

SILICON CARBIDE COMPOSITES FOR FUSION REACTOR APPLICATION

L. L. Snead¹, T. Hinoki¹, Y. Katoh², T. Taguchi³, R. H. Jones⁴, A. Kohyama², N. Igawa³

- 1 Oak Ridge National Laboratory, Oak Ridge, TN, USA 37831-6087
- 2 IAE Kyoto University, Gakasho, Uji, Kyoto 611-0011, Japan
- 3 Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, 319-1195
- 4 Pacific Northwest National Laboratory, Richland WA USA 99352

Over the past decade, the international fusion materials community has sought to understand the performance of SiC composites in an irradiation environment, with the goal of developing advanced composites capable of withstanding structural application to 1000°C and radiation damage corresponding to hundreds of displacements per atom (dpa). This paper will review research, development, and the significant progress made in the area of radiation-hardened SiC composites. Specifically, this paper reviews the results of a systematic study into the radiation effects on the mechanical properties of stoichiometric and off-stoichiometric SiC fiber reinforced, chemically vapor infiltrated (CVI) SiC composites. Materials have been manufactured by forced flow CVI at ORNL with fibers containing a range of oxygen (the Nicalon™ fiber family) and carbon interphases. Neutron irradiation was carried out in the High Flux Isotope Reactor in temperature and dose ranges of 300-800°C and 1-10 dpa, respectively. Results indicate that where degradation occurs at the 1 dpa level for non-stoichiometry fibers, there is essentially no degradation for the stoichiometric fibers. This paper will also review the recent trends in development of composite engineering for potential fusion reactor application.

1. Fusion Environment and Structures

The potential benefit of silicon carbide based materials for fusion reactors has been discussed for many years^{1,2} primarily due to their inherently low induced radioactivities. The application of such a low activation material offers several advantages in the areas of safety, maintenance and disposal, and is one of the reasons that fusion is considered an attractive future energy source. This was in fact the conclusion of the 1988 U.S. Department of Energy sponsored report² "Exploring the Competitive Potential of Magnetic Fusion Energy," which compared the future outlook of fossil, fission and fusion energy. Since this time there have been active programs exploring the use of SiC in fusion reactor systems, such as the ARIES³ designs in the US, the TAURO⁴ design in Europe, and the Japanese DREAM⁵ concept. In each of these cases the approach to handling the very high heat fluxes produced by the plasma is somewhat different, requiring somewhat different performance requirements for the SiC/SiC. An example of the scale and design for a SiC fusion reactor structure reproduced from the work of Giancarli⁶ is shown in Figure 1. Such structures are building blocks to surround the toroidal plasma and can be on the

order of meters in dimension. For the case of figure 1, the left side of the figure would face the fusion plasma, thus receive the greatest heat flux and highest stresses in the system. The performance requirements for SiC composites have been determined by designers keeping in mind practical extrapolations of the state-of-the-art for SiC composite properties. Table 1 shown typical performance requirements generated in the reactor design studies as compiled by Jones⁷. In parallel with these efforts, fundamental and applied programs in development and understanding the behavior of these materials in nuclear systems have been undertaken internationally. Reviews conducted in support of international fusion power development programs have been presented biannually⁸⁻¹³.

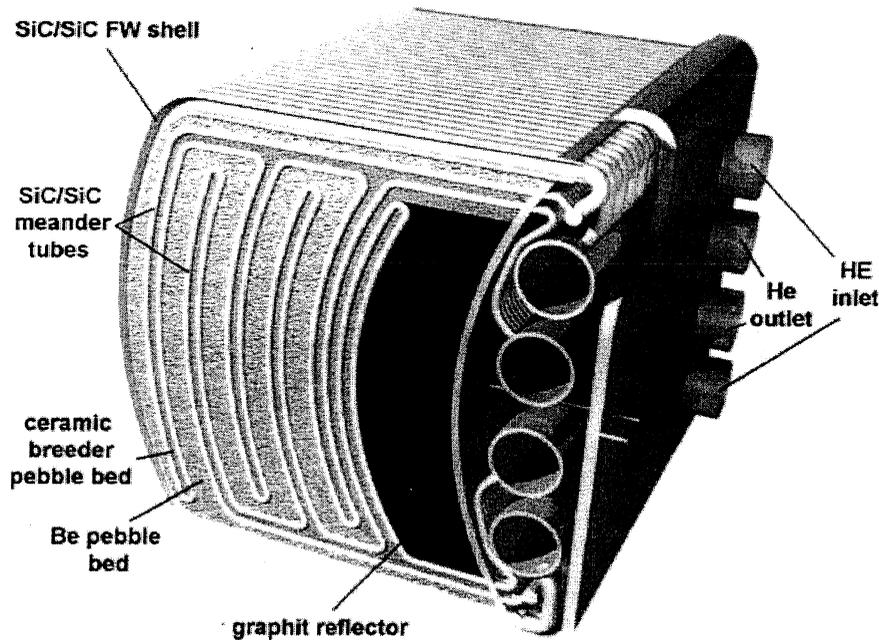


FIGURE 1 : Illustration of SiC blanket module for fusion power reactor.⁶

2. Radiation Damage in Silicon Carbide and Composites

Silicon carbide fibers are commercially processed through many different routes. The most widely studied, developed and commercialized SiC fiber is derived from the polymer precursor process first introduced by Yajima¹⁴. These fibers are commercially available under the trade name of NicalonTM. The first stage of the NicalonTM fiber process involves the low temperature melt-spinning of the polycarbosilane (PCS) polymer. These spun fibers, which are in the "green state", are then stabilized by elevated temperature exposure to oxygen and successively ceramized in an inert atmosphere to a final temperature of 1300 °C.

	ARIES-1	TAURO	DREAM-3
Fiber architecture	2D, 3D	3D	3D
Temperature (°C)	~1000	~1100	900–1100
Strength (MPa)	Pr. stresses <140; sec. Stresses <190	NS*	300
Elastic modulus (GPa)	NS	200 (100°C)	200
CTE (°C ⁻¹)	NS	4 × 10 ⁻⁶ (RT–1000°C)	3.3 × 10 ⁻⁶
Creep rate (s ⁻¹)	NS	NS	NS
Thermal conduct (W m ⁻¹ K ⁻¹)	17.5	~15	15
Specific heat (J kg ⁻¹ per m ³)	NS	NS	1200
Thermal shock	NS	NS	NS
DENSITY (g cm ⁻³)	NS	2.6 (800°C)	2.5
Chemical compatibility	He (750°C) Li ₂ O or (800°C), Be at 800°C	Pb–17 Li (~700°C) up to 1 m s ⁻¹	He:Li ₂ O, Li ₂ ZrO ₃
Lifetime (year)	NS	5 (12.5 MW a m ⁻²)	30 (15 MW a m ⁻²)
Impurity limits	Dictated by safety (and waste disposal) for all materials	Dictated by dose (safety) for SiC/SiC, after heat for all, recycling for Pb–17 Li	NS
Hermeticity (leak tightness)	10 MPa–He (tritium)	NS	NS
Brazing joining—strength (MPa)	NS	50	Low
Elect. conditions	No limits	NS	NS

* Not specified.

TABLE 1 : Material requirements for fusion power reactors following Jones ⁸

It is important to note that due to the presence of excess oxygen and carbon, these fibers are more correctly classified as SiC-based fibers, rather than SiC fibers. The manufacturer's quoted composition for Nicalon NLM-202, which is close to figures given by Yajima¹⁵ for pre-production fibers, is 65 % β-SiC with 23 % SiO₂ and 11 % free carbon. The microstructure of these fibers are of dispersed β-SiC crystallites of a few nanometers in size embedded in a continuum glassy silicon oxycarbide matrix (Si-O_x-C_y, where x+y is approximately 4).

A second generation of Nicalon™ fibers have been produced by improving the method of cross-linking the spun polymer. Rather than curing the PCS in air, the polymer is subjected to ionizing radiation in a helium environment. Cross linking the PCS in this manner first used ultraviolet light¹⁶⁻¹⁷, although the most successful demonstration is for the Nicalon pre-ceramic polymer and uses electron irradiation¹⁸⁻¹⁹. This process reduces the atomic oxygen content from greater than

15 % (standard Nicalon fiber) to less than 0.5 % and is the process with which Hi-Nicalon fiber is made¹⁹. The average SiC crystallite size for this product increases by more than a factor of two over the ceramic grade fiber, and the fiber elastic modulus undergoes a large increase while the strength decreases slightly. The density of the Hi-Nicalon fiber is also increased from 2.55 g/cc (ceramic grade Nicalon fiber) to 2.74 g/cc, which is approximately 85 % theoretical SiC density. Also of interest for nuclear applications, the Hi-Nicalon fiber density was seen not to undergo the dramatic densification seen in ceramic grade Nicalon fiber, at least for low-dose neutron irradiation²⁰. It is the densification of these fibers that was identified early on as the source of the poor irradiation performance of SiC composites²¹. Recently, a further improvement in the Nicalon™ system has been achieved (Type-S Nicalon™.) Essentially, the Hi-Nicalon™ process has been taken a step further with the result of a near theoretical density fiber with very low excess carbon and oxygen (< 0.1%).

Upon irradiation, the early composites using ceramic grade Nicalon yielded a disturbing loss in mechanical properties. Essentially, the composite lost more than 40% of its bending strength at the 1 displacement per atom (dpa.)²¹ This level of neutron damage is equivalent to that which would occur in less than a month of service in a fusion power application. It soon became clear that the reason for the degradation in composite properties under irradiation was the densification of the SiC-based Nicalon fiber. This densification caused debonding of the interface between the fiber and the composite interphase material eliminating the load transfer between the matrix and the fiber. Evidence of this debonding was clearly seen through TEM^{22,23}, and is shown in figure 2. It is noted that densification under irradiation is atypical for crystalline ceramics, with glass being the only exception. For this reason it was thought that elimination of the glassy phase in Nicalon fibers would improve the radiation performance, and the development of the new, lower oxygen containing fibers was welcome.

Figure 3 shows the irradiation performance of SiC/SiC composites indicating the clear trend toward better irradiation performance with the more advance, low oxygen-content fibers. In this case, all composites were fabricated with identical carbon interphases and chemically vapor infiltrated with SiC. This work gave the first promise of a radiation stable SiC/SiC material, albeit at relatively low irradiation damage levels. Figure 4 gives the most recent summary of the effect of neutron dose on the normalized strength of SiC/SiC composites taken to more application-relevant neutron damage levels.²⁴ Data on monolithic CVD is also included. From the figure it is clear that the near stoichiometric fibers, exhibit continued stability under irradiation to doses approaching 10 dpa. As physical properties of ceramics tend to saturate before this dose level, it is argued that the composite will not degrade due to neutron irradiation even at the design lifetime of fusion reactor components (up to 100 dpa.)

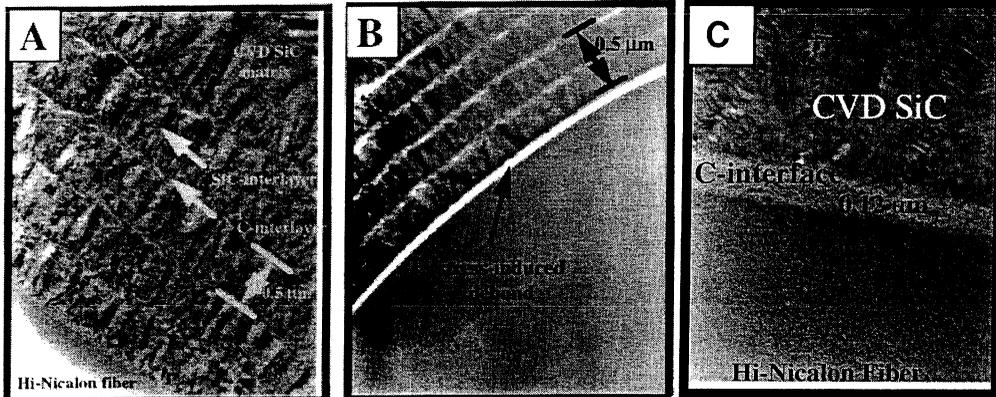


FIGURE 2 : TEM micrograph of irradiation-induced debonding of interphase

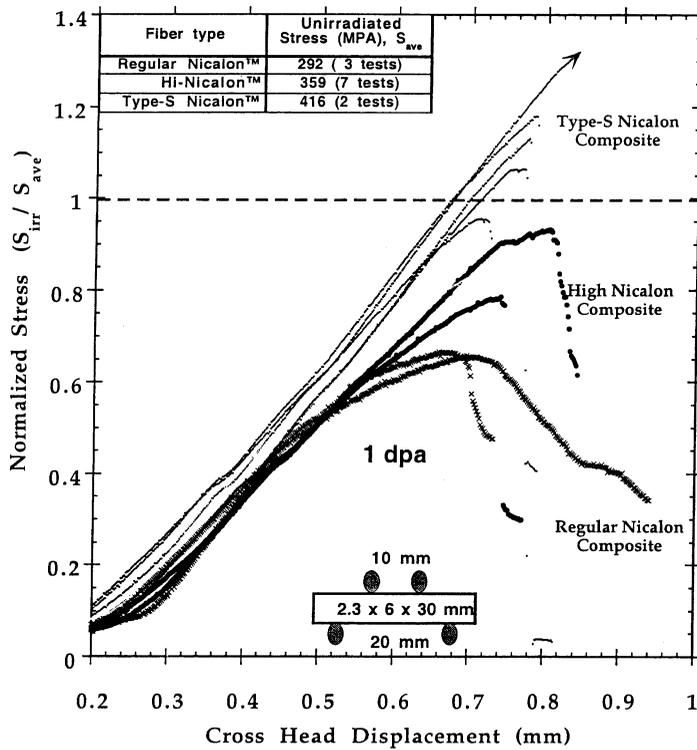
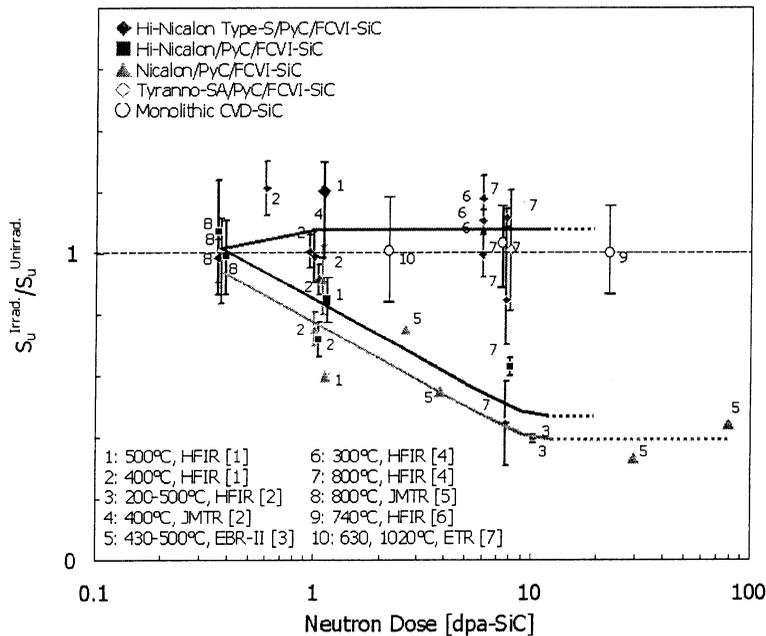


FIGURE 3 : Effect of low-dose neutron irradiation on SiC/SiC composites of Nicalon-family fibers.



- [1] L.L. Snead, et al., J. Nucl. Mater., 283-287 (2000) 551-555. [5] T. Nozawa, et al., J. Nucl. Mater., (2002) to be published.
 [2] T. Hinoki, et al., Mater. Trans., JIM, 43 [4] (2002) to be published. [6] R.J. Price, et al., J. Nucl. Mater., 108-109 (1982) 732-738.
 [3] R.H. Jones, et al., 1st IEA-SiC/SiC (1996). [7] R.J. Price, J. Nucl. Mater. 33 (1969) 17-22.
 [4] T. Hinoki, et al., J. Nucl. Mater., (2002) to be published.

FIGURE 4 : Effect of high-dose neutron irradiation on strength of SiC/SiC

It is well known that the effect of irradiation is to reduce the thermal conductivity of ceramics under irradiation. For monolithic materials, this reduction is generally due to the creation of defects such as vacancies and vacancy loops. Additionally, the disruption of grain boundaries can increase phonon scattering, also reducing thermal conductivity. For SiC/ SiC composites the situation is substantially more complex due to the presence of voids and interfaces (ie fiber/matrix) and internal cracking. It has been shown²⁵ that for CVI SiC infiltrated Hi-Nicalon composites, nearly all the thermal conduction takes place in the matrix material.

3. Development and Performance of Advanced Composites for Fusion

With the previous work on development of SiC for fusion systems now yielding a material which appears capable of withstanding the high neutron fluences associated with fusion systems, the emphasis of new work is shifting to optimization of properties and composite engineering to address design needs. Optimization of the "radiation hard" composites are being carried out on low-oxygen content, near stoichiometric, and highly crystalline fibers, Hi-Nicalon™ Type-S and Tyranno™ SA. Typical properties of fibers provided by the manufacture are shown in Table 2. As example, these composites have been fabricated by the forced-flow thermal-gradient chemical vapor infiltration (FCVI). Carbon, SiC/C or multilayer (SiC/C) were applied as the fiber/matrix

interphase followed by matrix SiC deposition. Sizes have varied from 75 to 300 mm in diameter for ~12.5 mm thick parts. The first consideration in fabrication conditions using the high-purity fibers was optimization to improve composite density and the uniformity in thickness of fiber/matrix interphase, thus ensuring uniformity of mechanical properties. Results from this study were recently presented by Taguchi²⁶ and Igawa²⁷. The density of composites fabricated by FCVI was significantly improved by optimization of temperature and gas flow and increasing fiber volume fraction. Matrix porosity was decreased to approximately 15%. The variability of fiber/matrix interphase thickness was significantly improved by reversing the up-stream side and down-stream side of the gas in the middle of deposition as shown in Figure 5. This figure shows the distribution of the interphase thickness at nine regions in a composite.

SiC Fiber	C/Si Atomic Ratio	Oxygen Content (wt%)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Thermal conductivity (W/mK)	Density (g/cm ³)	Diameter (μm)
Tyranno SA	1.08	<1	2.5	400	65	3.10	7.5
Hi-Nicalon Type-S	1.05	0.8	2.6	410	24.1	3.10	13
Hi-Nicalon	1.39	0.5	2.8	270	7.77	2.74	14
Nicalon CG	1.31	11.7	3.0	220	2.97	2.55	14

TABLE 2 : Properties of SiC fibers of interest

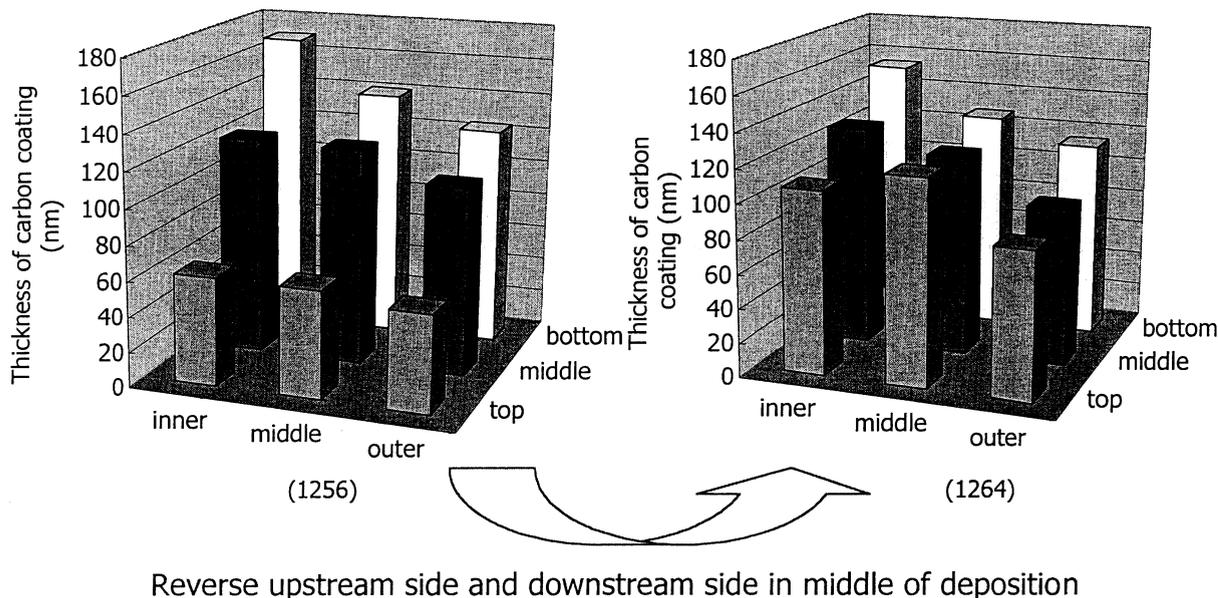


FIGURE 5 : Effect of reversed infiltration on the uniformity of interfacial thickness

Significant effort has been put towards understanding the role of the fiber/matrix interphase in SiC composites as the interphase is critical for transferring load from the matrix to the high-strength

fibers. If the interphase it is too weak load will not be transferred to the high strength fibers. However, if the bond between fiber and matrix is too strong, the interphase will not serve as a crack deflection site, eliminating the principle benefit of the composite-higher strength and more uniform properties due to micro-crack tolerance. It is well know that graphite and boron nitride, which are the two most popular SiC/SiC candidate interphases, will not respond well under neutron irradiation. For this reason, development of alternative interphases such as porous and multilayer SiC has being conducted.²⁵ A comparison of the mechanical properties for composites manufactured with carbon, C/SiC and multilayer SiC is given in Figure 6. It is seen that for this case of FCVI SiC matrix Hi-Nicalon fibers, the mechanical properties for the three interphases are comparable. Furthermore, the elastic modulus of these composites is almost twice that reported for composites reinforced with Nicalon fibers fabricated by CVI ²⁸. The fracture strain of composites fabricated in this work is less than half of that of composites reinforced with Nicalon fibers. These properties are attributed to the intrinsic fiber properties. Both tensile strength and proportional limit stress of composites fabricated in this work are superior to those of composites reinforced with Nicalon fibers. The thickness range of C interphase in figure 6 was about 20~300 nm. The average thickness of SiC layer of the SiC/C interphase was approximately 60 nm. No apparent effects of C interphase thickness and the first SiC layer on tensile properties were observed. In the case of the SiC/C interphase, the first thin SiC layer (50 nm) strengthens the bond between fiber and interphase. The next three SiC layers (200 nm) serve the function of crack deflection and debonding of the fibers. The next two thick SiC layers (500 nm) serve a similar function for the bundles themselves. Thin C layers (50 nm) are used just to separate SiC layers. Multiple fractures outside of the fiber bundles is represented in the SEM image of Figure 7. The tensile strength of the composites with the multilayer was nearly 30 % higher than the composites with C interphase and with SiC/C interphase.

Due to the very high heat loading expected in fusion systems combined with the significant degradation in thermal conductivity associated with neutron damage, enhanced thermal conductivity has been a key issue in the development of SiC composites. Modeling to understand the thermal transport across fiber/matrix boundaries, including asymmetric voids and irradiation conditions are being carried out. It is clear that simply increasing the initial quality of the composite, and thereby increasing the thermal conductivity is desirable. Process methods such as studying the effect of crystallinity of the matrix have been studied with good results. A second method for improving the composite conductivity is by using a combination of SiC matrix and high-conductivity graphite fibers. Figure 8 shows an optical micrograph of the polished surface of a CVI SiC matrix, graphite fiber composite.²⁹ In this case, the polished surface shows the z-stitched Amoco K-1100 graphite fibers of an unbalanced (1,1,6) weave where in the x and y direction a lower modulus Amoco P-55 fiber was woven. This three dimensional composite yielded

reasonably good strength and, from an analysis of the flexure curves²⁵ and fracture surfaces, possessed a fair amount of toughness. In the major fiber direction, the four-point bend strength was 267 ± 28 MPa, which is comparable to CVI SiC/SiC fiber materials.³⁰ Strength of bend bars across the major fiber direction would be considerably reduced due to the reduced fraction of (P 55) fibers in this orientation.

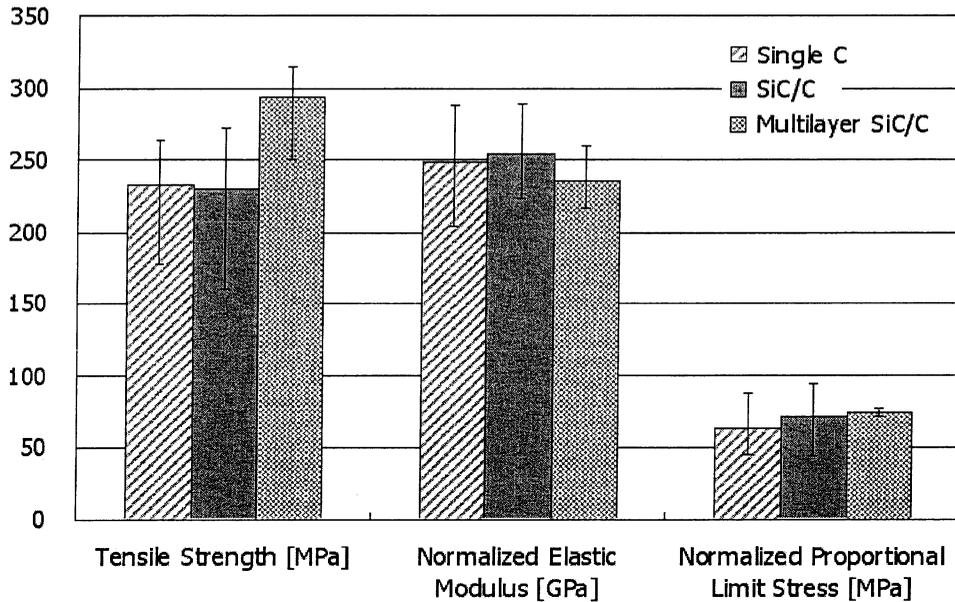


FIGURE 6: The effect of fiber/matrix interphase on tensile properties

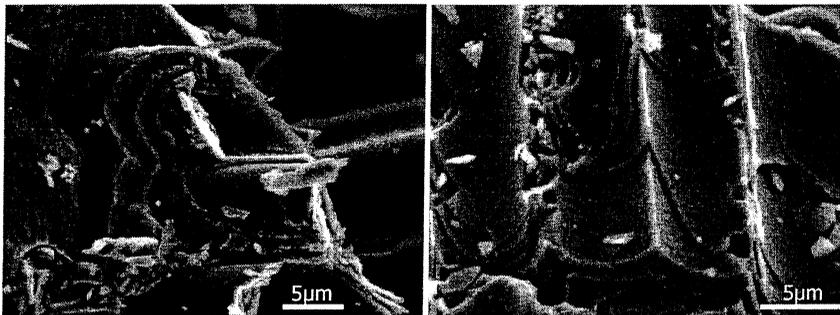


FIGURE 7: Multiple fracture of interphase of the composite with SiC/C multilayer

The thermal conductivity of both SiC/graphite produced in this study is given in Figure 9. Along with the thermal conductivity of the CVI SiC/graphite composites, the thermal conductivity of a very high quality monolithic CVD SiC material produced by Morton (now Rohm Haas), and the transverse thermal conductivity of an FCVI SiC/Type S Nicalon composite is shown. As expected, due to the significantly higher thermal conductivity of the graphite fibers (~ 950 and, ~ 120 W/m-K at ambient for K1100 and P55, respectively) as compared to the SiC fiber (~ 15 W/m-K at ambient),

the SiC/graphite composites have much higher thermal conductivity in their major fiber direction. In their minor fiber direction, the thermal conductivity was ~ 15 W/m-K, or about the same as the SiC/SiC composite. At approximately 200°C, the thermal conductivity of the CVI SiC/K1100 composite exceeds that of the high quality CVD SiC while the P55 composite approaches this value at the highest temperatures measured.

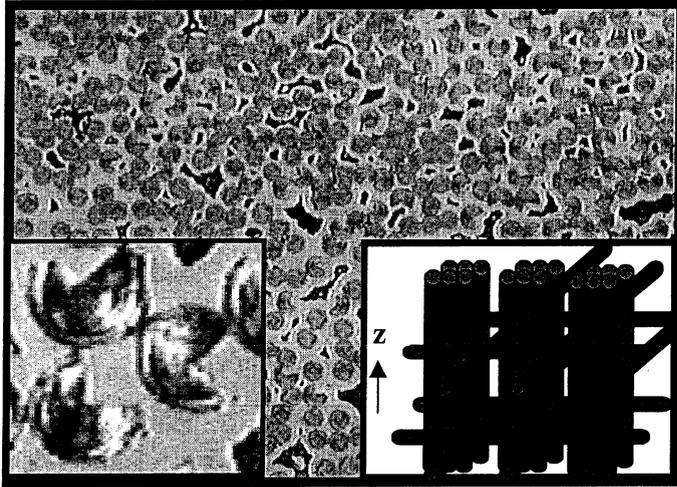


FIGURE 8 : Optical image of SiC/g composite

Alternative matrix densification processes for SiC/SiC composites are being extensively studied in parallel to the advancement of CVI process. This is primarily due to the limitations inherent to the CVI systems including high cost, large matrix void volume, and limitations in component geometries possible for infiltration. The polymer impregnation and pyrolysis (PIP) method is the most industrially developed process for SiC-matrix composites, though it has been regarded not to qualify as nuclear grade composite process due to the generally poor crystallinity and non-stoichiometry of the matrix. However, recent development of near-stoichiometry SiC precursors³¹ and application of high temperature pyrolysis process³² for improved crystallinity will potentially overcome these shortcomings. Melt-infiltration (MI) is also an attractive technique in terms that it produces fully-dense crystalline SiC-based matrix that leads to high thermal conductivity. The control of non-reacted silicon and relatively severe process-induced structural damages are the issues for MI process and are extensively studied mostly in non-nuclear programs.

In addition to the advancement of these rather conventional methods, an innovative processing technique through a liquid phase-sintering route was recently developed³³⁻³⁵. The technique named NITE (nano-infiltration and transient eutectic phase process) so far demonstrates very encouraging mechanical properties and trans-thickness thermal conductivity, owed to its near-fully dense crystalline SiC matrix as shown in the transmission electron micrograph is shown in Figure

10. The NITE composite also demonstrated tightness against helium permeation (in the unstressed condition) that meets requirements in gas-cooled fusion blanket, for the first time for ceramic composites³⁶. Since this processing technique is quite new to the ceramic composite research field, characterization and evaluation in a broad scope needs to be conducted. As a potential fusion material, radiation effects and creep resistance are the primary issues that have to be assessed.

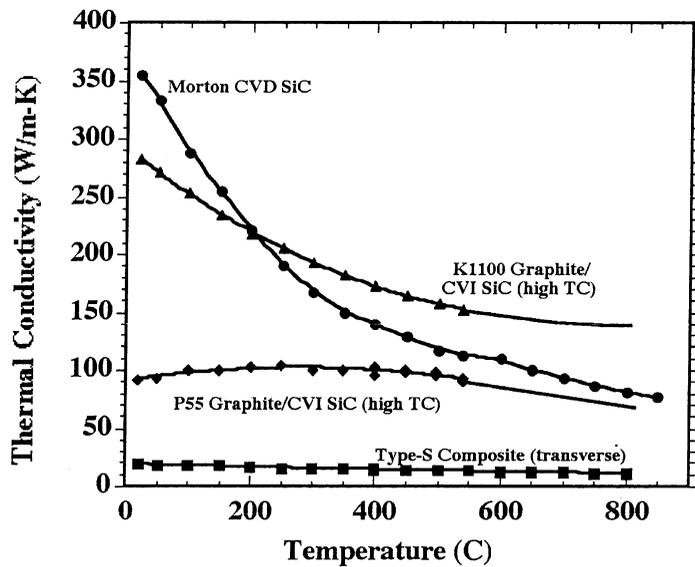


FIGURE 9 : Thermal conductivity of monolithic SiC, SiC/SiC and SiC/graphite fiber composites

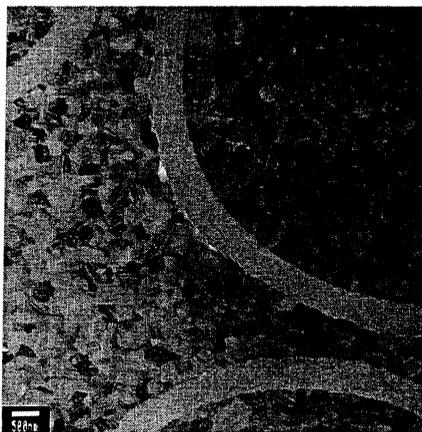


FIGURE 10 : TEM cross sectional micrograph of NITE processed composite.

ACKNOWLEDGEMENT

Research sponsored by the Office of Fusion Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

REFERENCES

- 1) G.R. Hopkins, in: IAEA Symp. on Plasma Physics and controlled Nucl. Fusion Res., Tokyo, Japan, vol. IAEA-CN-33/s3-3, IAEA, 1974
- 2) L.H. Rovner, G.R. Hopkins, Nucl. Tech. 29 (1976) 274.
- 3) F. Najmabadi, University of California Los Angeles Volume 2 Report UCLA-PPG-1323 (1991).
- 4) L. Giancarli, et al, IEA Int. Workshop on SiC/SiC ceramic. JRC Ispra, V. EUT 17352 EN 35.
- 5) S. Ueda, et. al, Workshop on Low Activation Mater. for Fusion App., Oarai, Japan, May 1996
- 6) L. Giancarli, M. Ferrari, M.A. Futterer, S. Malang, Fusion Eng. and Design 49 (2000) 445.
- 7) R.H. Jones, L.L. Snead, A. Kohyama, P. Fenici, Fusion Eng. and Design 41 (1998) 15.
- 8) R.H. Jones, C.H. Henager, G. Hollenberg, J. Nucl. Mat. 191-194 (1992) 75.
- 9) L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mat. 233-237 (1996) 26.
- 10) A. Hasegawa, et al., J. Nucl. Mat. 283-287 (2000) 128.
- 11) P. Fenici, et al., J. Nucl. Mat. 258-263 (1998) 215.
- 12) P. Fenici, J. Nucl. Mat. 212-215 (1994) 60.
- 13) A. Kohyama, et al, J. Nucl. Mat. to be published (2002).
- 14) S. Yajima, J. Hiyashi, M. Omori, Chem. Lett. 9 (1975) 931.
- 15) S. Yajima, K. Okamura, T. Matsuzawa, Y. Hasegawa, T. Shishido, Nature 279 (1979) 706.
- 16) K.J. Wynne, R.W. Rice, Ann. Rev. Mater. Sci. 14 (1984) 297.
- 17) R. West, L.D. David, P.I. Djurovich, H. Yu, Bull. Amer. Ceram. Soc. 62 (1983) 899903.
- 18) K. Okamura, T. Seguchi, J. Inorg. and Organometallic Polymers 2 (1992) 171.
- 19) T. Seguchi, N. Kasai, K. Okamura, Proc. of Int. Conf. on Evolution in Beam Applications, 1991
- 20) L.L. Snead, M. Osborne, K.L. More, J. Mater. Res. 10 (1995) 736.
- 21) L.L. Snead, D. Steiner, S.J. Zinkle, J. Nucl. Mat. 191-194 (1992) 566.
- 22) L.L. Snead, Ph.D Thesis, Dept. of Nuclear Engineering and Engineering Physics, RPI, 1992.
- 23) L.L. Snead, E. LaraCurzio, Microstructure of Irrad. Mat., Boston MA, MRS Vol 540, (1999) 273.
- 24) T. Hinoki, L.L. Snead, T. Nozawa, Y. Katoh, A. Kohyama, J Nucl Mat (submitted 2002).
- 25) L.L. Snead, O.J. Schwarz, J. Nucl. Mat. 219 (1995) 3.
- 26) T. Taguch, Sub. ICFRM 10. Baden Baden, Germany. To be pub. J. of Nucl. Mat. 2002.
- 27) N. Igawa, Subm. ICFRM 10. Baden Baden, Germany. To be pub. J. Nucl. Mat. 2002.
- 28) P. Lipetzky, G.J. Dvorak, N.S. Stoloff, Mater. Sci. Eng. A216 (1996) 11.
- 29) L.L. Snead, M. Balden, R.A. Causey, H. Atsumi, J. Nucl. Mat. accepted, 2002 (2002).
- 30) E. Lara-Curzio, in: Comprehensive Composites Encyclopedia vol. 4.18, 2000) p. 533.
- 31) T. Nakayusa, et al, Ceram. Eng. and Sci. Proc. 20 (1999) 301.
- 32) Y. Katoh, M. Kotani, H. Kishimoto, W. Yang, A. Kohyama, J Nucl Mat 289 (2001) 42.
- 33) Y. katoh, A. Kohyama, D.M. Dong, T. Hinoki, J.J. Kai, Ceram. Eng. and Sci. Proc. (in press).
- 34) A. Kohyama, S.M. Dong, Y. Katoh, Ceramic Engineering and Science Proceedings (in press).
- 35) Y. Katoh, S.M. Dong, A. Kohyama, Fusion Engineering and Design (in press).
- 36) Y. Hirohata et al., Fusion engineering and Design (submitted).