

CARBON-CARBON COMPOSITES FOR THERMAL MANAGEMENT

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ABSTRACT

Composite materials based on vapor grown carbon fibers (VGCF) have the potential of thermal conductivity greater than 1200 W/m-K. Challenges are to create composite materials that can exploit the thermal properties of VGCF while meeting the cost demands of the emerging applications. In situ polymerization of wetting monomers is a method of carbon-carbon infiltration which offers significant advantages in thermal properties, infiltration time and production cost. Composites densified using this method showed excellent thermal conductivity in comparison to previous carbon-carbon composite data obtained. Additionally, with the use of in situ polymerization to densify the composites, the composite processing time was dramatically reduced, establishing feasibility of fabricating high performance composites for thermal management with rapid turn-around and at significantly lower cost over conventional pitch impregnation or chemical vapor infiltration. A single densification cycle required only 4 hours, in contrast to the approximate 100 to 200 hours per cycle required for CVI and pitch infiltration. The combination of VGCF and in situ densification offers new degrees of freedom in design of high performance thermal management materials with controlled CTE.

Keywords

(vapor grown carbon fiber, carbon composites, thermal management)

INTRODUCTION

The market for high thermal conductivity materials is an emerging market driven by the continuing trend toward miniaturization at all levels of electronic packaging.¹ However, along with being highly thermally conductive, ideal electronics thermal management materials must also meet other stringent requirements, including low coefficients of thermal expansion (CTE) to minimize thermal stresses that affect reliability and performance.

Materials are needed with thermal conductivity much higher than conventional electronic packaging materials – up to a factor of three higher than copper. In response to these needs, an increasing number of ultrahigh-thermal-conductivity advanced materials have been developed that offer significant improvements, such as Vapor Grown Carbon Fiber (VGCF).

VGCF is synthesized from the pyrolysis of hydrocarbons or carbon monoxide in the gaseous state in the presence of a catalyst; in contrast to a melt-spinning process common to other types of carbon fiber. The thermal conductivity of VGCF is unmatched by pitch- or PAN-based carbon fibers, approaching that of single crystal graphite and diamond. The room temperature conductivity of individual VGCF fibers has been measured at 1950 W/m-K. Composites of VGCF hold records for thermal conductivity in various polymer matrices, as well as aluminum, copper and carbon matrices. The highest observed values of thermal conductivity in a carbon fiber composite are in VGCF-carbon composites; however, the cost and preparation time have been two major impediments to higher utilization of carbon-carbon composites.

¹ According to the Georgia Institute of Technology National Science Foundation Packaging Research Institute, the worldwide market for just microelectronic packaging in 2000 was \$100 billion.

The physical properties of VGCF in some instances can approach those of single-crystal graphite. Single-fiber physical properties of VGCF were shown to approach those of single crystal graphite in measurements by Tibbetts and Beetz² and Tibbetts *et al.*^{3,4} These values provide a representative view of the physical properties possible in vapor grown carbon fibers. Of the carbon fiber reinforcements available for carbon/carbon composites, vapor grown carbon fibers have the highest known thermal conductivity.

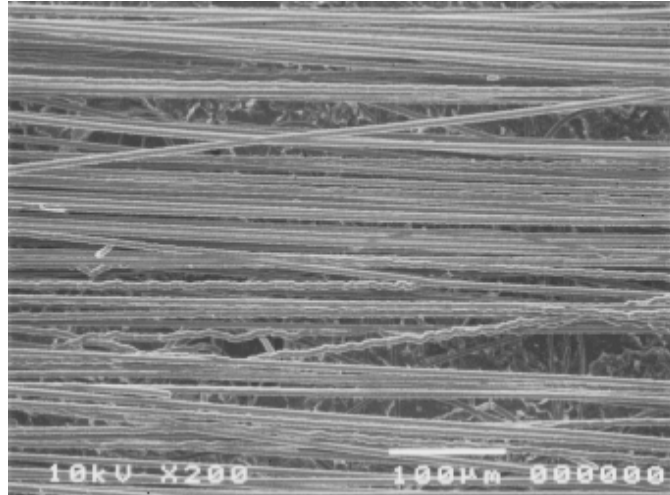


Figure 1. Micrograph of fixed catalyst VGCF showing the fibers are semi-aligned and semi-continuous. Composites of VGCF in matrices of carbon, metal and polymers hold records for thermal conductivity.

Carbon Nanofibers (CNF), a form of VGCF, are graphitic filaments having a diameter of approximately 100 nm and an aspect ratio greater than 100. In properties of physical size, performance improvement, and production cost, CNF completes a continuum bounded by carbon black, fullerenes, and single wall to multi-wall carbon nanotubes on one end and continuous carbon fiber on the other. Carbon nanofibers are able to combine many of the advantages of these other forms of carbon for reinforcement in engineered polymers. Carbon nanofibers exhibit a graphitic index that approaches that of single crystal graphite, suggesting similarly comparable values for transport and mechanical properties, but can be made in high volumes at low cost — ultimately lower than conventional carbon fibers. CNF provide enhanced electrical conductivity and mechanical reinforcement of certain matrix materials, as well as improved heat distortion temperatures.

². G.G. Tibbetts and C.P. Beetz, Jr. *J. Phys D: Appl. Phys.* **20**, 292 (1987).

³. G.G. Tibbetts, M. Endo, M., and C.P. Beetz, *SAMPE Journal*, **22** No. 5 (1986).

⁴. G.G. Tibbetts, G.L. Doll, D.W. Gorkiewicz, J.J. Moleski, T.A. Perry, C.J. Dasch, and M.J. Balogh, *Carbon*, **31**, No. 7, pp. 1039-1047 (1993).

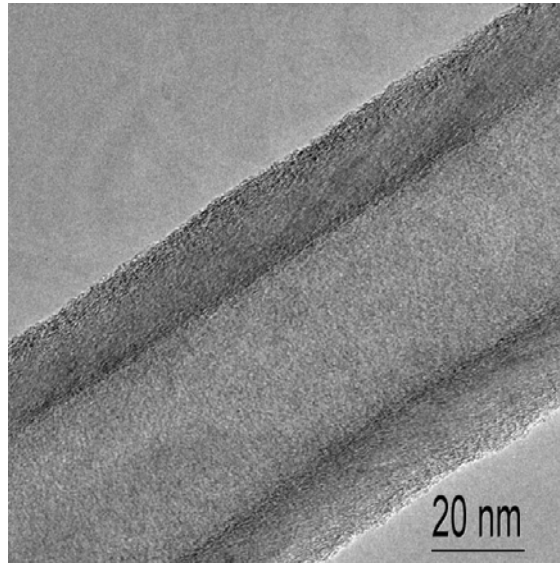


Figure 2. TEM showing the structure of a VGCF, including the hollow core, conical interior planes, and exterior disordered layer

One objective of this work is to assess the benefit of a combination of these novel graphitic additives as well as graphitic flake (EG30 from SGL Carbon) to achieve an optimal loading of graphite in the composite.

EXPERIMENTAL

Composite Design

Composites were designed to yield highest possible thermal conductivity in a single direction (X direction), with sufficient reinforcements placed in off-axis direction to provide mechanical strength and heat spreading. Four fiber architectures were studied under this effort. The first design (see figure 3) was a total of 60% by volume of primary high thermal conductivity VGCF carbon fiber reinforcement, with 80% in the X direction, and 10% fiber in each for the ± 45 degree directions from the X axis. The second design (see figure 4) was also 60 % volume fraction, with 80 % VGCF in the X direction, but with 10% volume fraction YSH pitch based carbon fiber fabric (Nippon Graphite) balanced plain weave in a 0/90 orientation, and 10% volume fraction in a ± 45 orientation with respect to the X axis.⁵ The third design was again 60 % volume fraction and had only YSH pitch weave with 50 % in a 0/90 orientation and 50 % in a $\pm 45^\circ$ orientation to determine the conductivity contribution of the fabric material in a carbon-carbon composite. The fourth design was 60 % volume fraction with 90 % VGCF in the X direction and 10 % volume fraction YSH pitch weave in 0/90 orientation.

A second set of preforms was prepared to test the contributions to thermal conductivity from addition of nanoscale graphitic components such as CNF and graphite flake. Several designs were used which varied the amounts of VGCF and VGCNF to test the effect of total graphite loading. One composite design was composed exclusively of VGCF with a 70 % fiber volume; one composite design was composed of only EG30 graphite flake from SGL Carbon, while other designs included VGCNF and EG30 at varied weight loadings as well as varied VGCF loadings. The VGCF type used was mat fiber that has undergone a heat treatment to 3000°C, from Applied Sciences, Inc. The VGCNF type used was PR-24 HHT XT LD from Pyrograf Products, Inc. Table 1 lists the design and compositions of the composites.

⁵ YSH is the only high thermal conductivity mesophase-pitch-derived fiber available in fabric and in small quantities.

Table 1. Composite Compositions

	VGCF Fiber Volume %	EG30 Graphite Flake Weight %	VGCNF Weight %
Comp. 1	70	0	0
Comp. 2	70	7	4
Comp. 3	0	85	0
Comp. 4	60	20	5

Preform Fabrication

Appropriate lengths of VGCF were spread by hand on the base of a compression mold in the designed fiber lay-ups. The thin layers of the aligned fibers were saturated with furfuryl alcohol through drop-wise addition. VGCNF and graphite flake were incorporated into the preform by weighing the appropriate amounts and dispersing the materials combination in the furfuryl alcohol through sonication for 5 minutes. The furfuryl alcohol, when heated in the presence of maleic anhydride powder, acts as a binder to create a rigidized preform of carbon fiber. The rigidized preform is then molded for 4 hours at 180°C and 3500 psi. The fiber volumes in the preforms were controlled by compression to prescribed volumes using mold stops. After molding, the resulting panels were trimmed, measured, and weighed in preparation for carbonization.

The rigidized preforms were framed between graphite plates during carbonization. Carbonization was conducted by slowly heating the panels to 1000°C (1832 °F), at a ramp rate of 0.3 °C/min., in a nitrogen atmosphere. This process was carried out over a 3 day period. After carbonization, the composites were heat-treated to 3000°C. at GrafTech. Following graphitization the composites were sent Ohio University for initial thermal conductivity testing.

Composite Densification

Composites were densified using in-situ polymerization. This technique is a rapid, low-cost method which imparts a highly graphitizable matrix, and is capable of uniform densification of thick parts. Rigidized preforms are impregnated with low-viscosity, low molecular weight monomers such as naphthalene. Following impregnation, polymerization is initiated to yield a high molecular weight matrix precursor, which is then pyrolyzed.

Thermal Conductivity Measurement

The laser flash diffusivity method was used to determine thermal conductivity. This testing was conducted at Ohio University, in Athens, OH. In this method, the diffusivity, α , is measured directly, as well as the specific heat, C_p , and the density, d . The relationship between the thermal conductivity, λ , and the aforementioned directly measured quantities is

$$\lambda = \alpha C_p d \quad (1)$$

The specific heat and density can be accurately measured on small specimens. The diffusivity measurement is obtained by heating the front face of a small specimen with a short (one millisecond or less) burst of radiant energy, usually a laser or xenon flash lamp. The temperature rise on the back face of the specimen is measured by thermocouple or an infrared detector.

The typical sample thickness, l , for this test is approximately one to two millimeters; however, with materials of high thermal conductivity, $t_{1/2}$ is sufficiently short that the diffusivity measurement is noisy, and less accurate. Therefore, samples of VGCF-reinforced carbon composites were cut to a thickness of 0.5 inches. The temperature range for these measurements is typically from room temperature to 600°C. The thermal conductivity measurements performed for this work were performed at room temperature.

RESULTS

The thermal conductivity values listed in Table 1 compare very favorably with all previous data on VGCF-carbon composites. Previous to this work, the highest known final thermal conductivity value for any carbon-carbon composite, 910 W/m-K, was achieved with a VGCF/carbon composite. These values have been reached when using higher fiber loadings (70%), achieving a higher final density (1.88 gm/cc), and heat treating to 3100°C. Extrapolating from the data in Table 1, a composite with comparable loading and density would be expected to exhibit a thermal conductivity of approximately 1150 W/m-K. The thermal conductivity value is enhanced by a significant contribution from the matrix carbon introduced through in situ polymerization. Initial testing of VGCF/carbon composites produced using the in situ method for densification yielded a thermal conductivity contribution from the matrix of approximately 800 w/m-K/gm, comparable to that obtained from one-dimensional VGCF preforms alone. Two densification cycles, each followed by a graphitization step, have yielded composite densities of approximately 1.6 gm/cc.

	Sample ID	Thermal Diffusivity (cm ² /s)				Density (kg/m ³)		Thermal Conductivity (W/mK)			
		Composite w/ Advanced Precursor		Composite w/ Naphthalene Precursor		Advanced Precursor	Naphthalene Precursor	Composite w/ Advanced Precursor		Composite w/ Naphthalene Precursor	
		x	y	x	y			x	y	x	y
VGCF Pyrograf-I	2294-1	1.26	4.81	1.11	5.07	1566	1580	142	542	126	577
	2294-3	0.93	4.91	1.01	5.14	1566	1580	105	554	115	585
	2294-5	1.05	4.98	1.19	4.00	1566	1580	119	562	135	455
	2294-7	1.21	4.64	1.06	5.14	1566	1580	136	523	121	584
	2294-8	1.19	4.70	1.10	5.13	1566	1580	134	530	125	584
VGCF & Pitch	2294-2	1.03	4.18	1.24	3.05	1497	1508	111	450	134	331
	2294-4	1.12	3.74	1.25	4.46	1497	1508	121	403	136	484
	2294-6	1.22	4.29	1.30	4.68	1497	1508	132	463	141	509
	2294-9	1.33	3.77	1.53	4.47	1497	1508	143	407	166	485
	2294-10	1.16	3.86	1.14	4.08	1497	1508	125	416	124	443
All Pitch	2294-18	2.14	2.39	1.96	1.97	1623	1656	250	280	234	234

Table 2. Thermal Conductivity results for composites densified by in situ polymerization.

Thermal conductivity measurements were made on VGCF/CNF and VGCF/CNF/graphite flake preforms following one graphitization cycle to 3000 °C. Thermal conductivity measurements are listed in Table 3. Densification cycles using in situ polymerization are in progress.

Table 3. VGCF/CNF Preform Characteristics

COMPOSITE #	Density (kg/m ³)	Heat Capacity (J/kg K)	1-D Thermal Conductivity (W/m K)
1	1179.5	720	513.9
2	1209.8	720	495.2
3	1366.0	720	132.9
4	1426.0	720	405.1

CONCLUSIONS

Miniaturization and increased power loads on electronics defines a need for materials with very high thermal conductivity. Carbon-Carbon composites have potential for high thermal conductivity, but cost and preparation time have been prohibitive factors in their widespread use. This work is part of an investigation into maximizing the thermal conductivity of carbon-carbon composites while minimizing the preparation time as well as cost. In this investigation several composites were fabricated using VGCF and CNF with varied graphite loadings. Although the work is still underway, the investigation to this point has revealed a hierarchy of factors that determines the thermal conductivity in carbon-carbon composites, dominated by aspect ratio of the filler material, and followed by total graphite loading and interphase characteristics between the graphitic fillers.

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