

INFLUENCE OF HEAT TREATMENT ON THE PROPERTIES OF HIGH THERMAL CONDUCTIVITY GRAPHITE COMPOSITES

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Introduction

Thermal management is key to improving the performance and reliability of electronics systems. The use of ‘traditional’ packaging materials (e.g. aluminium and copper), limits conductive cooling efficiency, especially for high heat fluxes. This has driven development of ‘third generation’ high-performance materials which have ultra-high thermal conductivities, low coefficients of thermal expansion and low densities (1). Most of these materials incorporate carbon in some form. Natural crystalline graphite, with its high in-plane thermal conductivity and relatively low cost, is very attractive for thermal management. Foil materials are well-established, and anisotropic composites are marketed (e.g. for heat sinks), and continue to be developed. There are several examples of carbon-bonded materials in the literature. Mesophase pitch as a binder could, quite reasonably, be expected to produce the highest conductivity composites (2,3). However, factors of cost, availability and processing requirements, remain drivers to look at alternative binders.

Experimental

Composites were made with a commercial large flake graphite (average flake size 450 μm) mixed with a phenolic (novolak) resin. Typically less than 10% binder is used, and one level used throughout this report. Plates were pressed at room temperature, and subsequently pressed at temperature (typically 100 to 150C).

In-plane (IP) thermal conductivity was measured on the plates using a ‘Searle’s Bar’ method. Tests with copper and aluminium plates showed good agreement with expected conductivity values. Through-plane (TP) conductivities were calculated from thermal diffusivity values obtained by conventional laser flash method. IP electrical conductivity was measured by standard four-probe method. TP electrical conductivities were measured using a two-probe method

Results and Discussion

The presence of the large flake graphite particles produced, upon pressing, a highly-aligned composite material, with consequent anisotropy of the bulk properties. Although the electrical and thermal transport mechanisms are different, the properties for some carbons have been correlated (4). It became clear that correlations could be established for the composites in this work (see Fig. 1). Here, the plots are for one composition processed under a number of conditions before curing (cold-pressed material having the lowest conductivities after heat treatment). The plots can be fitted to

straight lines with R-squared values of 0.93 and 0.98 for heat treatment to 900C and 2500C respectively. The linear correlation demonstrates that the improvements in the continuity and alignment induced in the structure have equivalent effects on both transport properties.

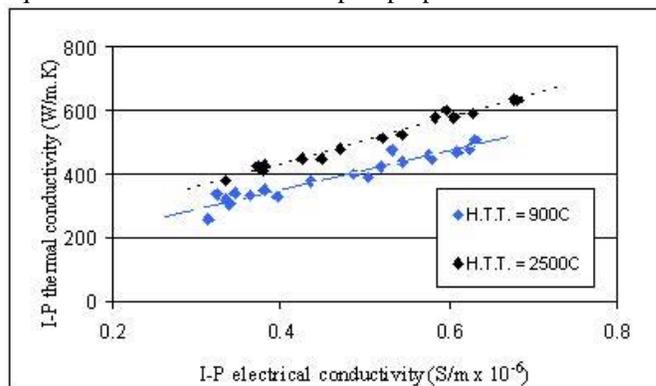


Fig. 1 IP thermal conductivity against electrical conductivity for a range of different forming conditions.

The IP thermal conductivity increases markedly (typ.c.27%), between the heat treatment temperatures of 900C and 2500C. The magnitude of this increase was unexpected, given the low content of a binder which is ‘non-graphitising’ in nature. Not so unexpected was the increase (typ. c.22%), in conductivity from the cured to the carbonised state (see Fig. 3.2). Here, a significant increase in conductivity of the binder was expected with its transformation to a glassy, ‘turbostratic’ carbon.

Comparative trials made with graphite pre-heat treated at 2500C showed that the conductivity increase upon ‘graphitisation’ was not simply enhancement of the graphite filler. There were no significant differences between the thermal conductivities after 900C and 2500C heat treatments (Table 1). A difference was found, however, between electrical conductivities of the materials after curing. The composite of pre-treated graphite exhibited lower weight losses and slightly higher densities. This may result from the effects that different carbon fillers can have on the decomposition of novolak resins (5).

Table 1: In-plane Conductivities of Composites made with ‘As-received’ and Pre-treated (2500C) Graphite Filler

HTT	Hot-pressed	Cured	Carbonised		Graphitised	
		250C	900C		2500C	
	Elec.	Elec	Elec.	Therm	Elec	Therm.
	$\mu\text{S/m}$	$\mu\text{S/m}$	$\mu\text{S/m}$	W/m.K	$\mu\text{S/m}$	W/m.K
As-received	0.21	0.16	0.54	487	0.56	640
Pre-treated	0.21	0.14	0.49	522	0.52	622
<i>t-test P-value</i>	<i>0.717</i>	<i>0.013</i>	<i>0.026</i>	<i>0.192</i>	<i>0.020</i>	<i>0.403</i>

Microstructural examination of carbonised samples, viewed under polarised light with a tint plate, found the binder in a carbonised hot-pressed material to be a generally thin (typically < 5 microns thick) isotropic phase between the optically-anisotropic graphite flakes (Fig. 2.1). In the equivalent graphitised material, the binder exhibited interference colours (Fig. 2.2), showing that it had undergone

a structural change as a result of the heat treatment. This is direct evidence that the binder has developed a graphitic character.



Fig. 2.1 Optical micrograph of carbonised composite



Fig. 2.2 Optical micrograph of graphitised composite

The thinnest layers between graphite flakes generally exhibited interference colours corresponding to the adjacent graphite, with equivalent change in colour upon rotation, indicating that the binder structure was aligned with that of the flake's (basal) surface. Where the alignment of flakes was poorer or disrupted the binder in these regions took on a more 'microcrystalline' appearance, indicating a lower structural alignment with the flakes. The transformation was found for cold and hot-pressed materials, consistent with the conductivity increase upon graphitisation of both materials.

The significant increases in thermal conductivity upon graphitisation for composites made from both as-received (0.16 wt% ash) and pre-treated (ash <0.01%) graphites (Table 1), together with the observed formation of anisotropic binder in both cases suggest that this was not impurity-catalysed graphitisation. More likely is 'stress graphitisation', resulting from differential shrinkage of the graphite and resin (6,7).

Although there are correlations between the IP thermal and electrical conductivities, the responses of the electrical and thermal properties to heat treatment temperature have some significant differences. It is evident from Fig. 3.1 that electrical conductivity is sensitive to heat treatment between the cured and carbonised state, both IP and TP (c.4x and 10x increases respectively). Similarly, Fig. 3.2, the IP and TP thermal conductivities also increase on heat treatment to 900C, though to a lesser extent than electrical. The greater response of the TP conductivities may be expected, considering the influence the increase in conductivity of the binder phase will

have in such an anisotropic material. It was further noted that the ratio of the % increase through-plane to that in-plane was the same ($\% \Delta TP / \% \Delta IP = 2.9$) for electrical and thermal conductivity, which might be predicted for an isotropic binder. The value of this ratio should be related to the microstructure of the composite.

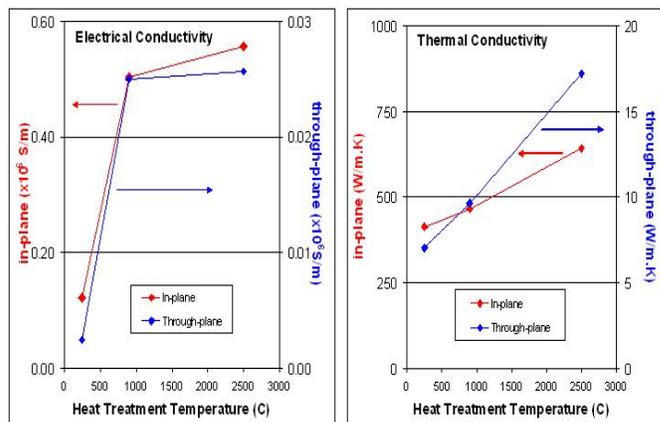


Fig. 3.1 and Fig. 3.2 IP and TP conductivities vs. HTT

Upon heat treatment to 2500C, despite noted change in the binder, there is relatively little effect on electrical conductivities. However, the effect on thermal conductivity is significant, and, again, the relative increase in TP conductivity is greater ($\% \Delta TP / \% \Delta IP = 2.1$).

Conclusions

With optimised conditions, composites made from a commercial large flake graphite and resin can achieve in-plane thermal conductivities exceeding 600 W/m.K. Correlations were established between the in-plane thermal and electrical conductivities, the apparent direct relationship resulting from the dependence of these properties on the composite's structure. Transformation of an ostensibly 'non-graphitisable' binder, first from the cured state to an optically-isotropic carbon, then from the carbon to an optically-anisotropic phase, can have significant effects on conductivity (both thermal and electrical), more so for the through-plane than the in-plane properties. Graphitisation of the binder had little effect on the electrical conductivity of the composite, indicating that this microstructural change was of more consequence for phonon transport than transport of charge carriers.

Acknowledgment. Acknowledgment is made to the Morgan Crucible Company for permission to publish.

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