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Effects of fibers and fabrication processes on mechanical properties of neutron irradiated SiC/SiC composites

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Abstract

Radiation effects on flexural properties of SiC/SiC composites fabricated by forced thermal gradient chemical vapor infiltration (F-CVI) process, reaction sintered (RS) process and polymer impregnation and pyrolysis (PIP) process were investigated. In this study, neutron irradiation at 1073 K up to 0.4×10^{25} n/m^2 ($E > 0.1$ MeV) was performed. For F-CVI and RS SiC/SiC, due to the irradiation damage of interphase like pyrolytic carbon and boron nitride, which were sensitive to neutron irradiation, composite stiffness was slightly decreased. On the contrary, for PIP SiC/SiC, there was no significant change in stiffness before and after irradiation. Composite strength, however, was nearly stable against high-temperature irradiation with such a low fluence, except for RS SiC/SiC, since mechanical characteristics of fiber and matrix themselves were still stable to neutron irradiation. However RS SiC/SiC had a slight reduction of flexural strength due to the severe degradation of the interface by neutron irradiation.
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1. Introduction

SiC/SiC composites are attractive materials for fusion structural applications, because of superior chemical and mechanical stability at high temperature, inherently possessed low induced-activation energy and after-heat [1,2], and others. In particular, recent improvement of radiation stability has been achieved by the development of fabrication technique as well as by using high-crystalline silicon carbide fibers with few impurities [3,4].

SiC/SiC composites fabricated by CVI process have been conventionally used in irradiation researches because of several advantages like high purity and high crystallinity of their matrix. CVI derived SiC matrix composites with pyrolytic carbon (PyC) interphase were known to degrade due to the neutron irradiation >1 displacement per atom (dpa) [4–7]. This is because the partial detachment of fiber and matrix (F/M) interface occurred due to the degradation of PyC by neutron irradiation and F/M interface partially lost load transfer function. Besides under neutron irradiation with much higher fluence, complete detachment of F/M interface and hence large stress reduction occurred [8,9]. Moreover it was reported that shrinkage of amorphous fibers like Nicalon™ and Hi-Nicalon™ fibers (Nippon Carbon Co. Ltd., Tokyo, Japan) and swelling of highly crystalline β-SiC matrix produced irradiation-induced internal stresses in the F/M interface [7]. By the presence of these stresses, reduction of composite strength was enhanced. However this kind of stresses could be reduced by using stoichiometric SiC fiber, such as Hi-Nicalon™ Type-S (Nippon Carbon Co. Ltd., Tokyo, Japan) or Tyranno™ SA (Ube Industries, Ltd., Ube, Japan). This is because both fiber and matrix swelled in the same direction by neutron irradiation due to their high-crystalline, near stoichiometric structure [10]. On the while, there is another advantage that severe

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degradation of stoichiometric fibers themselves does not occur after neutron irradiation up to 10 dpa [8,9]. Consequently, the composite structure and strength became more stable against neutron exposure. However, there are few studies on the stability of SiC/SiC against neutron exposure, especially far fluences <1 dpa. This will be important to give us useful knowledge about initial behavior of SiC/SiC for neutron irradiation.

Also, it is considered to be more important to identify neutron effects for SiC/SiC derived by recently developed alternate processes such as RS or PIP processes promising for commercial applications. However, radiation stability of SiC/SiC fabricated by advanced processes still remains unrevealed.

The objective of this study is to evaluate effects of neutron irradiation, especially low fluence irradiation <1 dpa, on structural and mechanical stability of SiC/SiC composites from the viewpoints of the influences of crystallinity and impurities of reinforced fibers, and micro-structural changes of matrix and F/M interface formed by each fabrication process.

2. Experimental

Several kinds of SiC/SiC composites were fabricated by F-CVI, RS and PIP processes, respectively (Table 1). Highly crystalline, low oxygen content fibers such as Hi-Nicalon™ Type-S and Tyranno™ SA were used as reinforcements. For comparison, Hi-Nicalon™ fiber, with lower crystalline microstructure, reinforced SiC matrix composites were also prepared. F-CVI, RS and PIP SiC/SiC composites had a thin PyC, boron nitride (BN) and gradient composition carbon as F/M interface, respectively. The last one was modified by specific thermo-chemical treatment called S6 treatment (Fig. 1) [11].

All the test (25 mm $\times$ 4 mm $\times$ 2 mm) pieces cut into from these composites respectively were irradiated in the Japan materials testing reactor (JMTR). They were irradiated to a fluence of 0.4×10^{25} n/m^2 ($E > 0.1$ MeV) at 1073 K. In this study, this fluence corresponds to 0.4 dpa (1 dpa $= 1 \times 10^{25}$ n/m^2).

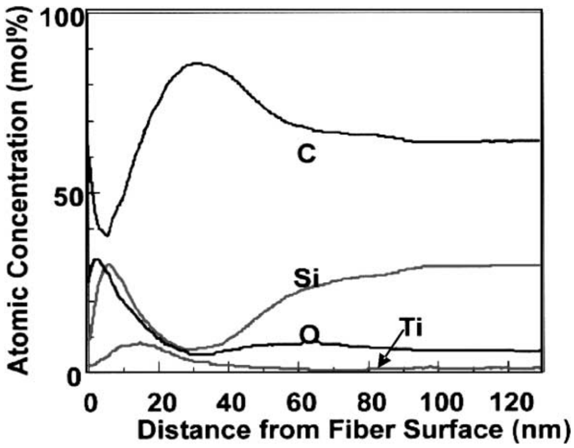

Fig. 1. Compositionally gradient SiC–C interphase.

Mechanical stabilities against neutron irradiation were evaluated by 3-point flexural tests. Support span of test beam was 18.0 mm. All the tests were conducted by using an electromechanical testing machine at room temperature with the crosshead control of 3.0×10^{-5} m/s, on the basis of ASTM C1341 [12]. Micro-structural observations were also conducted by using scanning electron microscopy (SEM) after mechanical tests.

3. Results and discussion

3.1. Neutron effect on F-CVI SiC/SiC

Significant reduction of flexural strength did not occur and flexural strength was quite stable for all F-CVI derived composites regardless of the fiber types as shown in Figs. 2 and 3. This is because dimensional changes in fiber and matrix might be quite small up to 0.4 dpa in neutron dose and also the strength of each component was still stable under such a low fluence irradiation [13,14]. In this experiment, volume changes of each F-CVI SiC/SiC were less than 0.6%. High crystalline SiC fibers like Hi-Nicalon™ Type-S, Tyranno SA

Table 1
Test materials

	CS01	CS02	CH01	RH01	PN01
Matrix	F-CVI SiC	F-CVI SiC	F-CVI SiC	RS SiC	PIP SiC
Fiber	Hi-Nicalon Type-S	Tyranno-SA	Hi-Nicalon	Hi-Nicalon	Tyranno-TE
Crystal structure of fiber	Crystal	Crystal	Micro crystal	Micro crystal	Amorphous
Architecture	S/W	P/W	P/W	UD	P/W
Interphase	PyC	PyC	PyC	BN	Gradient C
Thickness of interphase (nm)	150	150	150	–	~200
Density (Mg/m^3)	2.22	2.26	2.38	2.82	2.11
Supplier	ORNL	ORNL	ORNL	Toshiba	Ube

fibers and β-SiC as matrix swells due to the lattice expansion by the accumulation of radiation-induced point defects. However at higher temperature, most of them diminished easily because of their high mobility. Consequently the radiation effect was slightly limited. On the contrary, Hi-Nicalon^{TM} fibers are known to shrink and to increase their strength slightly by densification. However fiber shrinkage was also hard to occur in such a low dose and high temperature irradiation for the same reason. Similarly, proportional limit stress of all F-CVI SiC/SiC was not also changed against the irradiation up to 0.4 dpa because of good stabilities of fiber and matrix.

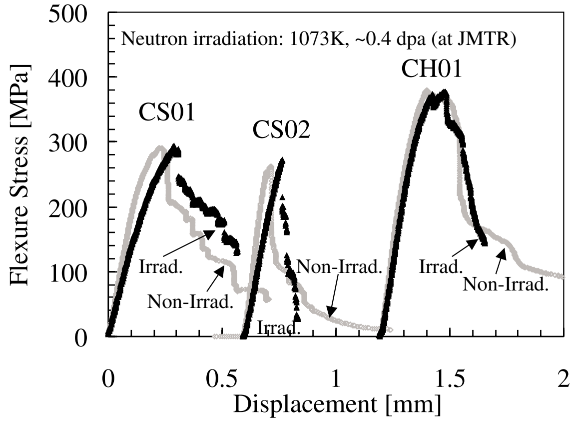

Fig. 2. Stress–displacement relationships of irradiated and non-irradiated F-CVI SiC/SiC composites.

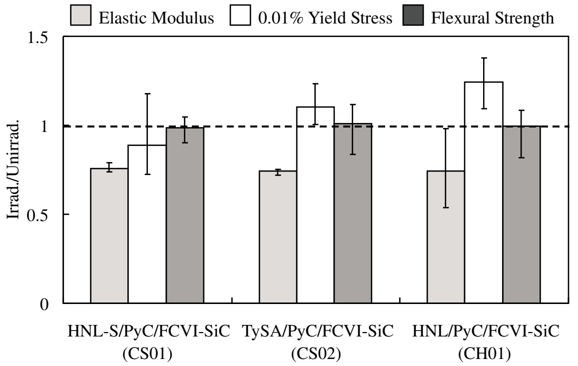

Fig. 3. Neutron irradiation effect on flexural properties of F-CVI SiC/SiC composites.

However reduction of elastic modulus of F-CVI SiC/SiC cannot be ignored. According to Osborne et al., the elastic modulus of β-SiC composing matrix and high-crystalline SiC fibers has severe degradation against neutron irradiation at about 773 K up to about 0.5 dpa [15]. This degradation of stiffness was attributed to lattice expansion of high-crystalline SiC caused by swelling. However, as mentioned previously, influences of dimensional changes of fiber and matrix were considered to be quite small in the irradiation at higher temperatures like this experiment. From this reason, reduction of composite stiffness seems mainly due to another mechanism. Possibly, degradation of F/M interface resulted in a decreasing composite stiffness, although there were no visible differences in fracture behaviors before and after neutron irradiation (Figs. 4 and 5). The F/M interface lost its load transferring function due to the degradation of PyC, which is sensitive to radiation [16], even at low dose neutron irradiation.

3.2. Neutron effect on RS SiC/SiC

Hi-Nicalon^{TM} fiber reinforced RS derived SiC matrix composite with BN interphase was damaged by neutron irradiation up to 0.4 dpa (Figs. 6 and 7). All mechanical characteristics such as flexural strength, elastic modulus and proportional limit stress tended to decrease after neutron irradiation.

Similar to F-CVI derived SiC matrix, RS derived SiC matrix is, in general, highly crystalline. Hence, it is

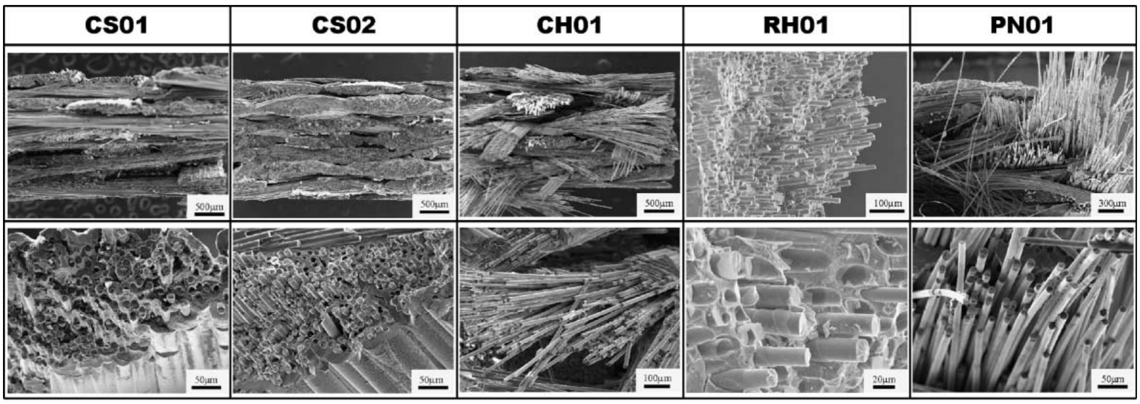

Fig. 4. Fracture appearances of non-irradiated F-CVI, RS and PIP SiC/SiC composites.

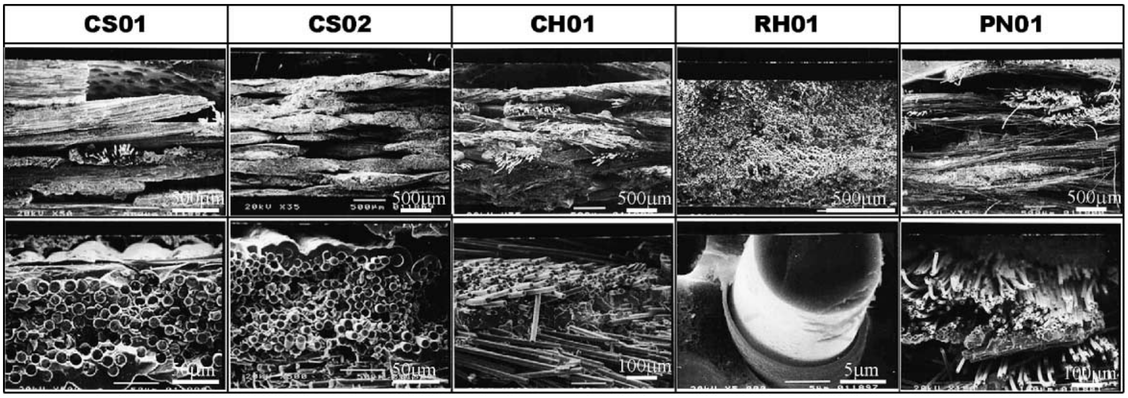

Fig. 5. Fracture appearances of irradiated F-CVI, RS and PIP SiC/SiC composites.

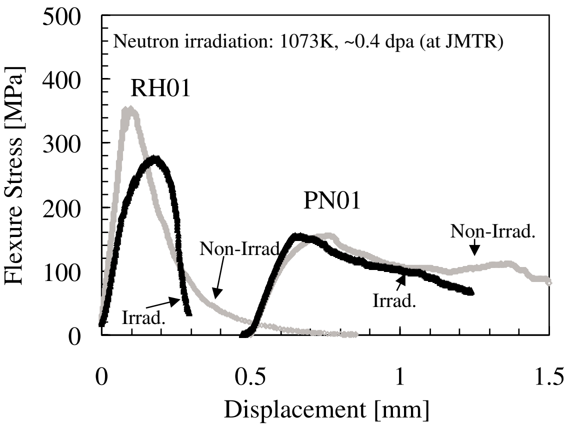

Fig. 6. Stress–displacement relationships of irradiated and non-irradiated RS and PIP SiC/SiC composites.

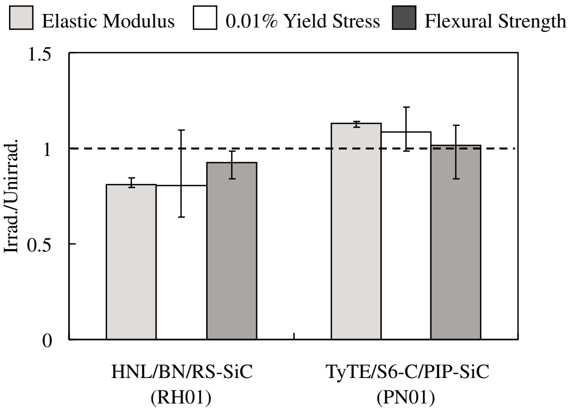

Fig. 7. Neutron irradiation effect on flexural properties of RS and PIP SiC/SiC composites.

natural that matrix was stable and independent of composite strength reduction by irradiation. However, it was revealed that this material contained small quantities of undesired excess carbon and boron in the matrix. These impurities might be induced during processing. They are known to be one of the most sensitive elements to neutron irradiation. Although helium production from boron by neutron irradiation was not identified in this study, it cannot be excluded. In this case, neutron damage of these impurities might result in a decreased matrix strength. Further investigations are necessary to discuss this.

Reduction of the elastic modulus can also be explained as follows. Obviously, non-irradiated composite failed just after the matrix cracking stress (Fig. 6). Also there were short pullouts of fibers at the fracture surface (Fig. 4). This means that the interfacial function to deflect cracks and to transfer load between fiber and matrix has nearly been lost before irradiation because cracks originating from the matrix penetrated into fibers due to the strong bonding between fiber and matrix. However, the BN interphase, was expected to be degraded by neutron irradiation and the F/M interface became much weaker after neutron irradiation. Spatial gaps between fiber and interphase, i.e. detachment of fiber and interphase, were defected frequently (Fig. 5). Hence the composite modulus decreased since the deflection of composite increased.

3.3. Neutron effect on PIP SiC/SiC

There were no significant changes in flexural properties of Tyranno^{TM} TE fiber reinforced PIP derived SiC matrix composite before and after neutron irradiation up to 0.4 dpa (Figs. 6 and 7). This is explained by no significant structural and physical change of fiber, matrix and also good performance of F/M interface before and after neutron irradiation.

Tyranno^{TM}-TE, which had an amorphous structure like Nicalon^{TM} fiber, might be non-sensitive to neutron irradiation up to 0.4 dpa, according to the stability of Nicalon^{TM} against low fluence neutron. Similarly it is possible that PIP derived SiC matrix with low crystalline structure showed little radiation effects. In short, combination of both polymer-derived fiber and matrix might have minimized the influence of irradiation-induced volume change. In addition to these facts, it can also be concluded that compositionally degraded SiC–C interphase (Fig. 1) might be effective for radiation-resistant composites, for the explanation of the good resistance of PIP SiC/SiC against neutron irradiation. However, slight increase in flexural modulus occurred likely due to the partial crystallization of polymer-derived amorphous SiC matrix and fibers. Otherwise, significant matrix defects like pre-existing pores and cracks might have masked irradiation-induced changes.

4. Conclusions

Radiation effects on flexural properties of F-CVI, RS and PIP SiC/SiC were investigated. This experiment was characteristic in neutron irradiation at low doses up to 0.4 dpa at high-temperature, 1073 K. Main conclusions were summarized as follows.

There were few influences of fibers and matrices on flexural properties of SiC/SiC against the neutron irradiation up to 0.4 dpa at 1073 K. Fiber and matrix themselves did not degrade significantly by neutron irradiation at such low fluences. On the contrary, F/M interface was significantly damaged by irradiation up to 0.4 dpa which resulted in the decrease of the composite strength, especially of the modulus of elasticity.

1. F-CVI SiC/SiC showed a slight decrease in the elastic modulus due to enlarged deflection by the degradation of PyC interphase. However the composite strength was still stable due to the dimensional and mechanical stability of fiber and matrix against neutron irradiation.
2. Composite strength and stiffness of RS SiC/SiC were degraded by radiation damages of the BN interphase.
3. PIP SiC/SiC was stable against neutron irradiation up to 0.4 dpa because no significant degradation of fiber, matrix and F/M interface occurred before and after irradiation. Amorphous SiC fiber and matrix did not degrade their flexural properties after neutron irradiation up to 0.4 dpa. Also compositionally degraded SiC–C interface might be very effective for neutron irradiation and it is considered to be a promising interface option for SiC/SiC composites.

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