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Optimizing the transverse thermal conductivity of 2D-SiC_f/SiC composites, II. Experimental

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Abstract

Model predictions of the transverse thermal conductivity (K_{eff}) are compared to experimentally determined values as a function of temperature for a commercial 2D-SiC_f/SiC made by DuPont from plain weave Hi-Nicalon™ fabric and with an ICVI-SiC matrix. Two versions of the DuPont composite were examined: one with a 'thin' and one with a 'thick' pyrolytic carbon (PyC) fiber coating of thickness 0.110 and 1.044 μm, respectively. Generally good agreement of either the Hasselman–Johnson or the Markworth model predictions (*see companion paper, I. Modeling*) with measured values of K_{eff} for this composite suggest that these models can be used to predict K_{eff} for composites with various 'non-ideal' fiber, interphase and matrix structures. Importantly, the models make it possible to separate the relative component contributions to K_{eff} so that individual component degradation mechanisms can be examined in detail. For the two versions of the well-bonded, as-received DuPont composite made with Hi-Nicalon™ woven fabric, at 200 °C constituent values $K_m = 22$–25 W/m K (matrix thermal conductivity), $K_c \approx 25$ W/m K (PyC-coating thermal conductivity) and $h_{eq} = 2.4 \times 10^7$ W/m^2 K (equivalent fiber–matrix interfacial thermal conductance) were determined.

1. Introduction

Many potential applications of continuous fiber-reinforced ceramic composites (CFCC) require relatively high thermal conductivity. This study will focus on the conditions for optimizing the transverse thermal conductivity (K_{eff}) for a CFCC consisting of a silicon carbide (SiC) matrix reinforced with SiC-type fibers (SiC_f). Usually the SiC matrix is made using the chemical vapor infiltration (CVI) process, but polymer infiltration and pyrolysis (PIP) and hybrid CVI-PIP processes also are being developed [1]. One of the goals of our work is to develop a SiC_f/SiC composite design with high K_{eff}-values.

To investigate the separate component contributions to K_{eff}, three different analytic models were described in a companion paper [2], namely (1) the Hasselman–Johnson (H–J) '2-cylinder' model [3], (2) the Markworth '3-cylinder' model [4] and (3) a newly developed '3-square' model with anisotropic thermal conduction. In this paper, to assess using these models, which describe heat transfer for somewhat 'ideal' composite systems, predicted K_{eff}-values are compared to K_{eff}-values determined experimentally for the following 'non-ideal' system made with woven SiC fabric layers, the DuPont 2D Hi-Nicalon™/pyrolytic carbon (PyC)/ICVI-SiC system. Later, the appropriate model will be selected to predict K_{eff} for this composite after irradiation to demonstrate their utility for analyzing degradation mechanisms. With better understanding of the degradation details, hopefully an acceptable composite can be designed and developed for potential nuclear fission or fusion reactor applications.

Recently, the design goal for a fusion reactor SiC_f/SiC first wall was set at 15 W/m K at 800 °C in service [5]. This translates roughly into a goal for unirradiated SiC_f/SiC to have $K_{eff} = 38$ W/m K at 800 °C,

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which is a value about three times that reported for even the best, currently available commercial 2D-SiC_f/SiC [6].

2. Experimental

Two similar plates of SiC_f/SiC were obtained from DuPont Lanxide. DuPont Lanxide used the isothermal CVI process to fabricate each plate, which was reinforced with plain weave Hi-Nicalon™ fabric and contained a nominal fiber volume content of 0.4. The fiber pre-forms were similarly coated with PyC applied by CVD prior to matrix infiltration. The only difference between the two plates was the thickness of the fiber PyC coating, which was nominally either 0.15 ('thin'), or 1.2 ('thick') μm thick. The average bulk densities were similar, 2.60 ± 0.03 and 2.63 ± 0.03 g/cc for the thin and thick composite versions, respectively. Several representative discs (6.2-mm diameter by 2.0-mm thick) were machined from the flat plates for thermal diffusivity measurements and analysis. Later, some of these discs were given oxidation or irradiation and thermal annealing treatments. These results will be discussed in a subsequent paper.

The thermal diffusivity (α) was measured in the transverse direction for representative samples of each composite version from RT up to at least 400 °C and sometimes up to 1000 °C by the laser flash diffusivity method [6]. Sometimes α was measured in a different atmosphere (vacuum, air, argon or helium) to examine the effects of possible fiber/matrix (f/m) debonding. As usual, for analysis K_{eff} was determined as the product of the calculated composite heat capacity together with measured α and bulk density (corrected for thermal expansion of SiC). The following expressions, based on a rule of mixtures, were used to estimate composite heat capacity values: $C_p(\text{thin}) = 1.044 + 0.000215(T) - 37893(T)^{-2}$ J/gK and $C_p(\text{thick}) = 1.059 + 0.000247(T) - 39950(T)^{-2}$ J/gK, the small difference being due to the different amounts of PyC in each version. Finally, polished cross-sections of representative samples were examined by optical and SEM methods. The fiber packing fraction and average diameter and the PyC-coating thickness were determined by analysis of the SEM micrographs.

3. Results

Typical SEM micrographs of composite cross-sections are given in Fig. 1(a)–(d) for the DuPont 2D-SiC_f/SiC composite with nominal coating thicknesses of 0.15 and 1.2 μm. The microstructures appear to be quite similar for each version. As observed in Fig. 1(a) and (b), the CVI-SiC infiltration was fairly uniform with only a few needle-like pores running parallel to the fiber axis contained within the bundles. A few rather large laminar-shaped pores, characteristic of composite fabricated by CVI infiltration of stacks of woven fabric layers, were observed typically at yarn cross-over points between the fabric layers. The higher magnification SEM views shown in Fig. 1(c) and (d) reveal that the thickness of the PyC coatings were extremely uniform and appear to be well-bonded to both the fiber and the matrix. Earlier, we reported average 4-pt bend strengths at RT of 628 ± 22 and 524 ± 45 MPa for these thin and thick versions of SiC_f/SiC, respectively [7]. All in all, these composites were considered to be high quality with bulk densities being 84% and 88% of theoretical, which implies total open porosity values of about 16% and 12% for the thin and thick versions, respectively.

The results from image analysis of several similar SEM micrographs of as-received material are given in Table 1. The number in parenthesis refers to the number of independent measurements.

The average fiber diameters for the thin and thick versions agree within the standard deviation with the nominal diameter of 14 μm quoted by the manufacturer for Hi-Nicalon™ fiber. The coating thickness values (determined from several high-magnification SEM views of single, isolated fiber cross-sections) were close to their nominal values of 0.15 (0.110) and 1.2 (1.044) μm. Although each version of the composite had a nominal average fiber packing fraction $f = 0.4$, the localized fiber packing within the individual tows was much higher, about 0.65 and 0.67 for the thin and thick versions, respectively. Fig. 1(a) and (b) reveal that the tow cross-sections have a lens shape with aspect ratios in the 6–9 range. Also, rather thick regions of single phase ICVI-SiC matrix exist around each fiber tow and as a seal coat on the outer surfaces of the plates.

In this paper, the notation and definitions used are the same as used in our companion paper (Ref. [2]), i.e. a is the fiber radius, t, fiber coating thickness, h, interfacial thermal conductance; K_m, K_c and K_f are the matrix, coating and fiber thermal conductivity, respectively; and R and $r = K_{eff}(T)/K_m(T)$ and $K_f(T)/K_m(T)$, the normalized effective transverse and fiber–matrix thermal conductivity, respectively.

In Fig. 2, the K_{eff}-data points (determined from measured α-values from RT to 1000 °C) are compared to the 3-cylinder model predictions for the thin and thick versions of the DuPont SiC_f/SiC for a range of K_c-values (10–30 W/m K). The experimentally determined K_{eff}-values increase slightly from RT up to about 150 °C, where K_{eff} has a maximum value for both versions of $\approx$14 W/m K, about the same value as that for stainless steel. Above 150 °C, K_{eff} decreases with increasing temperature with K_{eff} decreasing more rapidly for the thin than for the thick version.

The difference in K_{eff} for the thin and thick versions suggests that the thickness of the fiber coating is responsible. Therefore, the following protocol was developed

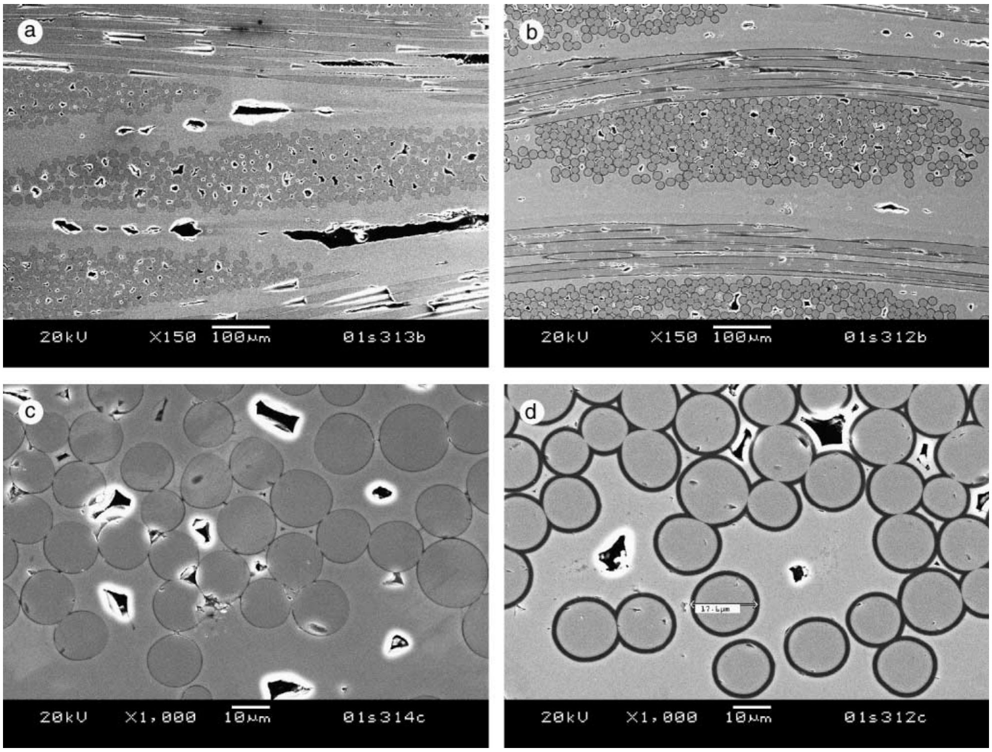

Fig. 1. (a–d) SEM micrographs of polished DuPont 2D-SiC$_f$/SiC cross-sections showing typical porosity and good infiltration of ICVI-SiC matrix into Hi-Nicalon™ bundles for (a) thin (0.110 μm) and (b) thick (1.040 μm) PyC fiber coating versions. Higher magnification (×1000) views illustrate connectivity of fibers and the PyC coating for the (c) thin and (d) thick versions.

Table 1
Image analysis results for DuPont 2D Hi-Nicalon™/PyC/ICVI-SiC composite

Type of PyC coating	Fiber diameter (μm)	Coating thickness (μm)	Tow fiber packing fraction (f_{tow})	Tow aspect ratio (width/ thickness)
Thin	14.0 ± 1.2 (70)	0.110 (5)	0.65 (3)	8.1 (2)
Thick	14.2 ± 1.6 (52)	1.044 (6)	0.67 (2)	6.5 (2)

to efficiently use the 3-cylinder model for analysis. First, previously measured values of $K_f(T)$ for Hi-Nicalon™ fiber were used [8]. These values are given in Table 2. Second, since the thin and thick versions each had similar ICVI-SiC structures, the same 'best-fit' reciprocal α-values, $1/\alpha_m(T)$, were used for the matrix contribution. The $K_m(T)$-values then were calculated from the common $\alpha_m(T)$-values for each version. These values are also given in Table 2. As a result, slight differences in the $K_m(T)$-values were introduced due to differences in density (porosity) of the ICVI-SiC matrices for each version. Third, the temperature dependence of K_c was ignored. This is a reasonable assumption because $K_c(T)$ is governed primarily by the pyrocarbon defect structure, not intrinsic phonon–phonon scattering, and should be rather temperature insensitive.

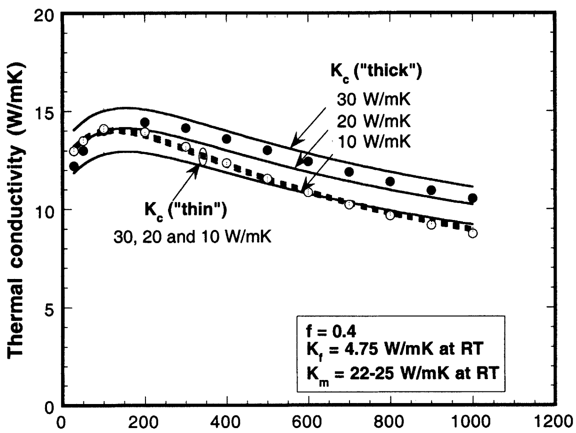

Fig. 2. Comparison of analytic solutions for the Markworth model to experimentally determined values of $K_{eff}(T)$ for DuPont 2D Hi-Nicalon™/PyC/ICVI-SiC composite with either a thin (0.110 μm, ○) or a thick (1.044 μm, ●) PyC fiber coating. Solutions for K_c-values of 10, 20 and 30 W/m K are shown as solid or dashed lines for the thick or thin versions, respectively.

Table 2
Measured values of $K_f(T)$ for Hi-Nicalon™ fiber from [8] and determined values of $K_m(T)$ for each version of the as-received DuPont composite made with Hi-Nicalon™ fabric and a ICVI-SiC matrix

Temperature (°C)	27	100	200	300	400	500	600	700	800	900	1000
$K_f(T)$	4.75	5.66	6.13	6.25	6.23	6.15	6.04	5.93	5.81	5.69	5.57
$K_m(T)$, thin	22.3	23.2	21.9	20.0	18.3	16.7	15.4	14.3	13.4	12.6	11.9
$K_m(T)$, thick	23.4	25.1	24.3	22.7	21.1	19.6	18.2	17.1	16.1	15.2	14.4

Table 3
Comparison of some interfacial conductance (*h*-values) for different composite systems

Composite systems	h ($\times 10^4$ W/m^2 K) at RT	Reference
Nicalon/MAS (delamination cracks)	0.01–2	[9]
1D Hi-Nicalon/amorphous PIP-SiC	20 (vacuum), 40 (He)	[10]
1D Nicalon/PyC/LAS (microcracked)	40	[11]
1D SCS6/RBSN (debonded)	4 (vacuum), 10 (He)	[12]
2D Hi-Nicalon/PyC/ICVI-SiC	2400	This study
Diamond (particulate)/cordierite	1500 (20 000 at 700 °C)	[13]
SiC (particulate)/aluminum	14 000	[14]

From Fig. 2, for $T > 200$ °C a good fit for the thick version was obtained for a K_c-value of about 25 W/m K, which is a reasonable value for 'ungraphitized' PyC. However, for $T > 200$ °C the measured $K_{eff}(T)$ data points fall below the predicted values, which is likely due to the neglect of the K_c temperature dependence. For the thin version, little difference in the fit was discerned over the range of K_c-values tested. When using the 3-cylinder model, the best fit to experimental data above $T = 200$ °C for the thick version of DuPont Hi-Nicalon™/PyC/ICVI-SiC system was obtained for $f = 0.4$, $K_c \approx 25$ W/m K and the values of $K_m(T)$ given in Table 2.

Using $K_c = 25$ W/m K, an equivalent interfacial conductance $h_{eq} = K_c/t$ can be calculated for the thick version. This value (2.4×10^7 W/m^2 K) appears bolded in Table 3 where it is compared to some other *h*-values listed in ascending order for various types of matrix-interface combinations from the literature.

4. Discussion

The H–J 2-cylinder and the Markworth 3-cylinder models are similar in that their thermal transport predictions depend upon the composite constituent (fiber, fiber coating and matrix) dimensions, thermal properties and their arrangement as well as the actual character of the different interfaces between these constituents [2]. Similar predictions of R are obtained for similar values of h or equivalently for $h_{eq} = K_c/t$ for the H–J and Markworth models, respectively. The only difference is that the Markworth model predicts higher values for R when $h_{eq} > 10^7$ W/m^2 K because then the coating also begins to contribute to K_{eff}. Therefore, to describe well-bonded SiC_f/SiC systems with high values of h_{eq} the Markworth model is preferred; while the H–J model is preferred when debonding and numerous f/m gas gaps occur so that *h*-values are relatively low. Thus, the Markworth model was used to analyze the K_{eff}-data for the well-bonded, as-received DuPont 2D Hi-Nicalon™/PyC/ICVI-SiC system.

Good agreement of the Markworth model predictions of K_{eff} with experimental data suggests that either of these models, Markworth or H–J, can be used to reliably estimate K_{eff} for a non-ideal SiC_f/SiC composite in terms of constituent properties even when the model assumptions of a uniform dispersion of parallel fibers within a uniform matrix are not fulfilled. Percolation effects through direct fiber–fiber contacts and through the inner-connected PyC coatings likely will enhance K_{eff}. Such effects will become more important as the number of contacts and inner-connections increase either as the average 'f' increases or as the local fiber packing within individual tows increases, as observed for the DuPont 2D-SiC_f/SiC system. Also, when K_c-values are high K_{eff} will increase as the coating thickness increases.

In this work, the Hi-Nicalon™ fiber had a K_f-value of 4.75 W/m K at RT so that $r < 1$ ($r \approx 0.2$ for the DuPont composite), which imposed the restriction that $R < 1$ regardless of the composite interface *h*-value. To achieve $R > 1$, a fiber with relatively high K_f-values must be used. Such a fiber would consist primarily of well-crystallized, stoichiometric SiC. Commercial fiber types that may fulfill this requirement are Hi-Nicalon™ type S (Nippon Carbon Co., Tokyo, JP, 20 W/m K), Tyranno™ SA (Ube Co., Ube City, JP, 65 W/m K) and Dow Sylramic™ (Dow Corning Co., Midland, MI, 50 W/m K). However, the DuPont composite made with a CVD PyC fiber coating and an ICVI-SiC matrix apparently had interfaces with a relatively high $h_{eq} \approx 2.4 \times 10^7$ W/m^2 K. If a composite were made by the same method with advanced

SiC-type fibers and the high h_{eq}-value retained, perhaps a high K_{eff} could be acquired. As an example (see Fig. 2(a) in the companion paper [2]), for the conditions $f = 0.4$, $K_f = 100$ W/m K and $h_{eq} = 2.4 \times 10^7$ W/m^2 K, $R \approx 1.5$. With $R = 1.5$ and $K_m = 22$–25 W/m K, $K_{eff} =$ 33–38 W/m K, values that approach the goal for unirradiated composite intended for use in many fusion reactor first wall designs.

In Table 2, several *h*-values for various types of interfaces taken from the literature are compared to the h_{eq}-value determined above. Relatively low *h*-values ($<$1–40 $\times 10^4$ W/m^2 K) occur when the fibers are thermally separated from the matrix due to f/m debonds, fabric layer delaminations or matrix microcracking. For these cases, K_{eff} will depend upon the atmospheric environment (and temperature). The *h*-values will be lowest for a vacuum environment, higher for a gaseous atmosphere, and highest with a helium atmosphere since helium has a relatively high gas thermal conductivity compared to other gases. Obviously, degradation due to f/m debonding or the presence of crack-like defects in irradiated or thermally or mechanically stressed composites can be quantified somewhat by determining K_{eff} for samples in vacuum and in different partial pressures and types of gas.

Furthermore, K_{eff} can be affected by the size of the fibers (or particulate) as expressed by the K_f/ah term in the H–J model, where '*a*' is a fiber (or particulate) radius. For instance, attempts have been made to toughen cordierite or strengthen aluminum substrates by adding diamond or SiC particulate, respectively. At the same time, it was thought that K_{eff} would also improve since these particulates them-selves have relatively high *K*-values. Even though the interface *h*-values were quite high ($h > 10^7$ W/m^2 K), in these cases this strategy didn't work due to the small size of '*a*'. Rather than making a contribution to K_{eff}, the smaller particulates acted more like insulating voids because of a size-effect [13,14]. The overall K_{eff} may similarly be reduced for a composite reinforced by SiC fiber with a high K_f, but also too small a diameter. The possibility of a size-effect must be considered for each individual case. The H–J model will be useful for such analysis.

Finally, the derived $K_m(T)$-values are themselves effective values in that they describe the net thermal conductivity for a matrix containing numerous, fairly large pores primarily located between the dense CVI-SiC bundle coating layers. A subsequent paper will investigate the details of the effect of porosity content and shape on $K_m(T)$ and $K_{eff}(T)$.

5. Summary

1. The H–J 2-cylinder and/or the Markworth 3-cylinder models are appropriate for designing 2D-woven SiC_f/SiC composites with a high K_{eff}-value or for analyzing $K_{eff}(T)$ to obtain individual constituent $K_m(T)$, $K_c(T)$ (or *h*) values.
2. By comparing experimentally determined values of $K_{eff}(T)$ to Markworth model predictions for a commercial DuPont 2D Hi-Nicalon^{TM}/PyC/ICVI-SiC composite, the constituent values $K_m = 22$–25 W/m K, $K_c \approx 25$ W/m K and $h_{eq} = 2.4 \times 10^7$ W/m^2 K were determined for this composite.
3. For composite with debonds or delaminations, K_{eff} depends upon the atmosphere. In such cases, the H–J model is preferred for analysis.
4. For a composite with well-bonded f/m interfaces, the Markworth model is the most useful. In this case, K_{eff} should be independent of atmosphere.
5. A size-effect may reduce K_{eff} if the radius of the reinforcing particulate or fiber is too small.

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