

THERMAL CONDUCTIVITY OF SiC AND C FIBERS - I - G. E. Youngblood and D. J. Senor (Pacific Northwest National Laboratory), W. Kowbel and J. Webb (MER Corporation), and Akira Kohyama (Kyoto University, Japan).

OBJECTIVE

The objective of this task is to examine SiC fibers and SiC/SiC composites fabricated by various processing methods designed to improve the composite thermal conductivity. Specifically, it is desired to increase the thermal conductivity of these composites to meet expected thermal transport requirements for advanced fusion energy systems.

SUMMARY

Several rod-shaped specimens with uniaxially packed fibers (Hi-Nicalon, Hi-Nicalon Type S, Tyranno SA and Amoco K1100 types) and a pre-ceramic polymer matrix have been fabricated. By using appropriate analytic models, the bare fiber thermal conductivity (K_f) and the interface thermal conductance (h) will be determined as a function of temperature up to 1000°C before and after irradiation for samples cut from these rods. Initial results are: (1) for unirradiated Hi-Nicalon SiC fiber, K_f varied from 4.3 up to 5.9 W/mK for the 27-1000°C range, (2) for unirradiated K1100 graphite fiber, K_f varied from 576 down to 242 W/mK for the 27-1000°C range, and (3) $h = 43 \text{ W/cm}^2\text{K}$ at 27°C as a typical fiber/matrix interface conductance.

PROGRESS AND STATUS

Currently available fiber-reinforced (Hi-Nicalon) SiC/SiC composites with a chemical vapor infiltrated (CVI) SiC matrix have a transverse thermal conductivity (K_t) of about 13 and 8 W/mK at 300K and 1273K, respectively. Neutron irradiation tends to degrade the K_t -values of this type of SiC/SiC by about 25% and 50% for 300K and 1273K, respectively (i.e., to 4 W/mK or below) [1]. A K_t -value of 4 W/mK for SiC/SiC is at most about 25% of that desired for anticipated fusion power system applications [2]. By comparison, thermal conductivity values of unirradiated, high-purity and dense monolithic CVD-SiC, whose values represent an upper limit attainable for SiC, can exceed 300 and 60 W/mK at 300K and 1273K, respectively [3]. These high K -values indicate that there is room for substantial improvement of the thermal transport properties in SiC/SiC. Nevertheless, attaining a K_t -value of 30 W/mK at 1273K for unirradiated SiC/SiC, one-half that of monolithic CVD-SiC at this temperature and the approximate K_t -value needed to provide a desired 15 W/mK material during irradiation, will present a serious challenge.

The cause of low K_t -values for SiC/SiC has been attributed to the approximately 10-15% porosity in the matrix, and particularly to the presence of numerous, fairly large interlaminar voids [4]. The relatively low K -values of the fiber reinforcement, which makes up about another 40% of a typical composite volume, also contribute to low overall K_t -values. Furthermore, thermal conductance across the various interfaces (fiber/matrix or matrix/matrix) or thin interphases (purposely applied at the fiber/matrix interface to provide composite toughness) is a very important factor affecting K_t [5]. Better control of the porosity geometry and amount (especially the reduction of the interlaminar void content) can help improve the K_t -values somewhat. However, to achieve significant improvement in the SiC/SiC K_t -values, both the fiber thermal conductivity and the interface thermal conductances must be improved.

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Fortunately, new near-stoichiometric SiC fibers have recently become available that claim to have K-values of about 50 W/mK (e.g., Tyranno™ SA and Dow™ Sylramic), a value significantly greater than the K-values of widely used Nicalon™ or Hi-Nicalon™ fibers (≈ 2 and 5 W/mK, respectively) [6,7]. Furthermore, the new SiC fibers promise to be more radiation resistant, in which case the rather large differential swelling/shrinking observed between the fiber and matrix components in composites made with first generation Nicalon SiC fibers should be considerably alleviated [8]. Improved dimensional stability of the fibers, in turn, should lead to improved fiber/matrix interface conductances in SiC/SiC composites. By using such new fibers and by careful design of the fiber/matrix interface, the opportunity to make significant improvements in the thermal transport of SiC/SiC composites now exists.

The use of 3D SiC fiber architectures has shown some promise to improve K_T -values [9]. Another method to improve K_T -values, now being investigated by MER Corp. (Tucson, AZ) under an SBIR program with the DOE Office of Fusion Energy Sciences, consists of “spiking” conventional 2D-SiC/SiC composite with high thermal conductivity, graphite fiber bundles in the transverse or Z-direction. The thermal conductivity of high modulus graphite fibers is very anisotropic, but can exceed 1000 W/mK along the fiber length [10].

In common, all strategies to improve K_T -values of SiC/SiC will require the use of fibers with correspondingly high K-values. This work describes a method to evaluate fiber K-values before and after irradiation up to 1000°C, which covers the relevant temperature range 600-1000°C for potential SiC/SiC fusion applications.

In this method, rod-shaped composites (20 mm long x 6.0 mm dia) with uniaxial fiber alignment were fabricated. The rods were sliced into several discs (about 2.0 mm thick) appropriate for thermal diffusivity measurements [11]. The composite matrix was made from Cereset™, a pre-ceramic liquid polymer at RT that is converted to SiC by pyrolyzing in an argon atmosphere. The Cereset matrix was purposely made amorphous so that the fiber contribution would dominate the overall composite K-values. To do this, a final heat treatment was given at 1100°C, a temperature high enough to exsolve most of the gaseous components but well below the 1600°C temperature required for SiC crystallization in Cereset. Also, to further improve the accuracy of the fiber K-value determinations a high fiber packing density (>60%) was used.

The thermal diffusivity also will be measured for SiC/SiC samples with normal 2D- or 3D- fiber architectures. Knowing the K-values of the bare fiber and matrix components and by using appropriate constituent thermal conductivity models that represent the particular SiC/SiC composite architecture, the interface thermal conductance values can then be investigated.

Analysis

First, the overall thermal diffusivity $\alpha(T)$ of a uniaxial composite with the fibers aligned parallel to the heat transport direction (assumed to be one-dimensional and effectively homogeneous) was measured using the laser flash diffusivity technique [11]. The effective composite thermal conductivity (K_{eff}) was calculated from:

$$K_{\text{eff}}(T) = \alpha_{\text{meas}}(T)C_{\text{eff}}(T)\rho_{\text{bulk}}(T) \quad (1)$$

where the composite specific heat $C_{\text{eff}}(T)$ was calculated from:

$$C_{\text{eff}}(T) = F_f C_f(T) + F_m C_m(T) \quad (2)$$

with F_i = weight fractions and $C_i(T)$ = component specific heats. In the above equations, several terms were determined as functions of temperature (T) and the subscript $i = f$ or m stands for fiber and matrix, respectively. The bulk density, $\rho_{\text{bulk}}(T)$, was determined from the sample weight and geometrical volume corrected for volume change due to thermal expansion.

Second, the bare fiber thermal conductivity, $K_f(T)$, was extracted from a simple series model expression for the parallel fiber alignment case given by:

$$K_{\text{eff}}(T) \approx f_f K_f(T) + f_m K_m(T) \quad (3)$$

with f_i = volume fractions and K_i = component K-values. Note that the sum of f_f and f_m , estimated by image analysis from several micrographic views of polished rod cross-sections, may not necessarily be equal to one since the rods also contained a void fraction. The matrix contribution (K_m) was determined separately by measuring $\alpha(T)$ of a sample formed only from matrix material (monolithic Cereset™ heat-treated at 1100°C).

The use of Eqns (1) and (3) assumes 1D heat flow or equilibrium conditions perpendicular to the heat flow direction. Then Eqn (3) can be used to calculate $K_f(T)$, and Eqn (1) is used again to calculate the fiber thermal diffusivity, $\alpha_f(T)$, from values of fiber specific heat, density and $K_f(T)$.

Third, $\alpha(T)$ was measured for a SiC/SiC sample with transverse fiber alignments. For the simple case of uniaxial fibers perpendicular to the heat transport direction, according to Hasselman and Johnson [12], $K_{\text{eff}}(T)$ is approximately given by:

$$K_{\text{eff}} \approx K_m \left[\frac{(K_f/K_m - 1 - K_f/ah)f_f + (1 + K_f/K_m + K_f/ah)}{(1 - K_f/K_m + K_f/ah)f_f + (1 + K_f/K_m + K_f/ah)} \right] \quad (4)$$

with K_i = component conductivity, a = fiber radius, f_f = fiber volume fraction, and h = the interfacial thermal conductance in $\text{W/m}^2\text{K}$. From the measured value of $K_{\text{eff}}(T)$ for the transverse configuration of the composite, and the already determined values of a , f_f , K_m and K_f , $h(T)$ was backed out of Eqn (4).

The approximation given by Eqn (4) is fairly good for the range $0.1 < K_f/K_m < 10$ and when $f_f < 30\%$ [13]. In this expression, the product "ah" is equivalent to the thermal conductivity of an interphase layer making perfect thermal contact with both the fiber and matrix. For the limiting case $(ah) \gg K_f$ (perfect fiber/matrix thermal contact), Eqn (4) reduces to the Releigh-Maxwell conductivity expression for a dilute distribution of conducting cylinders in a matrix. When $ah \rightarrow 0$ (perfectly insulated fibers), K_{eff} approaches the limiting value $K_m(1-f_f)/(1+f_f)$.

For this analysis, $h(T)$ includes the combined effect of transverse conduction through a thin interphase coating and across any porosity or other mismatch thermal barriers that might occur at the fiber/matrix interface. For temperatures less than about 1200K, $h(T)$ will be dominated by the asperities of the interface contacts and the conduction through any gaseous medium contained within intervening porosity. A separation of the relative conductance contributions through actual contacts and a gaseous medium can be obtained by performing the thermal diffusivity measurements in vacuum and in a controlled atmosphere [14]. Furthermore, K_m itself may be an effective conductivity when the matrix contains porosity or filler particles.

Results

In this section, some preliminary results are presented for the Hi-Nicalon™ and K1100™ fibers. Hi-Nicalon™ is a SiC-based fiber type made by Nippon Carbon Co. while K1100™ is a high

modulus graphite fiber with high thermal conductivity made by Amoco. Preliminary values of $C_{\text{eff}}(T)$, $k_f(T)$ and $\alpha_f(T)$ determined for the Hi-Nicalon fiber and $k_f(T)$ for the K1100 graphite fiber are given in Table 1.

Table 1. Thermal transport properties of Hi-Nicalon SiC and K1100 graphite fibers.

Temperature (K)	Hi-Nic $C_{\text{eff}}(T)$ (J/gK)	Hi-Nic $k_f(T)$ (W/mK)	Hi-Nic $\alpha_f(T)$ (cm ² /s)	K1100 $k_f(T)$ (W/mK)
300	0.689	4.29	0.0232	576
400	0.904	5.41	0.0223	495
500	1.016	5.68	0.0208	430
600	1.088	5.75	0.0197	380
700	1.140	5.72	0.0187	342
800	1.183	5.65	0.0178	313
900	1.219	5.61	0.0172	293
1000	1.252	5.59	0.0167	278
1100	1.283	5.67	0.0166	266
1200	1.312	5.78	0.0165	255
1300	1.339	5.91	0.0166	242

The bulk density of the particular batch of Hi-Nicalon fiber examined, measured by the liquid gradient technique, was 2.69 g/cc. The average Hi-Nicalon fiber diameter, determined by image analysis, was $13.8 \pm 1.8 \mu\text{m}$ [8]. The manufacturer (Nippon Carbon Co.) lists the chemical composition (in wt. %): Si (62.4), C (37.1), O (0.5) and C/Si (atomic) = 1.39. From these values, the weight and volume fractions of the components SiC, C and SiO₂ in Hi-Nicalon fiber were calculated to be: 0.882, 0.107 and 0.011 (weight) and 0.819, 0.168 and 0.013 (volume), respectively.

The free C-content in Hi-Nicalon fiber is relatively high and consists of turbostratic aggregates. According to Hochet, et al, in Hi-Nicalon the C-aggregates are approximately 8-10 atomic layers thick by 2-5 nm in length [15]. These C-aggregates probably have a marked influence on the thermal (and electrical) conductivity of Hi-Nicalon fiber and likely are responsible for the peculiar temperature dependence of $K_f(T)$ exhibited by Hi-Nicalon. Furthermore, the presence of these C-aggregates probably affects the dimensional stability of Hi-Nicalon during irradiation.

Although there is considerable uncertainty when using Eqn (4) to calculate $h(T)$, the 300K value of $h(T)$ was $\approx 43 \text{ W/cm}^2\text{K}$, which agrees fairly well with literature values determined for similar composites: $40 \text{ W/cm}^2\text{K}$ and $29 \text{ W/cm}^2\text{K}$ (by S. Graham [13] and H. Bhatt, et al [5], respectively). Obviously, a radiation induced swelling/shrinking mismatch between fiber and matrix components could also affect $h(T)$. Such an effect on the transverse thermal conductivity in irradiated SiC/SiC has been neglected in previous studies, and needs to be analyzed. As previously discussed, high values of both K_f and h are necessary to ensure high transverse thermal conduction in a SiC/SiC composite. Also, high values of K_f and h are desired to provide effective thermal conduction paths around micro-cracked regions in the matrix for conduction parallel to the fibers in a SiC/SiC composite. The behavior of $h(T)$ during and after irradiation should be of keen interest and importance.

Finally, the extremely high K_f -values determined for the K1100 graphite fiber (40-100 times that of Hi-Nicalon) confirm that the strategy of spiking 2D-SiC/SiC in the Z-direction with these fibers to improve K_t has merit. The effect of irradiation on $K_f(T)$ for the K1100 fiber also will be of keen interest and importance.

FUTURE WORK

The thermal diffusivity data for the uniaxial rod samples made from the Hi-Nicalon, Hi-Nicalon Type S and Tyranno SA SiC fibers and the K1100 graphite fibers will be analyzed before and after irradiation. Twenty-eight (28) fiber and four (4) CVD-SiC thermal diffusivity disc samples will be irradiated in the ATR reactor at 300°C to a dose of 1.5 dpa commencing in June, 2000. The samples should be available for final analysis by the end of year 2000.

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