HIGH THERMAL CONDUCTIVITY PANELS FROM MESOPHASE PITCH FIBERS

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INTRODUCTION

Thermal management has become a challenge for systems where heat generation limits efficiency or leads to component failure. High power electronic devices, high energy friction and braking systems, propulsion and energy generation equipment, as well as processing equipment operating in corrosive environments are some areas where traditional thermal management approaches are no longer adequate. The development of pitch fiber-based, high modulus materials can be viewed as a breakthrough in the search for more effective conductive cooling devices. It is the exceptionally high thermal conductivity, negative coefficient of thermal expansion, and low density that make these graphite fibers so suitable for thermal management purposes. Mesophase pitch fibers can be used to make a variety of ThermalGraph™ product forms which include: binderless fused panels (discussed herein), continuous and discontinuous fibers, two and three dimensional fabrics and non-woven broadgoods.

In this paper, the preparation and properties of highly graphitic panels are presented. Two major classes of product are discussed, high density nearly unidirectional graphite and lower density impregnated panels with varied anisotropy. Thermal conductivities are related to fiber alignment and densities of graphitized panels and are compared to the properties of high modulus, high thermal conductivity graphite fiber.

EXPERIMENTAL

Properties of the petroleum mesophase pitches, fiber spinning conditions, and the application of an oxidizing spin size were typical of those described by Schulz and Nelson [1]. Mesophase pitches were melt spun to give a continuous fiber with 2000 filaments in the tow. Sized fiber (approximately 2.7 kg) was wound on a ten cm diameter bobbin with a wind angle of +/-0.5 to +/- 40 degrees. The wind angle is the measure of the deviation from a circumferential (parallel) wind pattern on the spool. The fiber package was cut lengthwise, the bobbin removed, and the fiber pressed into a flat mat. After trimming to square the edges, the mat was aged in a polyethylene bag for several days. A properly aged sample softens during subsequent heat treatment and the filaments fuse together; however, the preferred orientation induced by spinning is retained. At the completion of the aging step, mats are stacked between graphite plates in an induction furnace with weight applied to produce a pressure of 0.07 to 0.14 kg/cm^2. Graphitization is carried out by heating to temperatures of 3100 to 3300°C in an inert atmosphere. Volume fractions of graphitized articles are the ratio of panel bulk density to K-1100 graphite fiber density (2.2 Mg/m^3). Thermal conductivities were measured by Research Opportunities, Inc. using a Fourier method to analyze the thermal gradient from a known heat flux [2].

RESULTS AND DISCUSSION

ThermalGraph™ panels are comprised of mesophase pitch fibers fused into coherent panels and heat treated to form self-reinforced graphite. While lower density panels require infiltration with carbonaceous, metallic, or polymeric materials, panels made with densities just below graphite are used without impregnation. Highly anisotropic panels are made from mesophase fiber with very small wind angles. The nearly unidirectional pattern promotes nesting of tows and aids in maximizing the fusion bonding needed to produce a high density panel with good structural integrity. Figure 1(a) is a scanning electron micrograph of a high volume fraction panel air etched to show the extensive bonding between filaments. By adjusting the degree of infusibilization of the mesophase filaments and the pressure applied during heat treatment, the V_f of coherent graphite panels has been varied from 0.45 to 0.97. The linear relationship ($r^2 = 0.82$) between density and longitudinal thermal conductivity for graphitized panels is given in Figure 2. Extrapolation to a density of 2.2 Mg/m^3 (K-1100 value) predicts a longitudinal thermal conductivity of 1020 W/mK, which is similar to the K-1100 value. Thermal conductivities increase with rising density with a slope greater than predicted by volume fractions because of the increasing network of interfilament bonding. Decreasing networking of the fused filaments is illustrated in the micrograph, Figure 1(b), of a lower density panel. Transverse thermal conductivity follows a similar trend with the maximum conductivity predicted to be approximately 60 W/mK.

Mechanical properties of a finished panel vary with material orientation, density, and processing conditions. Properties of a nearly unidirectional panel with a density of 1.81 Mg/m^3 (0.82 V_f) are shown in Table 1. Tensile properties are highly anisotropic with a longitudinal to transverse ratio greater than 50:1. This level of anisotropy is much higher than bulk graphites, e.g. AGSX, which exhibits a 2:1 modulus ratio of parallel (12.4 GPa) to perpendicular (6 GPa) to the grain. The panel has four times the tensile strength and over twice the compressive strength of ATJ, one of the stronger grades of graphite. Further development has produced improved properties. On panels of various densities, the highest longitudinal values measured have been a compressive modulus of 821 GPa (0.97V_f), a tensile strength of 406 MPa (0.80V_f), and an electrical resistivity of 1.35 micro-ohm meter (0.80V_f). These properties are between those achieved by filamentary and composite forms of K-1100. Shear properties for these panels reflect their graphitic nature. Figure 3 displays specific moduli for several materials. The 428 x 10^3 meter specific modulus of both K-1100 fiber and ThermalGraph™ is 37% higher than K-1100/epoxy composites, natural diamond, or thick polycrystalline diamond films. The stiffest aluminum alloys (4000 series) have specific moduli only seven percent that of oriented ThermalGraph™; bulk graphite is less than two percent.

X-ray diffraction measurements (Table 2) confirm the link between ThermalGraph™ and K-1100 fiber. Compared to K-1100 fiber, similarly graphitized ThermalGraph™ appears less oriented because of wind angle and tow misalignment effects. However, d_{002} and L_c (004) are at least equal to fiber values.

Panel fiber orientation can be tailored to meet system design needs. In figure 4, the difference in thermal conductivity in longitudinal and transverse directions decreases as the wind angle approaches +/- 45°. Experimental conductivity data (normalized to 0.63 Vf) are in good agreement with values calculated [2] using CLASS® software from Materials Sciences Corporation. The effect of wind angle on CTE is shown in Figure 5. The transverse CTE trend is from 43 ppm/K (unidirectional) to -1.3 ppm/K (+/- 40 degrees). Lower longitudinal CTE values (more negative) at intermediate wind angles are caused by the interaction of transverse expansion with the +/- ply angle construction.

Table 1. Mechanical Properties of a ThermalGraph™ Panel

Property		Axial	Transverse
Tensile Strength	MPa	101.4	2.1
Tensile Modulus	GPa	371.7	2.1
Compressive Strength	MPa	146.9	
Compressive Modulus	GPa	363.4	
In-Plane Shear Strength	MPa	11.7	
In-Plane Shear Modulus	GPa	8.3	
Bulk Density	Mg/m³	1.81	

CONCLUSIONS

ThermalGraph™ panels possess the thermal, electrical, and material properties of high thermal conductivity K-1100 graphite fiber and its composites. Properties are highly dependent on fiber orientation and panel density. Density is controlled by infusibilization conditions and pressure applied during heat treatment. This self-reinforced graphite has great utility in transferring heat, modifying thermal expansion, and stiffening structures as required in the design of advanced systems.

ACKNOWLEDGMENTS

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REFERENCES

1. David A. Schulz and Loren C. Nelson, U.S. Patent 5,266,294 (1993).
2. William C. Riley, Research Opportunities, Inc., personal communication.
3. William Phillips, Mater. Res. Soc. Symp. Proc. **306**, 111 (1993).

Table 2. X-ray Diffraction Data for High Conductivity Fiber and ThermalGraph™

	Orientation	[002] Å	[002] Å	[004] Å	[004] Å
Sample	[FWHM]	C_0	L_c	C_0	L_c
K-1100	3.40	3.372	366	3.368	186
				3.364	221
ThermalGraph	7.13*	3.368	402	3.364	241
	*Includes misalignment of filaments in formed mat.				

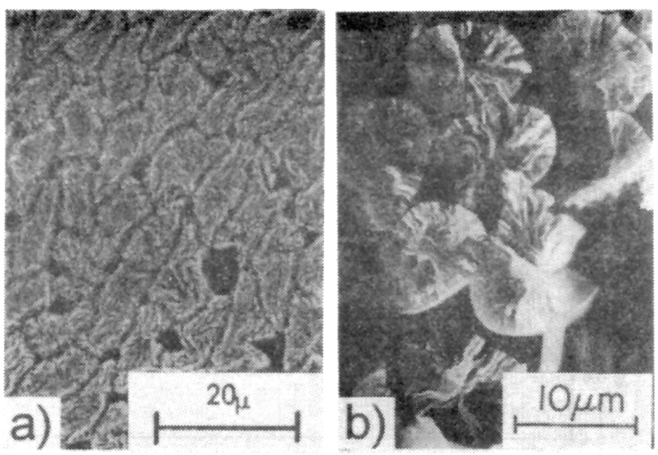

Figure 1. SEM photographs of graphitized panels showing filament shapes and packing: (a) high density, air etched; (b) lower density

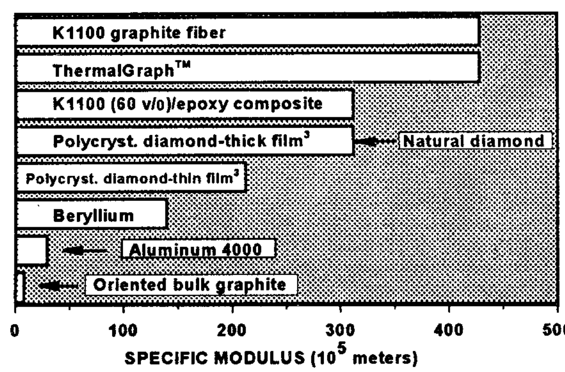

Figure 3. Longitudinal specific modulus of carbons/metals.

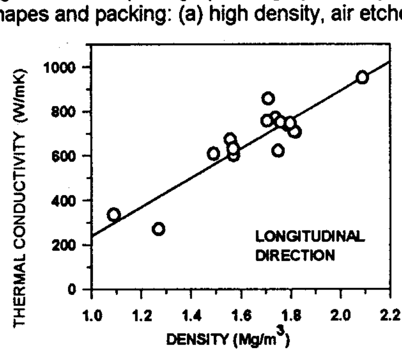

Figure 2. Thermal conductivity - density plot.

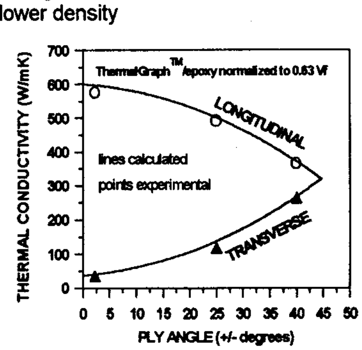

Figure 4. Thermal conductivity - ply angle plot.

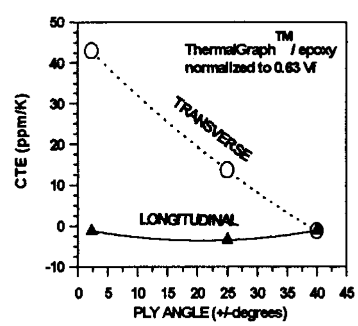

Figure 5. CTE as a function of ply angle.