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PREPARATION OF CVD DIAMOND WIRES, FIBRES AND TUBES

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Solid and hollow diamond fibres have been produced by depositing CVD diamond onto the surface of thin metal wires or ceramic fibres using a hot filament reactor. The diamond fibres are substantially stiffer and stronger than non-coated wires. Etching away the metal core in a suitable chemical reagent allows hollow diamond fibres, or tubes, to be made, of typical dimensions 1 cm long with an internal diameter of 50-150 μm and a 5 μm wall thickness.

INTRODUCTION

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). The outstanding physical and chemical properties of diamond promise many potential applications for thin film diamond (3,4), including uses in optical components, semiconducting devices and hard wear-resistant coatings. Until now, most reports of diamond CVD have been restricted to planar substrates, usually of materials such as silicon or molybdenum. We now demonstrate that diamond coatings can be grown uniformly on the surface of metallic wires or ceramic fibres.

APPARATUS

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 sccm and a pressure of about 30 Torr. Here, 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 μm h^{-1}.

Uniformity of deposition around the wire depended upon the position of the substrate relative to the filament. If the wire was placed parallel to, and a few mm 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 $> 250\ \mu m$. Alternatively, if the wire was positioned centrally and coaxially *within* the coils of the filament (see fig. 1), uniform coatings on wires and fibres with a wide range of diameters were achieved. In this case, for thicker wires or fibres (up to a few mm 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, and also that the flux of H atoms at the growing diamond surface was adequate to prevent graphite formation (5). The surface temperature of the wire was not measured due to the difficulty in placing a thermocouple through the filament. However, comparing the growth rate of diamond on planar substrates with that found on wires and fibres, we estimate the surface temperature to be around 900°C.

The metal wires used were made from copper, titanium or tungsten, ranging in thickness from 10-350 μm and length typically 1-2 cm. Silicon carbide fibres (Textron SCS6) were also used. The wires or fibres were manually abraded with 1-3 μm diamond grit prior to diamond deposition in order to promote nucleation sites for the diamond (1).

RESULTS

Fig. 2 shows a cross-section of a 145 μm-diameter SiC fibre coated with a 7 μm layer of diamond. The diamond coating is continuous, uniform and adherent. The quality of the diamond coating 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. 3 shows a diamond-coated W wire, which has been partially etched in acid to highlight the diamond layer. Tungsten is a particularly good wire material upon which to grow diamond because of its high melting point and stiffness, and also because its carbide-forming properties help to make the diamond layer adhere.

Copper wires were also used as substrates, but diamond was found not to adhere very well to wires of thickness $> 100\ \mu m$. This is because of the lack of an intermediate carbide layer, and also the large thermal expansion mismatch between copper and diamond. Consequently, diamond films grown on thick copper wires cracked and flaked off. Alternatively, copper wires $< 100\ \mu m$ in diameter were found to be suitable for diamond deposition, since the increased volume fraction of diamond was sufficient to overcome these problems.

By growing diamond upon copper wires and then etching away the metal in nitric acid, free-standing tubes, or hollow diamond fibres, can be manufactured. Fig. 4 shows such a hollow fibre, which is 5 mm long with a 50 μm internal diameter, with wall thickness 5 μm. Fig. 5 shows an end view of the same fibre. Larger diameter wires ($> 100\ \mu m$) 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 etched away (see fig. 6). Thinner wires are harder to handle, but require diamond layers of only a few μm thickness to produce free-standing hollow fibres.

Such solid or hollow diamond fibres may have many important applications in fibre-reinforced metal matrix composites (MMCs). For example, if CVD diamond

replaced the SiC in conventional SiC fibres (6) (140 μm diameter fibre containing a 20 μm diameter W core), Young's modulus, E, of the CVD diamond fibre would be 880 GPa compared with 400 GPa for the SiC fibre. Hollow diamond fibres with 50% void volume fraction would have a modulus of 445 GPa (greater than solid SiC fibre), and both types of diamond fibres would have a specific stiffness (E/d, where d = relative density) of 230 GPa. This is about a factor of 2 greater than SiC fibre (117 GPa), and comparable with values for high modulus carbon fibres. Based upon the rule of mixtures, a 40% volume fraction diamond fibre / Ti MMC would have a specific stiffness about 1.8 times greater than the equivalent SiC fibre composite.

These diamond fibres may also lead to high strength, high stiffness composite thermal conductors, since the thermal conductivity of CVD diamond along the direction of the fibre is 2-4 times greater than high conductivity Cu or Al, and is combined with an E/d value 10-18 times greater than the metals.

In theory, the properties of a composite containing hollow fibres may also be modified by filling the hollow fibres with suitable materials.

CONCLUSIONS

We have demonstrated that it is possible to deposit diamond layers onto wires and fibres, although it is by no means easy to handle such small diameter objects. In order to exploit this technology, however, it is essential that the coated wires be increased in length from the 5 mm-1 cm lengths currently produced to metres or even kilometres. Problems of manipulation of the wires in and out of the deposition chamber, coiling of the stiffened wires after deposition, and large scale etching to produce the hollow fibres will also need to be addressed.

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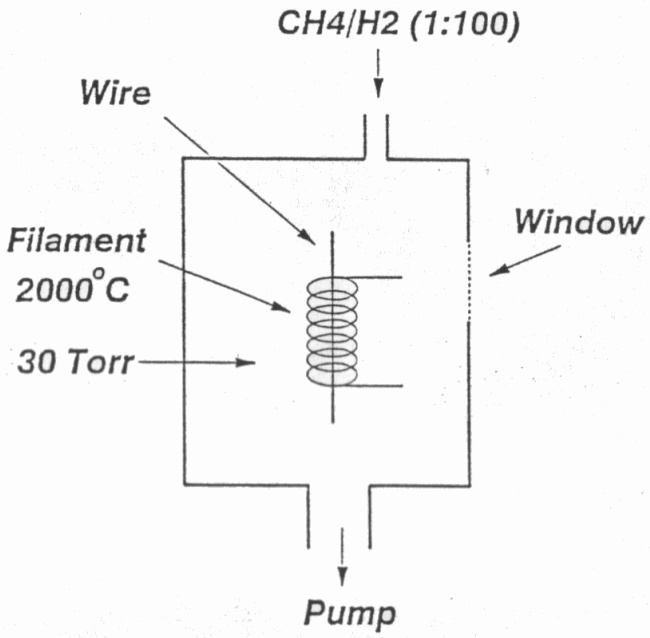

Fig. 1. Schematic diagram of the hot filament CVD reactor modified such that the wire or fibre is positioned coaxially and centrally within the coils of the filament.

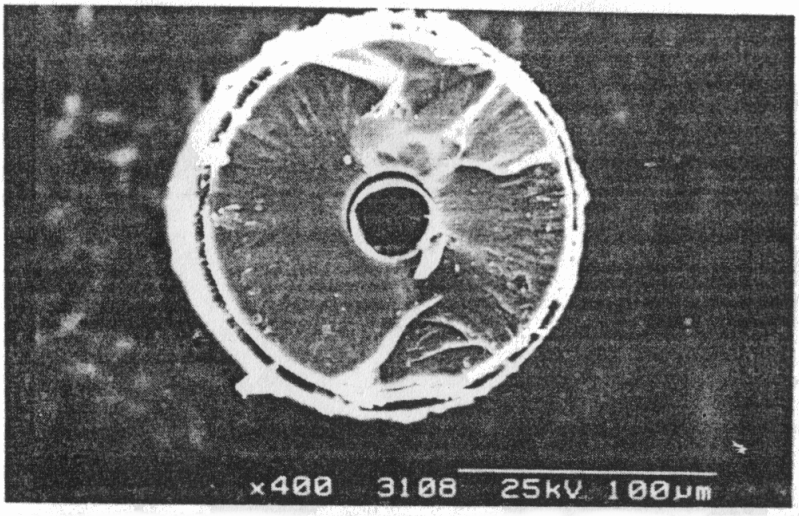

Fig. 2. End view of a diamond-coated SiC fibre (Textron SCS6, 33 μm diameter carbon-fibre with 56 μm-thick CVD SiC). The diamond coating is continuous, uniform and about 7 μm thick.

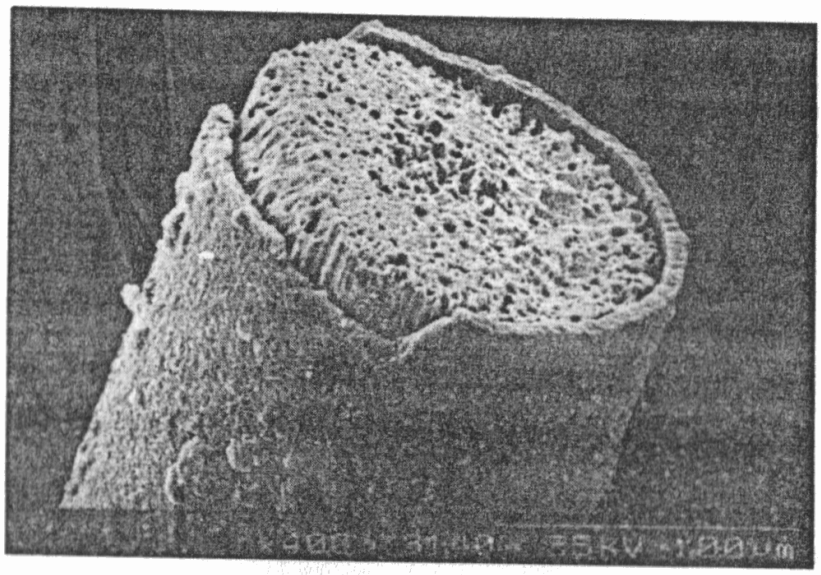

Fig. 3. 150 μm diameter tungsten wire coated with 7 μm of polycrystalline CVD diamond. The cut end of the wire has been etched in a 50:50 HF/HNO_3 solution to highlight the diamond coating.

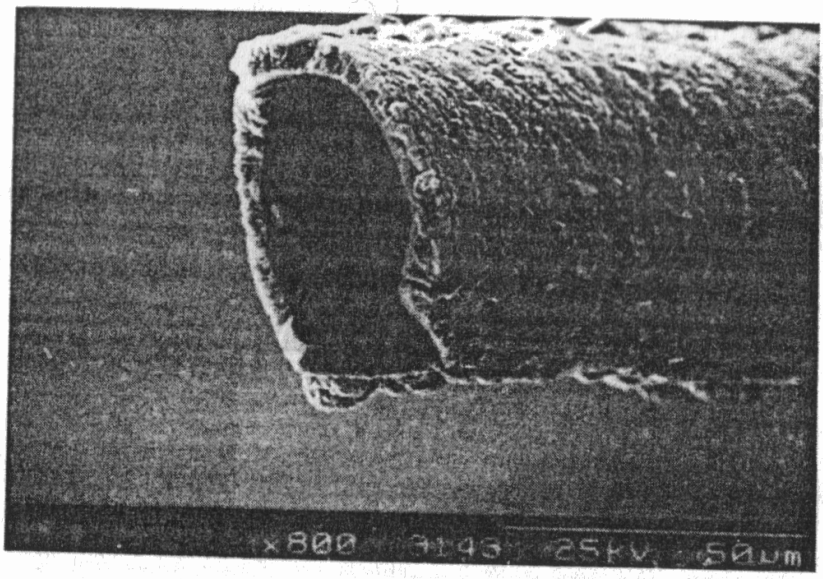

Fig. 4. Free-standing hollow diamond fibre, 50 μm internal diameter, 5 μm wall thickness. The cracking around the end was caused during sectioning.

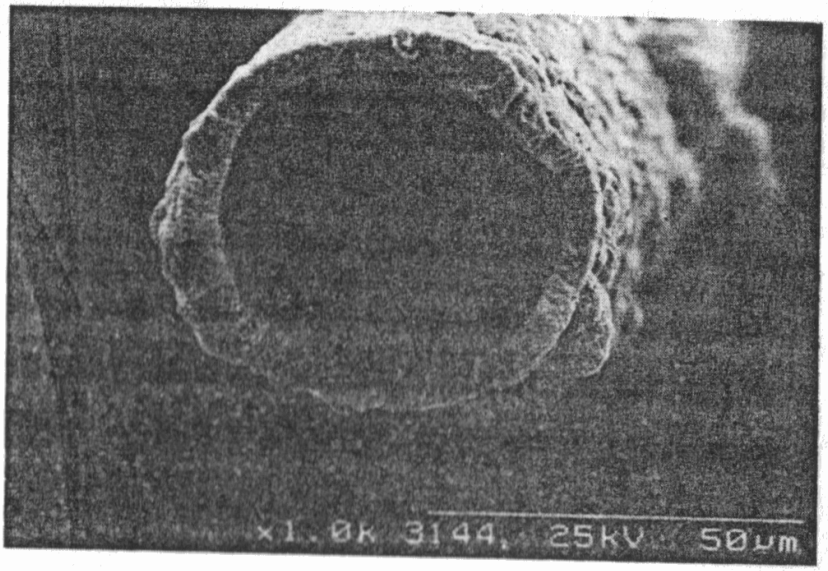

Fig. 5. Cross-section of the hollow fibre shown in Fig. 4. A few diamond nodules are visible on the outside surface of the fibre, indicating increased growth rates in these areas. This may be due to non-uniform abrasion.

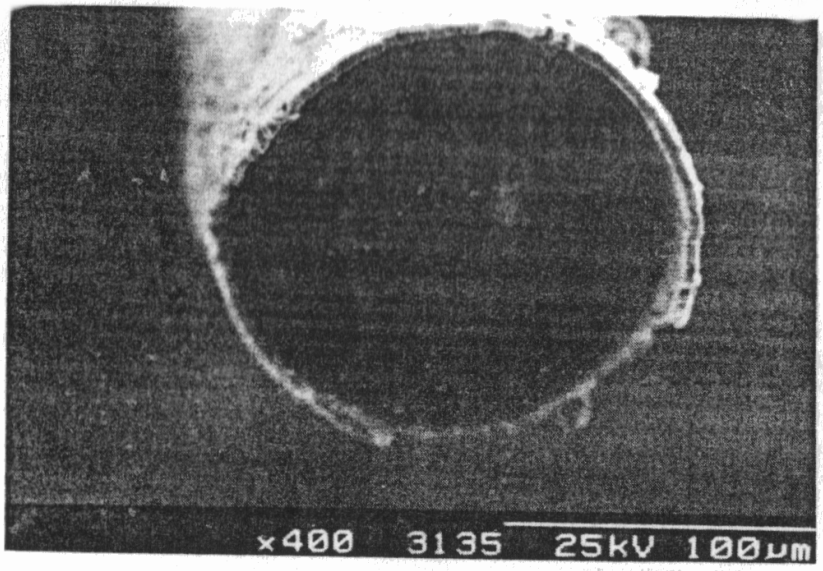

Fig. 6. Larger diameter hollow diamond fibre, made by growing on a titanium wire and then etching it away with HF solution.