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# Effect of Fiber Properties on Neutron Irradiated SiC/SiC Composites

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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 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 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 this material did not degrade, even after neutron irradiation up to 10 dpa, while the other materials with non-highly crystalline SiC fibers degraded significantly.

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***Keywords***: *silicon carbide, neutron irradiation, mechanical property, highly crystalline fiber, fracture behavior*

## 1. Introduction

The superior high temperature mechanical properties and low radio activity of SiC/SiC composite are very attractive as fission and fusion reactor materials.[1,2] In fusion reactor environment, nuclear collision and reaction by high-energy neutrons and particles from fusion plasma strongly affect on material properties through the production of displacement damage and transmutation effects.[3,4] Degradation of material performance such as mechanical properties, thermal properties and so on is important issue and extensive efforts have 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-assisted oxidation,[7] irradiation-induced recrystallization of microcrystalline fibers,[8,9] and to dimensional changes of carbon[10] interphase applied to the fibers, while matrix swells a little by irradiation-induced point defect. Fiber shrinkage leads to fiber/matrix debonding as being reported by Hollenberg[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 avoid or to minimize these radiation effects, development of SiC fiber with lower oxygen content, reduced free carbon and enhanced crystallization is recent trend. The development of SiC composite with radiation-resistance is based on the use of stoichiometric SiC fibers with lower oxygen and 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.

## 2. Experimental Procedure

The SiC/SiC composites used in this study were fabricated at National Research Institute for Metals (NRIM), using Hi-Nicalon™, Hi-Nicalon™ Type-S, Tyranno™ TE or Tyranno™ ZE SiC fibers. The Type-S fiber contains lower oxygen and has near-stoichiometric chemical composition and highly crystalline structure, while the other low oxygen fibers are composed of excess carbon and insufficiently crystalline structure. Representative properties and chemical compositions of the fibers[12,15] are compiled in Table 1. The matrix of a unidirectional fiber-reinforced composite was formed by chemical vapor infiltration (CVI) method.[16] A pyrolitic carbon interphase was applied to the fibers by CVI prior to matrix CVI processing. The thickness of carbon interphase on fiber preforms was 200 nm, and the plate size was $40^{\Phi} \times 2^{t}$ mm. The composites were square-cut into $25^{l} \times 4^{w} \times 2^{t}$ mm bar for bend bars irradiated at Japan Material Testing Reactor (JMTR),[17] and $20^{l} \times 1.5^{w} \times 1.5^{t}$ mm bar for the bend bars irradiated at High Flux Isotope Reactor (HFIR).[18] The composites prepared for JMTR irradiation had an extra SiC layer with 300 μm in thickness at one side, which was deposited on the infiltrated SiC/SiC composites.

Neutron irradiations were carried out in the 97M-33U capsule at JMTR, Research Establishment of Japan Atomic Energy Research Institute and in the HFIR 13J capsule at Oak Ridge National Laboratory. The fluence for the 97M-33U irradiation was $1.0 \times 10^{25}$ n/m$^2$ ($E > 0.1$ MeV). It is assumed an equivalence of one displacement per atom (dpa) $= 1.0 \times 10^{25}$ n/m$^2$ ($E > 0.1$ MeV). The samples were irradiated at 400°C. The fluence for the 13J irradiation was $1.0 \times 10^{26}$ n/m$^2$ ($E > 0.1$ MeV). The temperature of samples was controlled by electric heaters. The samples were irradiated at a constant temperature of 350°C, 500°C, in periodically-variable temperature of 300°C and 500°C or

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Table 1 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 |

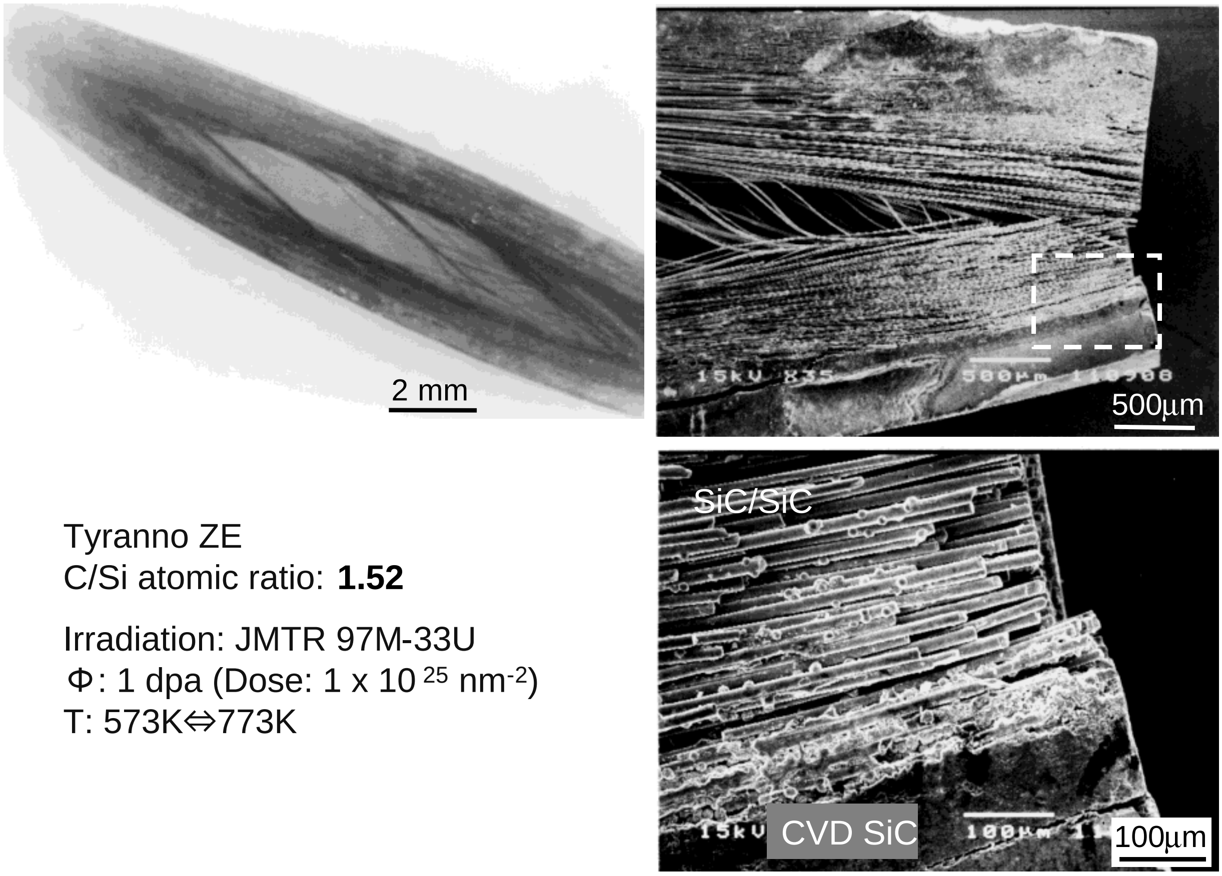


Fig. 1 Effect of neutron irradiation on Tyranno ZE/C/SiC.

200°C and 350°C. The details regarding HFIR-13J irradiation were reported in Ref. 19). After irradiations, the capsules were cooled to low radiation activity level, and then moved to the hot cell. The samples were transferred to hot lab for the observation of the microstructure and the flexural tests.

Three-points flexural tests for the sample irradiated at JMTR 97M-33U were carried out at ambient temperature before and after irradiations, and the support span was 18 mm and the crosshead speed was 0.03 mm/s. The support span was 16 mm and the crosshead speed was 0.02 mm/s for the sample irradiated at HFIR 13J. The size of the bend bar used at JMTR 97M-33U irradiation was different from that used at HFIR 13J irradiation because of limitation of the capsules. And different experimental conditions were applied. These flexural tests were carried out in a plastic bag.

## 3. Results

### 3.1 Effect of neutron irradiation of JMTR 97M-33U

The representative shape figures for three kinds of SiC/SiC composites with Hi- Nicalon, Tyranno TE or Tyranno ZE fibers neutron-irradiated are shown in Fig. 1. The deformation during irradiation was not observed in the SiC/SiC composites with Hi-Nicalon Type-S fibers. An example of the figures is shown in Fig. 2. The extra CVD SiC layers at one side are also observed in Fig. 1 and Fig. 2. The three kinds of fibers used for the deformed composites are not stoichiometric SiC composition, although they are lower oxygen content fibers. The shrinkage of non-crystalline SiC fiber[9] due to recrystallization[20] and the swelling of $\beta$-SiC by neutron irradiation[6,21] have been reported. According to the papers, this deformation was attributed to the mismatch between the fiber shrinkage and $\beta$-SiC swelling.

Only the samples of Hi-Nicalon Type-S were examined by flexural tests because the other samples were previously de-

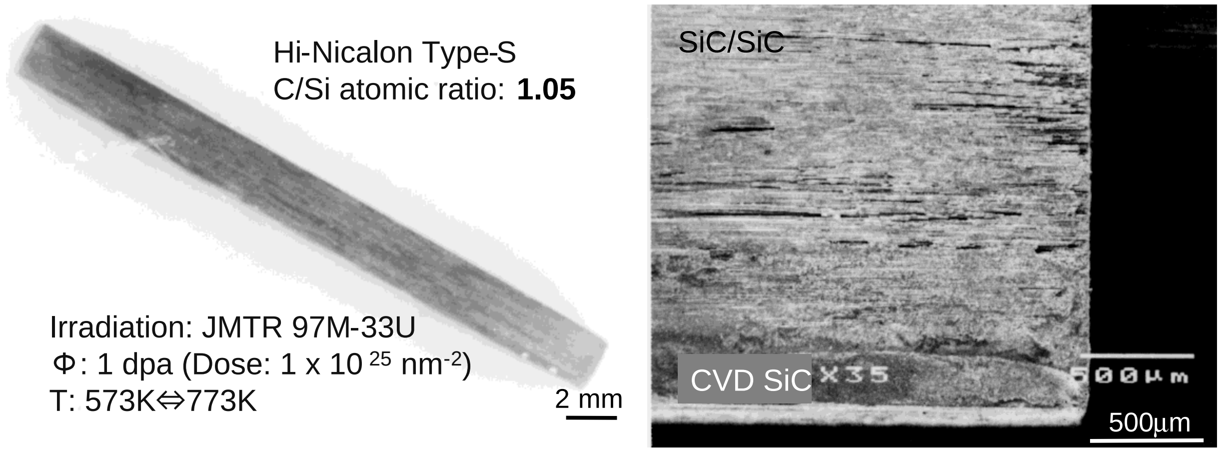


Fig. 2 Effect of Neutron Irradiation on Hi-Nicalon Type-S/C/SiC.

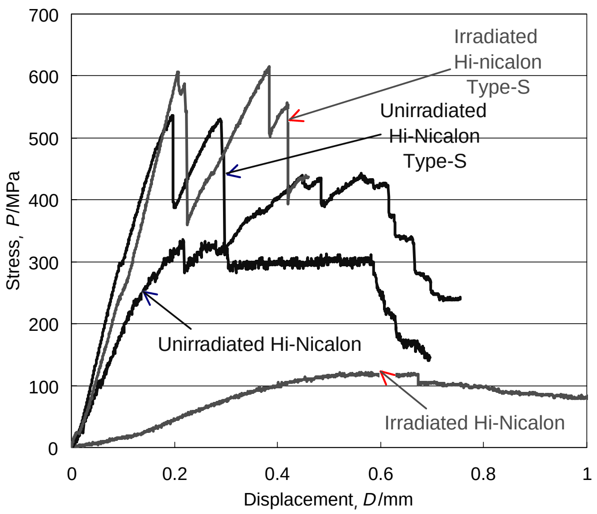


Fig. 3 Effect of neutron irradiation on flexural curves of SiC/SiC composites with Hi-Nicalon and with Hi-Nicalon Type-S.

formed by irradiation. Obvious degradation by the neutron irradiation was not seen in modulus, proportional limit stress (PLS), which was evaluated at 0.01% strain offset, and flexural strength. Most of pull-out fibers in the fracture surface of the irradiated sample were separated. On the other hand pull-out fibers of the unirradiated sample bonded with several fibers. The pull-out length of the irradiated sample was longer than that of the unirradiated sample. The similar results were reported for the composites with Hi-Nicalon Type-S in the Ref. 22).

### 3.2 Effect of neutron irradiation of HFIR 13J

Influence of the fiber properties on flexural properties of neutron irradiated SiC/SiC composites were studied for the SiC/SiC composites with Hi-Nicalon fiber and with Hi-Nicalon Type-S fiber, and some of the samples were deformed or delaminated. Figure 3 shows a typical example of degradation behavior on the flexural curve of SiC/SiC composites. The Type-S sample was stable to the neutron irradiation, while the Hi-Nicalon sample degraded significantly after neutron irradiation to 10 dpa. The fiber pull-out length of the irradiated Hi-Nicalon sample was larger than that of the irradiated Type-S sample as shown in Fig. 4. The data obtained were scattered in this experiment, because the samples were relatively small, and were prepared three years ago and the quality of the samples were also not as high as the latest samples. However the obvious neutron irradiation effect was observed in Fig. 5. Error bars show maximum and minimum values. In the Hi-Nicalon sample, the flexural properties, modulus, PLS and flexural strength were significantly degraded. In contrast to the Hi-Nicalon samples, the Type-S samples showed stable behavior to the neutron irradiation. The average flexural strength improved, while PLS showed a slight degradation. The effect of irradiation temperature on mechanical properties and fracture behavior were not seen in this result.

## 4. Discussions

SiC/SiC composites with lower oxygen content SiC fiber being not near stoichiometric were expected for nuclear application, because the lower oxygen content fibers showed superior stability to neutron irradiation to commercial grade SiC fiber[8)] such as Nicalon and Tyranno Lox M.[15)] Even the composites with these lower oxygen content fibers reduced their mechanical performance due to mismatch of swelling behavior between fiber and matrix of $\beta$-SiC. The interfacial shear strength was significantly decreased as a result of this mismatch. Degradation of interfacial shear strength is also given by following eqs. (1) and (2),[23,24)]

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

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

where $\sigma_m$ is the matrix cracking stress, $\tau$ the interfacial shear strength, $G_m$ the critical mode I energy release rate, $V_f$ the volume fraction of the fiber. $E_f$, $E_{cl}$ and $E_m$ are the modulus of the fiber, the composites and the matrix, respectively. $r$ is the fiber radius, $\sigma_r$ the residual stress and $h$ the pull-out length. The cracking stress of matrix depends on the proportional limit stress (PLS). The PLS of the Hi-Nicalon samples decreased significantly. It is reported that the Hi-Nicalon fiber modulus slightly increases and the fiber radius of Hi-Nicalon

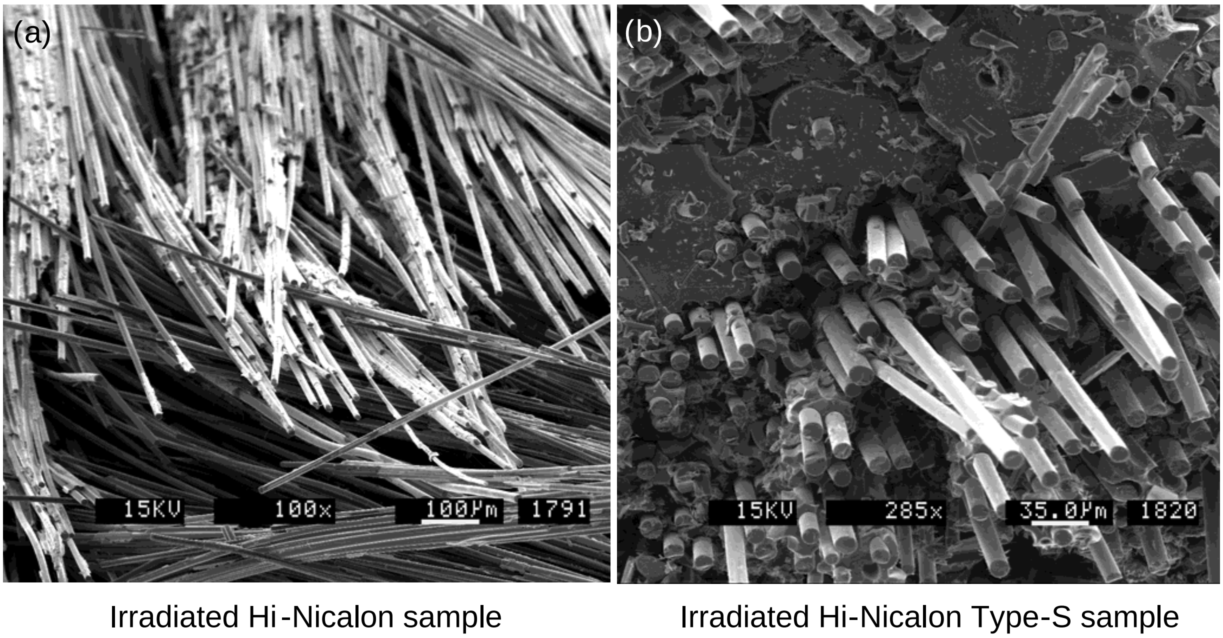


Fig. 4 Comparison of fracture surface of the irradiated Hi-Nicalon sample and the irradiated Hi-Nicalon Type-S sample.

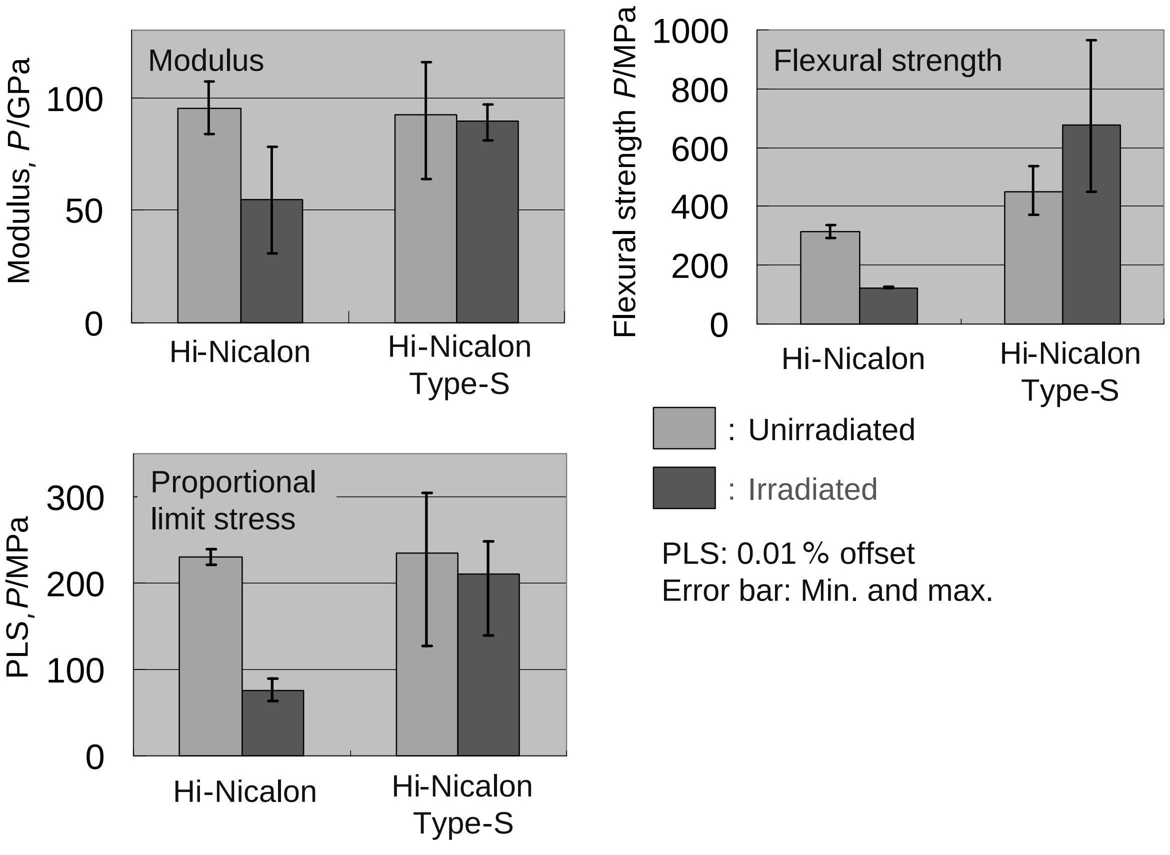


Fig. 5 Summary of the effect of neutron irradiation on flexural properties.

decreases by the densification after the irradiation.[9] The modulus of CVD SiC decreases by irradiation.[20] The pull-out length increased greatly by irradiation. These results suggest the significant reduction of the interfacial shear strength of the Hi- Nicalon samples after neutron irradiation.

In the case of the SiC/SiC composites with Hi-Nicalon Type-S fibers, which are low oxygen content, near stoichiometric atomic composition and highly crystalline structure, the flexural strength was not decreased by the neutron irradiation. The excellent stability to the neutron irradiation is attributed to the similar behavior for swelling of the fiber and $\beta$-SiC matrix after neutron irradiation. Another advantage of this material is that the swelling saturates at less than irradiation of 10 dpa at irradiation temperature $<1000^{\circ}$C,[25,26] while the displacement damage of saturation depends on the irradiation temperature. At lower temperatures, SiC swells

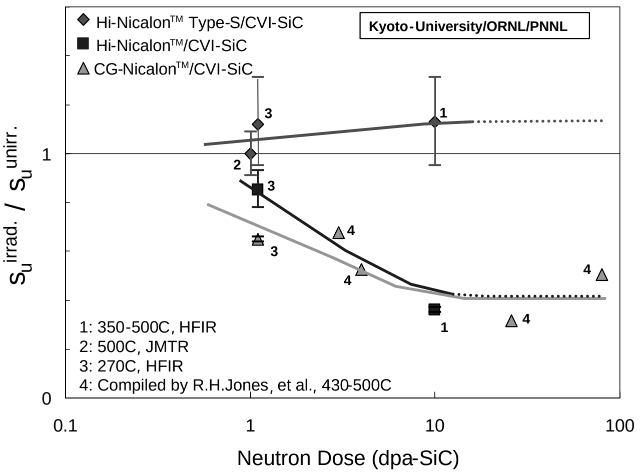


Fig. 6 Effect of neutron irradiation on flexural strength of SiC/SiC composites with various Nicalon type fibers.

by accumulation of point defects in the lattice. This swelling phenomenon saturates at lower damage levels and the total swelling decreases with increasing temperature. It was showed that void driven swelling, which would not saturate but increase monotonically with irradiation damage, do not occur below about 1000°C.[27] These results suggest that the SiC/SiC composites with reduced oxygen contents and near stoichiometric atomic composition might be stable to higher neutron irradiation above 10 dpa. The stability to neutron irradiation of the SiC/SiC composites with various Nicalon type fibers is summarized in Fig. 6. Error bars show maximum and minimum values.

The slight degradation of PLS was recognized in the Hi-Nicalon Type-S samples, but pull-out length did not change by the neutron irradiation. These results and eq. (2) suggest the degradation of the interfacial shear strength. The SiC/SiC composites irradiated had carbon interphase. Degradation of carbon interphase was mentioned in the previous paper.[11] Alternative interphase which is stable to the irradiation[28] is also required.

## 5. 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 fission reactors.

The conclusions are;

(1) In the SiC/SiC composites with a low oxygen content SiC fiber which is not near stoichiometric SiC, the deformation and the delamination by the shrinkage of the fibers were observed and the mechanical performance degraded significantly with poor fiber/matrix interfacial properties.

(2) The SiC/SiC composites with a low oxygen content, near-stoichiometric and highly crystalline SiC fibers showed the excellent stability to neutron irradiation. The mechanical performance of this material did not degrade, even following the neutron irradiation of 10 dpa.

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## REFERENCES

1) P. Fenici, A. J. Frias Rebelo, R. H. Jones, A. Kohyama and L. L. Snead: J. Nucl. Mater. **258–263** (1998) 215–225.
2) A. Hasegawa, A. Kohyama, R. H. Jones, L. L. Snead, B. Riccardi and P. Fenici: J. Nucl. Mater. **283–287** (2000) 128–137.
3) L. Giancarli, J. P. Bonal, A. Caso, G. Le Marois, N. B. Morley and J. F. Salavy: Fusion Engineering and Design **41** (1998) 165–171.
4) A. Kohyama, M. Seki, K. Abe, T. Muroga, H. Matsui, S. Jitsukawa and S. Matsuda: J. Nucl. Mater. **283–287** (2000) 20–27.
5) L. L. Snead, R. H. Jones, A. Kohyama and P. Fenici: J. Nucl. Mater. **233–237** (1996) 26–36.
6) L. L. Snead, M. C. Osborne, R. A. Lowden, J. Strizak, R. J. Shinavski, K. L. More, W. S. Eatherly, J. Bailey and A. M. Williams: J. Nucl. Mater. **253** (1998) 20–30.
7) L. L. Snead, M. C. Osborne and K. L. More: J. Mater. Res. **10** (3) (1995) 736–747.
8) A. Hasegawa, G. E. Youngblood and R. H. Jones: J. Nucl. Mater. **231** (1996) 245–248.
9) M. C. Osborne, C. R. Hubbard, L. L. Snead and D. Steiner: J. Nucl. Mater. **253** (1998) 67–77.
10) J. H. W. Simmons: *Radiation Damage in Graphite*, (Pergamon Press, 1965).
11) G. W. Hollenberg, C. H. Henager, Jr., G. E. Youngblood, D. J. Trimble, S. A. Simonson, G. A. Newsome and E. Lewis: J. Nucl. Mater. **219** (1995) 70–86.
12) M. Takeda, A. Urano, J. Sakamoto and Y. Imai: J. Nucl. Mater. **258–263** (1998) 1594–1599.
13) R. E. Jones, D. Petrak, J. Rabe and A. Szweda: J. Nucl. Mater. **283–287** (2000) 556–559.
14) T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura and T. Nagasawa: Nature **391** (1998) 773–775.
15) K. Kumagawa, H. Yamaoka, M. Shibuya and T. Yamamura: Ceram. Eng. Sci. Proc. **18** [3] (1997) 113–118.
16) H. Araki and T. Noda: J. Nucl. Mater. **258–263** (1998) 1540–1545.
17) M. Narui, H. Kurishita, H. Kayano, T. Sagawa, N. Yoshida and M. Kiritani: J. Nucl. Mater. **212–215** (1994) 1665–1670.
18) A. L. Qualls and T. Muroga: J. Nucl. Mater. **258–263** (1998) 407–412.
19) A. L. Qualls and T. Muroga: Fusion Reactor Materials Semiannual Report, **DOE/ER-0313-25**, US Department of Energy (2001) 302–306.
20) Y. Katoh, T. Hinoki, A. Kohyama, T. Shibayama and H. Takahashi: Ceram. Eng. Sci. Proc. **20** [4] (1999) 325–332.
21) M. C. Osborne, J. C. Hay, L. L. Snead and D. Steiner: J. Am. Ceram. Soc. **82** [9] (1999) 2490–2496.
22) L. L. Snead, Y. Katoh, A. Kohyama, J. L. Bailey, N. L. Vaughn and R. A. Lowden: J. Nucl. Mater. **283–287** (2000) 551–555.
23) B. Budiansky, J. W. Hutchinson and A. G. Evans: J. Mech. Phys. Solids **34** (1986) 167.
24) R. W. Davidge: *Applications of Fracture Mechanics to Composite Materials*, (K. Friedrich (Ed.), Elsevier, New York, 1989) 547.
25) L. L. Snead and J. C. Hay: J. Nucl. Mater. **273** (1999) 213–220.
26) H. Kishimoto, Y. Katoh, A. Kohyama, M. Ando, H. Tanigawa and K. Jimbo: (Proc. 4th IEA workshop on SiC/SiC Ceramic Matrix Composites for Fusion Structural Applications, Frascati, Italy, 2000) 59–66.
27) R. J. Price: J. Nucl. Mater. **33** (1969) 17–22.
28) T. Hinoki, L. L. Snead, Y. Katoh, A. Kohyama and R. Shinavski: J. Nucl. Mater. **283–287** (2000) 376–379.