7 dpa and 800 °C on mechanical properties.

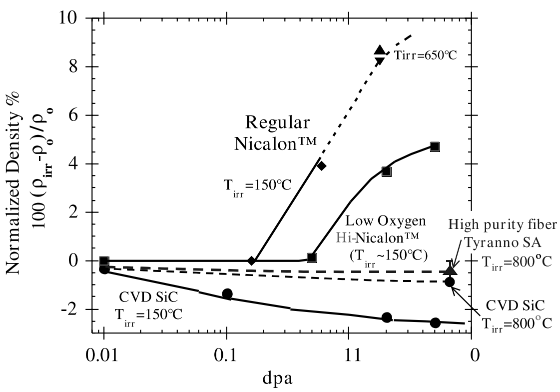

Fig. 8. Relative density change of SiC fibers and CVD SiC by neutron irradiation.

4. Discussions

Both composites reinforced with Hi-Nicalon Type-S and Tyranno SA fibers showed stable mechanical properties to even high dose and high temperature irradiation. Of particular note, the fracture behavior was completely different from previous composites reinforced with non-high purity fibers. In composites reinforced with non-high purity fibers, the composites fractured with long fiber pull-out following irradiation due to debonding of fiber/matrix interface. However, composites reinforced with Hi-Nicalon Type-S and Tyranno SA fibers fractured with relatively short fiber pull-out even with C interphase, and the fracture behavior of the composites following irradiation was similar with that of non-irradiated composites. C interphase was considered one of the critical issues for the degradation of interfacial shear strength. However the apparent effect of C interphase degradation on mechanical properties were not seen in this results. Composites reinforced with Tyranno SA fibers showed brittle fracture behavior even following irradiation due to weaker fiber strength and rough fiber surface attributed to larger grain size than Hi-Nicalon Type-S even with same fiber/matrix interphase. This fracture behavior is not ideal for composite materials. However, it was completely different from previous composites after irradiation. Tyranno SA fiber have been improved. The grain size decreased and the fiber strength increased. Composites reinforced with the current Tyranno SA fibers are expected to show superior mechanical properties.

Similar fracture behavior between irradiated composites and unirradiated composites with relatively short fiber pull-out is attributed to similar swelling behavior between the fiber and matrix. As shown in Fig. 8, there was a large mismatch of swelling between previous fiber, such as Nicalon and Hi-Nicalon, and CVD SiC. This mismatch caused fiber/matrix interfacial debonding and reduced mechanical properties with long fiber pull-out. Normalized density of Tyranno SA is quite similar to CVD SiC irradiated at same condition. That is the reason that both composites reinforced with Hi-Nicalon Type-S and Tyranno SA fibers retain their fiber/matrix integrity and mechanical properties.

In most of composites, degradation of modulus was seen. The degradation of elastic modulus of CVD SiC following irradiation has been reported [20,21] and considered that the degradation is inversely proportional to the amount of swelling. Fig. 8 shows slight swelling of both fiber and CVD SiC, and it is considered that the modulus of both fiber and matrix decreased. However effect of irradiation temperature on elastic modulus was not clear, while the amount of swelling of CVD SiC depends on irradiation temperature.

Typically, swelling and mechanical properties of ceramics saturate by a few dpa [21,22]. Perhaps this indicates that composite will be stable to much higher dpa, although further experiment of much higher dpa is required to confirm it.

5. Conclusions

1. Stoichiometric fibers are dimensionally stable to doses and temperatures of this study like CVD SiC.
2. The SiC/SiC composites with reinforced with high purity fibers showed stable mechanical properties to high dose (7.7 dpa)/high temperature (800 °C) irradiation.

Acknowledgements

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