MODELING THE TRANSVERSE THERMAL CONDUCTIVITY OF 2D-SIC$_F$/SIC COMPOSITES
– G. E. Youngblood, D. J. Senor and R. H. Jones (Pacific Northwest National Laboratory)*

OBJECTIVE

The primary objective of this task is to assess the thermal conductivity of SiC/SiC composites made from SiC fibers (with various SiC-type matrices, fiber coatings and architectures) before and after irradiation and to develop analytic models that describe the transverse and in-plane thermal conductivity of these composites as a function of constituent properties and geometry as well as temperature and dose.

SUMMARY

A hierarchical model was developed to describe the effective transverse thermal conductivity, K_{eff}, of a 2D-SiC/SiC composite made from stacked and infiltrated woven fabric layers in terms of constituent properties and microstructural and architectural variables. The model includes the expected effects of fiber-matrix interfacial conductance as well as the effects of high fiber packing fractions within individual tows and the non-uniform nature of 2D-fabric layers that include a significant amount of interlayer porosity. Model predictions were obtained for two versions of DuPont 2D-Hi Nicalon™/PyC/ICVI-SiC composite, one with a "thin" (0.110 μm) and the other with a "thick" (1.040 μm) PyC fiber coating. The model predicts that the matrix porosity content and porosity shape factor have a major influence on $K_{eff}(T)$ for such a composite.

PROGRESS AND STATUS

Introduction

In previous work, the Hasselman-Johnson (H-J) model for the effective transverse thermal conductivity (K_{eff}) of 2D-SiC/SiC was used to predict K_{eff} for a hypothetical composite made with high conductivity fiber and matrix components [1,2]. The H-J model includes the effect of the interfacial conductance, which in a composite with numerous fiber/matrix (f/m) interfaces can have a profound influence on K_{eff}. The model itself shows that for a composite with dispersed fibers the most important factor needed to achieve high K_{eff} is high thermal conductivity of the continuous matrix phase. Nevertheless, both high fiber and high interface conductivity also will be necessary.

The H-J model was derived for an ideal f/m geometry consisting of dispersed uniaxial fibers with relatively low volume fractions in a uniform matrix so that fiber-fiber interactions could be neglected. The model should especially be useful to describe the effects of f/m separation or debonding [3], which might occur during irradiation as a result of differential fiber-matrix swelling or fiber densification. A second model, the Markworth "3-Cylinder" model, was developed to examine the detailed contribution of a fiber coating characterized by the thickness of the coating and its thermal conductivity [4]. The 3-cylinder model proved to be most useful to describe K_{eff} for a composite with an f/m interface consisting of a well-bonded, uniform isotropic pyrocarbon (PyC) fiber coating [5]. Apparent agreement between Markworth model predictions and measured K_{eff}-values as a function of temperature for two different versions of a commercial, plain-woven 2D-SiC/SiC composite suggested that the Markworth model (and the H-J model) describe the general behavior of K_{eff} as a function of constituent thermal properties.

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Furthermore, depending on conditions each model should be useful to critically assess degradation mechanisms in these type composites [6].

Two versions of 2D-SiC/SiC were similarly fabricated by DuPont Lanxide (now Honeywell Advanced Composites) using fabric layers of Hi-Nicalon™ SiC fiber stacked in 0-90 sequence. Each version contained a nominal fiber volume fraction f = 0.4. The SiC matrix was applied by isothermal chemical vapor infiltration (ICVI). The only major difference between the two versions was that in one version the PyC fiber coating was "thin" (nominally 150 nm) while in the other the coating was "thick" (nominally 1.2 μm). The fiber thermal conductivity (K_f) and K_{eff} were separately determined from thermal diffusivity measurements as a function of temperature over the RT-1000°C range by methods described previously [7,8]. By using these data and the Markworth model, preliminary values of thermal conductivity for the matrix and coating constituents (K_m = 22-25 W/mK for an ICVI-SiC matrix and K_c = 25 W/mK for a PyC fiber coating at RT, respectively) were estimated [5]. The effective interfacial conductance (h) for the composite with the thin PyC coating also was estimated by $h \sim K_c/t = 24 \times 10^6$ W/m^{2}K. Typical SEM micrographs of composite cross-sections for the two DuPont 2D-SiC$_f$/SiC composite versions with different coating thickness are given in Figs. 1(a-d).

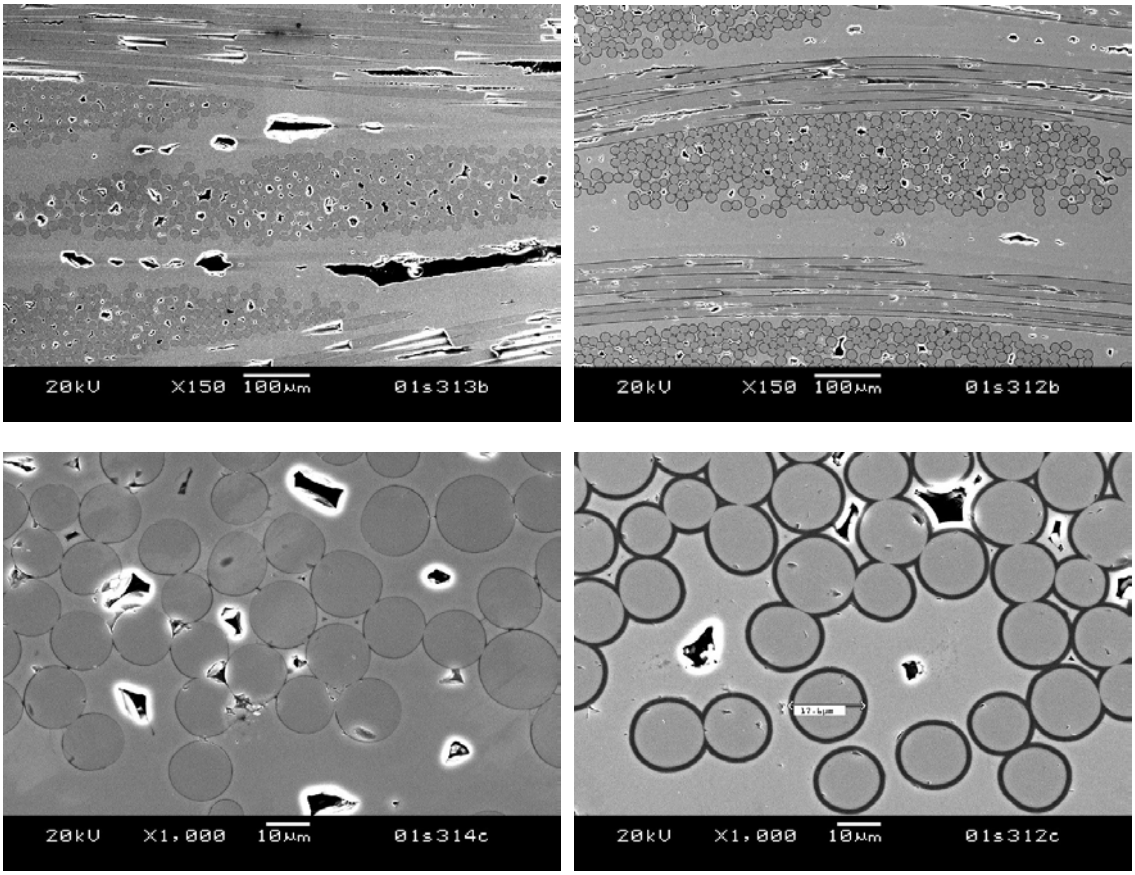

Figure 1. SEM micrographs of polished DuPont 2D-SiC/SiC cross-sections showing typical porosity and good infiltration of ICVI-SiC matrix within plain-woven Hi-Nicalon™ bundles for (lhs) "thin" (0.110 μm) and (rhs) "thick" (1.040 μm) PyC fiber coating versions. The higher magnification views (lower) illustrate good f/m bonding through the PyC fiber coating for each version of the as-received composite.

The 2D-woven pattern and the microstructures appear to be quite similar for each version. As observed in Figures 1(a-d), the CVI-SiC infiltration was fairly uniform with only a few needle-like pores running parallel to the fiber axis contained within the 0-90 bundles. The apparently tight f/m bonding through either the thin or thick PyC fiber coatings suggests that the fibers were thermally well-coupled to the matrix. However, a number of rather large laminar-shaped pores, characteristic of composite fabricated by CVI infiltration of stacks of woven fabric layers, were observed typically in the interlayer region between the fabric layers. Although each version of the composite had a nominal fiber packing fraction of 0.4, the localized fiber packing within the individual tows obviously is much higher. Also, rather thick regions of single phase ICVI-SiC matrix exist around each fiber tow and also existed as a seal coat on the outer surfaces of the composite plates.

Neither the H-J nor the Markworth models account for the non-homogeneous nature of a composite with 2D plain-woven fabric layers. A refined model based on the actual architectural design is needed to reliably examine irradiation degradation mechanisms in detail for such a composite. For instance, due to expected high fiber packing fractions within individual fiber tows, the effects on K_{eff} of potential fiber-fiber interaction, and even direct fiber or fiber coating connectivity, needs to be considered. Furthermore, the non-uniform nature of the 2D fabric layers separated by dense matrix layers, but which typically contain numerous, relatively large laminar-shaped pores, needs to be included in a realistic model. Such a model, based on a hierarchical approach, is presented below.

The hierarchical model approach

The hierarchical model approach is based on the schematic representation of the 2D-SiC/SiC architecture for a typical composite made from stacked and infiltrated fabric layers, as illustrated in Figures 2(a-b). A major consideration is to include the effects of the dense CVD-SiC layers that separate the infiltrated 2D-fabric layers and of the numerous laminar-shaped pores contained in the interlayer between the dense CVD layers. In the schematic representation the composite is divided into two layers, an infiltrated 2D-fabric layer and a dense CVD-SiC layer of relative thickness f_F and f_M, respectively. The layers are aligned perpendicular to the heat flux.

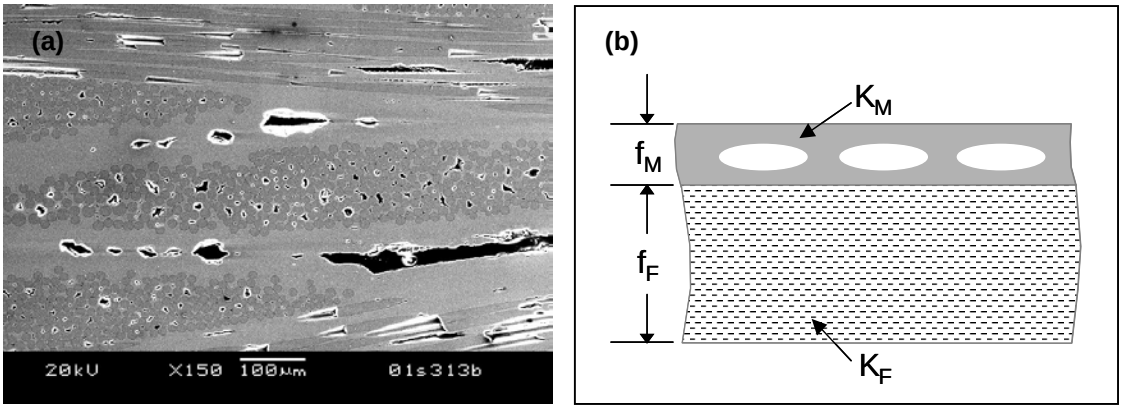

Figure 2. (a) SEM micrograph of a polished DuPont 2D-SiC/CVI-SiC cross-section showing the typical fabric and matrix layer pattern. Most of the laminar-shaped porosity is contained within the interlayer region between the fabric layers. (b) Schematic depiction of the composite two-layer architecture.

The average composite porosity (P_{avg}) can be estimated from the values of the overall fiber volume fraction (f) and composite bulk density (ρ_b), the fiber density (ρ_f), and the theoretical composite density (ρ_o) by

$$P_{avg} = 1 - f - (\rho_b - f\rho_f)/\rho_o \qquad (1)$$

Since most of the porosity is assumed to be contained within the dense CVI-SiC layer, P_{avg} must be adjusted to give the volume fraction porosity (P) contained within this layer by $P = P_{avg}/f_M$. Then the effective thermal conductivity in the CVI-layer (K_M) is estimated by the Maxwell-Eucken expression

$$K_M = K_m(1 - P)/(1 + \beta P) \qquad (2)$$

where β is a pore shape factor (e.g., $\beta = 0$ for needle-shaped pores parallel to the heat flux, $\beta = 1/2$ for isolated spherical pores, $\beta = 2/3$ for randomly dispersed cylindrical pores, and $\beta > 2/3$ for oblate spherical-shaped pores aligned perpendicular to the heat flux) [9,10].

The effective thermal conductivity in the 2D-fabric layer (K_F) is approximated by the H-J equation

$$K_F = K_m[1 - (B/A)p]/[1 + (B/A)p] \qquad (3)$$

where p, the actual packing fraction of the fibers within the fabric layers, has been substituted for f as the representative fiber volume fraction. As developed in Reference [1], $A = 1 + x + r$ and $B = 1 + x - r$, where $r = K_f/K_m$ and $x = K_f/ah$, and x is the reciprocal Biot number for heat transfer at the f/m interface with interfacial conductance (h) and fiber radius (a). In Equations (2) and (3), K_m now becomes the intrinsic ICVI-SiC matrix thermal conductivity. The effective transverse thermal conductivity of this two-layer composite model is then simply given by the expression for a fabric and matrix layer in series with thermal conductivities K_F and K_M, respectively:

$$1/K_{eff} = f_F/K_F + f_M/K_M \qquad (4)$$

As was discovered later, the H-J equation does not adequately treat thermal conduction in a composite with a rather thick, well-bonded fiber coating since the coating itself can contribute to the overall conduction. For a composite with a thin fiber coating, the substitution $h \sim K_c/t$ (where K_c and t are the fiber coating thermal conductivity and thickness, respectively) in the H-J equation gives representative results for K_F. For a composite with a well-bonded, "thick" fiber coating the somewhat more complex Markworth or "3-cylinder" model is used to describe K_F. For this latter case,

$$K_F = K_m\{f(K_f, K_m, K_c; p, t, a)/g(K_f, K_m, K_c; p, t, a)\} \qquad (5)$$

where the functions f and g are given by

$$f = 2c(r + c)[1 + p(1 + u)^2] + [(c - 1) + p(1 + u)^2(c + 1)]\{ (r - c)/(1 + u)^2 - (r + c)\} \qquad (6)$$

$$g = 2c(r + c)[1 - p(1 + u)^2] + [(c - 1) - p(1 + u)^2(c + 1)]\{ (r - c)/(1 + u)^2 - (r + c)\} \qquad (7)$$

In Equations (6) and (7), $u = t/a$ and $c = K_c/K_m$. As before, $r = K_f/K_m$ and p is the actual fiber packing fraction within a fabric layer.

Results

The temperature dependent thermal conductivity data $K_f(T)$ and the bulk density and average radius of Hi-Nicalon™ fiber (ρ_f = 2.74 g/cc and a = 7.0 ± 0.6 μm, respectively) were obtained in a separate experiment [8]. Other measured or calculated microstructural quantities used in the model descriptions for the "thin" and "thick" versions of the DuPont 2D Hi-Nic/PyC/ICVI-SiC composite are listed in Table 1.

Table 1. Microstructural data for "thin" and "thick" versions of DuPont 2D Hi-Nic/PyC/ICVI-SiC composite.

Version	t (μm)	ρ_o (g/cc)	ρ_b (g/cc)	P_{avg}	f_M	f_F	p	P	β
"thin"	0.110 (0.020)*	3.106	2.597 (0.030)	0.117	0.294 (0.07)	0.706 (0.08)	0.65 (0.02)	0.36 (0.10)	2.3 (1.3)
"thick"	1.044 (0.020)	2.991	2.627 (0.027)	0.088	0.314 (0.07)	0.686 (0.08)	0.67 (0.02)	0.25 (0.06)	2.3 (1.3)

* Numbers in parenthesis indicate approximate range of values based on repeated measurements at different locations.

In Table 1, ρ_o was calculated from a rule of mixtures based on the composition of Hi-Nicalon™ fiber and the dimensions and an assumed density of 1.90 g/cc for the PyC fiber coating. The bulk density of the composite (ρ_b) was determined by weighing and dimensioning the individual samples used for thermal diffusivity measurements. The values for f_M and f_F were approximated by scaling from a number of SEM views of composite cross-sections similar to Figure 1. Likewise, p and β were estimated in this manner. In particular, an approximation (β ~ 1/2 a/c for an oblate spheroid with large and small axes, a and c, respectively) was used to represent the interlayer pores having elliptically shaped cross-sections as depicted in Figure 2(b). Using the appropriate f_F-factor, P_{avg} was calculated from Equation (1) and adjusted to give P.

The model results based on the measured values of $K_{eff}(T)$ and $K_f(T)$ and on the microstructural data given in Table 1 are depicted in Figures 3 (a,b) for the "thin" and "thick" versions of the DuPont composite, respectively. In Figures 3(a,b), the large difference between the intrinsic $K_m(T)$ and $K_M(T)$ curves is due to the large influence of the porosity content within the matrix layer (P) and its shape factor (β). The "thin" version of the DuPont composite had a slightly higher ρ_o-value (due to a lower PyC content) and a lower ρ_b-value compared to the "thick" version. Since both versions were fabricated by the same CVI-process, the $K_m(T)$-values and the fiber coating thermal conductivity $K_c(T)$-values were required to be approximately the same during the model curve fitting. The coating $K_c(T)$-values ranged from 24 (@27°C) up to 40 (@200°C) and down to 32.5 W/mK (@1000°C). Then the major difference between the two versions is the significantly smaller $K_M(T)$-values for the "thin" version, with a larger difference occurring at lower temperatures. The fabric layer $K_F(T)$-values were about the same for each version, although the thicker PyC coating contributes more to the overall $K_{eff}(T)$ than the thinner coating. Finally, note that the $K_{eff}(T)$ curve lies between the $K_F(T)$ and $K_M(T)$ curves due to the layer configuration being in series.

The quantitative measurement of the microstructural features in 2D-woven composite generally exhibit a wide variation, as indicated by the relatively large uncertainties listed for these quantities in Table 1. In Figure 3(a), the sensitivity of $K_m(T)$ to a range of β-values from 1-4 (equivalent to an ellipse aspect ratio range 2-8) is examined. The basic difference between

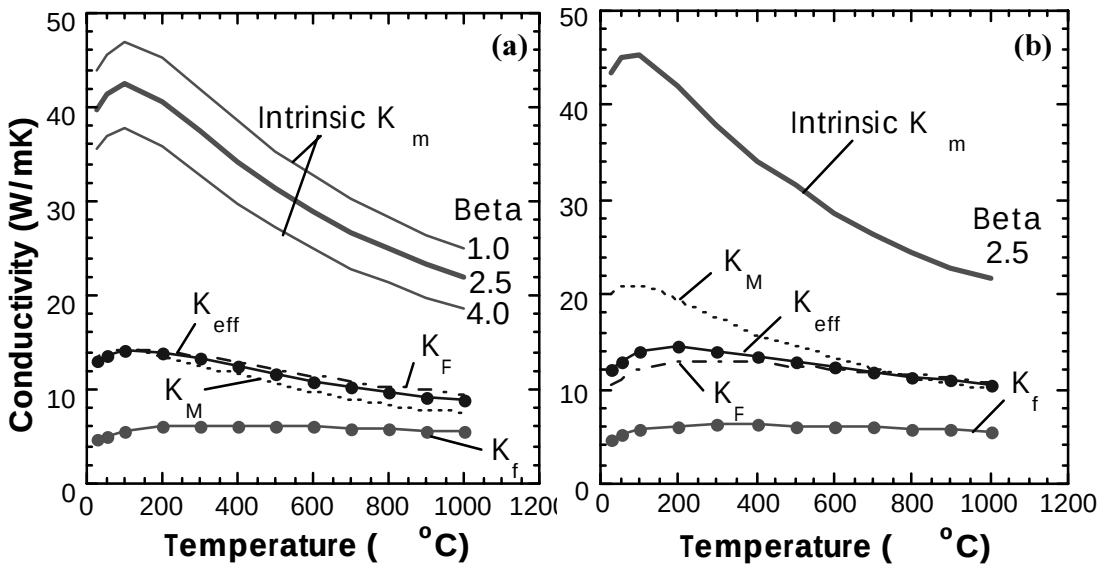

Figure 3. Hierarchical model predictions based on measured values of $K_{eff}(T)$, $K_f(T)$ and the porosity shape factor β for DuPont 2D-Hi Nic/PyC/ICVI-SiC composite versions with (a) "thin" and (b) "thick" PyC fiber coatings. The quantities derived from model fitting are the intrinsic ICVI-SiC matrix conductivity, K_m, and the effective fabric and matrix layer conductivities, K_F and K_M, respectively, as well as $K_c(T)$ that is not shown.

$K_m(T)$ and $K_M(T)$ is relatively unchanged for the range of β-values examined.

The large impact of the matrix porosity content and shape factor is not unexpected, but the hierarchical model is the first time that porosity has realistically been represented in a model for 2D-woven composite. The much smaller intra-bundle, needle-shaped pore content is not expected to exert much influence on $K_{eff}(T)$. Irradiation is expected to affect $K_m(T)$ by the introduction of point defects, but will have little affect on the porosity factor. At the same time, $K_F(T)$ will be affected primarily by thermal f/m decoupling (decrease in h).

FUTURE WORK

Using the hierarchical model, sensitivity studies will be performed to examine other composite systems. In particular, systems made with other SiC fibers (such as Tyranno™ SA with higher $K_f(T)$-values than Hi-Nicalon™) and other SiC-matrices (such as PIP with lower $K_m(T)$-values and different P and β-factors) will be examined. Expected irradiation effects then will be examined for these systems.

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