The Development of a Natural Graphite Heat-Spreader

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Abstract

The ongoing need for miniaturization and speed in the electronics industry has brought about a requirement for better performing thermal management systems. Thermal management technology remains a vital part of electronics innovations for notebook computers, high-performing CPU chipsets, mobile electronic appliances and power conversion [1]. Typical thermal management systems consist of external cooling mechanisms, heat dissipaters, and thermal interfaces. The primary function of the heat dissipaters, e.g. heat sinks, is to create the maximum effective surface area where heat is transferred into and carried away by the external cooling medium. Performance of a heat dissipater is conventionally characterized by its intrinsic thermal conductivity, physical surface area, and pressure drop (or drag) coefficient [2]. An additional variable, namely heat spreading coefficient (α), has been introduced by Tzeng [3]. The heat spreading coefficient has to be considered when the heat dissipater is a thermally anisotropic material. A high degree of thermal anisotropy reduces the temperature gradient in the plane of the part and increases the effective heat transfer area, characteristics that are most desirable for electronics with high heat-intensity components. The ability to direct heat in a preferred direction is an additional advantage of an anisotropic heat-spreader material. Carbon and graphite-based materials are attracting interest as anisotropic heat-spreaders, with an additional advantage being their low density. Most carbon and graphite-based materials used to date are based around carbon fibers. These are high cost by virtue of the need to conduct high temperature graphitization processes to develop the required thermal properties in the fiber. A new form of graphite heat-spreader material is described in this paper, based around naturally occurring graphite. Because this material has been graphitized "by nature", anisotropic heat-spreaders with high thermal conductivity can be manufactured without using traditional carbon fiber-based additives.

Manufacture of Natural Graphite Heat Sinks

Natural graphite, the mineral form of graphitic carbon, occurs worldwide [4]. The ore usually contains silicate materials which have to be removed. In its final form it is classified according to its purity, with high grade containing 95-96% carbon and low grade 90-94% carbon. It is possible to chemically purify the material to achieve a carbon content greater than 99.5%.

Graphite is a crystalline form of carbon wherein the atoms are bonded in flat layers (basal planes) with weaker van der Waals bonds between the layers. Each of the basal planes is comprised of hexagonal arrays or networks of carbon atoms. These basal planes are substantially flat and are oriented or ordered parallel to and equidistant from one another to form crystallites. Highly-ordered graphite consists of crystallites of considerable size, with the crystallites being highly aligned or oriented with respect to one another and having well-ordered basal planes. The graphite structure is typically described as having two axes -- the "a" and "c" axes or directions. In this context, the "a" axis is in a direction parallel to basal planes and the "c" axis is in a direction perpendicular to the basal planes and the "a" axis. Because of the markedly different nature of the bonding in the "a" and "c" directions, graphite exhibits structural anisotropy and possesses many properties that are highly directional, e.g., thermal and electrical conductivity. Natural graphites possess a very high degree of structural anisotropy which make them ideal starting materials for heat-spreader components.

Natural graphite is commonly obtained in the form of a flake. There are many ways of manufacturing products from this natural graphite material, depending on the finished shape required. In the manufacture of flexible graphite sheet for example [5], natural graphite flake is treated with an oxidizing agent such as a solution of nitric acid and sulfuric acid to form an intercalated compound with graphite. Upon heating at high temperature, the intercalants in the graphite crystal form a gas that causes the layers of the graphite to separate and the graphite flakes to expand or exfoliate in an accordion-like fashion in the c-direction, i.e., the direction perpendicular to the crystalline planes of the graphite. The result is the production of particles having a vermicular or worm-like structure. The expanded flakes are then compressed into sheets which are flexible and can be formed and cut into various shapes. The sheets retain the structural anisotropy of the raw flake. The material has found wide use as a thermal interface material [3] because of its combination of high thermal conductivity and excellent surface conformability. For heat-spreader applications, the same high thermal conductivity properties are important, together with the low density afforded by a graphite-based material. Described below are two forms of natural graphite heat-spreader developed to date, one of which uses a laminating process to produce thick plates of graphite, and the other which uses natural graphite in the form of a molding compound to allow manufacture of more complex net shapes by compression molding.

Laminate Material

This material is formed by chemically bonding individual sheets of graphite together to produce a laminate up to

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1.5 meters wide and several centimeters thick. The material can be heat treated after bonding to prevent outgassing during operation. If required in other than plate form, the material can be subsequently machined into components; materials at various stages of processing being shown in Figure 1. A typical cross-section through a laminate material is shown in Figure 2, with the bond lines between the individual graphite sheets being apparent.

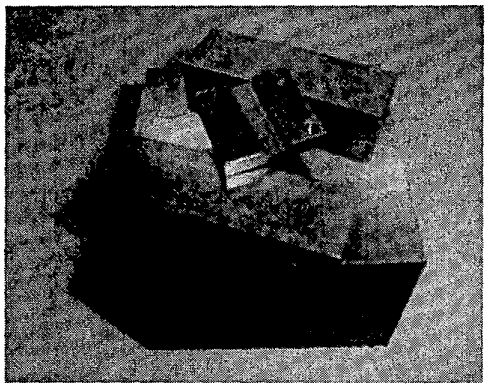

Figure 1 - Examples of Laminated Plate Material.

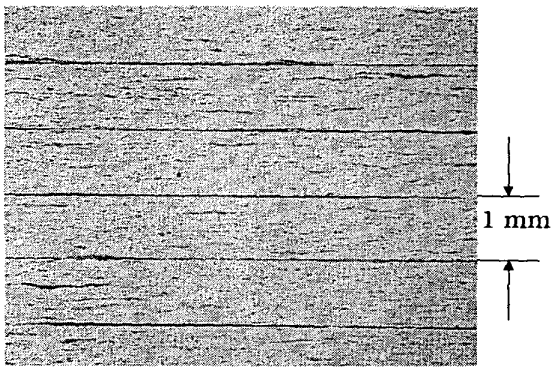

Figure 2 - Polished Cross-Section Through Graphite Laminate.

As discussed above, the material properties retain the characteristics of the graphite flake and are highly anisotropic. Typical properties of the material are shown in Table 1. All measurements were performed at room temperature unless otherwise specified. Thermal conductivity values were obtained using a thermal diffusivity technique (ASTM designation C 714-85). Electrical resistivity was measured according to ASTM C-611 with flexural strength (3 point, span/thickness = 8:1) and interlaminar shear strength (span/thickness = 4:1) being measured according to ASTM standards C1161-94 and D2344-84, respectively. Thermal expansion coefficient was measured using the Parma Automated Thermal Extensometer (PATE) method.

Table 1
Properties of Typical Graphite Laminate Materials

Property	Units	Direction	Value
Density	g/cm^3		1.33
Thermal Conductivity	$W/m \cdot K$	In-Plane	233
Thermal Conductivity	$W/m \cdot K$	Thickness	4.5
Thermal Anisotropy			52
CTE (30 °C-100 °C)	$10^{-6}m/m/°C$	In-Plane	-0.77
Resistivity	$\mu ohm \cdot m$	In-Plane	4.9
Young's Modulus	GPa	In-Plane	13
Flexural Strength	MPa	In-Plane	11
Shear Strength	MPa	In-Plane	0.18

The main feature of the material is its thermal anisotropy. In-plane thermal conductivity (in-plane is parallel to the sheet direction) is ~230 $Wm^{-1}K^{-1}$, compared to ~4.5 $Wm^{-1}K^{-1}$ through the thickness of the laminate. This yields a thermal anisotropy ratio of ~52 and allows for directional control of heat flow for applications in which this is desired. The low density of the material (~1.3 g/cm^3) results in specific in-plane thermal conductivity values 2.6 x that of aluminum 6061 and 3.8 x that of copper (Table 2). There is, therefore, the potential of significant weight savings using these graphite materials. Obviously, no directional control of heat flow is possible with isotropic metals. The low in-plane resistivity and negative thermal expansion values are typical of highly oriented graphitic materials. The Young's modulus and strength values are typical for a coarse grained graphite. The material is significantly lower in strength than carbon fiber-based polymer composites and cannot be considered a structural material, although this is not an issue for a number of passive heat management applications. In addition, in cases where it is required to directly retrofit a metal part with a natural graphite heat sink, the graphite can be cast within a metal casing.

The processing of the laminate allows some control of the density of the material, with densities varying in the range of 1.1 - 2.0 g/cm^3. Experience with graphite sheet [6] has shown that increasing density results in an increase in strength and thermal conductivity and a decrease in electrical resistivity. It seems reasonable that the thermal conductivity will approach that of copper as the density of the laminate approaches 2.0 g/cm^3. The density of the material needs to be optimized for the particular application.

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Table 2
Thermal Conductivity Comparison of Graphite Laminates with 6061 and Copper

	Graphite Laminate	Aluminum 6061	Pure Copper
Density (g/cm^3)	1.33	2.7	8.96
Thermal Conductivity (In-Plane) ($W/m \cdot K$)	233	180	400
Specific Thermal Conductivity ($W \cdot m^2/kg \cdot K$)	0.175	0.067	0.045
Thermal Anisotropy	52	1	1

The material contains no binder phase and so it can withstand temperatures typical for graphite materials (up to ~400 °C in air, up to 3000 °C in a non-oxidizing environment).

Some interesting composite derivatives of this material can be produced by laminating graphite with other metals, this process being well established in traditional markets for natural graphite sheet in fluid sealing and automotive applications. As an example, Figure 3 shows an optical micrograph of a laminate prepared using a perforated copper sheet. Perforation or tanging of the copper results in mechanical interlocking of the graphite sheets, increasing the strength, stiffness and toughness of the material. The thermal expansion coefficient, resistivity and thermal conductivity of the material is altered significantly by the addition of copper, allowing the ability to tailor properties according to the application.

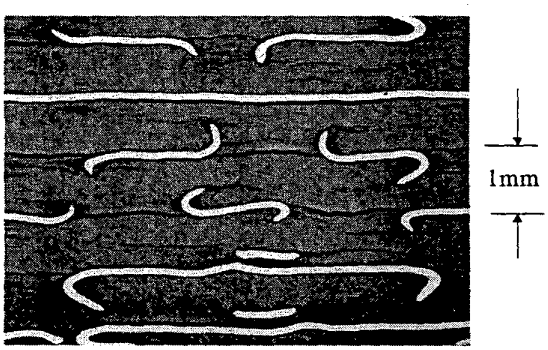

Figure 3 - Polished Cross-Section of Graphite/Copper Laminate.

Compression Molded Materials

In the manufacture of natural graphite sheet, various techniques have been developed for impregnating the expanded graphite with resin (as an example [7]) so that a composite material can be manufactured comprising natural graphite in a resin matrix. It is possible to produce molding compounds from these materials which can then be subsequently pressed into shapes using various methods (die-pressing, isomolding). Depending on the complexity of the heat-spreader design, it is possible to manufacture near-net shape components or to machine these blocks into the final shape. Examples of both net shape and machined products produced from epoxy-impregnated natural graphite are shown in Figure 4.

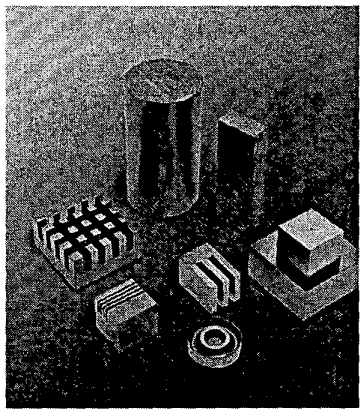

Figure 4 - Examples of Products Manufactured from Epoxy-Impregnated Natural Graphite.

A typical micrograph of an epoxy/graphite compression-molded part is shown in Figure 5. An intimate mixture of natural graphite and epoxy resin is apparent with very little porosity.

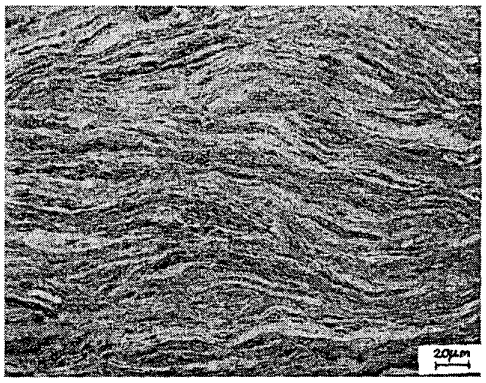

Figure 5 - Polished Cross-Section Through Epoxy/Graphite Compression-Molded Part.

The properties of the material can be varied over a broad range according to the proportions of resin and graphite and the molding technique used. Typical properties of the material are shown in Table 3. As with the laminate materials it is possible to produce highly anisotropic materials, with values of in-plane thermal conductivity as high as 200 $Wm^{-1}K^{-1}$, with corresponding through thickness values being ~ 8 $Wm^{-1}K^{-1}$. The ratio of the in-plane to through thickness thermal conductivity can be varied through processing changes, and nearly isotropic properties can be achieved. It is therefore possible to produce a material in which the relative amounts of heat flowing in different directions can be controlled, this not being possible with aluminum and copper.

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Table 3
Typical Properties of Compression Molded Materials

Property	Units	Direc-tion	Typical Value	Range
Volume Fraction Graphite	%		68	55-100
Volume Fraction Resin	%		32	0-45
Density	g/cm^3		1.59	1.5-1.9
Specific Heat Capacity (25 °C)	J/g°C		0.94	0.71-1.05
Thermal Conductivity	W/m·K	In-Plane	201	57-202
Thermal Conductivity	W/m·K	Thick-ness	7.7	7-71
Thermal Anisotropy			26	1-27
Resistivity	μohm·m	In-Plane	9	9-18
Resistivity	μohm·m	Thick-ness	98	52-98
CTE (30-100 °C)	10^{-6}m/m°C	In-Plane	20	3-24
CTE (30-100 °C)	10^{-6}m/m°C	Thick-ness	28	9-41
Flexural Strength	MPa	In-Plane	37	31-40
Young's Modulus	GPa	In-Plane	20	19-24

The density of the materials produced via this method is in the range of 1.5-1.9 g/cm^3, so significant weight benefits can still be achieved compared with aluminum and copper.

The electrical resistivity also varies with direction, and the degree of anisotropy can again be modified. Typical values are ~9 μohmm in-plane and ~100 μohmm through thickness.

The thermal expansion coefficient is largely dominated by the epoxy resin, usually resulting in much higher values than those reported for the laminate material. Reducing the mass fraction of resin reduces both the in-plane and through thickness values of thermal expansion coefficient.

The strength and modulus of these materials are significantly higher than those of the laminate materials (by a factor of three for strength and two for modulus), by virtue of the epoxy matrix. Machinability of the compression-molded materials is also superior.

The upper use temperature of these materials is limited by the epoxy resin system. Some resin systems (e.g., phenolics) can be used which can be converted to a carbon matrix during inert atmosphere pyrolysis to produce a graphite/carbon composite material. This will extend the temperature capability of this type of material.

Conclusions

New natural graphite-based heat-spreader materials have been developed, being available in the form of both laminates and compression-molded products. The materials are anisotropic, with the ratio of in-plane to through-plane thermal conductivity typically ranging from 5 to 50. The ability to control the anisotropy of these materials offers thermal engineers flexibility to channel heat in a preferred direction, and offers new design options that can reduce thermal failures in electronic devices. In addition, the low density offers the potential for replacing aluminum and copper in weight-sensitive applications.

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