**THERMAL DIFFUSIVITY/CONDUCTIVITY OF IRRADIATED HI-NICALON™ 2D-SIC$_F$/SIC COMPOSITE-**

G. E. Youngblood, D. J. Senor and R. H. Jones (Pacific Northwest National Laboratory)*

NOTE: This report was inadvertently left out of the previous FMSPR (DOE/ER-0313/33). Two companion papers did appear in the previous FMSPR, "Thermal diffusivity/conductivity of irradiated Sylramic™ 2D-SiCf/SiC composite" and "Thermal diffusivity/conductivity of irradiated monolithic CVD-SiC." For continuity, these reports should be read in sequence since the details for all three experiments and the description of the H2L model are given in this report.

## 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 neutron 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 radiation dose.

## SUMMARY

The H2L model was used to critically assess degradation within the individual fiber, fiber coating and matrix components for irradiated 2D-SiC$_f$/SiC composite made with an ICVI-SiC matrix and Hi-Nicalon™ fabric. The composites were made with either a 1.044-µm ("thick") or a 0.110-µm ("thin") PyC fiber coating and were irradiated in the HFIR reactor as part of the JUPITER 12J (355°C, 7.1 dpa-SiC) or 14J (330 and 800°C, 5.8 and 7.2 dpa-SiC, respectively) series. Laser flash diffusivity measurements were made on representative samples before and after irradiation and after various annealing treatments.

The ratio of the transverse thermal conductivity after to before irradiation ($K_{irr}/K_o$) determined at the irradiation temperatures and predicted by the H2L model were: 0.18, 0.23 and 0.29 for the 330, 355 and 800°C irradiations, respectively. Thermal diffusivity measurements in air, argon, helium and vacuum indicated that physical separation of the fiber/matrix interface was minimal after the irradiations, but was significant after annealing irradiated composites to 1200°C. These results suggest that during irradiation to 6 dpa or more radial swelling of the PyC interface would compensate for the radial shrinkage of the Hi-Nicalon™ fiber and the SiC matrix swelling. The fiber shrinkage is due to irradiation-induced grain-growth and recrystallization and the matrix swelling is due to accumulation of irradiation-induced point defects. However, when the irradiation induced swelling in the matrix and fiber coating components was removed by recombination of point defects during high temperature annealing there was significant fiber/matrix separation.

## PROGRESS AND STATUS

### Introduction

To predict the overall thermal conductivity ($K_{eff}$) for a SiC$_f$/SiC composite made with stacked, woven fabric layers, the hierarchical two-layer (H2L) model was developed [1]. In this H2L model, the composite architecture is represented by alternating SiC fabric layers in series with SiC matrix layers that usually contain considerable amounts of porosity. The H2L model describes $K_{eff}$ in terms of the composite constituent (fiber, fiber coating and matrix) properties as well as the fiber/matrix (f/m) interfacial effects and the porosity amount, distribution, shape and orientation. In this report, the H2L model is used to critically assess degradation within the individual constituents for irradiated SiC$_f$/SiC composites made

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

with an ICVI-SiC matrix and Hi-Nicalon™ fabric. The model equations and definitions were presented in a previous semi-annual report and at the recent 5th IEA SiC/SiC workshop where they were applied to the unirradiated 2D-$SiC_f$/CVI-SiC systems made with either Hi-Nicalon™ or Tyranno™ SA fabrics [1,2].

Composite Samples

The Hi-Nicalon™ composite was made by DuPont with either a "thin" (0.110 μm) or a "thick" (1.044 μm) pyrolytic carbon (PyC) fiber coating applied by CVD prior to matrix infiltration. The Hi-Nicalon™ fabric was plain-weave (PW) in a 0-90 layup for both cases. Four thermal diffusivity samples of each type (9.3 mm dia. X 2.3 mm thick) were diamond-cored from plates. The bulk density values, determined by simple weighing and measuring of the disc dimensions, were in the range 2.50-2.60 g/cc. Several flexural bars of each type composite also were cut from the plates. Example SEM views of the typical two-layer fabric/matrix macroscopic structures for these composites were given in a previous report [1].

Irradiation and Test Conditions

The thermal diffusivity of the unirradiated discs was measured in air as a function of temperature up to about 400°C by the laser flash method described elsewhere [3]. The sample discs with "thick" and "thin" interfaces were irradiated in the HFIR reactor at ORNL as part of the JUPITER 12J and 14J test series, respectively. Only two discs with "thick" interface (D1 and D2) were recovered after irradiation at 355 ± 35 °C to an equivalent dose of 7.1 dpa-SiC in 12J. Three discs were recovered after irradiation in 14J (JD2 at 330 ± 20°C, 5.8 dpa-SiC and JD3 and JD4 at 800 ± 5°C, 7.2 dpa-SiC).

Two separate laser flash diffusivity systems, a "low" and a "high" temperature one, were used to make the thermal diffusivity measurements after irradiation. Measurements in the low temperature system were made in air from RT up to about 400°C. The high temperature system was contained inside a steel bell jar so that diffusivity measurements could be made in vacuum or in different inert atmospheres (argon or helium). Measurements in the high temperature system were made from about 200°C up to the irradiation temperature. In addition, in situ post-irradiation annealing treatments in argon up to the irradiation temperature and beyond to 1200°C also were made in the high temperature system. Finally, four other unirradiated disc samples (two with each fiber coating thickness) were heated in air for 15 hours at 700°C to remove the PyC fiber coating by oxidation. The coating "burn-out" temperature was about 100°C below that where significant $SiO_2$ formation begins, so the PyC coatings were removed without sealing off the interface layers. Later, weight change measurements confirmed that this likely was the case. In an attempt to determine the composite matrix contribution to the thermal conductivity alone, the thermal diffusivity was then remeasured for each pair of samples, now with the fibers physically separated from the matrix. Other diffusivity measurements were made sequentially on specific samples before and after irradiation (and during and after annealing treatments) and in different atmospheres.

**Results and Discussion**

In Figures 1(a-b), the thermal diffusivity values as a function of temperature for the Hi-Nicalon™ ICVI-SiC composites with (a) "thick" and (b) "thin" PyC interfaces for various conditions are presented. The conditions in sequence of performance were: [1] average diffusivity values for four as-received samples (heavy solid line) and [2] average values for two unirradiated samples with PyC interface removed by oxidation (light solid line). Then for two specific irradiated samples in sequence of performance ("thick" = D1 and D2, irradiated at 355°C, 7.1 dpa and "thin" = JD2 irradiated at 330°C, 5.8 dpa-SiC and JD3 at 800°C, 7.2 dpa-SiC) and with open or filled data points separating the pairs of samples: [3] values in air (dashed lines), [4] values in vacuum (short dashed lines), [5] values in argon during in situ annealing from about 200°C up to 1200°C (2-hr hold time) and after as the temperature was decreased back to 200°C (diamond data points with dashed-dot lines), [6] values in vacuum from 200-400°C (short dashed lines), [7] values in helium from 200-400°C (long dashed lines), and finally [8] values in air again from RT up to

400°C (dashed lines).

Previously reported H2L-model results for the as-received Hi-Nicalon™ composites indicated that the matrix porosity content and shape factors had a large impact on $K_{eff}$. The relevant measured and calculated data from reference [1] are reviewed in Table 1.

Table 1. Measured and calculated data for Hi-Nicalon™ composites with different interface thickness.

| Type | t (μm) | $\rho_b$ (g/cc) | $f_M$ | $f_p$ | $P_{avg}$ | $P_M$ | β | $K_{eff}$ 200C (W/mK) | $K_{eff}$ 1000C (W/mK) |
|---|---|---|---|---|---|---|---|---|---|
| "thick" | 1.044 | 2.63 | 0.31 | 0.65 | 0.073 | 0.062 | 1.3 | 15 | 10 |
| "thin" | 0.110 | 2.60 | 0.29 | 0.67 | 0.126 | 0.107 | 1.3 | 15 | 8.5 |

In Table 1: t is the PyC interface thickness; $\rho_b$ is the composite bulk density; $f_M$, $f_p$ and $P_M$ (measured from several SEM views) are the fractional matrix layer, fabric layer fiber packing and matrix layer macroporosity contents, respectively; $P_{avg}$ is the calculated overall composite porosity content; β is the matrix layer macroporosity shape and orientation factor; and $K_{eff}$ is the measured composite thermal conductivity at 200°C and 1000°C, respectively. Both composite types, made by the same isothermal-CVI process with similar Hi-Nicalon™ fabric layups, had similar values of $\rho_b$, $f_M$, $f_p$ and β. However, the composite with the "thin" interface had noticeably higher porosity contents ($P_{avg}$ and $P_M$) compared to the composite with the "thick" interface, which likely is somewhat responsible for the slightly lower $K_{eff}$-values observed for the "thin" interface composite.

Assuming that the temperature dependent equivalent fiber coating and the "intrinsic" matrix thermal conductivity values ($K_c(T)$ and $K_m(T)$, respectively) each were the same for each composite type (which primarily differed only in the thickness of their PyC interface), the H2L-model predicted that values of $K_c$ and $K_m$ ranged from maximum values of 34 and 40 W/mK (at 200°C) down to 28 and 18-20 W/mK (at 1000°C), respectively. Apparently $K_c$ had more impact on $K_{eff}$ for the composite with the thick interface where conduction along the interface begins to become important. For this reason, the somewhat shallow temperature dependence predicted for $K_c(T)$ was responsible for the separation between the $K_{eff}$-values observed for the "thick" and "thin" composites, particularly as temperatures were increased.

When the PyC interfaces were removed by oxidation, the thermal diffusivity values for each composite dramatically decreased about 60% of their as-received values (Figures 1(a-b)). If it is assumed that only the individual fiber filaments were thermally separated by the oxidation treatment (i.e., equivalent to treating the fiber content simply as an additional porosity content), the H2L model would predict that the decrease in values should have been about 40% rather than the observed 60%. Apparently entire fiber bundles (and the included continuous matrix within the bundles) were thermally separated by the treatment. In fact, if about 85% of the fiber bundles were assumed thermally separated from the matrix in their entirety, the H2L model predictions would match the observed results.

Detailed SEM cross-section views near the edge of a fiber bundle in the composite with a "thick" interface before and after the oxidation treatment are shown in Figures 2(a-b), respectively. In Figure 2a, generally good infiltration of the ICVI-SiC matrix with pore-free bonding to the individual filaments is observed. A few needle-like pores (axis parallel to the fiber lengths) are observed at interstices between the matrix radial growth patterns. A significant amount of fiber coating interconnectivity also is observed. As shown in Figure 2b, when the interconnected PyC fiber coating was removed large sections of the matrix within the fiber bundle also became separated from the remaining matrix. The thermal diffusivity of the samples with their interface removed by oxidation also was measured in vacuum and in helium atmospheres. Compared to the values measured in air, the thermal diffusivity increased by 15-30% when measured in

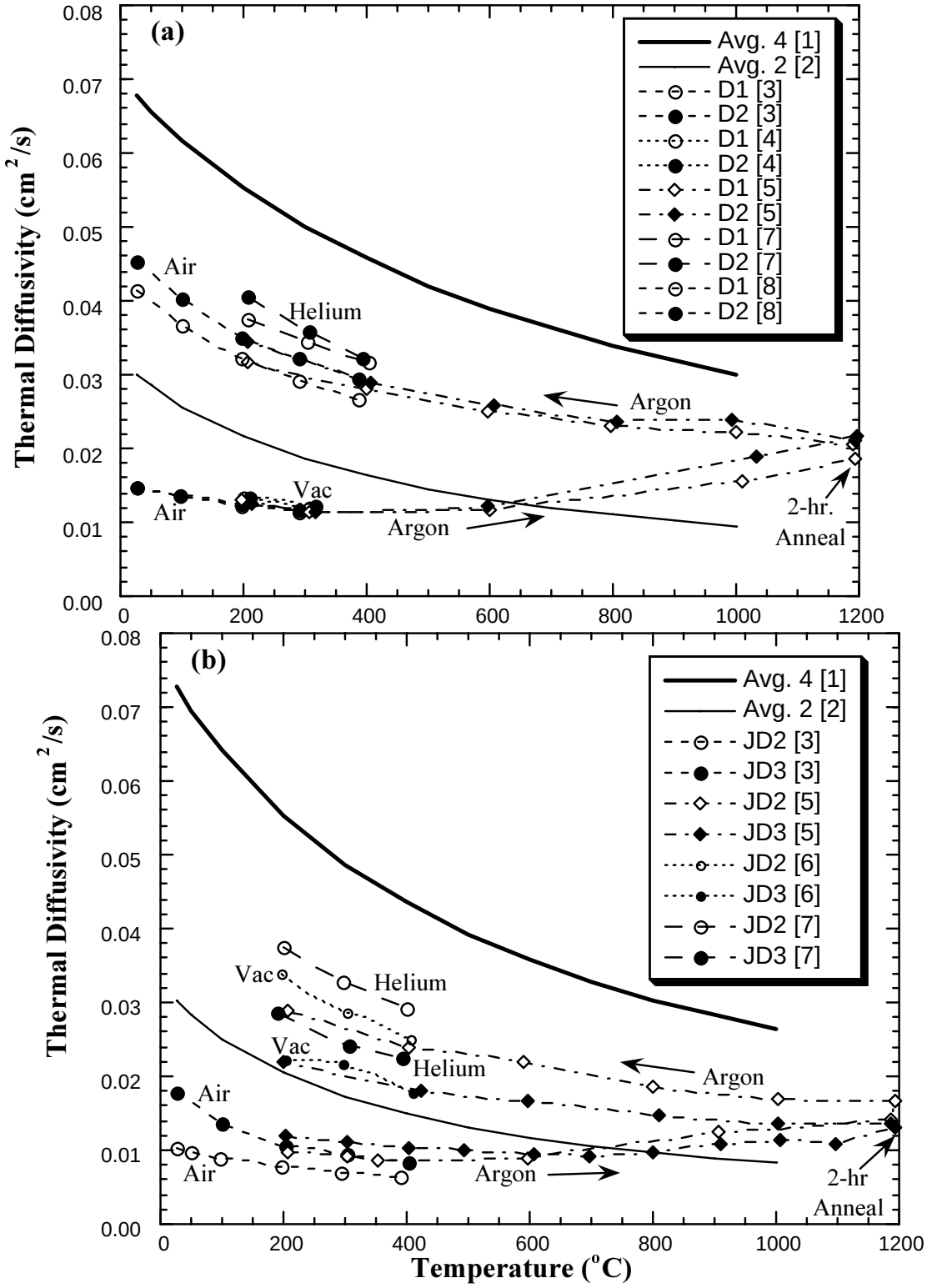
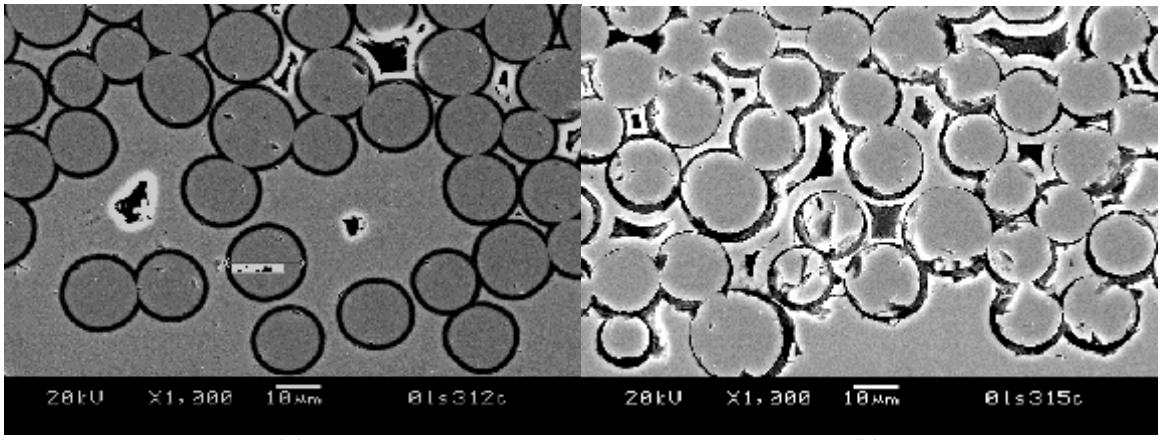



Figure 1(a-b). Thermal diffusivity of 2D Hi-Nicalon™/ICVI-SiC composites with (a) "thick" and (b) "thin" PyC interface for various unirradiated and irradiated conditions. See text for key.




(a) (b)

Figure 2(a-b). Cross-section SEM views of a region near the edge of a fiber bundle in the Hi-Nicalon™ composite with a "thick" interface (a) before and (b) after removal of the interface by oxidation in air at 700°C for 15 hours.

helium, and it decreased by 20-40% when measured in vacuum (data not shown in Figure 1). Such effects are expected for composites with physical gaps formed at numerous fiber/matrix interfaces where the interfacial conductance depends upon the thermal conduction of the atmosphere within these gaps [6].

After irradiation, the thermal diffusivity of each composite was severely degraded. The degradation was significantly larger for the irradiations at 330 and 355°C compared to those at 800°C. The actual thermal diffusivity values before and after irradiation determined from Figures 1(a-b) at three different irradiation temperatures are listed in Table 2. If it is assumed that the density and heat capacity values weren't significantly affected by the irradiation, then the ratio of the thermal diffusivity values after to before irradiation is approximately equal to the ratio of the thermal conductivity after to before irradiation, $K_{effi}/K_{effo}$. This ratio also is listed in Table 2.

Table 2. Comparison of thermal diffusivity values for the Hi-Nicalon™ composites with "thick" and "thin" PyC interfaces determined at their irradiation temperature.

| Quantity | "Thick," 355°C | "Thin," 330°C | "Thin," 800°C |
|---|---|---|---|
| T Diff (before irrad.), $cm^2/s$ | 0.047 | 0.049 | 0.031 |
| T Diff (after irrad.), $cm^2/s$ | 0.0108 | 0.0090 | 0.0088 |
| $K_{effi}/K_{effo}$ (after/before) | 0.23 | 0.18 | 0.29 |
| H2L-model T Diff predict after irradiation,* $cm^2/s$ | 0.0113 | 0.0088 | 0.0086 |

* Assumed constituent values $K_{fi} = 0.5K_{fo}$, $K_{ci} = 0.5K_{co}$ and $K_{mi} = 0.1K_{mo}$ after irradiation.

The relative degradation ratios are slightly lower than similar ratios determined previously for 2D-$SiC_f$/SiC composite made with Nicalon™ CG fabric with a "thin" PyC interface and irradiated to doses in excess of 25 dpa-SiC (0.27 at 500°C, 0.40 at 800°C and 0.50 at 1000°C) [5]. However, the general trend that this ratio tends to gradually increase with increasing irradiation temperature is consistent. Note that all the thermal diffusivity values measured for irradiated samples represent saturated conditions, i.e., all the irradiation doses were well above saturation doses for SiC.

After measuring the thermal diffusivity in air up to about 400°C in the low temperature system, the samples were remounted in the high temperature system and measurements continued in argon up to 1200°C. Excellent agreement of the thermal diffusivity values occurred for the 200-400°C overlap region for the composite with "thick" interface, while the agreement was within 20% for the composite with "thin"

interface when measured in the different laser systems in air or argon. Agreement within 20% is considered barely within uncertainty limits for such measurements; nevertheless continuity of the thermal diffusivity values through the temperature overlap region was assumed.

Once the annealing temperature exceeded the irradiation temperature, the thermal diffusivity was observed to increase with further increase in temperature in three steps up to 1200°C, where the samples were held for two hours to complete the anneal of the irradiation induced point defects. After the 2-hr anneal at 1200°C, the thermal diffusivity values at 1200°C for each composite returned to about 70-80% of expected unirradiated values at that temperature. Further thermal diffusivity measurements were made in argon as the temperature was then decreased in several steps from 1200°C down to 200°C. Although sample JD3 irradiated at 800°C initially had higher thermal diffusivity than sample JD2 irradiated at 300°C, after annealing at 1200°C the reverse situation occurred, i.e., the thermal diffusivity of JD2 was significantly higher than that of JD3. This observation can be qualitatively explained if the thermal diffusivity degradation is considered primarily due to the accumulation and recombination of irradiation induced point defects in the matrix constituent. Since saturation in SiC occurs for a lower concentration of defects at higher irradiation temperatures (at least up to 800°C, or so), the thermal diffusivity degradation for the 800°C irradiation is expected to be less than for the 330-355°C irradiations, as observed. However, in SiC after an 800°C irradiation to saturation the relative amount of recovery is less than after a similar 330-355°C irradiation. In fact, after the annealing treatment and returning to 200°C the thermal diffusivity of the composite irradiated at 330°C is about 25% higher than that of the composite irradiated at 800°C. Similar trends have been observed in the recovery of volume swelling for irradiated and annealed monolithic SiC [7].

The thermal diffusivity of a fiber-reinforced SiC/SiC composite has been shown to be sensitive in some cases to the actual condition of the relatively thin fiber/matrix (f/m) interface [6]. In particular, if physical gaps are formed at composite f/m interfaces, e.g., due to removal of a PyC fiber coating by oxidation or due to differential f/m shrinkage-swelling caused by the different effects of the irradiation in each constituent, the thermal diffusivity becomes dependent on the gas atmosphere within the gaps. Interestingly, after the 355°C irradiation of the composite with a “thick” PyC interface, the thermal diffusivity measured in vacuum was almost identical to the values measured in air or argon in the 200-350°C overlap region. Apparently, at this point physical f/m gaps did not exist in the irradiated composites even though the matrix was expected to swell about 0.8% and the Hi-Nicalon™ fiber was expected to shrink about 1.7%. The radial swelling in the irradiated PyC fiber coating with its somewhat anisotropic microstructure is estimated to be larger than 2% (with a commensurate axial shrinkage of about 0.7%). At least it is plausible that the expected swelling at 6 dpa in the PyC interface compensated somewhat for the differential shrinkage-swelling in the f/m components, and significant f/m thermal decoupling in the composite no longer existed. However, radial tensile stresses generated at lower doses (1-2 dpa, i.e., low enough so that swelling in the PyC fiber coating were not yet substantial) likely were sufficient to cause serious f/m debonding and loss of composite strength.

After annealing and cooling the composites to the 200-400°C range, the thermal diffusivity was remeasured with different atmospheres (vacuum and helium) admitted into the bell-jar enclosure. Although some inconsistency occurred for the measurements made in vacuum, for the measurements made in helium the thermal diffusivity values were significantly greater than values measured in air, argon or vacuum for all three cases.

Apparently, the relative shrinkage-swelling situation changed when the irradiated and annealed composites were then cooled back to the 200-400°C temperature range. The shrinkage in the irradiated Hi-Nicalon fiber, caused by irreversible recrystallization and grain growth, was permanent. Meanwhile, the swelling and partial recovery in the irradiated and annealed SiC matrix, caused by accumulation and then recombination of point defects, was reversible. Therefore, the final situation appears to be a matrix with dimensions similar to the pre-irradiation conditions, while the fiber dimensions were significantly reduced. The shrinkage-swelling situation in the irradiated and annealed PyC interface is more complex,

since irradiated PyC does not exhibit saturation effects, and the swelling (or shrinkage) is highly temperature and dose dependent. Nevertheless, significant physical f/m separation must have occurred in the irradiated, annealed and cooled composites to account for the noticeable dependence of their thermal diffusivity values on atmosphere.

Finally, the H2L model was used to predict the expected thermal diffusivity values from RT to 200°C for the Hi-Nicalon™ composites with complete thermal decoupling of the fiber constituent (i.e., let $K_c = 0$), but with no other changes in the matrix or porosity factors. For each composite, the predicted values closely matched the observed magnitudes and slopes of the measured thermal diffusivity values, at least in this narrow temperature range. Perhaps somewhat fortuitous, such agreement with model predictions nevertheless suggests that the described thermal and dimensional behavior of the irradiated and annealed Hi-Nicalon™ composites is consistent.

**Future Work**

Flexural stress-strain measurements will be made on bar samples of the Hi-Nicalon™ composites with "thick" and "thin" PyC interfaces, also irradiated in the 12J and 14J experiments. Results will be compared to a recently developed stress-strain model for such composites. The mechanical property results will be correlated with the thermal property results.

**Acknowledgments**

The U.S. DOE Nuclear Energy Research Initiative (NERI) funded the model development work.

**References**

[1] G. E. Youngblood, D. J. Senor and R. H. Jones, "Modeling the transverse thermal conductivity of 2D-$SiC_f$/SiC composites," p. 57 in the Fusion Materials Semiannual Progress Report for Period Ending December 31, 2001. (DOE/ER-0313/31).

[2] G. E. Youngblood, D. J. Senor, R. H. Jones and Y. Katoh, "Modeling the thermal conductivity of 2D-$SiC_f$/SiC composites with woven architectures," p. 36 in the Proceedings of the 5th IEA SiC/SiC Workshop April 12-13, 2002, San Diego, CA (PNN-SA-37623).

[3] D. J. Senor, G. E. Youngblood, D. V. Archer and C. E. Chamberlin, "Recent progress in thermal diffusivity testing of SiC-based materials for fusion reactor applications," p. 102 in the Proceedings of the 3rd IEA SiC/SiC Workshop, January 29-30, 1999, Cocoa Beach, Florida.

[4] G. E. Youngblood, D. J. Senor, W. Kowbel, J. Webb and Akira Kohyama, "Thermal conductivity of SiC and C fibers," p. 113 in Fusion Materials Semiannual Progress Report for period ending December 31, 1999 (DOE/ER-0313/27).

[5] 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).

[6] G. E. Youngblood and R. H. Jones, "The transverse thermal conductivity of 2D-$SiC_f$/SiC composites," p. 190 in the Proceedings of the 4th IEA SiC/SiC Workshop, October 12-13, 2000, Frascati, Italy.

[7] R. J. Price, "Annealing behavior of neutron-irradiated SiC temperature monitors," Nuclear Technology 16, 536-542 (1972).