EFFECT OF FIBER PROPERTIES ON NEUTRON IRRADIATED SiC/SiC COMPOSITES

T. Hinoki*, A. Kohyama and Y. Katoh (Kyoto University), L.L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

Several kinds of SiC fibers have been developed recently. The objective of this work is to understand the effect of fiber properties on neutron irradiated SiC/SiC composites.

SUMMARY

The use of SiC/SiC composites for nuclear application has recently been considered because of intrinsic low activation and superior high temperature mechanical properties of SiC. The property of SiC fiber is a key issue in order to improve mechanical properties of SiC/SiC composites following irradiation. SiC/SiC composites reinforced with unidirectional fibers were fabricated by chemical vapor infiltration method. Low oxygen and highly crystalline fibers or just low oxygen fibers were used in the composites. The specimens were irradiated at Japan Material Testing Reactor and High Flux Isotope Reactor. The effects of neutron irradiation on mechanical properties were examined by three points flexural test. Microstructure and fracture behavior were observed by scanning electron microscopy before and after neutron irradiation. The SiC/SiC composites reinforced with a low oxygen content, near-stoichiometric atomic composition, and highly crystalline SiC fibers showed the excellent stability to neutron irradiation. The mechanical property of the composites did not degrade, even after neutron irradiation up to 10 dpa, while the other materials reinforced with non-highly crystalline SiC fibers degraded significantly.

PROGRESS AND STATUS

Introduction

The superior high-temperature mechanical properties and low induced radioactivity of SiC/SiC composite make them very attractive as fission and fusion reactor structural materials. [1,2] In fusion reactor environment, nuclear collision and reaction with high-energy neutrons and particles from fusion plasma strongly affect on material properties through the production of displacement damage and transmutation products. [3,4] Degradations of material performance such as mechanical properties, thermal properties etc. are important issues and extensive effort has been conducted. [5]

Interfacial properties between the fiber and matrix of neutron-irradiated SiC/SiC composite influence mechanical performance. [6] This is attributed primarily to shrinkage in the SiC-based fibers due to irradiation-induced recrystallization of microcrystalline fibers [7,8], irradiation-assisted oxidation [9], and potential dimensional changes of carbon [10] interphase applied to the fibers, while matrix swells slightly by irradiation-induced point defect. Fiber shrinkage leads to fiber/matrix debonding as being reported by Snead [11] so that elastic modulus and fracture strength are decreased. Therefore, it is needed to optimize the microstructure of SiC/SiC composite (i.e. fiber, fiber/matrix interphase and matrix) in order to retain interfacial shear strength between fiber and matrix. In order to mitigate radiation effects, development of SiC fiber with lower oxygen content, reduced free carbon and enhanced crystallization is the recent trend. The development of SiC composite with radiation-resistance is based on the use of near stoichiometric SiC fibers with lower oxygen and

* Current affiliation: Oak Ridge National Laboratory

SiC-based interphase. Recently, stoichiometric SiC fibers have been developed such as Hi-Nicalon™ Type-S, [12] Sylramic™ [13] and Tyranno™ SA. [14]

The objective of this work is to understand the effect of fiber properties on neutron irradiated SiC/SiC composite and to improve the stability of SiC/SiC composite under fusion environment. The effects of neutron irradiation on microstructure and mechanical properties were studied.

Experimental

The SiC/SiC composites used in this work were fabricated at the National Research Institute for Metals using Hi-Nicalon™ SiC fibers, Hi-Nicalon™ Type-S advanced SiC fibers, Tyranno™ TE and Tyranno™ ZE. The Type-S fiber contains a reduced amount of oxygen and has near-stoichiometric chemical composition. Representative properties and chemical compositions of the fibers have been compiled in Table 1. The matrix of a unidirectional fiber-reinforced composite was formed by chemical vapor infiltration (CVI). A pyrolitic C interphase was applied to the fibers by CVI prior to the matrix CVI processing. The nominal thickness of the C interphase was 200 nm. The plate size was 40 (diameter) × 2 (thick) mm. The composites were square-cut into 25 (long) × 4 (wide) × 2 (thick) mm bar for the bend bars irradiated at Japan Material Testing Reactor (JMTR) [15], and 15 (long) × 1.5 (wide) × 1.5 (thick) mm bar for the bend bars irradiated at High Flux Isotope Reactor (HFIR) [16]. The composites prepared for JMTR irradiation had an extra SiC layer with approximately 300 μm in thickness, which deposited on the infiltrated SiC/SiC composites.

Table1: Properties of SiC fibers used in this work

SiC Fiber	C/Si Atomic Ratio	Oxygen Content (mass%)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)	Density (Mg/m^3)	Diameter (μm)
Hi-Nicalon	1.39	0.5	2.8	270	1	2.74	14
Hi-Nicalon Type-S	1.05	0.2	2.6	420	0.6	3.1	12
Tyranno TE	1.59	5	3.4	206	1.7	2.55	11
Tyranno ZE	1.52	2	3.5	233	1.5	2.55	11

Neutron irradiations were carried out in the 97M-33U capsule at JMTR, Oarai Research Establishment of Japan Atomic Energy Research Institute, Japan, and in the HFIR 13J capsule at Oak Ridge National Laboratory, USA. In the 97M-33U capsule, a dose equivalent of 1.0×10^{25} nm^{-2} (E>0.1 MeV) = 1.0 dpa was used. The sample temperature was controlled by the combination of gas gap conduction of the nuclear heat and electric heaters. The samples were irradiated at 400 °C. In the HFIR 13J capsule, a dose equivalent of 1.0×10^{26} nm^{-2} (E>0.1 MeV) = 10 dpa was used. The sample temperature was controlled by electric heaters. The samples were irradiated at a constant temperature of 350 °C or 500 °C or in periodically-variable temperature of 300 °C and 500 °C or 200 °C and 350 °C. After irradiation, the capsule was cooled to enough low activation level, and then the capsules were moved to the hotcell and disassembled by the manipulators. Fig. 1 shows the disassembly of the HFIR 13 capsule at the hotcell of ORNL. The samples were then shipped to ORNL LAMDA for observation of the microstructure and flexural tests.

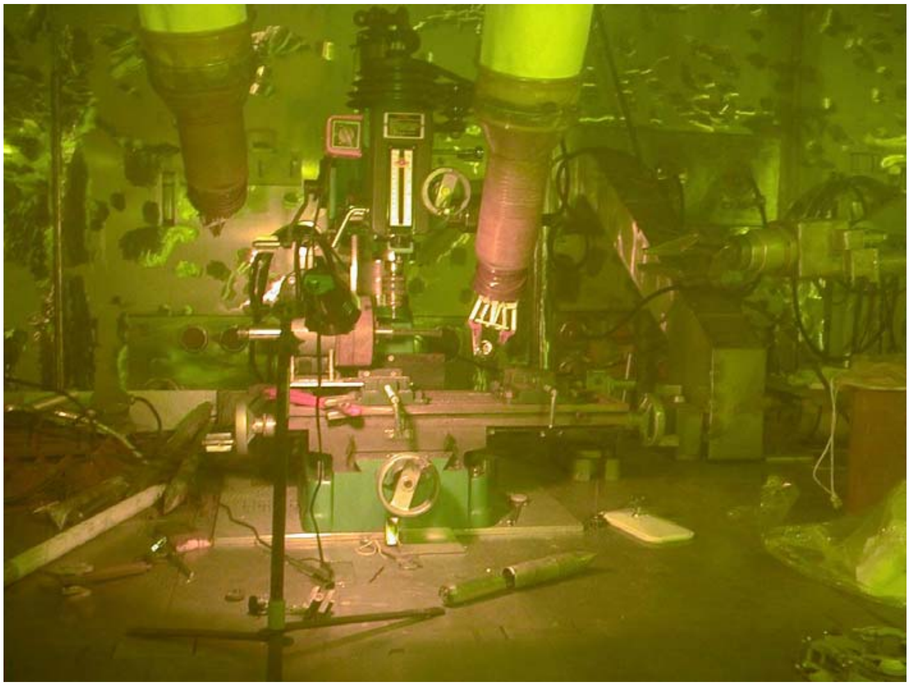


Fig. 1: The disassembly of the HFIR 13J capsule at hotcell of ORNL

Three-point flexural tests were carried out at ambient temperature after the irradiations. The support spans were 18 mm and the crosshead speed was 0.03 mm/sec for the sample irradiated at JMTR 97M-33U. The support spans were 16 mm and the crosshead speed was 0.02 mm/sec for the sample irradiated at HFIR 13J. The size of the bend bar used at JMTR 97M-33U irradiation was

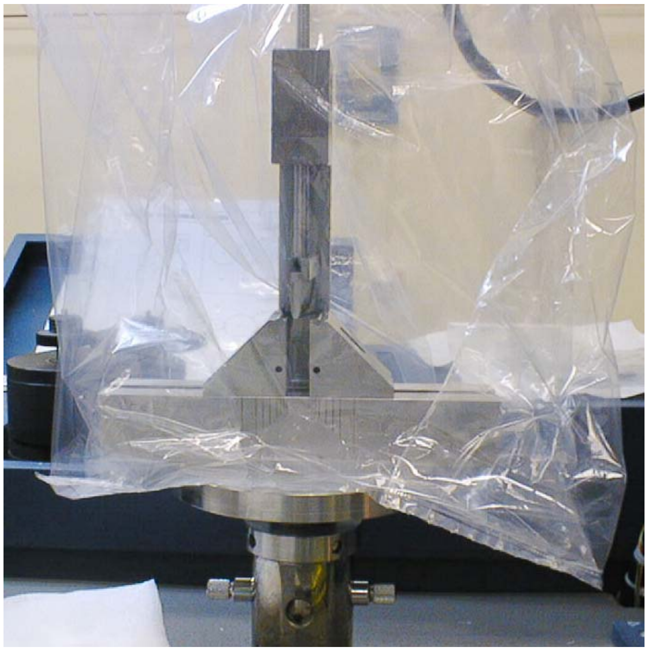


Fig. 2: The flexural test of SiC/SiC composites after neutron irradiation

different from that used at HFIR 13J irradiation because of limitation of each capsule. And different experimental conditions were applied. One of the serious problems to carry out the mechanical tests of SiC/SiC composites after neutron irradiation is the diffusion of the dust during the fracture. The flexural tests were carried out within a plastic bag as shown in Fig. 2.

Effect of neutron irradiation of 97M-33U

Four kinds of the SiC/SiC composites were irradiated. However, three kinds of composites reinforced with Hi-Nicalon, Tyranno TE and Tyranno ZE fibers could not keep their shape following the irradiation as shown in Fig. 3. In marked contrast to the deformed samples, any deformation after

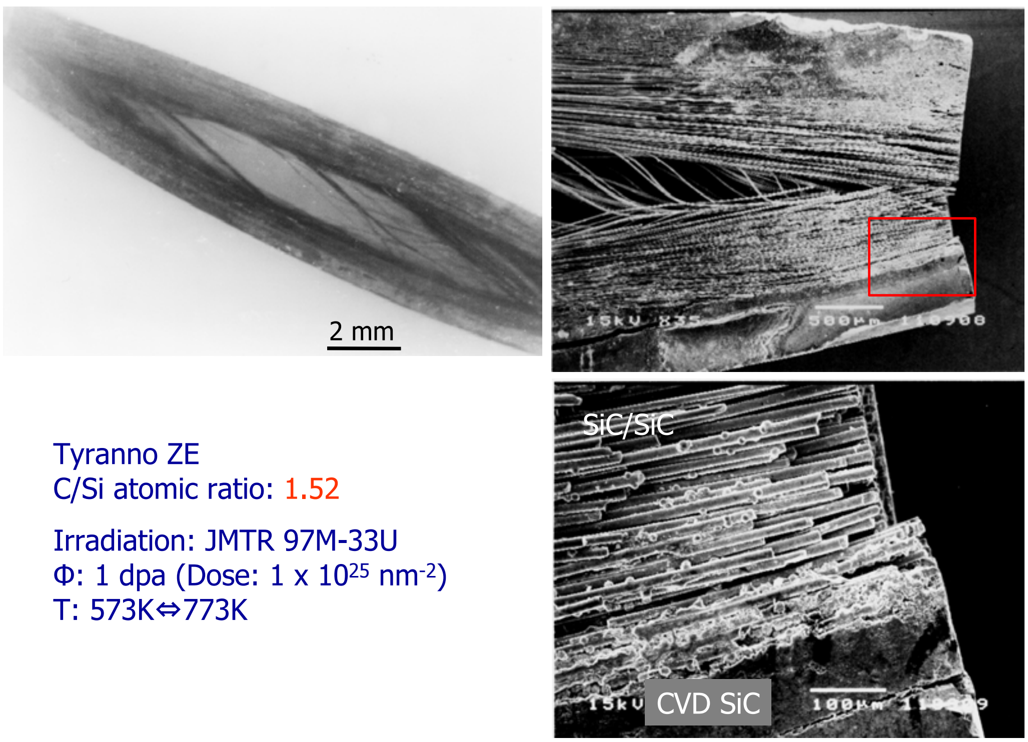


Fig. 3: Effect of neutron irradiation on Tyranno ZE/C/SiC

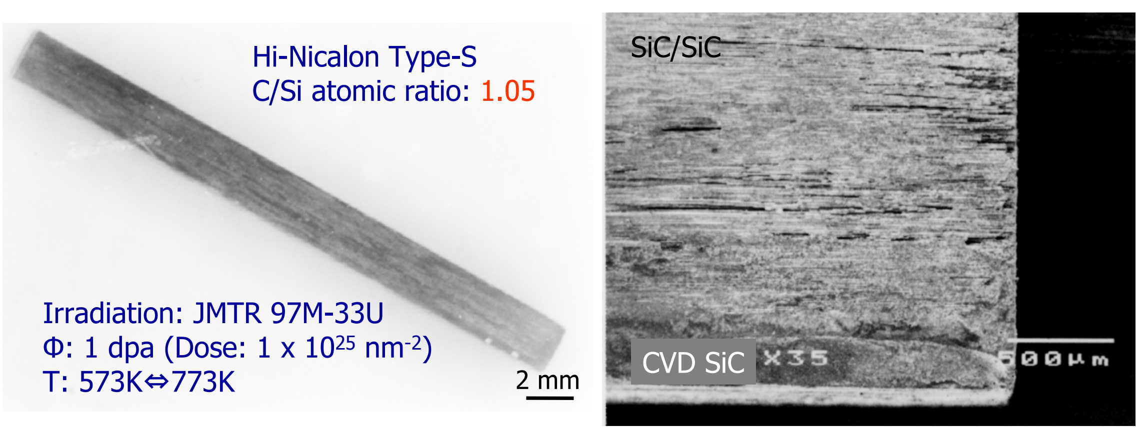


Fig. 4: Effect of Neutron Irradiation on Hi-Nicalon Type-S/C/SiC

the irradiation could not be observed in the SiC/SiC composites reinforced with Hi-Nicalon Type-S fibers as shown in Fig. 4. The composites used in this work had an extra thick SiC layer at one side. The three kinds of fibers used for the deformed composites dose not have near-stoichiometric SiC composition, although they are low oxygen content fibers. The shrinkage of the non-crystalline SiC fiber [9] due to recrystallization [17] and the swelling of β-SiC by neutron irradiation [18] have been reported. So, this deformation was attributed to the mismatch between the fiber shrinkage and β-SiC swelling as illustrated in Fig. 5.

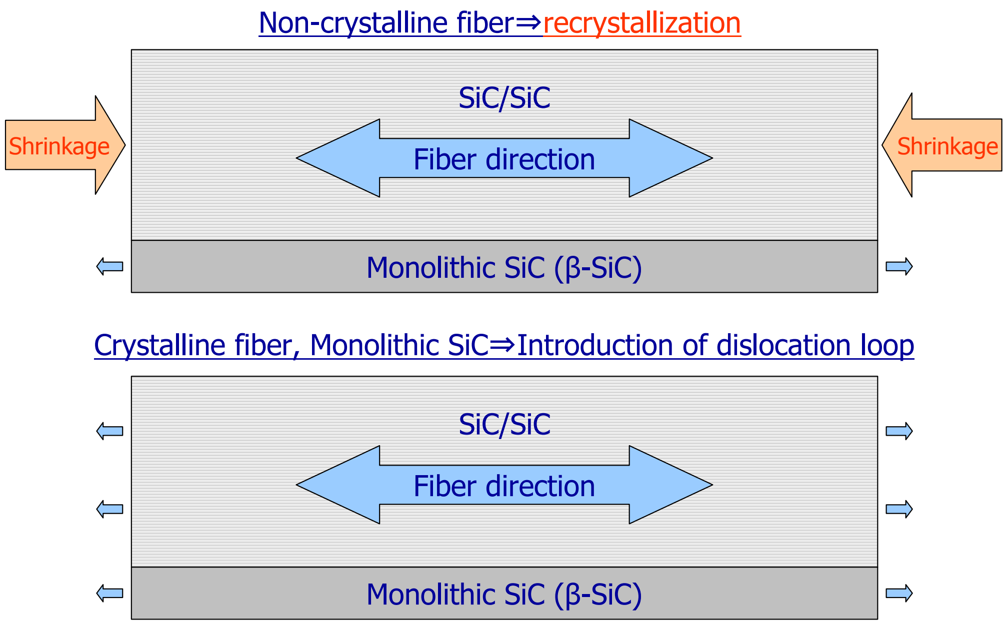


Fig. 5: Deformation mechanism of SiC/SiC composites after neutron irradiation

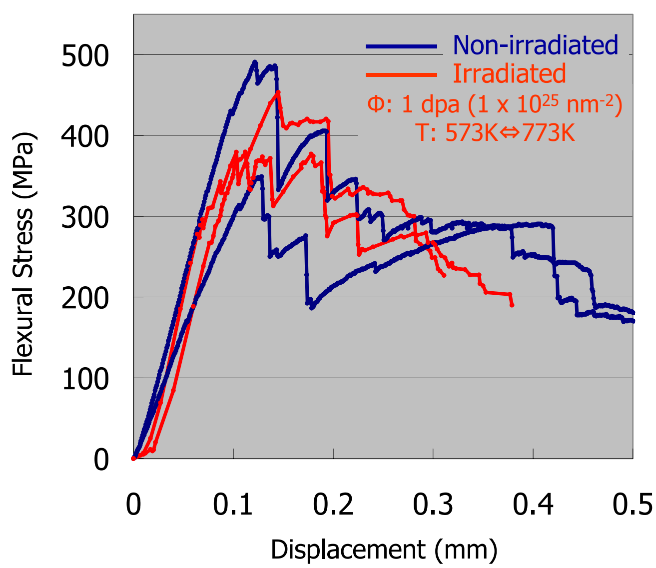


Fig. 6: Effect of Neutron Irradiation on flexural Properties of Hi-Nicalon Type-S/C/SiC

Only the composites reinforced with Hi-Nicalon Type-S fibers were evaluated by flexural tests due to the deformation of the other samples. Fig. 6 shows the effect of the neutron irradiation on the flexural properties of the composites reinforced with Hi-Nicalon Type-S fibers. Clear degradations due to the neutron irradiation were not seen in modulus, proportional limit stress (PLS) and flexural strength. However most of pull-out fibers in the fracture surface of the irradiated composites were separated, respectively, while most of pull-out fibers of the non-irradiated composites were gathering as shown in Fig. 7. And pull-out length of the irradiated sample was longer than that of the non-irradiated sample. The similar results regarding the effect of the neutron irradiation on the mechanical properties of composites reinforced with Hi-Nicalon Type-S were reported in the Ref. 19.

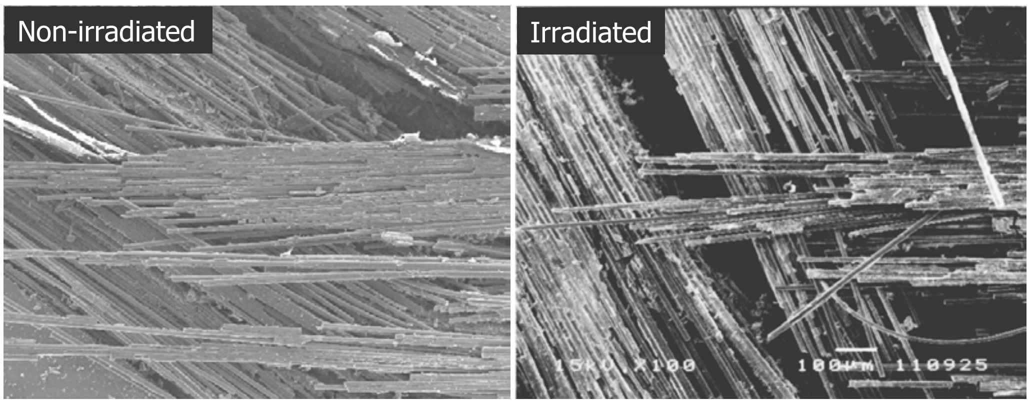


Fig. 7: Comparison of the fracture surface
of the non-irradiated and the irradiated sample with Hi-Nicalon Type-S

Effect of neutron irradiation of HFIR 13J

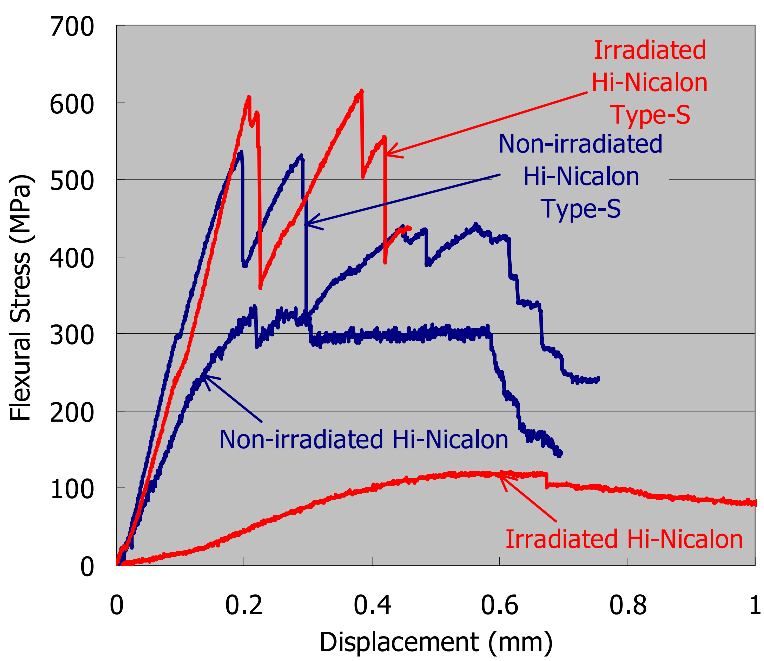
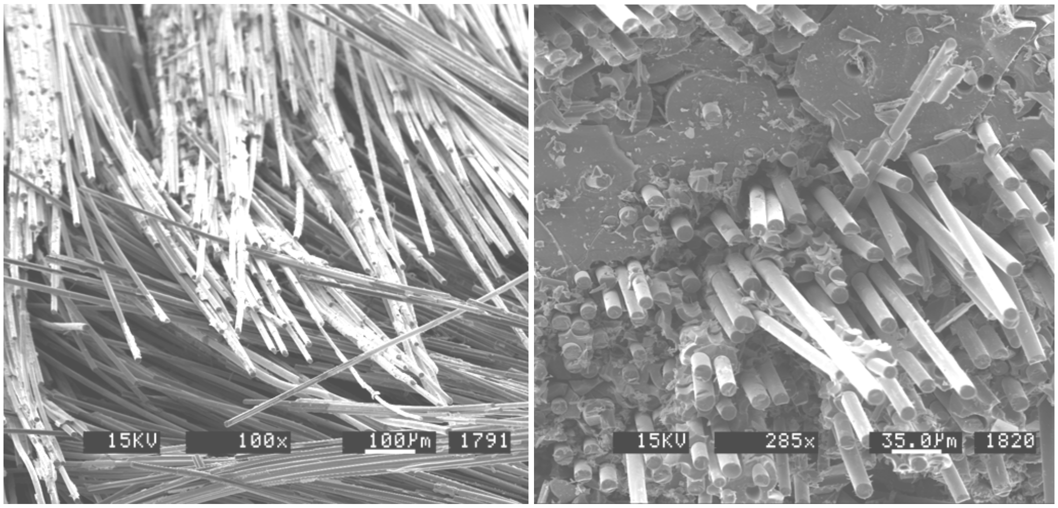


Fig. 8: Effect of neutron irradiation on flexural curves
of SiC/SiC composites with Hi-Nicalon and with Hi-Nicalon Type-S



Irradiated Hi-Nicalon sample Irradiated Hi-Nicalon Type-S sample

Fig. 9: Comparison of fracture surface of the irradiated Hi-Nicalon sample and the irradiated Hi-Nicalon Type-S sample

The SiC/SiC composites reinforced with Hi-Nicalon and Hi-Nicalon Type-S fibers were used in this experiment. Effect of the fiber properties on flexural properties of neutron irradiated SiC/SiC composites were evaluated, while some of the composites were deformed or delaminated during the irradiation. Fig. 8 shows a typical example of the effect of neutron irradiation on the flexural curve of SiC/SiC composites. This figure shows that composites reinforced with Hi-Nicalon Type-S fibers was very stable to the neutron irradiation, while composites reinforced with Hi-Nicalon fibers degraded significantly after the neutron irradiation of 10 dpa. The fiber pull-out length of the irradiated composites reinforced with Hi-Nicalon fibers was much longer than that of the irradiated composites

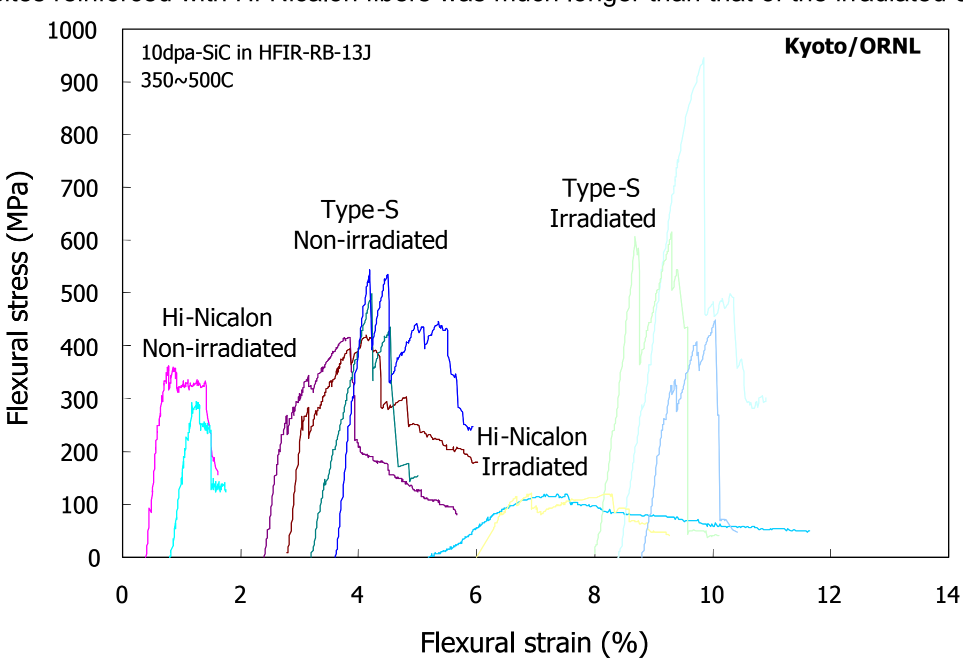


Fig. 10: The entire flexural curve of Hi-Nicalon and Hi-Nicalon Type-S samples prior to and after neutron irradiation

reinforced with Hi-Nicalon Type-S fibers as shown in Fig 9. The entire flexural curves obtained in this work are shown in Fig. 10. A lot of data scatter were seen in this experiment, since the composites used in this work were relatively small, and the composites were prepared three years ago and the quality of the composites were not as high as the present composites. However the obvious neutron irradiation effect was obtained from these data as shown in Fig. 11. In the composites reinforced with Hi-Nicalon fibers, the flexural properties, modulus, PLS and flexural strength were significantly degraded. In marked contrast to the composites reinforced with Hi-Nicalon fibers, the composites reinforced with Hi-Nicalon Type-S fibers showed stable behavior to the neutron irradiation. The average flexural strength improved, while PLS showed a slight degradation.

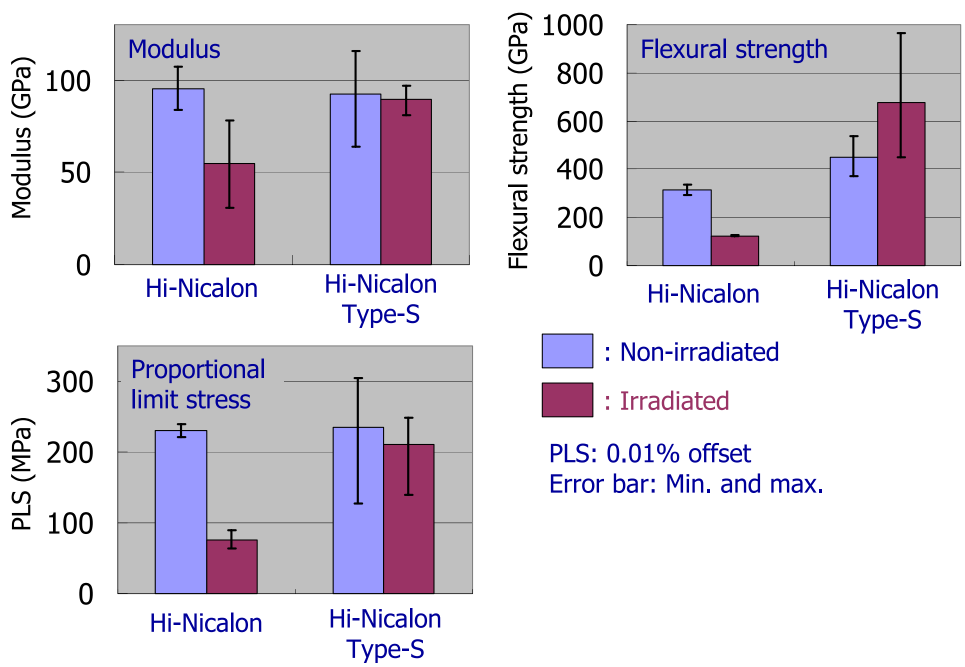


Fig. 11: Summary of the effect of neutron irradiation on flexural properties

Discussions

SiC/SiC composites reinforced with low oxygen SiC fibers which are not near stoichiometric such as Hi-Nicalon and Tyranno TE are anticipated for nuclear application, since it was reported that the low oxygen content fibers showed stability to neutron irradiation compared with commercial grade SiC fiber such as Nicalon and Tyranno Lox M [20]. Even the composites reinforced with these low oxygen content fibers degraded mechanical performance due to mismatch of swelling behavior of the fiber and matrix β-SiC. This mismatch reduced interfacial shear strength significantly. Degradation of interfacial shear strength is also explained by following Eq. (1) and (2) [21,22],

$$\sigma_m = \left(\frac{6\tau G_m V_f^{\,2} E_f E_{cl}^{\,2}}{(1-V_f) E_m^{\,2} r} \right)^{1/3} - \sigma_r \qquad (1)$$

$$h = \frac{\sigma_m^{\,2} r}{2\tau} \qquad (2)$$

where σ_m is the matrix cracking stress, τ is the interfacial shear strength, G_m is the critical mode I energy release rate, V_f is the volume fraction of the fiber, E_f, E_{cl} and E_m is the modulus of the fiber, the composites and the matrix, r is the fiber radius, σ_r is the residual stress and h is the pull-out length. The matrix cracking stress depends on the proportional limit stress (PLS) and the PLS of the composites reinforced with Hi-Nicalon fibers decreased significantly. And it is reported that the Hi-Nicalon fiber modulus slightly increased and the fiber radius of Hi-Nicalon decreases by the densification after the irradiation [9]. The modulus of CVD SiC is seen to decrease by the irradiation [18,23]. The pull-out length increased a lot by the irradiation. These results mean the significant reduction of the interfacial shear strength of the composites reinforced with Hi-Nicalon fibers.

In the case of the SiC/SiC composites reinforced with Hi-Nicalon Type-S fibers, which are low oxygen content, near stoichiometric atomic composition and highly crystalline, the flexural strength was not decreased by the neutron irradiation. Most of the reasons of the excellent stability to the neutron irradiation are attributed to the similar swelling behavior of the fiber and β-SiC matrix to the neutron irradiation. The significant reduction of the interfacial shear strength as shown in the composites reinforced with Hi-Nicalon fibers was not observed in these composites. The slight degradation of PLS was obtained in the composites reinforced with Hi-Nicalon Type-S fibers, while pull-out length did not change by the neutron irradiation. These results and Eq. (2) suggests the degradation of the interfacial shear strength. The SiC/SiC composites irradiated in this work had C interphase. So alternative interphase which is stable to the irradiation is required.

CONCLUSIONS

The SiC/SiC composites were developed with the newly developed fibers. The effect of the irradiation on mechanical properties was evaluated following the neutron irradiation in several fusion reactors.

The conclusions are;

(1) In the SiC/SiC composites reinforced with low oxygen SiC fiber which is not near stoichiometric SiC, the deformation and the delamination due to the shrinkage of the fibers were observed and the mechanical performance degraded significantly with poor fiber/matrix interfacial properties.
(2) The SiC/SiC composites reinforced with a low oxygen content, near-stoichiometric and highly crystalline SiC fibers showed the excellent stability to neutron irradiation. The mechanical performance of the composites did not degrade, even following the neutron irradiation of 10 dpa.

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