THERMAL DIFFUSIVITY/CONDUCTIVITY OF IRRADIATED SYLRAMIC™ 2D-SIC$_F$/SIC COMPOSITE

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 conduction properties of SiC_f/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 2D-SiC_f/SiC composite was made by Hypertherm with an ICVI-SiC matrix and with multilayer C/SiC coatings on high thermal conductivity Sylramic™ fibers woven into 5HS fabric layers. Thermal diffusivity measurements were made on representative samples of this Sylramic™ composite before and after irradiations in the HFIR reactor as part of the JUPITER 14J test series. The irradiations took place at about 290 and 800°C to equivalent doses of 4.2 and 7.0 dpa-SiC, respectively. The ratios of the transverse thermal conductivity after-to-before irradiation (K_{irr}/K_o) determined at the irradiation temperature were estimated from thermal diffusivity measurements to be about 0.12 and 0.37 at 290 and 800°C, respectively. However, the measured thermal diffusivity values of the unirradiated Sylramic™ composite with multilayer C/SiC fiber coatings were about 40% less than values predicted by the H2L model for this composite. This observation could be explained if the net interface conductance of the C/SiC multilayer was less than 0.1 of the interface conductance of a single layer PyC fiber coating.

PROGRESS AND STATUS

Introduction

The purpose of this study was to examine the effects of a C/SiC multilayer fiber coating on the thermal conduction properties of a SiC_f/SiC composite reinforced with a high conductivity SiC fiber. In particular, the H2L thermal conductivity model predicts that a composite with low fiber-matrix (f/m) interface conductance would thermally decouple the fiber from the matrix [1]. If the C/SiC multilayer interface, in fact, exhibits a low net interface conductance, the expected beneficial influence of using a fiber with a high thermal conductivity to achieve a composite with an overall high transverse thermal conductivity may be nullified.

It is noted that SiC_f/SiC composites with a multilayer interphase have exhibited improved toughness [2] and oxidation resistance [3] compared to composites similarly made except with a single layer PyC interphase. Furthermore, Snead and Lara-Curzio showed that for a set of similar SiC_f/SiC composites made with Hi-Nicalon™ fabric, but with a conventional single layer carbon, a pseudo-porous SiC, or a multilayer C/SiC interphase, the composite with the multilayer C/SiC interphase exhibited the least degradation (8-20%) in the ultimate bend stress after irradiation to 1.1 dpa at 385°C [4]. Thus, the multilayer C/SiC fiber coatings are expected in some cases to promote improved mechanical performance in both unirradiated and irradiated SiC_f/SiC composite.

In this companion report to [1], the H2L model is used to critically assess the overall transverse thermal conductivity before and after irradiation for a 2D-SiC_f/SiC composite made with a high thermal conductivity fabric and a C/SiC multilayer fiber coating. The examined composite was made by

* Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

Hypertherm using a Sylramic™ fabric. The primary differences in this composite compared to the Hi-Nicalon™ composites discussed in the previous report were replacing the Hi-Nicalon™ fabric and its single layer PyC fiber coating with Sylramic™ fabric and its multilayer C/SiC fiber coating. Otherwise, the Sylramic™ and Hi-Nicalon™ composites had a similar ICVI-SiC matrix and similar bulk density values.

Composite Samples

The Sylramic™ fiber was prepared from a polymer-derived Si-C-O fiber by Dow Corning Corporation and had the following nominal properties: mean fiber diameter 10 µm, density 3.0-3.1 g/cc, tensile strength 3.2 GPa, tensile modulus 380 GPa, thermal conductivity 40-46 W/mK, crystallite grain size 100 nm, and thermal stability to 1600°C [5]. By using several processing steps including a high temperature sinter, a crystalline fiber results with essentially stoichiometric SiC (95% wt.), TiB_2 grains (3% wt.) at triple points and small amounts of B_4C (1% wt.) and BN. The high density and high degree of crystallinity in the fiber promote a high elastic modulus and thermal conductivity. Because the diameter is small, this fiber can be readily woven into 2D fabrics, even though the modulus of the Sylramic™ fiber is quite high.

The Sylramic™ composite, made by Hypertherm with a x4 C/SiC multilayer fiber coating applied by CVD prior to matrix infiltration by ICVI, was provided by G. Newsome (KAPL) as a 0.125” x 2.0” x 4.0” plate. The Sylramic™ fabric had 800 filaments/tow and was five-harness satin weave (5HS). In the composite plate, thirteen plies were stacked with a 0-90 lay-up. Prior to cutting out individual samples, the plate was diamond milled on one surface to a constant 2.26-mm thickness. Four thermal diffusivity samples (TS1-4, 9.3 mm dia. X 2.26 mm thick) and 21 flexural bars (30 x 6.0 x 2.26 mm) were diamond cored or sawed from the milled plate. The bulk density values, determined by simple weighing and measuring of the sample dimensions, were in a similar range as the composites made with Hi-Nicalon™ fabric (2.44-2.60 g/cc). These bulk density values suggest that the macroporosity values were in the 15-20% range for the Sylramic™ composites, whereas the Hi-Nicalon™ composites had macroporosity values in the 7-13% range.

Irradiation and Test Conditions

Thermal diffusivity measurements were made simultaneously on several sample discs at various temperature steps in air from RT to 400°C before and after irradiation using the “low temperature” laser flash diffusivity system as described previously [1]. By plotting the reciprocal of the measured thermal diffusivity values versus temperature in degrees K, the resulting linear fit was used to extend diffusivity values to higher temperatures for analysis. The Sylramic™ composite disc samples were irradiated in the HFIR reactor at ORNL as part of the JUPITER 14J test series (TS1-2 at 290 ± 20°C, 4.2 dpa-SiC and TS3-4 at 800 ± 5°C, 7.0 dpa-SiC). All diffusivity measurements were made in air, but no annealing treatments were given to these Sylramic™ composites (as were carried out for the Hi-Nicalon™ composites).

Results and Discussion

In Figure 1, the thermal diffusivity values as a function of temperature for the Sylramic™ ICVI-SiC composite with a multilayer C/SiC interface are presented for various conditions. The conditions were: [1] as-received sample TS4 with a bulk density of 2.60 g/cc, [2] samples TS3 and TS4 irradiated at 800°C to an equivalent dose of 7.0 dpa-SiC, and [3] samples TS1 and TS2 irradiated at 290°C to an equivalent dose of 4.2 dpa-SiC. Although not accurately determined by simple dimensional measurements, a volume change of the disc samples irradiated at 290°C and 800°C appeared to exhibit roughly a 2.5-4.0% and 1.5-2.5% expansion, respectively.

In general, the unirradiated samples with higher bulk density values exhibited higher thermal diffusivity values. Since sample TS4 had approximately the same bulk density (2.60 g/cc) as the previously tested

Hi-Nicalon™ samples with the "thin" interface, the thermal diffusivity data for this specific sample with a high thermal conductivity Sylramic™ fiber component was used for detailed analysis. The measured thermal diffusivity of this sample was about 0.076 cm^2/s at RT and decreased continuously with increasing temperature to about 0.04 cm^2/s at 500°C. The thermal diffusivity curve for sample TS4 approximately matches the curve determined for the Hi-Nicalon™ composite with a "thin" PyC interphase [1]. The corresponding transverse thermal conductivity values also approximately match the Hi-Nicalon composite values (14 and 9 W/mK at RT and 1000°C, respectively).

Assuming that the ICVI-SiC matrix in the Sylramic™ composite has the same thermal conductivity values as determined for the ICVI-SiC matrix in the Hi-Nicalon™ composite, the H2L model predicts thermal diffusivity values that should be about 40% higher than the observed values. This is the case even if the somewhat higher porosity factors in the Sylramic™ composite are considered. This observation can be explained if the net interface conductance for the x4 C/SiC multilayer fiber coating is less than 0.1 of the value determined for the single layer PyC fiber coating. At this time, microstructural analysis has not

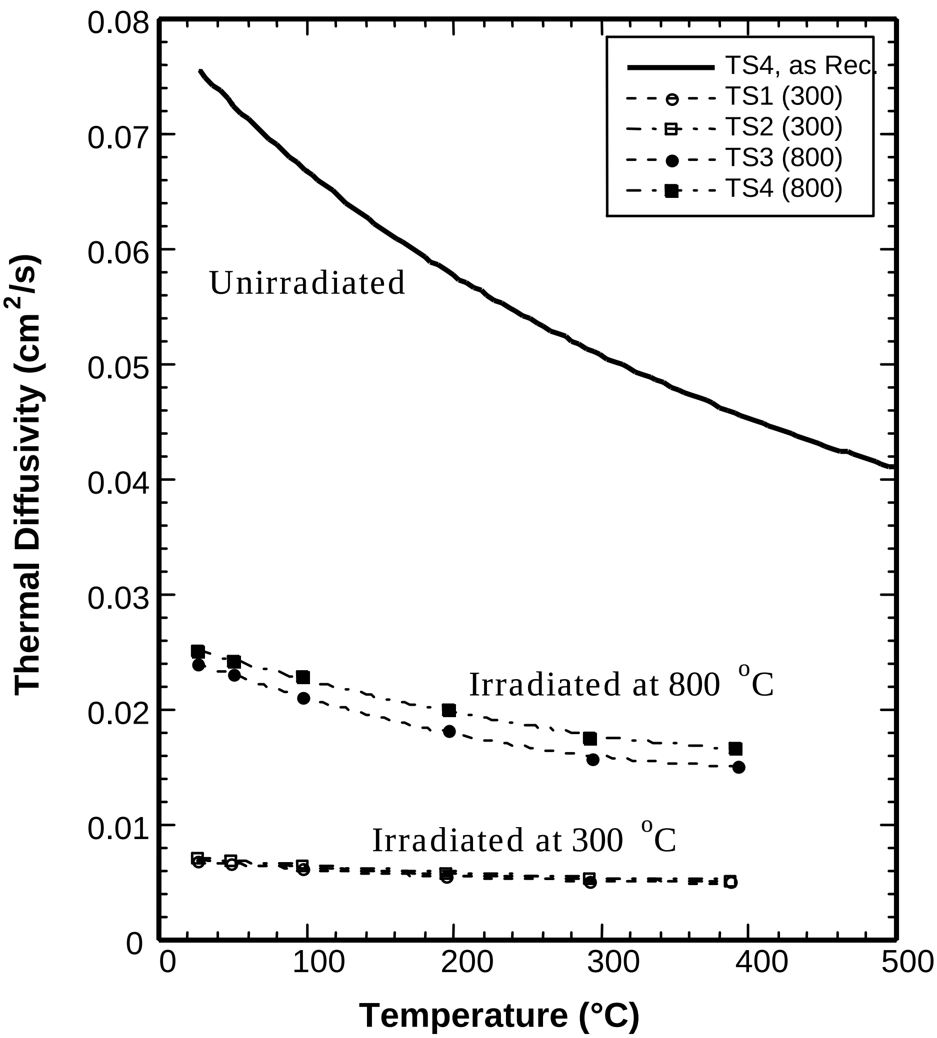

Figure 1. The measured thermal diffusivity values for representative Sylramic™ fiber-reinforced 2D-SiC_f/SiC composite samples made with multilayer C/SiC interphase before and after irradiation at 290°C (4.2 dpa-SiC) and 800°C (7.0 dpa-SiC).

been carried out on these Sylramic™ composites. Nevertheless, further analysis of this potential thermal conduction problem for other SiC_f/SiC composites made with multilayer fiber coatings is warranted.

After irradiation beyond saturation doses, the thermal diffusivity of the Sylramic™ composite was severely degraded as expected (Figure 1). Similar to the Hi-Nicalon™ composite case, the degradation was significantly larger for the irradiations at 290°C compared to those at 800°C. If it is assumed that the density and heat capacity values weren't significantly affected by the irradiation, then the ratio K_{effi}/K_{effo} is approximately 0.12 or 0.37 at 290 and 800°C, respectively. Again, the general trend that this ratio tends to gradually increase with increasing temperature for irradiated SiC_f/SiC composites and monolithic SiC is observed [6].

Further analysis of these data is not warranted until microstructural examinations have been carried out. Also, at this point the potential negative influence on the irradiation performance of the Sylramic™ composite due to the enhanced helium production in the Sylramic™ fibers with substantial boron content has not been considered.

FUTURE WORK

Detailed dimensional analysis will be performed on bar samples of the Sylramic™ composite irradiated in the 14J experiment. Also, if warranted flexural stress-strain measurements and microstructural examinations will be made and correlated with the thermal property results.

REFERENCES

[1] G. E. Youngblood, D. J. Senor and R. H. Jones, "Thermal diffusivity/conductivity of irradiated Hi-Nicalon™ 2D-SiC_f/SiC composite," in this Fusion Materials Semiannual Progress Report.

[2] Sebastien Bertrand, Rene Pailler and Jacques Lamon, "Influence of strong fiber/coating interfaces on the mechanical behavior and lifetime of Hi-Nicalon/(PyC/SiC)n/SiC minicomposites," J. Amer. Ceram. Soc. 84(4), 787-794 (2001).

[3] Y. Katoh, K. Hironaka, T. Hinoki and A. Kohyama, "Environmental effects of interfacial integrity of advanced SiC fiber-reinforced SiC matrix composites," Ceram. Eng. and Sci. Proc. 22 (4), 2001.

[4] L. L. Snead and E. Lara-Curzio, "Interphase integrity of neutron irradiated silicon carbide composites," p. 100 in Fusion Materials Semiannual Progress Report for period ending December 31, 1998 (DOE/ER-0313/25).

[5] R. E. Jones, J. Rabe and D. Petrak, "Sylramic™ SiC fibers for CMC reinforcement," p. 22 in the Proceedings of the 3rd IEA SiC/SiC Workshop, January 29-30, 1999, Cocoa Beach, FL.

[6] D. J. Senor, G. E. Youngblood, C. E. Moore, D. J. Trimble, G. A. Newsome and J. J. Woods, "Effects of neutron irradiation on thermal conductivity of SiC-based composites and monolithic ceramics," Fusion Technology 30(3), 943-955 (1996).