**A NEW TYPE OF SIC COMPOSITE FOR FUSION** - G. E. Youngblood and R. H. Jones (Pacific Northwest National Laboratory*)

## 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

A new type of SiC composite called Tyrannohex™ is potentially suitable as a fusion reactor structural material. Tyrannohex™ composite plates are made by hot-pressing layups of Tyranno™ SA precursor fibers into various 1D and 2D configurations. The fiber-bonded composite plates contain nearly 100% fiber volume, so take advantage of the outstanding high temperature strength and creep properties of the Tyranno™ SA fiber, a nearly stoichiometric SiC fiber. The hot-pressed plates are dense, strong, rigid, tough, thermally conductive and have high temperature stability.

The microstructure and thermal conductivity of a SA-Tyrannohex™ material with a 2D-woven configuration was evaluated prior to irradiation testing. The microstructure contained some small, flat interlaminar pores and intrabundle needle-like pores, and the transverse thermal conductivity was 25 and 21 W/mK at ambient and 1000°C, respectively. These results suggest that careful control of the fiber-bonded interlayers and the fiber architecture are critical to achieve both high thermal conductivity and toughness in Tyrannohex™ type materials.

## PROGRESS AND STATUS

Considerable radiation performance data now exist for a two-dimensional (2D), woven $SiC_f$/SiC composite made with Hi-Nicalon™ fiber and a chemical vapor infiltrated (CVI) matrix [1]. Therefore, this composite serves as a useful standard even though its properties appear to be unacceptable for the most demanding (first wall) fusion reactor application [2]. In particular, its transverse thermal conductivity ($K_t$) is expected to degrade from about 13 and 10 W/mK unirradiated to about 5 W/mK irradiated at 300K and 1273K, respectively [3]. Several conceptual fusion reactor designs utilizing SiC/SiC call for $K_t$-values above 15 WmK at 1000°C for the first wall structure [4]. Since the $K_t$-values for monolithic SiC or SiC/SiC irradiated at 1000°C to saturation doses or above have been observed to degrade about 50% [3], unirradiated 1000°C $K_t$-values must exceed 30 W/mK. Obviously, the thermal conductivity performance of the 2D-woven SiC/SiC composite made with Hi-Nicalon fiber is far below this goal. In fact, it is unlikely that any 2D-woven SiC/SiC composite made by either the CVI-process or by polymer infiltration pyrolysis (PIP-process) will attain the $K_t$-values required for fusion (see reference [5]). To attain the thermal conductivity goal for fusion, a "new" type of SiC/SiC composite should be considered.

Currently, MER Corporation (Tucson, AZ) is pursuing the design and testing of SiC/SiC with a special 3D-type architecture to meet the fusion $K_t$ goal [6]. Ube Industries Ltd. (Ube City, JP) also is currently developing a new type of SiC composite that potentially could meet fusion

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requirements for $K_t$ [7]. This report presents a description and some test results for the latter material.

**Description of a "new type" of SiC composite for fusion**

The fabrication and properties of a new type of SiC composite developed by Ube Industries, called Tyrannohex™, have been described in recent papers [7, 8-10]. This new SiC composite consists of a 100% fiber-bonded ceramic made by hot-pressing sheets of polycrystalline SiC fibers (precursor fibers for Tyranno SA™) at temperatures over 1800°C and at a pressure of about 50 MPa.

The sintered Tyranno SA™ fiber itself exhibits outstanding high temperature tensile strength retention (2.8 GPa up to 1900°C in argon), and even in air chemical stability and creep resistance [11]. In Fig. 1, creep curves of representative SiC fibers in air at 1300°C for a 1 GPa applied stress are presented [12]. The creep resistance of the Tyranno™ SA fiber is significantly better than that of Hi-Nicalon™ fiber and earlier versions of the Tyranno™ SiC fiber. Furthermore, the SA fiber has a relatively high thermal conductivity (64 W/mK at ambient), which is 13 times higher than the thermal conductivity value for Hi-Nicalon™ fiber. These favorable properties are related to the densified and sintered fiber structure, which is composed of nearly stoichiometric SiC grains. The SA fiber composition ($Si_1C_{1.08}Al_{0.009}O_{0.006}$) contains a small amount of aluminum ($\leq$1%) which apparently controls grain growth during densification. Because oxidative rather than electron beam radiation curing is utilized, it is expected that fiber processing costs for the SA fiber also can be reduced. Preliminary estimates place the cost of SA fiber at about 1/3 that of Hi-Nicalon™ type S fiber, which is a comparable near-stoichiometric SiC fiber made using electron beam curing [13].

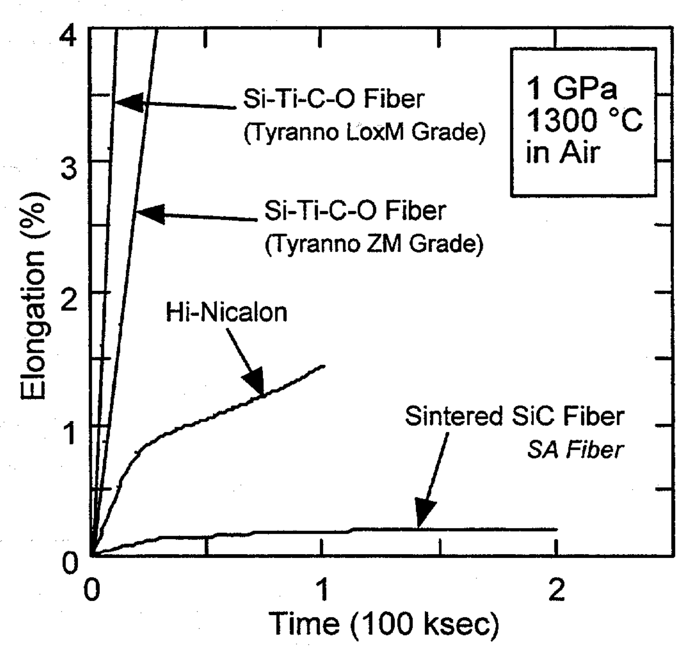


Figure 1. Creep curves for representative SiC fibers in air at 1300°C for 1 GPa.

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One version of the new type of SiC composite is synthesized by hot-pressing stacked sheets ($\approx$100 $\mu$m thick) of the Tyranno SA precursor fibers. The precursor fibers actually are amorphous Si-Al-C-O fibers, which have been cured but not sintered by heating in inert gas up to 1300°C. During hot-pressing, the amorphous Si-Al-C-O fibers deform and convert into sintered SiC fiber by way of a decomposition, which releases CO gas over the 1500-1700°C temperature range before completion of the sintering at temperatures over 1800°C. The sintered composite consists of a highly ordered, close-packed structure of fine hexagonal columnar fibers with a 100-400 nm grain size and a thin interfacial carbon layer between fibers. When made with the fibers aligned uniaxially in the sheets, this material had a tensile strength of 600 MPa in the longitudinal direction, which was retained when tested up to 1600°C. Because of the very thin interfacial carbon layer, the SiC fiber-bonded ceramic also exhibits fibrous fracture behavior similar to that exhibited by a conventional 2D-woven SiC/SiC composite. Likewise, the stress-strain curves for a 2D cross-plied version of the ceramic exhibit nonlinear fracture behavior, a maximum bend strength of 210 MPa, a maximum strain of 0.09%, a proportional limit of 120 MPa, a high elastic stiffness of 300 GPa, and a relatively high fracture energy of 2000 J/m$^2$. These properties are almost equivalent or better than comparable properties obtained for 2D-woven SiC/SiC made with Hi-Nicalon™ fiber and a CVI-SiC matrix (see Table 1). Furthermore, the fiber-bonded ceramic exhibits a desired high transverse thermal conductivity (20-65 W/mK at 1000°C, depending on configuration). The dense, low porosity structure made up of nearly 100% high quality, sintered crystalline SiC fibers accounts for the outstanding mechanical and thermal properties exhibited by the Tyrannohex™ fiber-bonded ceramic.

Generally, large improvements in mechanical properties of other types of SiC/SiC composites made with advanced fibers have been limited because of the high temperature strength limitation of the fiber. As an example, one way to improve the thermal conductivity of a SiC/SiC composite, especially one made by PIP-processing, is to give the composite a high temperature treatment (HTT). However, the HTT temperature required to achieve a significant improvement in the

Table 1. Comparison of properties for three types of SiC composites

| Property | Hi-Nic/PyC/CVI-SiC (2D-PW) | Tyrannohex™ 1D (parallel plies) | Tyrannohex™ 2D (8HS) |
|---|---|---|---|
| Bulk density (g/cc) | **2.6** | 3.1 | **3.0** |
| Porosity (%) | **10-15** | <3 | **<6** |
| Bend strength (MPa) | 350 [7]<br>(up to 1000°C) | 600 [7]<br>(up to 1600°C) | 280<br>210 (X-ply) [14] |
| Young's Modulus (GPa) | 200 (est) | NM | 320 (X-ply) [14] |
| Proportional limit (MPa) | NM | NM | 120 (X-ply) [14] |
| Ultimate strain (%) | **0.9** | NM | 0.09 (X-ply) [14] |
| Thermal conductivity (W/mK) | **13** | 37 (63 in plane) [7] | **25 (80 in plane)** |
| @ 1000°C | **10** | 27 (35 in plane) [7] | **21 (42 in plane)** |

PNNL measurements shown in bold type.

thermal conductivity is about 1800°C, which exceeds the stability limit of other advanced SiC fibers. Thus, at the expense of improving the thermal conduction properties of a composite the mechanical properties will be degraded by an 1800°C HTT. However, the high temperature stability of the Tyranno™ SA fiber allows an 1800°C HTT without sacrificing composite mechanical properties [11].

Recently, Ube discovered that by reducing the mean diameter of the SA fiber from 10 to 7.5 μm during processing the fiber tensile strength could be further improved [10]. Apparently, when starting with smaller diameter precursor fibers the gas evolution stage and grain growth are better controlled so that the resulting microstructure is made up of smaller (≈50 rather than 200 nm) grains, and the fiber surface is smoother. Contrary to expectation for a fiber with a smaller average grain size, the resulting creep resistance for this new version of Tyranno fiber (called SA-B) also is improved as depicted in Fig. 2 [12].

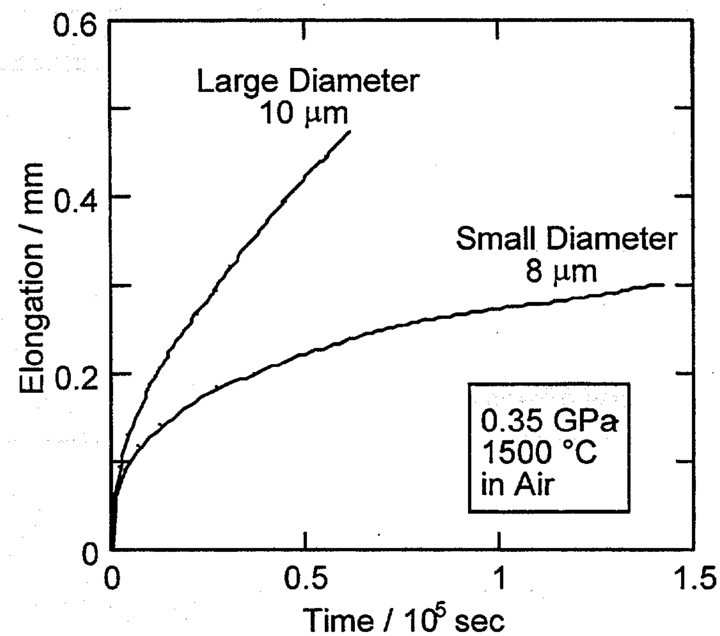



Figure 2. Creep resistance difference between two types of sintered SiC fiber (Tyranno™ SA) with different diameters.

By starting with smaller diameter fiber precursors, the strength of the fiber-bonded Tyrannohex™ composite also was improved. For instance, the 4-point bending strength of a cross-plied specimen increased from 300 to 500 MPa by using the 7.5 μm rather than the 10 μm fiber [10]. Other improvements in Tyrannohex™ composite properties are expected as fiber and composite development continues.

The Tyrannohex™ fiber-bonded SiC composite is dense, strong and rigid, tough, thermally conductive and has high temperature stability, all of which are desired attributes of a fusion grade SiC/SiC. The irradiation performance of this new type of SiC composite now needs to be assessed.

**Pre-irradiation experimental results**

A plate (50 x 16 x 2.0 $mm^3$, code UD-786) and two discs (6.5 mm dia x 2.0 mm thick, code UD-722) of 2D SA-Tyrannohex™ were obtained from Ube Industries for testing (courtesy of T. Ishikawa). The plate contained 22 fabric layers stacked and bonded together. Each layer was woven in a 0/90 satin weave (8HS) pattern, which is a different architecture option from that discussed previously. The surfaces of the as-received plate were lightly machined. The nominal density and bending strength were given as 3.1 g/cc and 280 MPa, respectively [12].

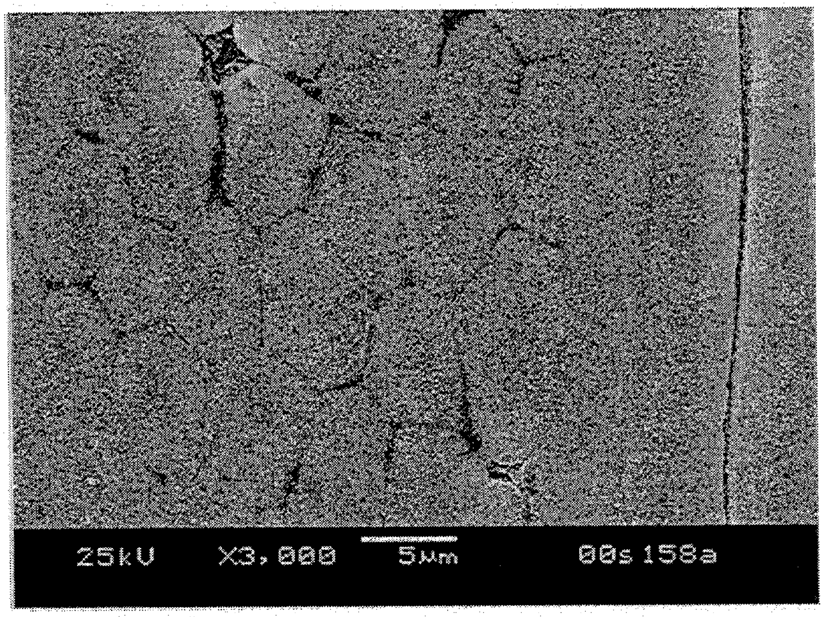
Seven discs (6.2 mm dia x 2.0 mm thick) for thermal diffusivity testing were core-drilled from the plate with the fabric layers normal to the heat flow direction. The remainder of the plate was cut into two flexure bars (50 x 3.6 x 2.0 $mm^3$). The two as-received discs were cut from a thicker piece of stock so that the heat flow direction was parallel to alternate fabric layers (i.e., 50% rather than 100% of the fibers were normal to the heat flow direction). These discs will be irradiated in the ATR and the HFR Petten reactors as part of the KFIB experiment (see Ref. [14] in this report). The thermal diffusivity was determined as a function of temperature up to 1000°C for each type of architecture by the laser flash technique described elsewhere [15].

SEM micrographs of polished pieces of the SA-Tyrannohex plate sample are presented in Figs. 3(a-b). In Fig. 3(a), the fibers on the left-hand side exhibit deformed hexagonal cross-sections with intervening thin carbon interfacial layers. However, sometimes needle-like pores remain between individual filaments. Such a pore is observed aligned parallel to the fiber axis in the right-hand side while two end-on views of pores are noted in the left-hand side of Fig. 3(a), respectively. Importantly, large interlaminar pores characteristic of 2D-woven SiC/SiC with a CVI-SiC matrix were not observed. However, for these SA-Tyrannohex samples made from layers of 8HS fabric a few smaller "interlaminar-type" pores were observed, as depicted in Fig. 3(b). Because of the more undulating weave pattern in this SA-Tyrannohex material, as compared to the unidirectional or simple 2D-layered architectures, porosity was low but not completely eliminated by hot-pressing. In fact, the average bulk density determined by weighing and dimensioning each disc sample was 2.97 ± 0.03 g/cc, a value slightly less than the given nominal 3.1 g/cc value.

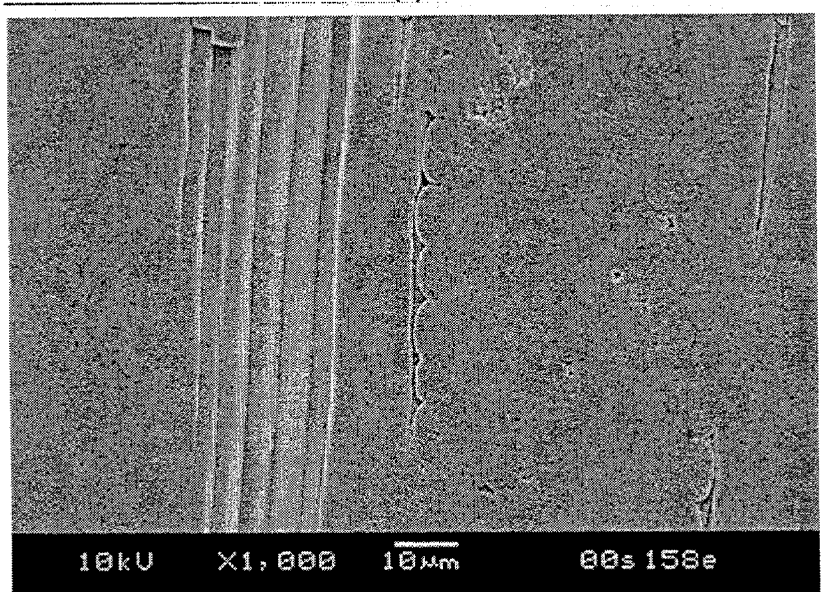
In Figures 4(a-b), the measured pre-irradiation thermal diffusivities and calculated thermal conductivities for the individual disc samples are given as a function of temperature. The heat flow in the samples labeled THt# was transverse to 100% of the fibers; in the samples labeled THp#, heat flow was transverse to 50% and parallel to the other 50% of the fibers. As expected, the thermal diffusivity values for samples with either architecture decreased with increasing temperature up to 1000°C, in a manner characteristic of thermal transport being governed by phonon conductivity. For the two samples with heat flow parallel to 50% of the fibers, the thermal conductivity ranged from about 80 W/mK at ambient down to 42 W/mK at 1000°C. However, in samples with the heat flow transverse to 100% of the fibers the thermal conductivity ranged from only 25 W/mK at ambient down to 21 W/mK at 1000°C.

The large difference in the thermal conductivity values between samples with the two different architectures is due primarily to the high conduction along the axis of 50% of the fibers for the THp material because the axial thermal conductivity of the Tyranno SA fibers is quite high (64 W/mK at ambient). Furthermore, the THt material contains approximately twice as many intervening carbon interlayers, which effectively act as thermal barriers.

Using a simple series-parallel combination model, the thermal conductivity of an interlayer ($K_i$) can be estimated from the difference in the thermal conductivity values for the two architectures. If the interlayer is assumed to be 50 or 100 nm thick, $K_i \approx 0.2$ or 0.4 W/mK, respectively. These



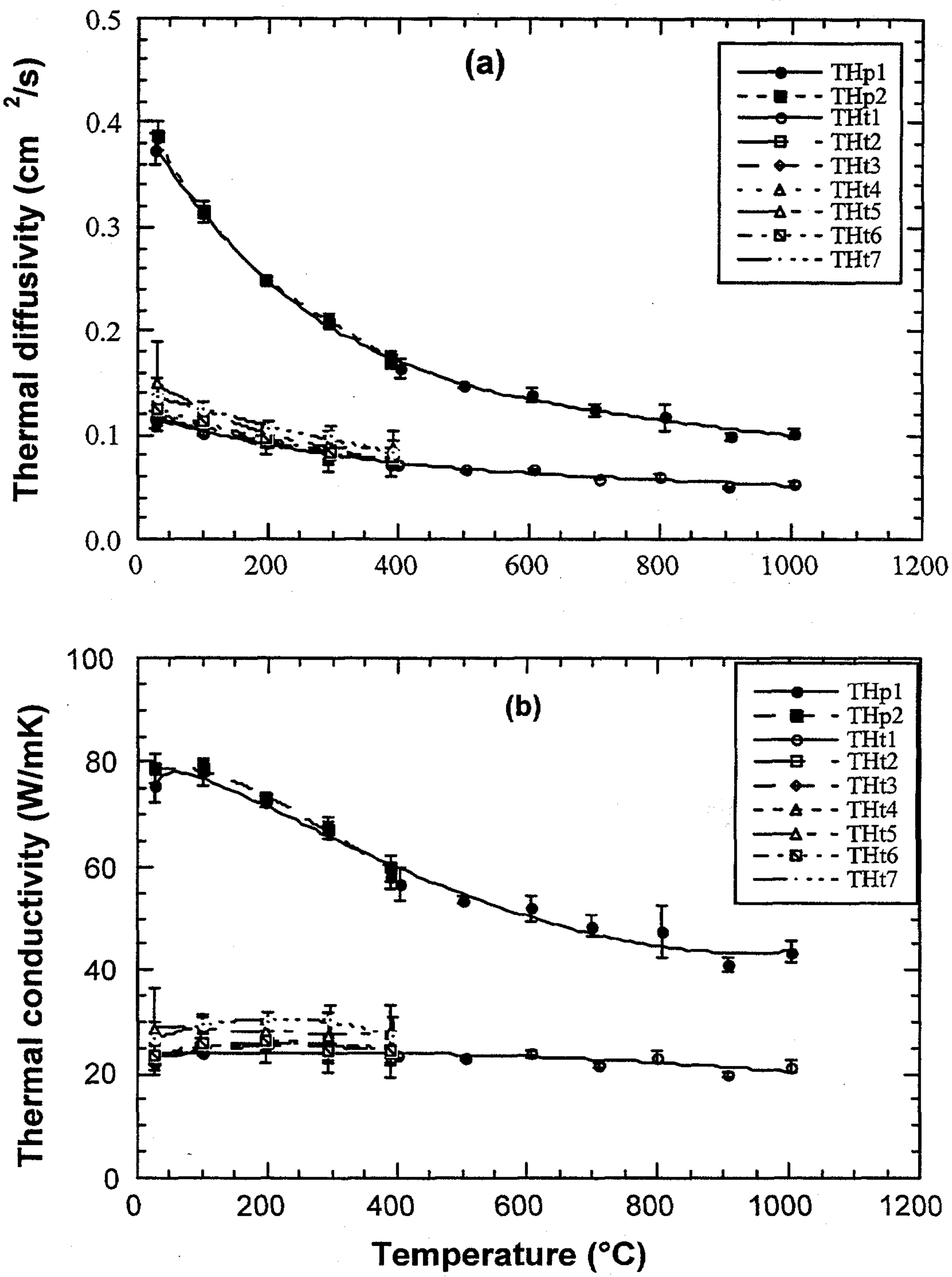

(a)




(b)

Figures 3(a-b). Typical SEM images of 2D SA-Tyrannohex showing cross-sectional views of material made by hot-pressing a layup of 8HS fabric layers. (a) Typical fiber-bonding arrangement with residual intrabundle needle-like porosity observed in both 0° and 90° bundles and (b) limited amount of small interlaminar type porosity observed between 0/90 layers.

low values confirm that the interlayers act as effective thermal barriers for transverse thermal conduction in the Tyrannohex™ 1D- or 2D-type materials.




Figures 4(a-b). Tyrannohex-SA (2D-HP from 8HS Tyranno SA fiber) pre-irradiation (a) measured thermal diffusivity and (b) calculated thermal conductivity for "KFIB Experiment" disc samples (see Ref. [14]). The heat flow was normal to 100% or 50% of the fibers for the samples labeled THt# or THp#, respectively.

If the interlayer is carbon, as is suggested by detailed chemical and microscopic analysis by Ube [10], the carbon must exist in a fairly unorganized form to exhibit such low thermal conductivity values. Of course, the small amount of porosity contained in the SA-Tyrannohex™ material with an initially woven fiber layup may also contribute to the low $K_i$ estimates. However, a carbon interlayer is necessary to provide the fibrous fracture and toughness in these materials so cannot be eliminated. The somewhat lower 21 W/mK transverse conductivity value observed at 1000°C for the THt material is only about two times comparable values for a conventional 2D-PW SiC/CVI-SiC made with Hi-Nicalon™ fibers. However, the 1000°C thermal conductivity of other types of the Tyrannohex material has been reported to be as high as 65 W/mK [10]. These results suggest that careful control of the fiber-bonded interlayers and the fiber architecture are critical to achieve both high thermal conductivity and toughness in Tyrannohex™ type materials.

## FUTURE WORK

The dimensional stability and transverse thermal conductivity of the 2D SA-Tyrannnohex™ material will be assessed after irradiation as part of the KFIB experiment.

## ACKNOWLEDGEMENTS

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