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Thermal conductivity of CVD diamond fibres and diamond fibre-reinforced epoxy composites

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Abstract

Diamond fibres were fabricated using hot filament chemical vapour deposition (CVD) with tungsten wire of varying diameters as the cores. A steady-state technique was used to measure the thermal conductivity along the length of the individual fibres over a distance of 6 cm. The room temperature thermal conductivity of the fibres ranged between 750 and 1088 W m^{-1} K^{-1}. This is lower than values measured for CVD diamond thin films by other groups, due to the fact that the measurements were made perpendicular to the growth direction, and hence involved traversing a large number of grain boundaries. Epoxy composites containing the fibres were produced. The thermal conductivity of these composites was compared to metal bars of the same dimensions for both heating and cooling cycles. It was found that diamond composites are more efficient heat conductors than metal rods and can combine good lengthwise heat transfer with low heat transfer to the surroundings, as well as high electrical insulation. This makes them suitable for applications such as 'heat pipes' in electrical circuits.

Keywords: Diamond fibres; Thermal conductivity; Composites

1. Introduction

Diamond has the highest known thermal conductivity of any material at room temperature, with values up to five times that of copper [1]. The applications of diamond in thermal management are extensive, especially as high thermal conductivity values are combined with electrical insulation and high thermal stability. In its natural form, it is not easy to exploit this property, however, using chemical vapour deposition (CVD) techniques, diamond can be produced cheaply and in the more compliant form of thin films. Thin diamond films are proving to be effective heat sinks in micro-electronic devices and have found applications as heat spreaders for high power laser diodes and submounts for integrated circuits [2].

A review of the advantages and disadvantages of the various thermal conductivity measurement methods used for hard materials, including diamond, is given in Ref. [3]. Some methods reported include: a steady-state technique which is a variation of the 'heated bar' method [4]; laser flash heating [5]; and a variation of Angstrom's method (a time-modulated technique) [6]. However, the results from measuring thermal conductivity of diamond have been varied. Values for natural, gem quality diamond have been measured as high as 2500 W m^{-1} K^{-1} at room temperature [1,7]. CVD diamond thin films have been found to approach, or in some cases equal, this value, depending on the deposition conditions and the microstructure of the films. In a 'round robin' investigation of methods of thermal conductivity measurement [8], mean values for the different CVD diamond film samples were in the range of 1300–2000 W m^{-1} K^{-1}. The variations were due to the anisotropy inherent in CVD diamond films. Methods measuring the thermal conductivity perpendicular to the plane of the film gave higher values than those measuring the in plane thermal conductivity. This is because CVD diamond has a

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columnar structure, with grains orientated perpendicular to the substrate which increase in size as the film grows thicker. Phonon scattering occurs along the columnar grain boundaries and this accounts for the anisotropic thermal conductivity.

Factors influencing the diamond thermal conductivity were investigated by Gu et al. [9]. Methane concentration during deposition was found to have an effect on the thermal conductivity. Diamond films grown in low methane conditions had higher thermal conductivity. This was due to the decrease in the number of impurities, such as graphite, in the samples. Thermal conductivity also increased with film thickness. The upper portion of a film was found to have a higher local conductivity than the lower portion. This was due to the decrease in the number of grain boundaries which caused phonon scattering. As the film became thicker, the grain crystal size increased and the number of defects and grain boundaries decreased, so the upper layers of thick films were of better quality than the layers near the substrate [9].

However, all of these previous measurements of thermal conductivity were from thin films of areas <10×10 mm. Indeed, the measurements made through the thickness of the film are only from thicknesses of a few 100 μm. In our laboratory, it is now possible to deposit CVD diamond onto metal wire cores of diameters between 25 and 250 μm to produce 'diamond fibres' [10–16]. These fibres can be made with lengths up to 10 cm, and so this provides us with an opportunity to measure the thermal conductivity of the diamond over a much longer distance (and hence through many more grain boundaries) than previously reported.

We have previously embedded bundles of diamond fibres into metal [17,18] and plastic matrices [19] in order to make lightweight, stiff reinforced composites [20,21]. Plastic composites reinforced with diamond fibres could combine the high thermal conductivity of diamond with the insulating properties of the plastic, to give a 'heat pipe' which would be able to transfer heat efficiently from one point to another while remaining electrically and thermally insulated from the surroundings. One application might be in electronics or computing, where the localised heat source from the microprocessor needs to be removed to a radiator at the rear of the machine, without affecting sensitive components along the way. It has also been suggested that diamond fibres could be used as microheaters [22], utilizing the electrical conductivity of the wire cores and the thermally conducting and electrically insulating diamond coating. A current can be passed along the metal core providing a method for resistive heating, perhaps in metal matrix composites.

However, thermal conductivity values have not yet been measured for diamond fibres. The high values, small diameter and delicate structure of the fibres make typical methods of thermal conductivity measurement difficult, and therefore specialised apparatus must be purpose-designed. In this paper, we shall describe the apparatus built to measure the thermal conductivity of these diamond fibres, and compare the conduction behaviour of epoxy composites reinforced with diamond fibres to values from metal rods of the same cross-sectional area.

2. Experimental

2.1. Fibre deposition

The diamond fibres were deposited in a specially designed hot filament CVD reactor, described elsewhere [19]. The wire cores were tungsten metal of length 10 cm and diameters varying between 25 and 250 μm. The process gas mixture was 1% CH_4 in H_2, with total gas flow 200 sccm and pressure 20 Torr, and an estimated substrate temperature of ~900 °C, which gave a typical diamond growth rate of 0.5 μm h^{-1}. Films were grown for periods between 26 and 150 h to give a range of diamond film thicknesses. An example of a diamond fibre is shown in Fig. 1.

2.2. Thermal conductivity apparatus

The thermal conductivity of individual fibres was measured in a specially built apparatus, depicted in Fig. 2, which was designed to minimise all heat transfers except those along the fibre. The whole apparatus was positioned inside a vacuum vessel at a pressure of ~50 mTorr to minimise convection losses. The apparatus consisted of a low thermal conductivity PTFE frame connected to a large block of copper which acted as a constant temperature heat sink. The fibre was suspended in the vacuum with only two points of contact (at either end of the sample) in order to minimise losses by conduction. One end of the fibre was inserted into a hole in the copper block which remained at room temperature, and the other end was inserted into a hole

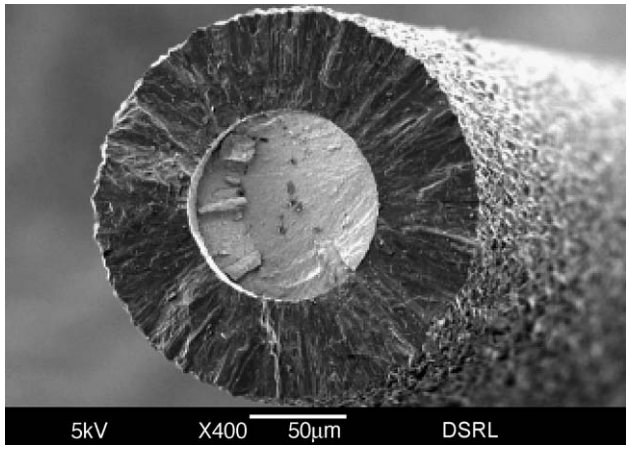

Fig. 1. Scanning electron micrograph of the cross-section of a typical diamond fibre, with tungsten core diameter 100 μm and diamond film thickness 50 μm.

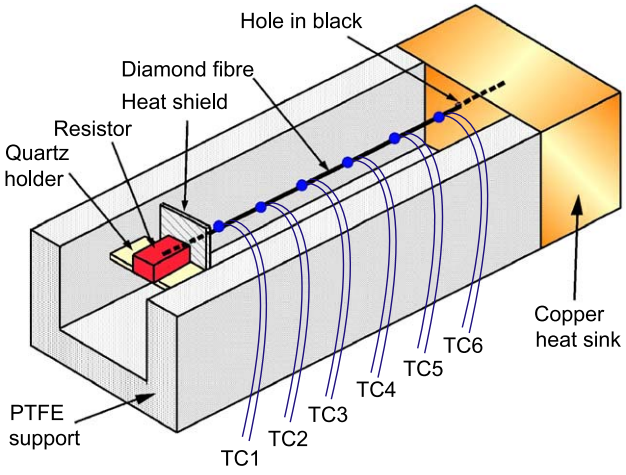

Fig. 2. Schematic diagram of the apparatus for measuring thermal conductivity of individual diamond fibres.

in a 100-Ω resistor, which provided the constant heat source. Six micro-thermocouples (Type K) were attached to the fibre at varying positions along its length using a tiny dab of heat-sink compound. Direct radiative heating of the thermocouples by infrared radiation from the heater was eliminated by a heat shield positioned immediately in front of the resistor. This heat shield was made from quartz wrapped in reflective Al foil.

Direct current (0.25–1.25 A) was passed through the resistor, and after about 10 min, the resistor achieved a steady-state temperature. At this time, the readings from the six thermocouples were collected by a data-logger and transferred to a computer. These measurements were then repeated for different values of the current through the resistor, and for all the different fibres under test.

2.3. Data analysis

The temperature values, T, were plotted against distance along the sample, l, and a straight line with gradient $\Delta T/\Delta l$ was fitted to the data. If a straight line was obtained, this showed that loss effects such as conduction and convection were negligible, and that the apparatus was measuring accurate values for heat transport. An example of such a plot is shown in Fig. 3. The gradient of this plot was then used to calculate the thermal conductivity using the equation [23,24]:

$$k = \frac{Q}{A\Delta T/\Delta l} \quad (1)$$

where k=thermal conductivity, Q=heat flux entering the fibre (in watts), A=cross-sectional area of fibre, and $\Delta T/\Delta l$=temperature gradient along sample.

2.4. Calibration

Since the efficiency of heat transfer from the resistor into the fibre was a function of fibre diameter, the value of Q (the amount of power in watts going into the fibre) was found to vary depending on the diameter of the fibre. The apparatus was therefore calibrated using different thickness copper wires (of known thermal conductivity), and Eq. (1) was used to calculate Q. These Q values were plotted against the cross-sectional area of the copper wires to give a calibration curve, from which the corresponding values of Q could then be read-off for diamond fibres of any thickness.

2.5. Composite fabrication

Transparent liquid epoxy (Araldite Vantico 2020) was used as a matrix for the diamond fibre composites. The epoxy was made by mixing a total of 5 cm^3 of the two components in a 3:1 ratio. The mixture was left to become more viscous for approximately 2 h and then poured into a V-shaped PTFE mould. A batch of identical diamond fibres was deposited (72 h on 100-μm tungsten cores) and then placed into the liquid so that they were parallel and lying lengthwise along the mould. The composite was then left to cure for 24 h. When hardened, the composite was removed from the mould and smoothed with wet-and-dry paper to give a composite test piece with a length of 8 cm and a cross-sectional area of 14 mm^2. The ends of the test pieces were filed smooth with the ends of the fibres exposed, to ensure efficient heat transfer into and out of the fibre.

The following composites test pieces were made (see Fig. 4):

1. Epoxy containing 100 diamond fibres in one bundle with the fibres in contact with one another.
2. Epoxy containing 100 diamond fibres in 3 layers. The composite was made in three stages. Each layer of epoxy contained 33 fibres and was left to harden before adding the next layer.
3. Epoxy containing 100 tungsten wires of 100-μm diameter in one bundle.
4. Epoxy (control sample).

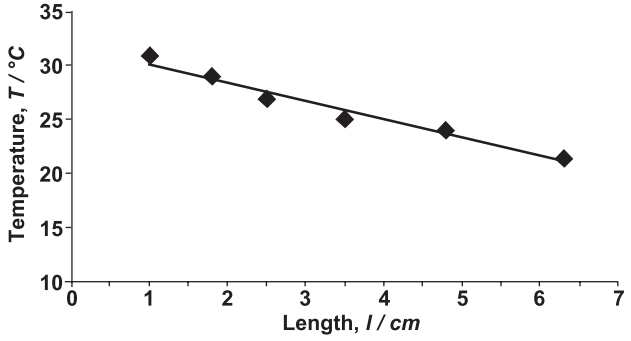

Fig. 3. Plot of temperature vs. length, l, along the diamond fibre (where l=0 is taken to be where the fibre exits the resistor) for a 180-μm diameter fibre (100-μm tungsten core with 40-μm diamond film) and with Q=2.97 mW.

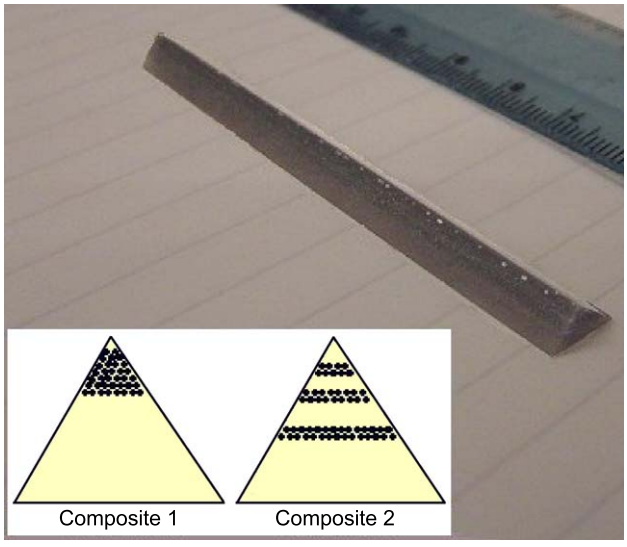

Fig. 4. Photograph of one of the epoxy composite test pieces. Inset shows a schematic diagram of the positions of the diamond fibres in composites 1 and 2 (note that the fibres are not drawn to scale).

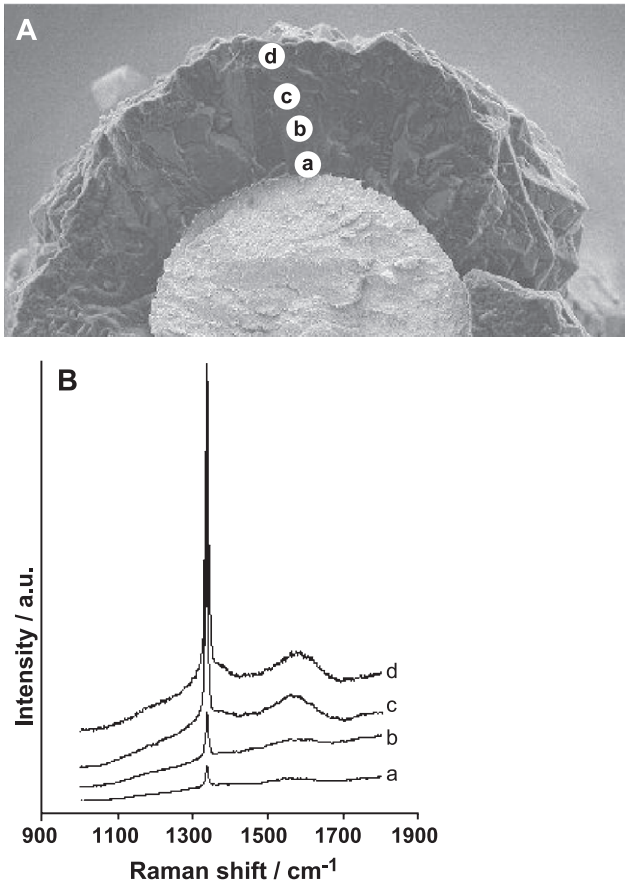

Fig. 5. (A) SEM cross-section through a diamond fibre showing the positions (a–d) from which laser Raman spectra in (B) were taken. The spectra were obtained in situ inside a Jeol scanning electron microscope using a combined laser Raman/SEM system (Renishaw) operating at 514 nm. The spectra were all taken with the same sensitivity, but have been offset vertically for clarity.

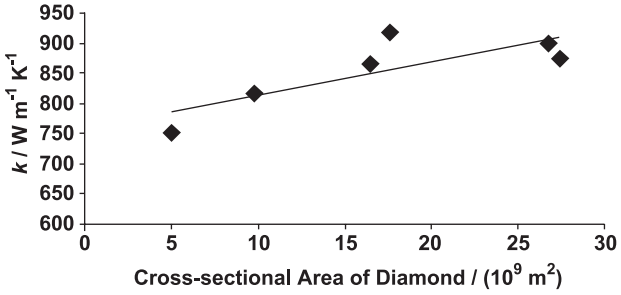

Fig. 6. The measured thermal conductivity, k, of diamond fibres grown onto 100-μm diameter tungsten cores, with varying diamond thickness. The horizontal scale is the area of the *diamond* annulus in the fibre.

2.6. Composite testing

A qualitative method was used to compare the diamond composites to solid aluminium, stainless steel and brass rods of the same length and cross-sectional area. The diamond composites had a diamond volume fraction of 12.6%. Therefore, although the solid metal rods were the same total volume as the epoxy composites, the diamond-to-metal volume ratio was 1:8.

To compare the thermal conductivity of the test pieces, each was held by a an insulated clamp and a thermocouple was attached to the top of the sample. The lower 1 cm of the 8-cm-long test piece was then placed into (a) a salted ice bath at a temperature of −4 °C, and then (b) boiling water at 100 °C. The temperature of the thermocouple was taken at intervals of 10–15 s, and plotted as a function of time.

3. Results

3.1. Fibre uniformity

Fig. 5 shows laser Raman spectra obtained at various depths into the diamond. The increasing height and FWHM of the diamond peak at 1332 cm^{-1} shows that the quality of the diamond film increases closer to the top of the coating, reflecting the increased grain size and smaller number of grain boundaries as the film grows in thickness.

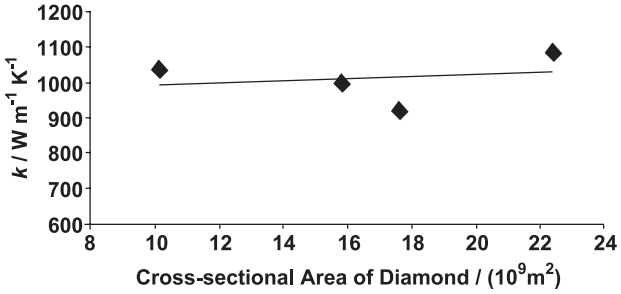

Fig. 7. The thermal conductivity, k, of diamond fibres grown on different diameter tungsten cores. The diamond thickness was 38 μm in all cases.

3.2. Thermal conductivity of individual fibres

Fig. 6 shows the thermal conductivity for diamond fibres with a range of diamond thicknesses (i.e. growth times) with the W core diameter constant at 100 μm. The magnitudes measured are around 750–900 W m^{-1} K^{-1}, which is around two times lower than values reported for CVD thin films in the literature, which vary between 1300 and 2000 W m^{-1} K^{-1} [8]. These lower values are due mainly to the fact that we are measuring perpendicularly to the growth direction, across many grain boundaries. Nevertheless, the measured values are still a factor of two to three times better than copper. The increase in thermal conductivity with diamond thickness is probably due to the increasing quality of the diamond as the film grows thicker, as discussed above.

Fig. 7 shows that for a constant diamond thickness deposited upon varying diameter W cores, the thermal conductivity is almost constant. This shows that the tungsten wire provides a negligible contribution to the thermal conductivity, which is determined solely by the amount and quality of the diamond.

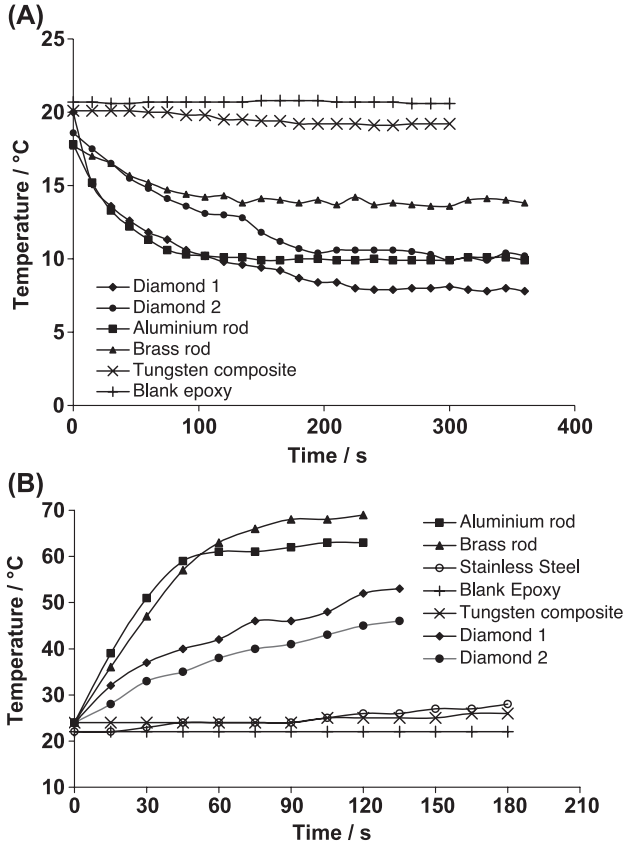

Fig. 8. The temperature response of the epoxy composites and metal rod test pieces for (A) cooling in a salted ice solution at −4 °C and (B) heating in boiling water at 100 °C, as measured by the thermocouple at the top of the sample. The 'blank epoxy' test piece had no fibre reinforcement, the one labelled 'tungsten composite' contained 100 tungsten wires of diameter 100 μm, 'diamond 1' refers to the epoxy composite containing 100 diamond fibres in a close packed bundle, 'diamond 2' refers to the epoxy composite containing 100 diamond fibres in 3 separate layers (see the inset in Fig. 4), and the 'aluminium rod' 'stainless steel' and 'brass rod' labels refer to solid metal control samples. Note that the volume of diamond in the diamond composites is 1/8th of the total volume.

3.3. Relative thermal conductivity of diamond fibre composites

In Figs. 8 (A) and (B) show the temperature change as a function of time, measured by the thermocouple on top of the test samples, when the lower 1 cm of the test piece was cooled or heated, respectively. Fig. 8(A) (cooling) shows that the diamond composites performed very well in comparison to the solid metal rods, both in terms of speed of cooling and lowest temperature reached. Diamond composite 1 (with the single bundle of fibres) reached the lowest temperature, even outperforming the test pieces made solid aluminium and brass. This is quite exceptional, considering that the volume of diamond in the composites was eight times less than the volume of the metal in the rods. Diamond composite 2 (three layers of diamond fibres) did not reach such low temperatures but still showed better thermal conductivity than brass, and similar conductivity to aluminium. The layered diamond composite did not reach such low values as the composite which contained all the fibres in one bundle. This can be explained by the fact that there is more surface area of the diamond in contact with the epoxy matrix, so there are more heat losses from the fibres and therefore heat transfer is less efficient. The tungsten composite and blank epoxy show very little change, confirming that the measurements from the diamond composites are due to the diamond.

Fig. 8(B) shows that for heating, the solid aluminium and brass rods outperform the diamond composites in terms of heat transfer. However, when the small volume fraction of diamond is taken into account, the diamond composites have much higher efficiency of heat transfer per unit volume.

4. Conclusions

We have shown that individual diamond fibres have room temperature thermal conductivity values that are two to three times that of copper, over lengths of up to 6 cm, and when embedded within epoxy matrices, they conduct heat extremely efficiently. Such diamond fibre-reinforced epoxy composites may be suitable for heat management applications, since they combine stiffness, lightness, high thermal conductivity, and are electrically insulating.

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