

ADVANCED SiC COMPOSITES FOR FUSION APPLICATIONS – Lance L Snead and Otto J Schwarz (Oak Ridge National Laboratory)

OBJECTIVE

This is a short review of the motivation for and progress in the development of ceramic matrix composites for fusion.

SUMMARY

Chemically vapor infiltrated silicon carbide (SiC) composites have been fabricated from continuous fibers of either SiC or graphite and tested for strength and thermal conductivity. Of significance is that the Hi-NicalonTM SiC based fiber composite has superior unirradiated properties as compared to the standard Nicalon grade. Based on previous results on the stability of the Hi-Nicalon fiber, this system should prove more resistant to neutron irradiation. A graphite fiber composite has been fabricated with very good mechanical properties and thermal conductivity an order of magnitude higher than typical SiC/SiC composites.

PROGRESS AND STATUS

Introduction

The 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 Department of Energy sponsored report,³ "Exploring the Competitive Potential of Magnetic Fusion Energy," which compared the future outlook of fossil, fission, and fusion energy.

It is important to note that considerable benefit can be achieved from selective utilization of low activation materials such as SiC composites without completely replacing the higher activity metallic structure, as was proposed in recent reactor studies such as ARIES.⁴ In fact, based on our current belief in what a commercial fusion plant will look like, the materials requirements for such a reactor are so diverse and demanding that the exclusive use of low activation materials is very unlikely. However, as the economic and safety benefit of these materials scales with volume of irradiated reactor structure, the goal for the application of low activation materials should be to gain as large a fraction of reactor structural material as possible.

At this time there are no large scale industrial applications of SiC composite materials as load bearing structures and there are only limited data on general engineering properties such as strength and fatigue. It is therefore premature to purport their use in the most extreme environments of a fusion reactor such as the first wall or the divertor plate. In these structures, not only will the static and cyclic loads be extremely high, but they would routinely be subjected to heat loads⁵ as high as 15 MW/m^2 , and would experience damage levels of tens of displacements per atom (DPA) per year.

There are far less harsh environments in a fusion machine where low activation ceramic composites could be applied in the near-term. Table 1 illustrates the possible regions where ceramic composites could replace metallic structure. This table is based on preliminary design reports for the international thermonuclear experimental reactor (ITER).⁵ The ITER fusion core structure is broken down in this table into 5 components and listed in order of decreasingly demanding material requirements (i.e. reduced heat flux and radiation dose). Of significance in this table is that the components which are subjected to the highest heat flux and radiation dose (i.e. areas in which the use of ceramic composites is the most speculative), also correspond to the components with the smallest reactor volume fraction. It is seen that the two reactor components which dominate the volume fraction are the shield and magnet which, due to their reactor location, are also subjected to moderate loads. At least in the near term, utilization of low activation

Table 1. Summary of Major Fusion Reactor Components

Component	Volume* m3 (%)	Fusion Core		Hermeticity	Development Timescale
		Dose Activation	Stress MPa		
First Wall					
Plasma Face	18 (0.2)	Highest	High	Not necessary	In-use
Structure	20 (0.2)				
Divertor					
Plasma Face	8 (0.1)		High	Not necessary	In-use
Structure	32 (0.3)				
Blanket					
Breeder Structure	1500 300 (3.2)		<200+	Desirable	Near to long term
Shield	1000 (11.0)		<150++	Not necessary	Near term
Magnet					
Conductor Structure	3040 8100 (85.5)	Lowest	300 (ave.)	Not necessary	Near to long term

materials such as silicon carbide should then focus on replacement of structure in these regions. Also of consideration in reducing the amount of activated structure is that some components are "lifetime" components, such as the vacuum vessel and magnet structure, and some components will require routine change-out, such as the blanket modules. Because of this it is necessary to take the frequency of change-out and the component volume into the overall assessment.

As the stresses expected in fusion reactor structures are substantial, monolithic ceramic components cannot be considered due to their brittle failure mode. For this reason, composite materials, which have a higher degree of toughness and a more uniform statistical distribution of failure (i.e. higher Weibull's modulus), are being considered. While there has been very limited study into the effects of neutrons on SiC composites, the available data show a substantial degradation in mechanical and thermal properties of conventional SiC/SiC at damage levels as low as 1 dpa.^{6,7} To this point, all SiC/SiC radiation effects studies have used material processed with Nippon Carbon's Ceramic Grade (Standard) Nicalon fiber. The choice of this fiber is largely due to its excellent mechanical properties and good weavability. The cost and availability of this fiber has also made it attractive to composite manufacturers.

The reason for the significant degradation in mechanical properties seen in Nicalon based SiC/SiC composites is not due to a response in the SiC phase itself, but to the non-SiC phases in the fiber. As discussed in a separate paper,⁸ the presence of a substantial siliconoxycarbide phase in the standard grade of Nicalon causes a radiation induced densification and subsequent interfacial debonding leading to reduced composite strength. The composite degradation is demonstrated in Figure 1, which shows flexure curves for both unirradiated and neutron irradiated composite. This plot includes both previously reported data⁶ and new data to 20 dpa (displacement energy of carbon assumed). Also given are measured elastic moduli for the matrix (E_m) and the fiber (E_f).

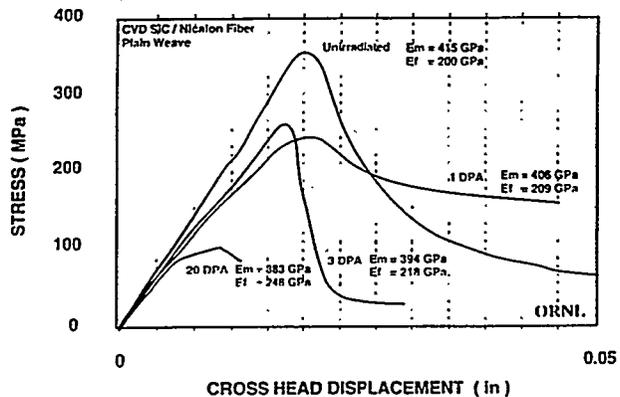


Figure 1: Effect of neutron irradiation on room temperature bend strength of Nicalon composites at temperatures under 500°C.

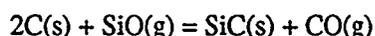
Table 2. Data on Candidate Fiber Reinforcements

Fiber	Make-up	Structure	σ (GPa)	E (GPa)	ρ (g/cc)	Comment
Nicalon	65% SiC, 23% SiO ₂ , 11% C	3 nm β -SiC	3	220	2.55	available
Hi-Nicalon	75% SiC, 21% C - other	\sim 6 nm β -SiC	2.8	270	2.74	limited availability
Textron SCS-6	SiC on C core	faulted β -SiC	3.45	370	3.15	not weavable
Dow Corning SiC	>95% SiC, free C	0.5 μ m β -SiC	2.6	420	\sim 3.1	not available
MER converted	SiC and free C	\sim 0.1 μ m β -SiC	2.0	-	<3.1	developmental
Amoco k1100	Graphite	highly aligned	2.76	900	2.15	limited availability

Based on the significant degradation of these SiC composites, a search for more radiation resistant fibers has been undertaken. Table 2 gives specifics of six candidate fibers including Nicalon for reference. Currently, the most interesting fiber from a radiation damage standpoint is the Hi-Nicalon material, which is processed from the same polymer precursor as standard Nicalon, but has been cured with electrons rather than oxygen.⁹ This process reduces the atomic oxygen content from greater than 15% (standard Nicalon) to less than 0.5%.⁹ Note from the table that the average SiC crystallite size has been increased for this material while the strength has been slightly reduced and the modulus of the fiber has significantly increased. The density of the Hi-Nicalon is also increased from 2.55 g/cc (standard Nicalon) to 2.74 g/cc, which is approximately 85% of the theoretical density. Recent measurements⁸ on Hi-Nicalon following low temperature, low fluence irradiation, showed that the rapid densification seen in standard Nicalon did not occur, and that the irradiated tensile properties behaved as would be expected for a "pure" SiC fiber.

Another popular commercial SiC fiber is processed by chemical vapor deposition of SiC on to a pitch carbon core. This is the process which is used to produce the Textron SCS-6 fiber, for example.¹⁰ The pitch carbon filament used is 33 μ m in diameter and the finished CVD SiC fiber is typically 140 μ m in diameter. The size of this fiber and consequently its stiffness makes it not possible to weave and fabricate composites with complex geometries. However, if the diameter were decreased substantially, this fiber would have very attractive features from a radiation resistance point of view, as its unirradiated and irradiated properties would be very similar to chemically vapor infiltrated (CVI) SiC matrix.

Also of interest is the MER¹¹ converted SiC fiber. The process for conversion follows the general reaction:



Graphite tows or fabric are simply reacted in a high temperature furnace (at 1300 to 2000°C) with silicon monoxide gas and converted from the outside of the fiber inward. Fiber strengths greater than 2 GPa have been reported¹² with elastic moduli approaching that of pure silicon carbide. The microstructure of these fibers depends on the grain structure of the starting graphite fiber but are typically microcrystalline with grain sizes varying from 25 nm to 100 nm. Fiber density is in the range of 2.8 to 3.1 g/cc, depending on processing conditions and the final composition being free of excess silicon. Of particular interest for these fibers is the good high temperature strength and excellent creep resistance.

There has recently been progress in both sintered SiC fibers¹³ and for advanced polymer precursor fibers.¹⁴ Dow Corning's polymer precursor fiber is melt-spun, cross linked and heated to above 1600°C under argon to drive off oxygen in the form of CO. Such a process would normally result in large-grained, porous material. However, through the incorporation of certain additives, a high density SiC fiber results. The quoted composition¹⁴ of the Dupont fiber is >95% β -SiC with a crystallite size of \sim 0.5 μ m, along with excess carbon in the form of graphite at the crystallite boundaries. The oxygen and nitrogen content is <0.1 weight percent.

The purpose of this paper is to show the progress made in the fabrication of composites of interest for fusion. Specifically, all composites have been fabricated through the chemical vapor infiltration (CVI) of SiC. Three fiber systems were chosen: Nicalon (standard and the low-oxygen "Hi-Nicalon"), MER converted SiC fiber from Amoco T-300 graphite cloth, and a high conductivity (Amoco K-1100) graphite fiber. The rationale behind studying a CVI SiC/graphite fiber composite system will be discussed later. Two of the SiC-based fibers listed in Table 2 were not fabricated into composites for this study for practical reasons. The Textron AVCO SCS-6 was not considered, primarily due to difficulty in weaving (as

mentioned earlier). The Dow Corning polymer precursor material was unavailable, though it would seem an attractive system from a radiation damage standpoint, and should be evaluated when material is released.

Experimental procedure

All materials for this study were processed at the High Temperature Materials Laboratory at the Oak Ridge National Laboratory using the forced chemical vapor infiltration (FCVI) method.¹⁵ The infiltrated silicon carbide matrix was deposited from methyltrichlorosilane. The typical process temperature and time for infiltration was 1200°C and 18 hrs, respectively. The dimensions of the as fabricated disks were 4.45 cm in diameter and 1.25 cm thickness. For each composite a graphitic interface was applied to the composite prior to SiC infiltration by decomposition of propylene gas at 1100°C. Previous work has shown that the structure of interfaces deposited in this manner on Nicalon are partially graphitic with basal planes lying normal to the axis of the fiber.¹⁶

For the case of SiC/SiC composites, 1k denier (thousand filament yarn) plain weave fabric was laid-up inside a graphite holder with a fiber volume fraction of approximately 40% in the case of the Nicalon fiber and approximately 30% for the MER converted SiC fiber. Due to the highly crystalline nature of the MER converted fiber, it was felt that applying pressure normal to the fabric lay-ups could crack the fibers, thus a reduced fiber volume was chosen. The Nicalon fiber composites were processed with an interfacial graphite thickness of ~0.3 μm, while a range of interfacial thicknesses were chosen for the MER converted SiC fiber. A third composite was fabricated from alternate layers of ceramic grade Nicalon and MER converted SiC fiber onto which an interface of 0.3 μm was applied to the Nicalon. The interface on the MER fabric in this hybrid composite was somewhat thinner.

Both ceramic grade (standard) Nicalon and low-oxygen-content, Hi-Nicalon were used for composite fabrication in this study. The Hi-Nicalon, from lot number NC9302, was obtained in fabric form from the Dow Corning Corporation, presumably manufactured by Nippon Carbon in February of 1993. Sizing of both fiber systems was removed with an acetone wash following fiber lay-up. Materials Electrochemical Research (MER) Corporation supplied their converted fabric as part of a U.S. Department of Energy SBIR Phase 2 contract dealing with the fabrication of SiC/SiC composites for use in fusion systems. This MER fabric was converted from the very high strength, PAN based Amoco T300 graphite fiber which had been converted ~60% such that a graphite core remained.

The graphite fiber preform was composed of a three dimensional, unbalanced weave of Amoco Corporation K1100 and P55 fibers. The P55 fiber was woven in 2-k tows in the x and y directions, while six 2-k tows of K1100 were woven through the orthogonal weave in the z-direction. Due to the high modulus of the K1100 fiber, there was a tendency for the fiber to break as it was looped. For this reason a fugitive nylon yarn was used to maintain preform stability. The preform was then rigidized with polymethylmethacrylate (PMMA). The overall fiber volume fraction was 43.9% of which 7.1% was in the x and y directions and 85.7% was in the z (K1100) direction. The graphite preform was machined into 4.45 cm diameter, 1.27 cm thick disks which were mounted in graphite holders for infiltration. The preform was then heated to 350°C in an argon flow gas to burn out the PMMA binder. Following this a graphite interface was deposited to the fibers followed by FCVI infiltration of SiC.

All materials with the exception of the K1100 composite were cut into bend bars of dimension 0.254 x 0.30 x 3.18 cm and tested in 4-point bending using an upper and lower span width of 0.635 cm and 1.9 cm, respectively. Nine bend bars of each material were tested at a cross head displacement rate of 0.05 cm/sec. Due to the larger unit cell for the K1100 graphite fiber composite material, a larger bend bar and bending fixture was desirable. For this case, bend bars of 0.300 x 0.400 x 5.0 cm were used with an upper and lower span of 1.9 cm and 3.8 cm, respectively.

Sample cubes of 1.27 cm on a side were machined from each composite and room temperature thermal diffusivity was measured using a thermal (xenon) flash technique. An infrared detector was used to measure the back surface temperature rise. The thermal conductivity was calculated as follows using a mass average of specific heats for the graphite fibers and silicon carbide matrix:

$$K = \alpha \rho_{\text{composite}} (V_F \rho_F C_p^F + V_M \rho_M C_p^M) / \rho_{\text{composite}}$$

where α is the measured diffusivity, V_F and V_M , ρ_F and ρ_M , C_p^F and C_p^M , are the volume fractions, densities and specific heats of the fiber and matrix respectively and $\rho_{\text{composite}}$ is the density of the composite.

Results

Bending Strength

The results of the four point bend tests on all composites fabricated are given in Table 3. For the case of the CVD SiC/Nicalon based fiber composites, a single interfacial coating thickness of 0.3 μm was chosen.

Table 3. Results on Infiltrated Composites

Fiber	Interface (μm)	VF Fiber (%)	σ UTS (MPa)	Std. Dev. (MPa)	Density (g/cc)	Void (%)
Nicalon	~0.3	41	292	26	2.5	~14
Hi-Nicalon	~0.3	42	348	27	2.6	~13
Nicalon-MER	~0.3	34	221	24	2.5	~19
MER-T-300	~0.15	~33	123	6	2.3	~20
MER T-300	~0.3	~34	144	9	2.4	~19
MER T-300	~1.0	~28	123	18	2.1	~30
MER T-300*	~0.3	~32	152	1	2.1	~15
Amoco k1100	~0.3	44	283	30	2.1	~20

*fabric overcoated with CVD SiC prior to graphite interface

This has been shown previously to yield the maximum bend strength for the ceramic grade Nicalon fiber. From the table it is seen that the low-oxygen-content Hi-Nicalon yielded an ultimate bend strength of 348 ± 27 MPa versus the 292 ± 26 MPa achieved for standard Nicalon. The standard deviation for each was approximately equal, as were the calculated volume fraction of fibers, composite density, and matrix void fraction.

The CVD SiC/MER converted fiber system had a substantially lower bend strength than the Nicalon composite. From Table 3 it can be seen that increasing the interfacial thickness from 0.15 to 0.3 μm increased the measured strength from 123 ± 6 to 144 ± 9 MPa. In both cases the fiber volume fraction was approximately equivalent at just over 30%. The void fraction for this material was fairly high, calculated at approximately 20%. The thickest interface applied to the MER fabric (1.0 μm) yielded a composite with decreased bend strength from the 0.3 μm interfacial material, and had a significantly higher standard deviation (123 ± 18 MPa). Of note is that this material also had a higher void fraction (30%) which would cause the variability in properties.

In order to explore the effect of the fiber surface roughness of the MER fabric composites, a second part was fabricated with the standard 0.3 μm graphitic interface. However, a thin layer of CVD SiC was applied to the converted fiber prior to the deposition of the graphitic interface. This material exhibited the best properties of the MER-only fiber composites with a bend strength of 152 MPa and a low standard deviation (Table 3). A composite was fabricated from alternate layers of the MER converted fabric and ceramic grade Nicalon yielded substantially higher strength (221 ± 25 MPa) than the MER-only fabric specimens.

The CVD SiC/K1100 graphite fiber system yielded quite good bend strength considering no process optimization was conducted (due to limited availability of material). The bend strength in this case was found to be 267 ± 26 MPa with the major fiber direction parallel to the axis of the bend bar. The estimated void fraction for this composite was approximately 20%, which is reasonable considering the three dimensional orthogonal weave necessarily has large cubic voids that are difficult to completely infiltrate.

The flexure curves for all materials tested are shown in Figure 2. Note that the curves presented in this figure are from representative tests (i.e. one of the nine bend bars tested). It is seen that the lower strength FCVI SiC/MER composites failed in a rather brittle manner while significant fiber pullout and toughness was exhibited by the standard Nicalon composite as well as the Nicalon/MER hybrid composite. Also of interest (Figure 2a) is that none of the curves for the Hi-Nicalon exhibited gradual post-ultimate load drop-

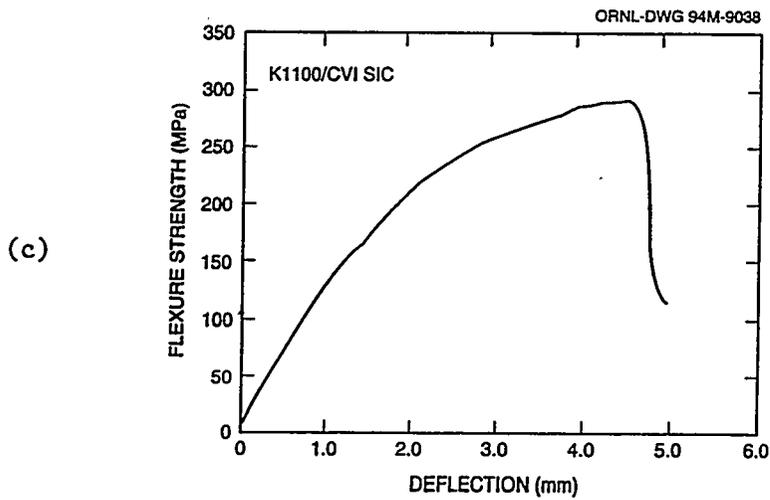
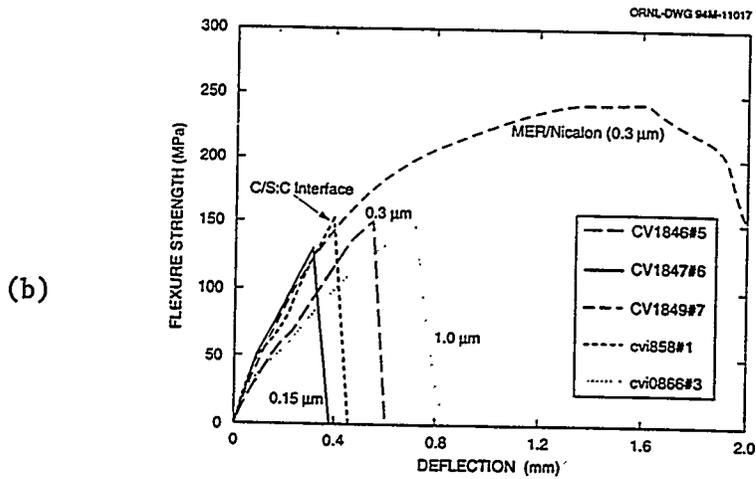
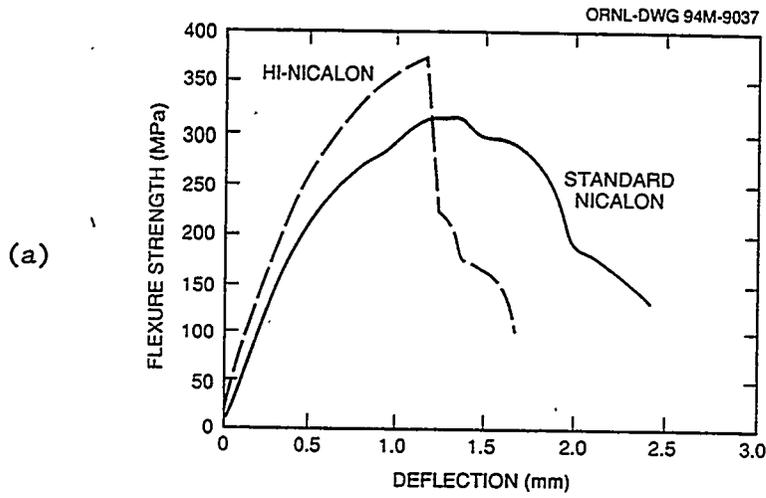


Figure 2: Flexure curves of composite materials: (a) Nicalon fabric composites, (b) MER fabric composites, and (c) K1100 fiber composite

off. A general trend exists for the standard Nicalon composites toward a more "brittle" failure for the materials with higher ultimate bend strength.

Thermal Conductivity

The thermal conductivities for these materials is given in Table 4 for different directions, both parallel (in-plane) and perpendicular (cross ply) to the fabric layers. For the case of the graphite fiber composite, results are given for directions along and perpendicular to the major fiber direction. It is seen that the Nicalon fiber composite has a relatively low thermal conductivity of 20.3 W/m-K in the plane of the fiber lay-ups and 7.4 W/m-K across the plies. The crystalline converted MER fiber shows slightly higher thermal

Table 4. Thermal Conductivity of Fabricated Composites

Composite	Diffusivity (cm ² /s)	Calculated Conductivity (W/m-K)
CVI SiC/Nicalon		
cross ply	0.044	7.4
in-plane	0.145	25.3
CVI SiC/Nicalon (Oxidized)		
cross ply	0.039	6.8
in-plane	0.141	24.7
CVI SiC/MER		
cross ply	0.60	10.0
in-plane	0.167	27.8
CVI SiC/MER (Oxidized)		
cross ply	0.052	8.7
in-plane	0.134	22.5
CVI SiC/k1100		
major fiber dir.	1.49	214
across major fiber dir.	0.08	12.0

conductivity both in plane (27.8 W/m-K) and cross plane (10.0 W/m-K), which is interesting in light of its greater void fraction. Table 4 also gives data for the SiC fiber composites following a six hour furnace oxidation (in air) at 600°C. This treatment removes the graphitic interface, thus eliminating the fiber contribution to conductivity in the cross ply direction. For the CVD SiC/Nicalon composite the cross ply thermal conductivity has been reduced from 7.4 to 6.8 W/m-K following oxidation. In the case of the MER fiber composites the cross ply conductivity has been somewhat more substantially reduced from 10 to 8.7 W/m-K. The CVD SiC/K1100 graphite fiber composite shows the highest thermal conductivity, yielding 214 W/m-K in the k1100 (major) fiber direction though only 12 W/m-K across the minor fiber direction.

DISCUSSION

Nicalon Based Composite Material

It has been previously demonstrated⁶ (Figure 1) that the Nicalon based SiC composites undergo substantial degradation in strength and toughness following neutron irradiation. At the 20 dpa level shown in Figure 1, the composite has become quite weak and fails in a more brittle manner, and therefore cannot be considered a candidate near the first wall of a fusion machine. In areas such as the shield and magnet, where the lifetime displacement level would not approach 1 dpa and the stress levels are more modest (Table 1), the material may be adequate, however.

The degradation in properties in this composite has been shown to be caused by fiber densification⁸ which is attributed to the glassy siliconoxycarbide phase (SiO_xC_y) phase present in the fiber. This phase is a by-product of the oxygen cross-linking step during fiber processing. This production step can be eliminated by the employment of electron beam curing of the fiber which effectively reduces the oxygen content from $>10\%$ in the case of standard Nicalon to $<0.5\%$ for the electron beam cured Hi-Nicalon. As was mentioned in the introduction, an initial assessment of the radiation response of these fibers indicates that the densification found in standard Nicalon does not occur.⁸ For this reason, composites fabricated from Hi-Nicalon fibers appears promising from a radiation-resistance standpoint.

A straightforward comparison of a composite fabricated from standard and Hi-Nicalon, processed at identical conditions, indicates that the unirradiated mechanical properties are superior for the Hi-Nicalon system (Figure 2 and Table 3). It is seen that the ultimate strength in four-point bending is approximately 20% greater for the Hi-Nicalon composite. One possible reason for this increased strength is due to the closer elastic moduli match between the Hi-Nicalon fiber and the matrix. Hi-Nicalon's modulus is quoted as 270 GPa, which is $\sim 23\%$ higher than the standard fiber, and should allow the matrix to take fuller advantage of the fibers strength prior to significant matrix micro cracking.

Of interest is that the load drop-off behavior (Figure 2a) for the Hi-Nicalon composite exhibits a more brittle failure than the ceramic grade Nicalon system. By SEM inspection of the composite fracture surfaces (given in Figure 3), it is apparent that the pull-out length of the fibers was less for the Hi-Nicalon system. The more brittle failure in the Hi-Nicalon composite is most likely an indication that the interfacial coating applied is not optimal. Previous work with standard Nicalon, which yielded a system optimized for high strength (interfacial thickness of $\sim 0.3 \mu\text{m}$), demonstrates that the type of failure seen for the Hi-Nicalon system is indicative of an interface that is too thin. Also, inferring from the previous work on standard Nicalon, the effect of increasing the Hi-Nicalon interfacial thickness would be to augment both strength and toughness of this composite. Due to the current high cost of the Hi-Nicalon, optimization of the interfacial layer was not possible in this study. At the time of this writing, Hi-Nicalon was available in only small quantities at a price of \$6,900 per kg of fiber tow or about \$30,000 per kg in plain weave.

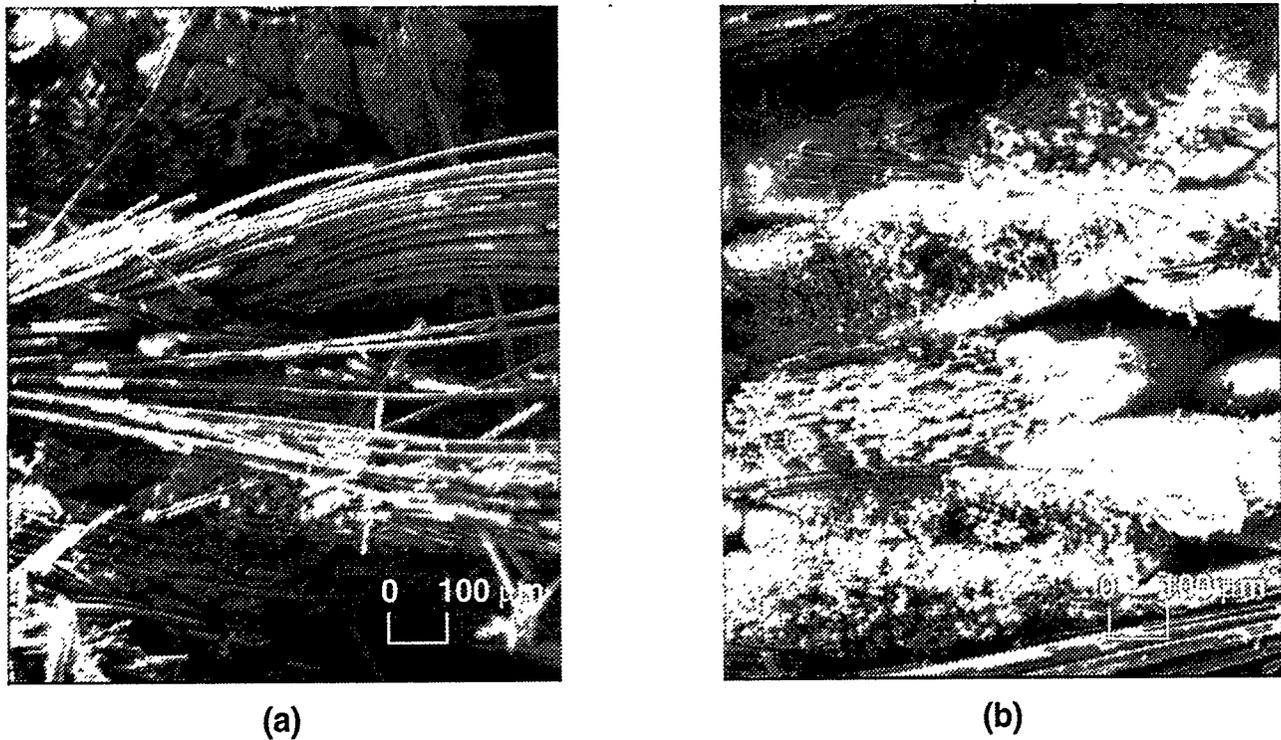


Figure 3: Scanning electron micrograph fracture surface comparing: (a) standard Nicalon and (b) Hi-Nicalon.

The measured thermal conductivity of the CVI SiC/Nicalon composite was found to be quite low both along and across the cloth lay-ups. Specifically, the room temperature thermal conductivity across the plies was only 7.4 W/m-K, which is significantly less than the measured value of high quality commercial (Morton, Inc.) CVD SiC of ~250 W/m-K.¹⁷ It is obvious that many factors could act to reduce the thermal conductivity from what would be expected from a simple rule of mixtures assuming ~40% matrix volume fraction of CVD SiC. Firstly, impurity content as well as the crystalline structure of the matrix will affect the thermal conductivity of the material and no attempt has been made to reduce impurity levels in composite materials. Secondly, during processing of the composite, significant micro cracking occurs during cool-down which significantly reduces the matrix thermal conductivity.

The presence of the Nicalon fibers will also reduce the composite thermal conductivity from that of pure CVD SiC, due to the low fiber conductivity (~13 W/m-K).¹⁸ In addition, the phonon scattering at the fiber/matrix interface could also be significant. The small contribution of the fibers to the composite conductivity was demonstrated by removing the graphitic interface through oxidation (Table 4). It was shown that, following oxidation of the graphite interface, the thermal conductivity of the Nicalon composite was reduced by <10%. As the conductivity from matrix to the fiber should have been essentially zero following the oxidation, this implies that the fiber contribution to conductivity is very low.

The low thermal conductivity of SiC/SiC composites is an important issue regarding their use in fusion systems. While some composite materials¹⁹ have been fabricated with room temperature thermal conductivities in the range of 100 W/m-K (through the use of BeO presumably as a sintering aid during hot pressing) the conductivity of typical CVI SiC composite is unacceptably low for thermal management applications such as the first wall of a fusion reactor. It should also be noted that the thermal conductivity will decrease following neutron irradiation. It is well known that the production of point defects in ceramics during irradiation quickly dominates the mean free path of phonons, thus reducing the thermal conductivity. For the case of SiC it has been shown²⁰ that fission neutron irradiation of pyrolytic β -SiC caused a reduction in the room temperature thermal conductivity by a factor of 9 following irradiation at 550°C and a factor of 3 following irradiation at 1100°C. For the case of irradiated SiC/Nicalon composite it was observed⁷ that the room temperature thermal conductivity was reduced from ~8 to ~3 W/m-K following an irradiation dose of 25 dpa.

MER Converted SiC Fiber Composite Material

Several interfacial coating thicknesses were tried in an effort to optimize both the composite strength and toughness of the MER fabric composite. It is seen by inspection of Table 2 and Figure 2, that for the thinner (0.15 and 0.3 μm) interfacial coatings, the MER fabric composite increased from 123 to 144 MPa in bend strength, though this absolute value is low in comparison with the Nicalon system. For these two coatings the composite still failed in a rather brittle manner. The brittle nature of the failure is seen clearly in the flexure curves (Figure 3) as well as by inspection of the typical fracture surfaces given in Figure 4. This figure shows a scanning electron micrograph of the fracture surface for the MER fiber composite with the ~0.3 μm interface. It is apparent that the amount of pull-out was quite limited,



Figure 4: Scanning electron micrograph fracture surface of MER fiber composite.

generally less than one fiber diameter. The graphite core can be easily distinguished in Figure 4, particularly in some cases where the outer SiC sheath has pulled away from the graphite core.

In an attempt to increase the amount of pull-out in the MER fabric composite system a very thick (~1 μm) interface was applied to the fabric before infiltration with CVD SiC. By increasing the interface thickness a degree of toughness was exhibited by the composite (Figure 3), though after a close inspection of the fracture surface of this material individual fiber pull-out was still not achieved. This material tended to pull out in large tow-sections of fabric (hundreds of fibers). Apparently, the deposited graphite completely encapsulated the fiber bundles, which were then overcoated with SiC and acted as single, large fibers. The associated strength of this composite was also low, 123 MPa, which is identical to the thinnest interface studied. It should be noted that due to very thick interface the void fraction of this material was quite low. Also, after examination of fibers which were properly coated with interface and matrix, pull-out was still very limited, on the order of one fiber diameter.

From these results the reason for the limited pull-out of the T-300 converted MER fabric has been associated with the surface non-uniformity of the fiber. Example of this non-uniformity can be seen in Figure 4. It is seen that the surface of the fiber has axial striations with a peak-to-valley dimension on the order of a tenth of a micron. Also, SEM analysis of bare fiber indicates that small axial undulations are present. These surface nonuniformities negate the effectiveness of the interfacial layer, causing mechanical interlocking of the fiber and matrix leading to the brittle-type failure exhibited in Figure 2b.

Further demonstration of the difference in the behavior of the Nicalon and MER converted fiber pull out is seen by inspection of the fracture surfaces of the hybrid CVI SiC/MER-Nicalon composite. Shown in Figure 5 is a low magnification SEM image of the composite showing one alternating layer of Nicalon (upper) and MER converted T-300 fabric (lower). Pull-out was seen in the case of the larger diameter Nicalon fibers, with the amount of pull-out ranging from several to more than ten times the fiber diameter. The smaller MER fibers, which should have a thinner interfacial layer, showed very limited pull out. A comparison of the interfaces of these fibers is given in Figure 6. Figures 6a and 6b show the thin graphitic interface on the MER fiber and demonstrate that the surface roughness of the fiber causes an correspondingly rough interface. This is to be compared to the smooth interface which has flaked off the Nicalon fiber in Figure 6c. The difference in scale should be noted in these micrographs.

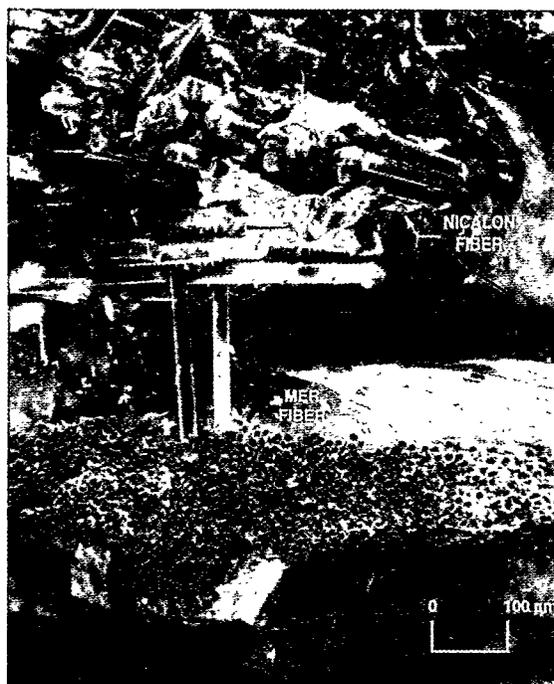
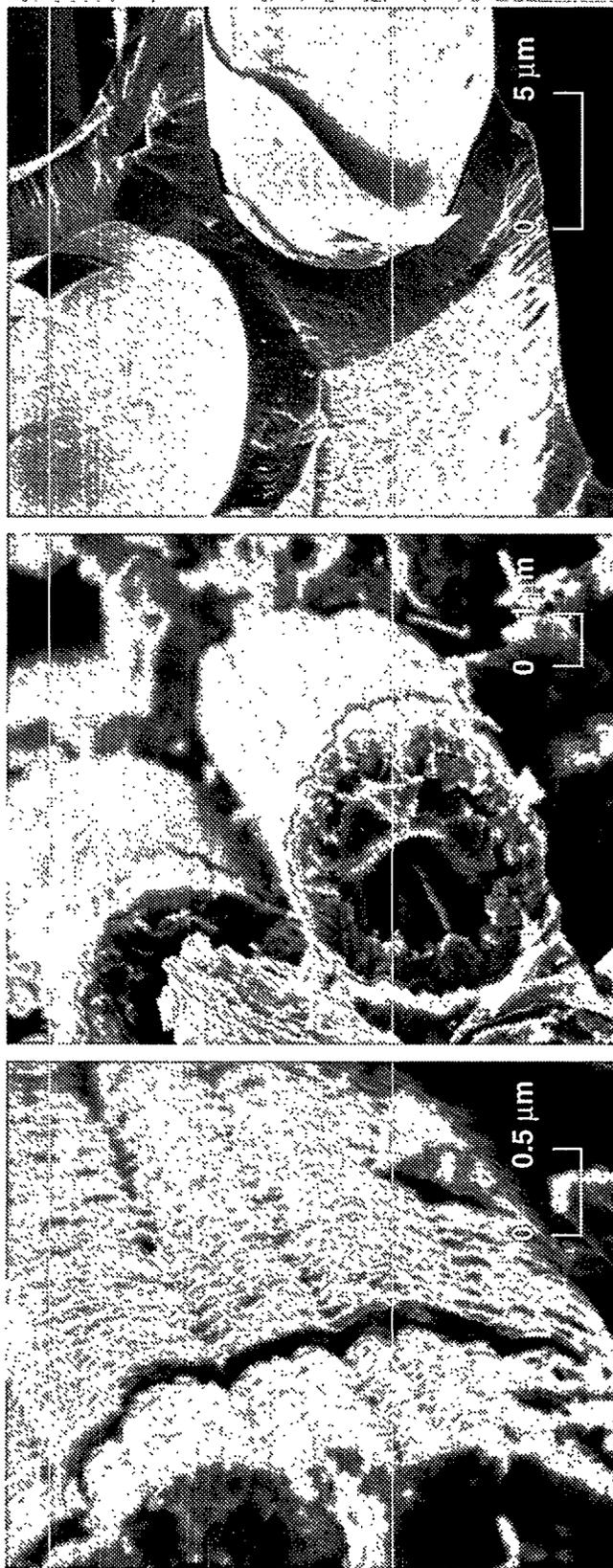


Figure 5: Scanning electron micrograph fracture surface of MER-Nicalon hybrid composite.

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(a) (b) (c)
Figure 6: Scanning electron micrograph comparing interfaces on MER and Nicalon fibers: (a,b) interface on MER fiber (c) interface on Nicalon fiber.

The nonuniformities in the MER converted T-300 fiber has been shown to be an attribute of the original graphite fiber.²¹ By starting with a more uniform graphite fiber, the converted fiber will be smoother and should yield superior composite properties. Graphite fibers such as Hercules IM-9 and AS-4, which have a smoother, rounded perimeter are currently being studied.¹⁹

Graphite Fiber Composite Material

The use of SiC matrix/graphite fiber composites is attractive for use in fusion systems for several reasons. Firstly, though development of this system has been limited, some authors²²⁻²⁶ have reported these materials to have similar strength to SiC/SiC composites, and in the case of CVI infiltration of very high strength 2-d lay-ups of T-300 graphite fiber,²⁵ composite bend strength as high as 800 MPa have been reported. Also, it has been shown²² that for CVI infiltrated graphite composite, the fracture toughness is somewhat higher than for SiC/SiC composites.

The potential for this composite in fusion applications is that it offers a high thermal conductivity composite with significantly lower tritium retention than the advanced carbon/carbon composites (C/C's) currently considered for plasma facing components. The thermal conductivity of the composite system can be engineered to be isotropic or optimized for high conductivity in a single direction, as needed. For the case of the three dimensional composite fabricated in this study, the thermal conductivity was 215 W/m-K in the direction of the high conductivity fibers. This conductivity is approximately one order of magnitude higher than that of SiC/SiC systems. It should be mentioned, by simple rule of mixtures, the calculated thermal conductivity for this SiC/graphite fiber composite should be greater than 400 W/m-K based on manufacturer's quoted fiber conductivity. Due to a processing problem with the early batch from which this fiber was purchased, the thermal conductivity of the composite was significantly reduced from this maximum value. It is reasonable to assume that if the composite were fabricated with a newer batch of fiber, the composite conductivity would be on the order of 400 W/m-k.

Atsumi has demonstrated²⁷ that the hydrogen retention in graphite is a strong function of the degree of perfection of the graphite crystal. Figure 7 demonstrates that the hydrogen solubility is reduced by more than an order of magnitude as the degree of graphitization (crystalline perfection) is increased from 50 to 80%. This is of particular interest because for typical C/C composites, the degree of graphitization of matrix material is significantly less than that of the highly oriented fibers, indicating that the majority of the tritium resides in the composite matrix. By replacing this (low perfection) graphite matrix with very low hydrogen solubility SiC,²⁸ the high thermal conductivity of the fibers is still utilized while the significant tritium retention problem associated with the matrix is avoided.

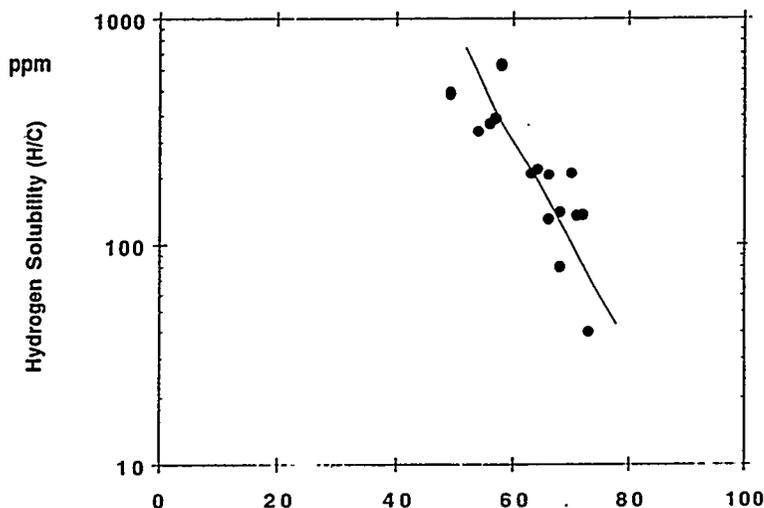


Figure 7: Effect of graphite perfection on hydrogen solubility.²⁷

The three dimensional CVD SiC/K1100 composite fabricated for this study yielded reasonably good strength and, from an analysis of the flexure curves and fracture surfaces, possessed a fair amount of toughness. In the major fiber direction, the four point bend strength was 267 ± 28 MPa, which was comparable to the Nicalon fabricated material. It should also be noted that the graphite fiber composite was a 3-d composite compared with the 2-d lay-up in the case of the SiC/SiC system. Strength of bend bars across the K1100 major fiber direction would be considerably reduced due to the reduced fraction of (P 55) fibers in this orientation.

Properties such as thermal conductivity and tritium retention, and composite strength will substantially change under irradiation. It has been shown²⁷ that irradiation can increase the solubility of hydrogen in graphite by a factor of ~17 following fission neutron irradiation to 6×10^{24} n/m² (E >1 MeV) at 600°C. Thermal conductivity degradation in graphite and C/C composites has been very well documented²⁹ and can decrease by over an order of magnitude at low fluence, depending on the irradiation temperature. This decrease in thermal conductivity typically saturates at a neutron fluence level between 0.1 and 1 dpa, depending on irradiation temperature. It could be expected, based on results on relatively high thermal conductivity graphite radiation damage, that at fusion relevant temperatures of 600 to 800°C, a saturation reduction in thermal conductivity of approximately 50% could be expected in the SiC/graphite system presented here. However, even taking this radiation-induced degradation into account, the thermal conductivity of the CVD SiC/graphite fiber system will still be greater than the CVD SiC/SiC composite. It should be mentioned that there is no data to indicate what the mechanical properties of this composite would be like following neutron irradiation. It can be assumed that the CVD SiC would undergo a slight (<0.1%) swelling at temperatures of ~1000°C, while the fibers would exhibit a significant radial expansion and corresponding axial shrinkage. To what extent these radiation induced dimensional changes would effect the mechanical properties needs to be examined.

Concluding Remarks

Several silicon carbide matrix composites have been fabricated with low activation, high strength fiber reinforcements. Of primary interest is that a composite made from Hi-Nicalon with an interfacial coating of 0.3 mm graphite exhibited ~20% higher bending strength than the standard Nicalon composite which possessed an interface optimized for strength. Further increases in strength and toughness can be expected upon further optimization of the interfacial layer for the Hi-Nicalon. Based on recent data regarding the superior radiation stability of the lower oxygen content Hi-Nicalon, a more radiation damage resistant composite compared to standard Nicalon composite is expected.

A high thermal conductivity 3d carbon fiber (K1100), CVD SiC matrix composite has been demonstrated to have high strength (283 MPa) as well as high thermal conductivity (215 W/m-K). The thermal conductivity for this composite is dominated by the fiber contribution and can be substantially increased with little effect on the composite strength by utilizing the current generation of high-conductivity Amoco K1100 fiber. This composite is of interest for thermal management application in fusion reactors not only because of the superior thermal conductivity but also due to the expected reduction in tritium retention in this composite as compared to carbon/carbon materials.

Lastly, a CVD SiC composite has been fabricated from polycrystalline SiC converted from T-300 graphite fibers by the MER Corporation. These fibers are nearly stoichiometric and have shown good strength and excellent creep resistance. The lack of oxygen in these fibers makes them excellent candidate materials for radiation resistance. The composites fabricated from this fiber have to this point yielded somewhat disappointing results. This is mainly due to the fact that the surface roughness intrinsic to the T-300 graphite fiber carries over onto the converted SiC fiber. This surface roughness makes the development of a compliant interface problematic. However, it is likely that this surface roughness problem can be avoided by the choice of a smoother starting graphite fiber, such as the Hercules AS-4 and IM-9.

FUTURE WORK

Low dose HFIR hydraulic tube (in-core) irradiations of Hi-Nicalon fiber composites are planned for both the Hi-Nicalon and Amoco K-1100 fiber composites. Development of improved interfaces for the Hi-Nicalon fiber composite is under way.

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