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A technique for the manufacture of long hollow diamond fibres by chemical vapour deposition

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Diamond possesses a unique combination of physical, mechanical and chemical properties, and many of these properties can now be obtained in diamond produced by chemical vapour deposition (CVD) [1–3]. Hitherto, CVD diamond has only been available as thin (micrometre) films on suitable substrates, which has limited CVD diamond applications to optical or wear resistant coatings and cutting tools [4]. Recently, continuous CVD diamond fibres have been produced by coating CVD diamond onto wires or ceramic fibre cores [5–7]. The diameter of the fibre cores can vary from $< 50\ \mu m$, typical of the commercial fibres present in flexible multifilament tows such as HI-nicalon, Altex and Nextel 480, to about 100–150 μm, typical of commercial fibre monofilaments such as SiC and Al_2O_3 (Saphikon) [5, 8]. CVD diamond fibres can have tensile modulus values of ~ 1000 GPa [8, 9], over twice that of monofilament SiC fibres [5], and are suitable for reinforcing polymer, metal [6, 10] or ceramic matrices. Thus, diamond fibres offer the engineer, for the first time, the possibility of exploiting the properties of diamond on a large scale in conventional engineering components and structures [5, 10].

In order to increase the compressive stiffness and decrease the density of glass fibre reinforced composites, hollow glass fibres, made by extruding and drawing, have been developed with the same mass per unit length as solid glass fibres [11]. Hollow diamond fibres have also been produced by etching out the diamond fibre core [6]. The possibility of obtaining the properties of diamond in hollow fibres is particularly attractive, but the etching method is unsuitable for very long, small diameter fibres. This letter describes a method for manufacturing long hollow fibres that does not rely on etching.

The manufacturing technique involves CVD of diamond onto a helical tungsten wire coil. The diameter of the tungsten wire was in the range $d_1 = 10$–$20\ \mu m$. The coil was made by winding annealed tungsten wire around a stiff wire or ceramic fibre core, as shown schematically in Fig. 1. After winding and relaxing the wire coil, the core was removed to leave a free-standing tungsten coil (Fig. 2a). Diamond deposition was carried out in a specially designed hot filament reactor (designed and built by Thomas Swan, Cambridge, UK) using a 1% CH_4/H_2 gas mixture and a flow rate of 200 standard cubic centimetres per minute at a pressure of about 20 torr (1 torr = 1.333×10^2 Pa). A vertical Ta filament at about 2000 °C dissociated the gases and deposited diamond on to the coil, which was radiantly heated to about 900 °C and held parallel to and about 5 mm from the filament [6].

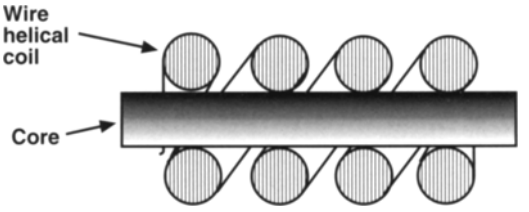

Figure 1 Schematic diagram of tungsten wire helical coil wound around a metallic or ceramic core.

The final diamond coated shape obtained depends on the dimensions of the coil (Fig. 2a). A continuous solid fibre wall will be produced when the space between the turns of the coil, s, is filled with diamond. This will occur when $s = 2x$, where x is the diamond deposit thickness (Fig. 2b). The critical deposition time, t_c, to form a continuous diamond coated coil is $t_c = x/R$, where R is the diamond deposition rate.

If $D > 2x$ and $t = t_c$, a hollow diamond fibre will be obtained (Fig. 2b). Continued coating for a total time $t = t_1 + t_c$ will increase the fibre wall thickness by $x_2 = Rt_1$ (Fig. 2c), but since the active gas radicals cannot gain access to the fibre core, diamond deposition on the internal surface ceases, and the hollow core diameter will remain constant at $(D - 2x)$. When $t < t_c$, $s > 2x$ and a diamond spring is produced. When $D = s = 2x$ and $t = t_c$, a solid fibre is produced; the fibre may contain built-in porosity, depending on the growth conditions.

A hollow diamond fibre with outside diameter 150 μm and internal hollow core diameter of ~70 μm is shown at A in Fig. 3. The fibre wall contained a 20 μm diameter tungsten wire coated with diamond to a thickness $x = 10\ \mu m$ to give 75 vol% diamond. At the end of the fibre (at B in Fig. 3) the spacing between the coil turns s was greater than $2x$ and the hollow fibre became a diamond coated tungsten wire spring. To illustrate the small size of hollow diamond fibres that can be manufactured by this method, a fibre inserted into a

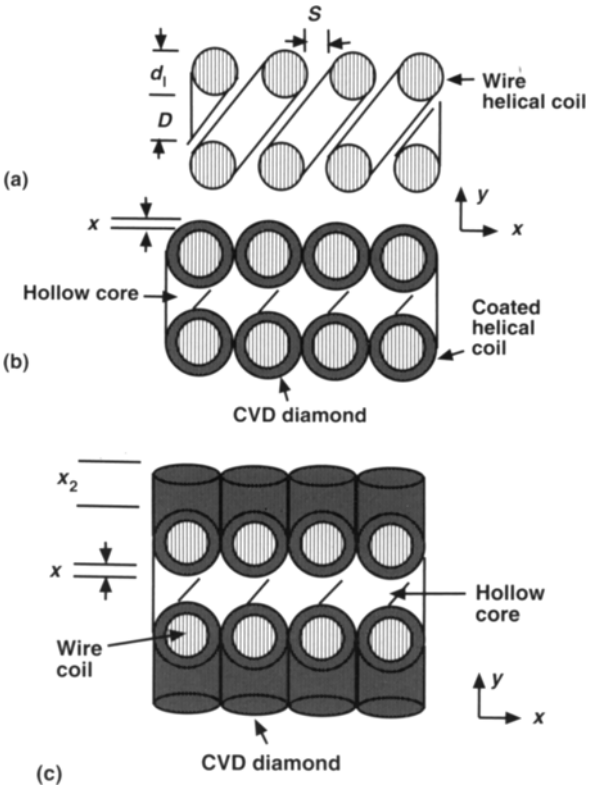

Figure 2 Schematic diagram of relaxed tungsten wire helical coil (a) after core removal, showing the dimensions of the coil, (b) after deposition of diamond to a thickness $x = s/2$ onto the coil in time $t = t_c$ to produce a hollow fibre and (c) diamond thickness in fibre wall, $2x + x_2$, after time $t = t_c + t_1$.

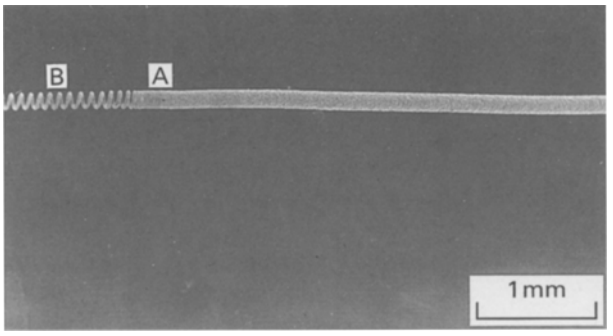

Figure 3 Scanning electron micrograph of hollow helical coil fibre at A where $s = 2x$, changing to diamond helical coil spring at B where $s > 2x$.

fine dental hypodermic needle of internal diameter 110 μm is shown in Fig. 4.

The fractured end of a hollow fibre is shown in Fig. 5a. For thin diamond coatings the outer fibre surface replicates the wire coil and appears corrugated, but these corrugations become less severe with increasing diamond thickness x_2, as shown schematically in Fig. 2b and c. The corrugations are also present on the internal surface. In this respect a hollow fibre made via the helical wire route differs from a hollow fibre made by deposition onto a smooth surface of a straight wire core followed by etching out the core, as shown in Fig. 5b. Both external and internal surfaces of this fibre are smooth.

The potential modulus for solid and hollow diamond fibres has been discussed elsewhere [5]. Tensile and bend tests on solid diamond/SiC core

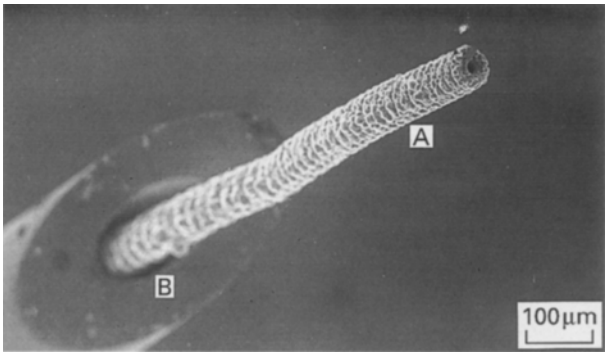

Figure 4 Scanning electron micrograph of small diameter hollow helical coil fibre at A, inserted into a hypodermic needle of internal diameter 110 μm at B.

fibres [8, 9] gave maximum moduli values of up to about 900–1000 GPa. The length of hollow fibres made via the helical coil route is at present limited by the dimensions of the reaction chamber to about 100 mm. Insufficient high quality hollow fibres have been produced to date to provide valid test data, but some comparisons between hollow fibres made by etching out a straight W-wire core and by coating a helical wire core can be made, based upon the rule of mixtures calculations and taking a published value for CVD diamond of 891 GPa [5].

Consider the manufacture of two hollow fibres by diamond deposition for the same time to produce the same diamond deposit thickness of 20.5 μm on a straight tungsten wire core of 99 μm diameter and on a 10 μm diameter helical tungsten wire, to form fibres with the same outside diameter of 140 μm.

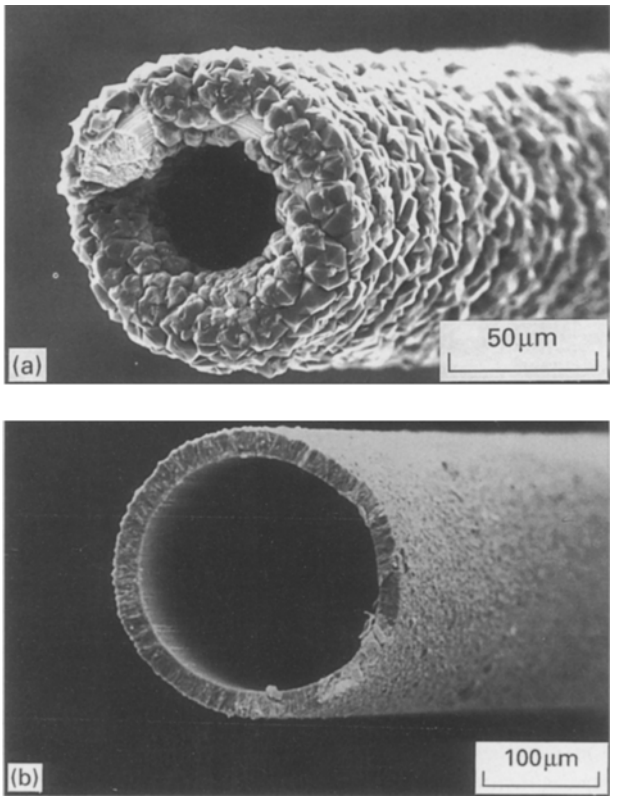

Figure 5 Scanning electron micrographs of (a) fractured end of helical coil fibre showing corrugated surfaces and (b) hollow fibre produced by etching out the core, showing smooth internal and external surfaces.

TABLE I Predicted density and modulus values for hollow diamond fibres

Fibre properties	Hollow diamond fibre with core removed by etching	Hollow diamond fibre made with helical wire	Commerial silicon carbide monofilament
Outside fibre diameter (μm)	140	140	100
Hollow core			
Diameter (μm)	99	38	(15, tungsten wire)
Volume fraction (%)	50	7.4	
Helical wire diameter (μm)		10	
Fibre wall thickness (μm)	20.5	51	
Diamond deposit thickness (μm)	20.5	20.5	
Wall of hollow fibre			
Volume fraction of diamond (%)	100	96.2	
Density (ρ)	3.5	4.1	
Hollow fibre			
Volume fraction of diamond (%)	50	89.1	
Effective density (ρ)	1.75	3.79	3.4
Effective fibre modulus			
E (GPa)	445	808	400
Specific modulus (E/ρ)	254	213	117

After etching out the 99 μm W-wire core, the final dimensions of the coated hollow fibres are as shown in Table I. Compared with the etched fibre, the helical coil fibre has a slightly lower volume fraction of diamond in the wall (96 vol% diamond and 4 vol% W), but has a greater fibre wall thickness and therefore a much greater mass of diamond. This is because the mass of diamond deposited per unit time is proportional to the surface area, which is greater for the helical coil. For the same deposition time, the helical fibre will therefore have a greater elastic modulus than the etched core fibre. Note that in this example the tungsten wire leads to a greater helical coil fibre density, whereas the etched hollow core represents 50% fibre volume fraction and leads to a very low etched fibre density. The net effect is two fibres with similar specific stiffness values, but with the helical coil fibre having a modulus that is greater by almost a factor of 2. Thus, only half the number of fibres with helical cores would be required for a given composite stiffness.

Also shown in Table I are values for a typical commercial SiC fibre monofilament. Values for the modulus of the helical wire fibre and for the specific stiffness E/ρ of both diamond fibres are predicted to be about a factor of 2 greater than those for the SiC fibre.

In conclusion, the helical coil route to hollow fibres provides great flexibility in the selection of the dimensions for hollow diamond fibres, since the internal diameter, the outside diameter and the wall thickness of the fibres can be varied independently to give different combinations of density and modulus. The helical coil fibre does not have to be straight and the internal and external diameters may taper along the fibre length. Many applications are envisaged for these hollow fibres in lightweight composites [5] and thermal management systems [12].

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