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Preparation of solid and hollow diamond fibres and the potential for diamond fibre metal matrix composites

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The development of techniques to grow diamond thin films using chemical vapour deposition (CVD) is now an area of active world-wide research [1, 2] and the unique physical and chemical properties of diamond promise many potential applications in optical components, semiconducting devices and hard wear-resistant coatings [3, 4]. Previous work has focused primarily on planar silicon on molybdenum substrates, but some preliminary results have recently been reported for coatings on wires [5, 6]. This paper describes a technique for producing uniform diamond coatings on the surface of metallic wires or ceramic fibres and the production of free-standing diamond tubes. The factors that affect the quality of the diamond fibres are discussed and their potential use in reinforced composites is considered.

In the present experiments, diamond-coating was carried out in a standard hot filament CVD reactor [1, 2], in which CH_4 and H_2 in a ratio of 1:100 were passed into a vacuum chamber at a total flow rate of 200 standard $cm^3\,min^{-1}$ and a pressure of about 4000 Pa. A Ta filament held at 2000 °C dissociated the gases allowing carbon to deposit on to the surface of the wires and fibres in the form of a polycrystalline diamond film at a rate of about 0.5 $\mu m\,h^{-1}$. If the wire was placed parallel to, and a few millimetres from, the filament (as for planar substrates) the uniformity of the diamond-coating was limited by the thickness of the wire, since diamond grew fastest on the side of the wire facing the filament. This effect became noticeable for wires and fibres with diameter $> 250\ \mu m$, placing an upper limit upon the thickness of wires or fibres that can be uniformly coated by this method of around 300 μm. Alternatively, if the wire was positioned centrally and coaxially *within* the coils of the filament, uniform coatings on wires and fibres with a wide range of diameters were achieved. In this case, for thicker wires or fibres (even up to a few millimetres diameter), the diameter of the filament coils was simply increased to maintain an optimum distance of about 4–5 mm between the surface of the wire and the filament. This ensured that the wire was heated to a sufficient temperature to favour diamond deposition (typically about 900 °C), and also that the flux of H atoms at the growing diamond surface was adequate to prevent graphite formation [7].

As for planar substrates, diamond grew best upon wires made from materials with relatively low thermal expansion coefficients and preferably having carbide-forming properties. Wires of tungsten, titanium, tantalum and copper, and fibres of silica and silicon carbide were manually abraded with 1–3 μm diamond grit prior to diamond deposition in order to promote nucleation sites for the diamond growth [1]. Fig. 1 shows a section through a 200 μm diameter tungsten wire coated with a 6.5 μm thick layer of diamond. The quality of the diamond was ascertained by laser Raman spectroscopy which showed the strong 1332 cm^{-1} peak characteristic of diamond, with no corresponding graphite peak at 1550 cm^{-1}. Fig. 2 shows a cross-section of a diamond-coated SiC fibre. The diamond coatings are continuous, uniform and adherent, and thicker coatings could lead to diamond fibres equivalent to the SiC fibres currently manufactured for metal matrix composities (MMCs) [8]. The coated wires and fibres show increased stiffness and strength over the non-coated materials.

By growing diamond upon wires and then etching away the metal in an appropriate chemical reagent (e.g. nitric acid for copper, hydrogen peroxide for tungsten, etc.), free-standing tubes, or hollow diamond fibres, can be manufactured. Fig. 3 shows such

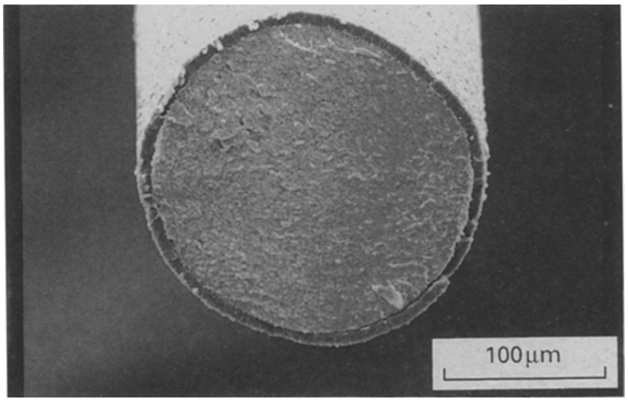

Figure 1 200 μm diameter tungsten wire coated with 6.5 μm of polycrystalline CVD diamond.

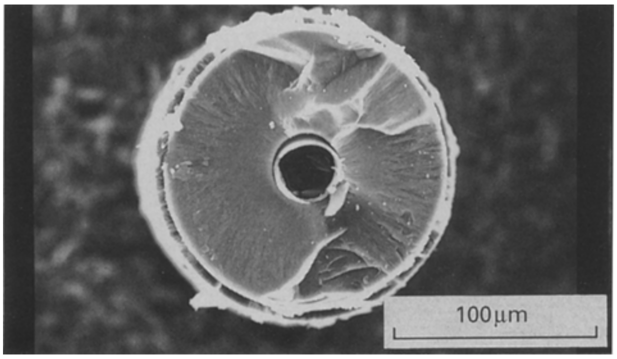

Figure 2 End view of a diamond-coated SiC fibre (Textron SCS6, 33 μm diameter carbon-fibre with 56 μm-thick CVD SiC). The diamond coating is continuous, uniform and about 7 μm thick.

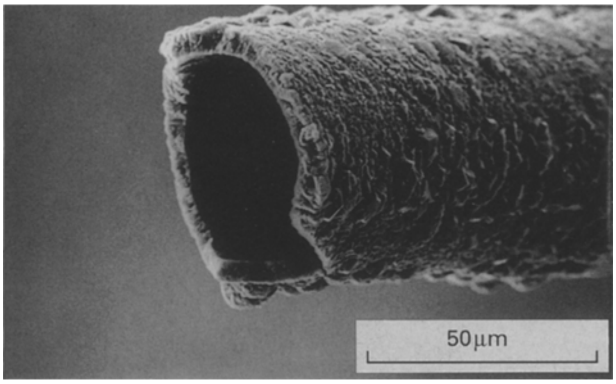

Figure 3 Free-standing hollow diamond fibre, 50 μm internal diameter, 5 μm wall thickness, made by depositing diamond upon a copper wire and then etching away the copper in nitric acid. The cracking around the end was caused during sectioning.

a hollow fibre, which is 5 mm long and has a 50 μm internal diameter, with wall thickness 5 μm. Fig. 4 shows an end view of the same fibre. Larger diameter wires (> 100 μm) are easier to handle and manipulate in and out of the deposition chamber, although they require longer deposition times in order to make a diamond coating thick enough to be self-supporting when the wire is elected away (see Fig. 5). Thinner wires are harder to handle, but require diamond layers of only a few micrometres thickness to produce free-standing hollow fibres.

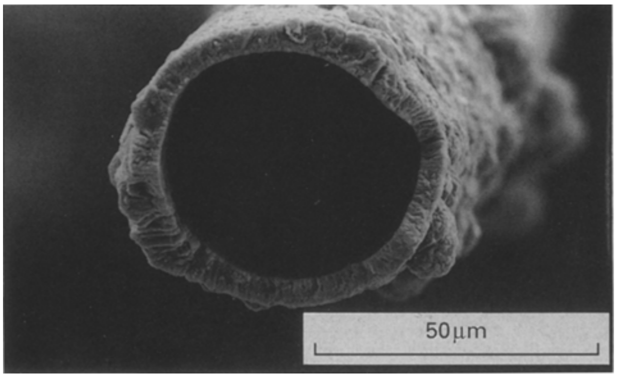

Figure 4 Cross-section of the hollow fibre shown in Fig. 3. A few diamond nodules are visible on the outside surface of the fibre, indicating increased growth rates in these areas. This may be due to non-uniform abrasion.

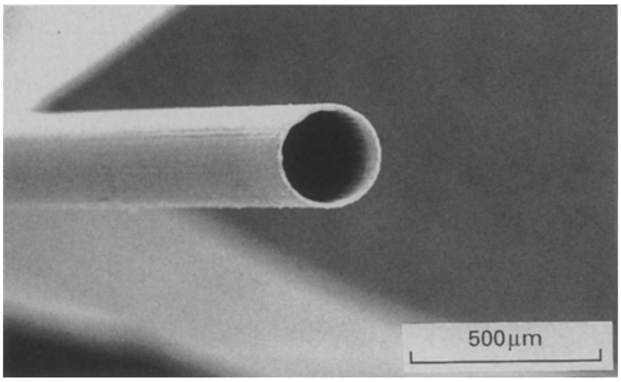

Figure 5 Larger diameter hollow diamond fibre, made by growing on a tungsten wire and then etching the metal away with hydrogen peroxide solution.

Solid diamond fibres have been considered for reinforcing ceramics [9] but only short fibres have been proposed for metals [10]. In fact the PVD matrix coated fibre technique [8] may produce continuous diamond fibre MMCs with an outstanding combination of properties [11]. The potential diamond fibre stiffness values are shown in Fig. 6. If, for example, CVD diamond replaced the SiC in conventional SiC fibre [8] (i.e. a 140 μm diameter fibre containing a 20 μm diameter W core), Young's modulus (E) of the CVD diamond fibre would be $\sim$880 GPa compared with 400 GPa for the SiC fibre. Other core materials such as Ti and silica have been demonstrated in the present work, and Cu-coated carbon-fibre elsewhere [6]. The core material would have little effect on fibre properties (Fig. 6) but will affect fibre cost. Unlike hollow glass fibres, the same diameter diamond fibre with a 50% void volume fraction would still have significant strength, with $E \sim 445$ GPa (greater than solid SiC), and both solid and hollow diamond fibres would have a specific stiffness (E/d, where d = relative density) of 230–250 GPa. This is about a factor of 2 greater than SiC fibre (117–142 GPa). The hollow fibre diameter could be increased to give the same mass as

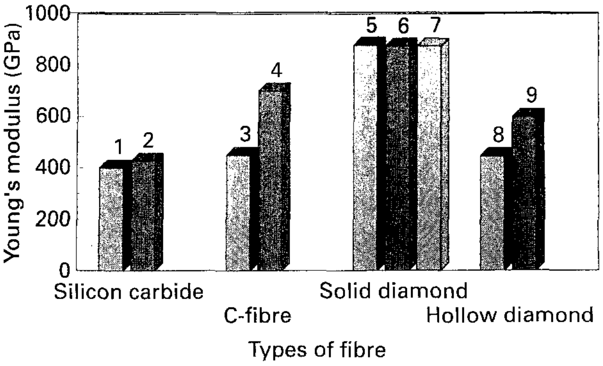

Figure 6 Comparison of achieved Young's modulus values for: (1) BP SiC fibre; (2) Textron SiC fibre; (3) PAN high modulus C-fibre; (4) pitch P100 C-fibre; with those predicted for 140 μm diameter diamond fibre with 20 μm diameter cores made from: (5) W wire; (6) Ti wire; (7) silica fibre; and for hollow diamond fibres with (8) 50% void and (9) 33% void with the same mass as solid diamond fibres.

the solid fibre, and the corresponding values would then be $E \sim 597$ GPa and $E/d \sim 260$ GPa.

These values are comparable with those reported for high modulus carbon fibres (Fig. 6). Such diamond fibres might be used in continuous fibre reinforced composites and allow, for the first time, the exploitation of the mechanical properties of diamond in large-scale engineering structures. For hollow fibres there is also the possibility of modifying the composite properties by filling the fibres with suitable materials, or of designing sensors for inserting into the fibres to make a smart composite.

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