Overview

Chemical vapour deposited diamond fibres: manufacture and potential properties

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The properties of chemical vapour deposited diamond are reviewed and many properties are shown to approach or equal those for natural diamond. The manufacture of solid diamond fibres via chemical vapour deposition on various wire and ceramic cores and the production of hollow diamond fibres by removal of the cores is described. The potential values of Young's modulus of continuous and discontinuous diamond fibres, calculated using the rule of mixtures, are predicted to be substantially higher than for current commercial SiC fibres. Corresponding increases in compressive stiffness are expected, with significant increases in specific buckling loads for hollow fibres. Hollow fibres may also allow the use of sensors in smart structures. The factors affecting the cost of diamond fibres are discussed. It is concluded that chemical vapour deposited diamond fibres offer for the first time the possibility of exploiting the properties of diamond on a large scale via diamond fibre composites.

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Introduction

The outstanding physical and mechanical properties of diamond have long been recognised.¹ The diagrams constructed by Ashby² provide an excellent comparison of the relative strength and stiffness values of natural diamond and other engineering materials (Fig. 1). They show that diamond combines a relatively low density with a strength greater than that of any other structural material. The combination of strong sp³ bonds and the highest volumetric density of any material is responsible for many of the outstanding properties of diamond.³ However, except for engineering applications involving wear resistant diamond particulate coatings, the mechanical properties of natural diamond have remained of academic interest to engineers because of product dimensions and cost.

Commercial particulate diamond composites contain either natural diamond grit or artificial diamonds synthesised under high pressures and temperatures in processes developed during the 1950s in the then USSR and the USA. In the initial work on low pressure chemical vapour deposition (CVD) of diamond carried out in the USA it was not possible to suppress codeposition of graphite and the yield of diamond was only about 1%. This diamond had to be extracted periodically and the process was extremely slow. The major effort then moved to the USSR where researchers made the significant discovery that atomic hydrogen could selectively etch and remove from a deposit graphite and amorphous carbon (with non-sp bonding) leaving diamond (with sp³ bonding). This breakthrough allowed continuous operation and faster deposition rates using plasmas having a high concentration of hydrogen. Intensive reseach by the Japanese led in the early 1980s to several routes for the continuous low temperature CVD of diamond thin films (Fig. 2) and to the production of large area high quality polycrystal and single crystal diamond films (100 mm diameter and 425 μ m thickness4) and free standing shapes of up to 600 µm thickness. 5.6 The potential for these CVD diamond films is indicated by the explosive growth in research activity, publications, and patents on this subject.

Thin diamond films are particularly suited for applications that make use of the exceptionally high transparency to radiation (wavelengths extending from the ultraviolet to the infrared), thermal conductivity, and hardness or wear resistance of diamond. In thick sections, diamond in common with many ceramic materials is limited by low toughness as well as by its tendency to cleave on (111) planes. One method of overcoming the problems associated with the toughness of brittle materials is to manufacture the material in the form of small diameter fibre. On the basis that a small volume is less likely to contain a critical defect than a large volume 7,8 (the volume of a fibre 1 m in length and 50-100 μm in diameter is about 2-8 mm³) and that surface flaws must be short, fibres will be less sensitive to defects than bulk material. With suitable surface preparation fibres can therefore be obtained having much higher strengths than the same material in bulk form. Furthermore, failure of one fibre will not lead to failure of the component. The recent manufacture of diamond fibres by CVD suggests⁹⁻¹³ that for the first time the properties of diamond may be capable of exploitation on a large scale via diamond fibre composites.

Various metal matrix composites (MMCs) based on continuous ceramic fibres embedded in a metal matrix are being developed for applications that require materials having a combination of high strength and stiffness. 14,15 Currently, the most widely used fibres for MMCs are based on boron or silicon carbide (SiC). Carbon fibre, widely used in carbon fibre reinforced polymer composites, is also considered for some MMCs. 17-20 Major research programmes are currently based on titanium alloy/SiC fibre composites for use in aeroengine power plants, 14,15 and continuous fibres are also being considered for toughening brittle ceramics.¹⁴ Composites containing continuous^{12,13} and discontinuous²¹ diamond fibres in a metal matrix or continuous SiC fibre in a diamond matrix¹⁰ have been proposed. Although the strength data for CVD diamond films is limited at present, there is evidence to suggest that CVD diamond could have much higher stiffness than CVD SiC, with a combination of strength, thermal conductivity, and corrosion resistance not obtainable in any other material. In this paper, the properties of CVD diamond are compared with those of natural diamond and techniques for the manufacture of continuous solid and hollow CVD diamond fibres are described. Using the rule of mixtures the potential values of stiffness of these diamond fibres have been calculated and compared with the stiffness of commerical fibres. The factors that may control diamond fibre properties and the relative fibre costs

f fibre; w whisker; SG specific gravity; M performance index

1 Design charts for a light strong composites based upon strength v. density and b light stiff composites based upon Young's modulus v. density²

Table 1 Properties of natural diamond (Ref. 1) and chemical vapour deposited (CVD) diamond (e.g. see Refs. 22-25)

Property	Natural diamond	CVD diamond
Relative density ρ Fracture stength $\sigma_{\rm f}$, GN m ⁻²	3·51 ~3−5	3·5 0·5–1·4 (in tension)
Young's modulus <i>E</i> , GN m ⁻² Hardness, GN m ⁻² Fracture toughness, MN m ^{-3/2} Poisson's ratio <i>v</i>	1050 55-113 $K_{lc} = 3.4-5.0$ 0.07	700–1079 31–90 K _c ≈ 6 0·07
Coefficient of thermal expansion (CTE) \times 10 ⁻⁶ , K ⁻¹ Thermal conductivity λ , W m ⁻¹ K ⁻¹	0·8 600–2200	0·8–1·05 1000–2400 (300 µm thick) 1000 (5 µm thick)
Specific heat C_v , C_p , J mol ⁻¹ Specific heat capacity, J kg ⁻¹ K ⁻¹ Electrical resistivity, Ω m	6·2 525	510
high low Surface roughness Sound velocity, m s ⁻¹	> 10 ¹⁴ 0·1–10 10 285	10 ¹⁴ 10 (B doped) 1–4 μm 16 200
Coefficient of friction Radiation absorption coefficients	0·02–0·1 Low over ultraviolet, visible,	(Ti = 4900) 0·15-0·52 Within factor of 2-3 of type
Hall mobility, cm² V ⁻¹ s ⁻¹ Dielectric constant	and infrared 325 5·7	11A diamond 3–10 5·7

Properties of diamond

NATURAL DIAMOND

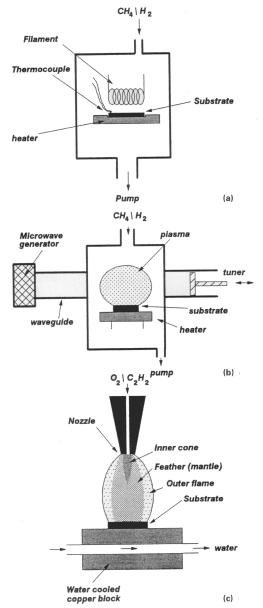
Some properties of natural diamond are given in Table 1 and the strength and stiffness of natural diamond relative to a wide range of structural materials is illustrated by Fig. 1 and Table 2. The physical properties have been investigated extensively and are well documented, but the strength data, obtained indirectly via compression or hardness measurements, are dependent on the value of Poisson's ratio^{1,26} and do not allow a reliable prediction of strength under tensile loading. Stress wave and crack growth velocities are greater in diamond than in any other material;1 the former makes diamond attractive for speaker diaphragms.5

CVD TECHNIQUES FOR DIAMOND

To date, only a few groups have demonstrated the ability to achieve CVD of diamond on metallic wires or non-metallic fibres.^{9,10-13} A microwave plasma enhanced CVD

Table 2 Specific stiffness of potential core materials for diamond fibres compared with Ti-6AI-4V and

odulus	Specific stiffness E/ρ
050	299
391	255
700	350
490	256
220	86
270	99
400	117
74	35
362	18
124	14
110	25
	700 190 220 270 100 74 1662

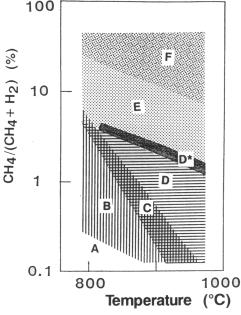


a hot filament and b microwave plasma techniques use low pressures (~30 torr) and hydrogen-hydrocarbon process gas mixtures; c oxyacetylene torch method operates at atmospheric pressure and can produce high growth rates over small areas

Schematic diagrams of techniques for chemical vapour deposition (CVD) of diamond (1 torr ≈ 133·3 Pa)

reactor or a hot filament reactor is usually used and the deposition conditions are identical to those used for planar substrates^{3,27,28} (Fig. 2).

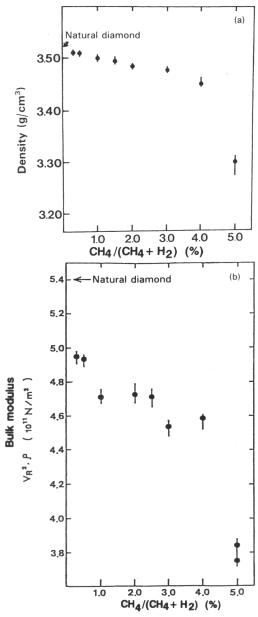
Wires and fibres have been coated in a hot filament reactor at a CH₄/H₂ ratio of 1:100, a flowrate of 200 cm³ min⁻¹ (STP), a pressure of 30 torr, and a filament temperature of $\sim 2000^{\circ} C.^{11,12}$ The substrate wire or fibre was lightly loaded to keep it straight and positioned vertically a few millimetres away from a vertical filament.



- A little or no deposition of either diamond or graphite
- 3 (111) facets predominate
- C (111) and (100) facets appear with comparable frequency
- D (100) facets predominate
- * (100)<001> texture predominates
- E film has smooth surface composed of nanocrystals of diamond and disordered graphite
- F film is composed of fibrous deposits of soot or disordered graphite growing normal to substrate
- 3 Schematic diagram showing morphology of diamond films as function of methane concentration and substrate temperature (After Ref. 32)

Provided the fibre or wire does not exceed about 200 μm in diameter, very uniform coatings can be produced at deposition rates of about 0·5–1·0 μm h⁻¹. On thicker wires, however, the coatings become non-uniform because of higher temperatures and hydrogen atom flux on the surface facing the filament. Larger diameter fibres can be coated if they are placed centrally and coaxially within a coiled filament. This leads to uniform coatings but has the disadvantage of poor process control, especially in monitoring the substrate temperature.

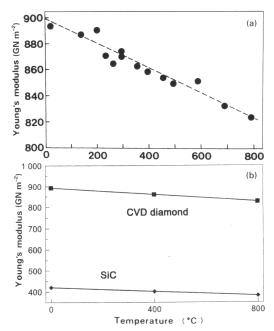
Other workers have deposited diamond on 100 µm dia. SiC fibres in a microwave reactor at 2.45 GHz excitation, with a total flowrate of 200-250 cm3 min-1 (STP) at 50-90 torr pressure.10 To avoid excessive heating of the fibres the applied power level was maintained within 500–1000 W. As for planar substrates, wires and fibres must be abraded, with diamond grit the most common abrasive, in order to promote diamond nucleation sites on the substrate surface. This can be achieved by drawing the wire or fibre through a die loaded with diamond-water slurry or by placing the substrates into a slurry bath with ultrasonic agitation. The fibres may also be coated with hydrocarbon oil to enhance growth. ¹³ Alternative methods for treating substrate surfaces to nucleate diamond will be required, since current techniques damage the fibre cores and are impracticable for thin fibres. The reported lengths of diamond fibres to date are of the order of only 100 mm, with a maximum diamond coating thickness of $\sim 20 \,\mu m$. Chemical vapour deposited diamond can contain hydrogen; it will be necessary to consider the effect of such hydrogen in subsequent applications.28



4 a Density and b bulk modulus of CVD diamond films at methane concentrations of 0·3-5% (bulk modulus calculated from velocity of surface acoustic waves and density)³¹

CVD DIAMOND

Some properties reported for CVD diamond films on planar substrates are compared with those for natural diamond in Table 1 (tensile strength, 9,10,22 modulus, 5,22-24,29 hardness, 22 fracture toughness 25,30). Certain properties of CVD diamond can approach or equal the value for natural diamond, e.g. Young's modulus, thermal conductivity, and radiation absorption, but all are dependent on deposition conditions and on microstructure, 3,31 For a CH₄-H₂ mixture, the effect of CH₄ concentration and substrate



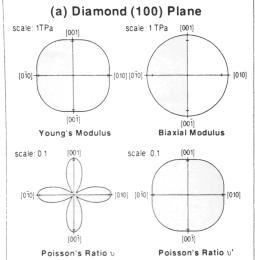
Variation of Young's modulus of CVD diamond film with test temperature:²⁹ in b, values can be compared with those for CVD SiC film^{29,34}

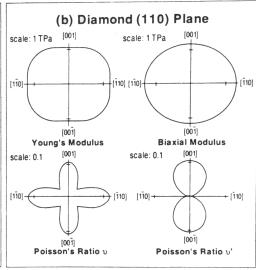
temperature on diamond film morphology and texture is shown in Fig. $3.^{32}$ At 30-80 torr pressure, about $1\%\text{CH}_4$, and substrate temperature in the range $900-1000^\circ\text{C}$, diamond films with well developed (111) and (100) facets are favoured

The initial grain size of CVD deposits depends on the diamond nucleation density, and the grain size increases with increase in deposit thickness.³³ The density and bulk

modulus (the latter calculated from the velocity of surface acoustic waves) of CVD films descreases rapidly with increasing CH₄ concentration above about 0.5% (Fig. 4).31 The decrease is attributed to codeposition of disordered graphite and H₂ absorption. The change in modulus is also reflected in the change in hardness. In some elegant experiments using a vibration reed technique, Seino and Nagai²⁹ determined the temperature dependence of Young's modulus up to 800°C, as shown in Fig. 5a. At room temperature the modulus of 891 GN m⁻² is about 17% less than that of bulk diamond (1050 GN m⁻²) but is twice the modulus of CVD β -SiC (Ref. 34) over this temperature range (Fig. 5b). The temperature sensitivities were 0.048 and 0.084 GN m⁻² K⁻¹ for β -SiC and CVD diamond respectively. The greater temperature sensitivity of CVD diamond compared with natural diamond is attributed to the presence of graphite. Some diamond films have been reported to have much higher modulus values, ^{22,23,25} and biaxial modulus values of 1180 GN m⁻² for randomly oriented and 1220 GN m⁻² for (110) textured films have been obtained.²⁶ In the principal planes and directions the anisotropy of the elastic properties is small, with isotropy in the (111) plane. Some uncertainty in the elastic constants has been caused by the use of different values for Poisson's ratio. 1,26 The ratio exhibits significant anisotropy away from the principal crystal directions (Fig. 6).²⁶

High elastic properties are more easily achieved in thin CVD diamond films than are high tensile fracture properties. Fracture in CVD diamond is dominated by transgranular cleavage on (111) planes; since these are also the growth planes, the preference for cleavage in these planes may be due to growth defects. There are few measured values of tensile strength as distinct from values of strength deduced from hardness, sompression tests, or diaphragm bulge tests. Since the strength of CVD diamond is very sensitive to impurities, surface roughness, and residual stresses. A low tensile fracture strength leads to low elastic strain and this could limit the ability to exploit the high modulus of CVD diamond as a fibre. The reported 19,22 tensile fracture strengths of ~0.7-1.4 GN m⁻² are a factor of ~3 lower than values predicted for natural diamond; this has been attributed to surface cracks of 2-10 µm in





a applied stresses within (100) planes; b applied stress in (110) planes

6 Rotational dependence of elastic modulus, biaxial modulus, and two values of Poisson's ratio v and v' for single crystal diamond: v and v' refer to longitudinal orthogonal elongation and transverse orthogonal elongation respectively²⁶

Table 3 Properties of fibre core materials compared with CVD diamond

Material	ρ	<i>E</i> , GN m ⁻²	$\sigma_{\rm f}$, GN m $^{-2}$	ν	CTE, 10 ⁻⁶ K ⁻¹	λ , W m ⁻¹ K ⁻¹	Specific heat, J kg ⁻¹ K ⁻¹	Electrical resistivity, Ωm	Fibre dia., μm
CVD diamond	3.5	~891 (film)	0.5-1.0	0.07	0.8-1.0	1000-2400	525	10 ¹⁴	
W wire	19.3	411		0.29	4.5	177	133	4.9×10^{-6}	25-100
SiC fibre (BP)	3.4	400 (BP)	3.75	0.14	4.8	110	820	1.5×10^4	100
Silica fibre	2.21	74	4	0.16	0.54	11	84	10 ¹²	9-60
C fibre	1.91 PAN	490 PAN	2.2-2.5	0.16	-1·4 P100	600 P100		$3 \times 10^{-6} \text{ P100}$	5-10
	2·15 P100	700 P100			−1·0 M50	10 T300 900 P140		$20 \times 10^{-6} \text{ T}300$	
Cu wire Ti wire	8.96	130	•••	0.34	16.7	403	379	0.016×10^{-6}	Wide range
Pure Ti	4.51	110	0.3-0.5	0.36	7.6	16	528	0.48×10^{-6}	Wide range
Ti-6AI-4V	4.42	110	1.1	0.31	8.0*	5.8*	610	1.68 × 10 ⁻⁶ *	Wide range

*IMI 318.

the CVD diamond film.²² The columnar grain boundaries show a surprising resistance to fracture under tensile stress normal to the grain growth direction.²⁴ This may be caused by crack blunting in amorphous layers at the grain boundaries and by the presence of high residual stresses, as suggested by Brown in Ref. 22. Fracture toughness at $\sim\!6~\mathrm{MN}~\mathrm{m}^{-3/2}$ (Refs. 25, 30) appears to be slightly greater than for natural diamond.

Optical transparency is dependent on surface roughness and, as is thermal conductivity, on grain size and impurities. $^{6.37}$ The thermal conductivity of CVD diamond $(1000-2400~W~m^{-1}~K^{-1})$ is greater than that of any other material. 37 Chemical vapour deposited diamond films having large columnar grains ($\sim 100~\mu m$ length $\times 12~\mu m$ dia.) can have remarkably high thermal conductivity values – up to 85% that of natural diamond (1700 W m $^{-1}~K^{-1}$). 33 However, typical values for CVD films are lower, in the range $1000-1200~W~m^{-1}~K^{-1}$, but still a factor 2–3 times greater than the value for copper (Table 3). Diamond is not a heat sink as is often reported (it has a rather low specific heat capacity 38) but it can redistribute heat rapidly from small hot spots to a larger lower temperature region.

Silicon carbide monofilaments and Nicalon fibres have excellent high temperature stability in oxidising and nonoxidising environments even at 1800°C, but in practice it is the reactions that occur at the fibre/matrix interface that limit the service temperature of MMCs, e.g. SiC fibres in a titanium alloy matrix are limited to about 600°C. It is likely that this will also be the maximum service temperature envisaged for diamond fibres without oxidation protection. The oxidation rate of CVD diamond depends on the presence of non-diamond carbon. At 600–800°C in air the activation energy for oxidation (213 kJ mol⁻¹) is similar to that for natural diamond. Coatings of SiC and TiB₂, used to protect carbon fibre from oxidation, could be used for diamond. In vacuum, the onset of bulk graphitisation occurs at 1700–1900°C.

Diamond is resistant to most acids and bases but reacts with carbide forming elements and some molten salts.⁶ Since CVD diamond combines the properties of an insulator with the highest thermal conductivity of any material, it may be superior to graphite in reinforcing magnesium alloys.^{17,18} Magnesium alloy matrix/diamond fibre composites may offer low density, high strength, and high thermal conductivity (see Fig. 24 of Ref. 2) without the galvanic corrosion problems associated with graphite fibres

Manufacture of high strength continuous fibres

COMMERCIAL FIBRES

Comprehensive reviews of commerical fibres have been presented by Harris³⁹ and Cooke⁴⁰ and the manufacture of

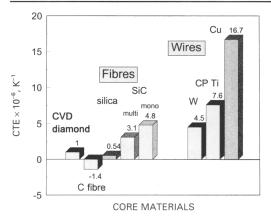
continuous fibre reinforced composites has been reviewed by Partridge and Ward-Close. The well known 10 μm dia. PAN carbon fibre used in reinforced plastics obtained by oxidising and pyrolysing a drawn textile fibre such as polyacrylonitrile. The Nicalon NL 200 Si–C–O fibre (made by the Nippon Carbon Co.) is 15 μm in diameter and consists primarily of β -SiC fibre with some silica, which makes it more reactive than pure SiC. It is made by pyrolysis of melt spun polycarbosilane at 1200–1300°C in nitrogen or vacuum. He HI-Nicalon fibre of lower silica content has higher strength and excellent strength retention at temperatures of about 1300°C.

The two large diameter (100–140 μ m) commerical β -SiC fibres, widely investigated for use in MMCs, are more difficult to handle than the thinner fibres, but a large diameter leads to higher composite compressive strengths. In the development of SiC fibres for MMCs, a diameter of 140 μ m was considered the best compromise for cost, composite properties, and acceptable residual stresses.⁴¹

The 100 μm dia. SiC fibre supplied by BP in the UK is made by CVD on moving electrically heated 20 μm dia. tungsten wire at temperatures of 1200–1400°C. The 140 μm dia fibre supplied by Textron in the USA has a 37 μm dia. carbon fibre core. 42 The fibres vary in grain size and composition with increasing distance from the core. 40,42,43 For use in titanium alloy MMCs, layers are produced near the fibre surface to control the strength and interdiffusion at the fibre/matrix interface, $^{44-46}$ e.g. a carbon rich layer of $1-2~\mu m$ thickness on Textron fibre and an inner carbon layer of 0.4 μm thickness with an outer TiB $_2$ layer of 1 μm thickness on BP fibre. Large diameter boron fibres are also produced on carbon fibre and tungsten wire cores but they tend to be more reactive in MMCs than SiC fibres. 40

POTENTIAL CORE MATERIALS FOR DIAMOND FIBRES

Since the diamond deposition temperature in the hot filament process (900-1000°C) is lower than for SiC, a wider range of fibre core materials can be considered for diamond. Some potential core materials and their properties are compared with CVD diamond and titanium in Tables 2 and 3; other cores used include molybdenum and alumina.9 In the hot plasma present during CVD of diamond, copper is not affected, SiC is slightly etched, and carbon fibre and silica are severely attacked. Carbon fibre has been coated with diamond after precoating with copper.13 The remaining core materials tungsten and titanium form carbides at the core/diamond interface. Graphite or other non-diamond carbon products may deposit first on all substrates before the nucleation of diamond. (The initial deposition of carbon can also occur during SiC fibre manufacture. 40) The high solid solubility of carbon in titanium alloys, nickel alloys, and ferrous materials may delay diamond nucleation and the subsequent formation of carbide phases may embrittle the



CP commercial purity

7 Coefficient of thermal expansion (CTE) for various core materials for CVD diamond fibres

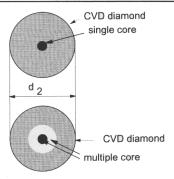
alloys. The non-metals and tungsten have adequate strength at the deposition temperature, but creep problems may arise with very thin titanium and copper wires.

The effect of these layers at the diamond/substrate interface has not yet been assessed. If the layers are not too thick they may help to relieve thermal mismatch stresses and provide adhesion between diamond and the core. A carbon coating has been recommended for carbon fibres before protecting with a SiC coating.⁴⁷

Diamond has a very low coefficient of thermal expansion and for carbon fibre, silica, and SiC the coefficient mismatch is much lower than for metal cores, as shown in Fig. 7. It is worth noting that the combination of high thermal conductivity and low coefficient of thermal expansion gives diamond excellent thermal shock resistance,1 which would be maximised in free standing hollow fibres. The intrinsic stresses that developed during CVD diamond film growth at temperature on silicon were tensile and thought to be associated with grain boundary phenomena.48 During cooling from the deposition temperature these stresses were reduced by the thermal stresses, Residual compressive stresses in polycrystalline CVD diamond films depend on substrate and deposition conditions, with reported values from 10 MN m^{-2} (Ref. 26) to $0.3-1.5 \text{ GN m}^{-2}$ (Refs. 32, 48). With metal cores the residual stresses may be reduced considerably via plastic deformation at temperatures well below the deposition temperature, and the high modulus of CVD diamond may allow the coating to withstand high uniform compressive stresses.

Fibre cores contribute to the ultimate cost of the fibre. (Note however that fibre cost may be only a small fraction of the composite cost, see 'Cost of diamond fibres' below.) The number of metres of filament per pound sterling⁴⁹ relative to titanium wire, for the above core materials, is roughly: carbon fibre 3537 m in a 2000 filament tow, Nicalon fibre 1200 m in a 500 filament tow, copper 84 m, Fe-Ni-Cr 25 m, iron 20 m, tungsten 20 m, SiC 2-6 m, and titanium 1 m. Depending on the core material, a diffusion barrier and/or a diamond nucleation coating or pretreatment may be necessary, involving additional processing cost. Obviously, if they can be coated, multifilament fibres would be attractive for cores.

In theory, diamond fibres can be made with any combination of internal core diameter and outside diameter. Small diameter non-metallic fibre cores ($10-15~\mu m$ dia.) are less costly than the thick fibres, but are supplied in tows containing hundreds or thousands of filaments. Liquid infiltration with metal is difficult and surface reactions can



8 Schematic diagram of CVD diamond fibre with single core and multiple cores

severely reduce the fibre cross-section. They have therefore tended to be used mostly for polymer matrixes. However, it may be possible to coat these fibres with CVD diamond by untwisting the fibre bundle until the interfilament spacing is greater than the mean free path in the deposition chamber. For CVD of diamond using a gas pressure of > 30 torr, the mean free path is < 3 μm .

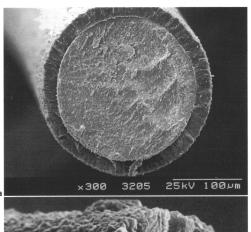
DIAMOND FIBRES

Cross-sections of solid diamond fibres having two types of core are shown schematically in Fig. 8. Various cores have been used, e.g. copper, tungsten, titanium and molybdenum wires, copper coated graphite fibre, and SiC, SiO2, and Al2O3 fibres. When a large diameter SiC fibre is used as a core for diamond fibres there will be three materials contributing directly to the fibre properties, as well as the indirect effects due to the interfaces present. Some examples of CVD diamond fibres with tungsten wire cores are shown in Fig. 9. Note the uniformity of the coating obtained using the hot filament technique. The characteristic columnar grain structure and the faceted surface of the diamond coating is apparent in Fig. 10, together with the furrowed surface of the drawn tungsten wire and the adherence of the coating. Copper wires less than 100 µm in diameter can be successfully coated with diamond, but the expansion mismatch leads to cracks with larger diameter wires, 11 as shown in Fig. 11.

Since diamond is resistant to attack by almost all chemicals, it is possible to remove metallic and ceramic fibre cores by etching to produce hollow diamond fibres with thick or thin walls (Fig. 12), and smooth internal surfaces (Fig. 12a), without affecting the diamond. These hollow fibres have potential not only for reducing the weight of composites, but also for providing channels for gases and sensors in smart composites. These sensors might involve electrorheological liquids for vibration control, si piezoelectric and optical materials to detect mechanical strain, 52,53 or optical fibres for damage detection, 4 all of particular importance for applications in the aerospace industry. 53,55 In common with amorphous glass fibres, 6 diamond fibres may also have potential for optical transmission, but over a much greater frequency range from the infrared to the ultraviolet (Table 1).

Potential modulus of diamond fibres

The fibre core can have a significant effect on fibre properties. The density ρ and thermal conductivity λ in the longitudinal fibre direction are given by the rule of mixtures^{2,8}





a 200 μm dia. tungsten wire core with 22 μm thick diamond coating to give volume fraction of diamond in fibre $V_d=0.33$, predicted effective fibre modulus E=537 GN m $^{-2}$, relative density $\rho=14\cdot1$, and specific stiffness $E/\rho=38$; b 25 μm dia. tungsten wire core with 10 μm thick diamond coating to give $V_d=0.69$, predicted effective modulus E=727 GN m $^{-2}$, fibre density $\rho=8\cdot4$, and specific stiffness $E/\rho=86$

9 Solid CVD diamond fibres produced at University of Bristol

where F, $F_{\rm c}$ and $F_{\rm d}$ are the properties of the fibre, fibre core, and CVD diamond coating and $V_{\rm c}$ and $V_{\rm d}$ are the volume fraction of core and diamond in the fibre cross-section. The upper bound values for Young's modulus E are also given by the rule of mixtures if the core and coating deform to the same strain.^{2,8,57}

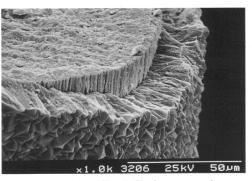
The volume fractions are determined by the diameter ratio k where

and d_1 and d_2 are the core and fibre diameters respectively (Fig. 8).

Values of ρ and E for solid diamond fibres having different types of core and for hollow diamond fibres have been calculated using the rule of mixtures and taking the measured value²⁹ for CVD diamond of E=891 GN m⁻².

SOLID CORE DIAMOND FIBRES

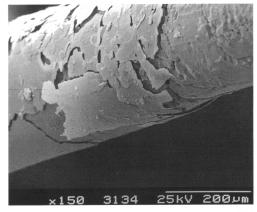
It is convenient to compare the properties of potential diamond fibres with the major commerical CVD fibres



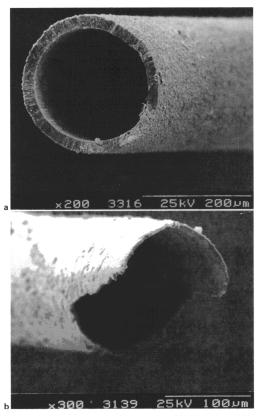
10 Fracture surface of fibre in Fig. 9a: note good contact between tungsten fibre and diamond coating, and columnar grain microstructure with faceted surface of coating

based on SiC. These are supplied in two sizes, 100 or 140 µm dia., with tungsten wire and carbon fibre cores respectively; these cores affect the fibre density. For example, a 20 μm dia. tungsten wire core in a 100 μm SiC fibre represents 4% of the fibre cross-section and increases the density and decreases the specific stiffness E/ρ of the SiC fibre (by about 12%). However, since the critical buckling load of a column in compression increases with the first power of the modulus but with the fourth power of the column diameter, thicker fibres are particularly attractive for composites loaded in compression (see 'Stiffness in compression' below). The combination of lower deposition temperature and exceptionally high modulus for CVD diamond coatings may permit not only a much wider choice of core materials, but also a wider range of core and fibre diameters than is possible for CVD SiC fibres.

The diamond coating thickness is given by $s=(d_2-d_1)/2$ and, for a given volume fraction of diamond in fibre, s will be less for a small diameter core. These fibres will require shorter deposition times, have smaller bend radii (allowing more complex shapes in a composite), and lower residual stresses than fibres having larger diameter (100 μ m) cores but an equivalent volume fraction of diamond. Clearly, small diameter diamond fibres may be in competition with carbon fibres. However, for a given composite modulus, a reduction in the number of fibres required would be possible with diamond fibres slightly larger than carbon fibres.



11 Multiple fracture of diamond coating on thick copper wire

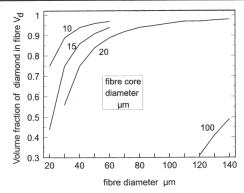


a 200 μm dia. fibre having 22 μm thick wall produced by etching out tungsten fibre core in fibre of Fig. 9a, $V_d=0$ -33, E=294 GN m $^{-2},~\rho=1\cdot15,~E/\rho=255;~b$ fibre having wall thickness of 3-5 μm

12 Hollow CVD diamond fibres

The effect of typical core and fibre diameters on the volume fraction of diamond in fibre, and hence on the fibre modulus, is shown in Fig. 13. With small fibre cores 10-15 μm in diameter, typical of carbon and Nicalon fibres, diamond volume fraction is very sensitive to diamond coating thickness up to about 40-50 µm fibre diameter. A larger diameter (100 µm) SiC fibre core having similar coating thicknesses of 10-20 µm will have much lower volume fractions. Carbon fibre is a particularly attractive core material and has been used as a core for CVD superconducting wires.⁷ The effect of 10 µm carbon fibre and 20 µm tungsten, titanium, and quartz cores on the potential elastic modulus of diamond fibres is indicated in Fig. 14a and Table 4. With the carbon fibre core the modulus is insensitive to coating thickness for fibre diameters in the range 50-150 µm, but for cores 20 µm in diameter modulus values are sensitive to fibre diameter below about 100 µm. Note the significant increase in fibre modulus for all diamond fibre cores compared with the values for commerical SiC fibres.

Of much greater significance is the effect of the core on the fibre specific modulus E/ρ , indicated in Fig. 14b and Table 4. For fibre diameters less than about 50 μ m the high density of tungsten reduces the E/ρ value for the diamond fibres to values below those for commercial SiC fibres (Fig. 14b, Table 4). Tungsten is therefore unsuitable for small diameter fibres compared with the lower density carbon fibre, SiC, and quartz cores. The inelastic behaviour



13 Volume fraction of diamond in fibre V_d versus fibre diameter for core diameters of 10, 15, 20, and 100 μ m

of tungsten cored boron fibre below 800°C (Ref. 40), which makes this fibre less thermally stable than SiC fibres, has been attributed to reaction products and stresses between boron and the tungsten core. The stability of diamond/core and diamond fibre/metal matrix interfaces has yet to be studied.

HOLLOW FIBRES

The possibility of manufacturing hollow glass fibres for reinforced plastics was considered in the mid 1960s. 88 Hollow fibres can be compared with solid fibres on the basis of either constant diameter or constant mass per unit length, as shown in Fig. 15. A wide range of effective density $\rho_{\rm f}$ and effective modulus $E_{\rm f}$ values are possible with hollow diamond fibres, depending on the volume fraction of hollow core $V_{\rm v}=k^2$ and given by

For a constant diameter fibre, increasing the volume fraction of hollow core increases the diameter ratio $k=i.d./o.d.=d_1/d_2$ and decreases the effective diamond fibre modulus (Fig. 16a and Table 4). At $V_{\rm v}=55\%$, the diamond fibre effective modulus $E_{\rm f}=400~{\rm GN~m^{-2}}$, the value for SiC fibre (Fig. 16a), but the diamond fibre effective density $\rho_{\rm f}=1.58$ compared with $\rho=3.4$ for SiC fibre.

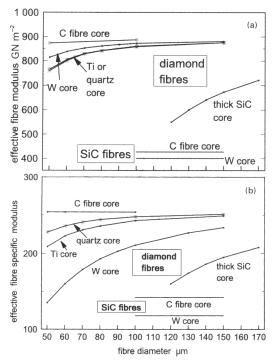
Thus, whereas with glass fibres it is necessary to keep the mass per unit length of a hollow fibre the same as that of the solid fibre in order to preserve the fibre strength, 58-60 this may not be necessary for hollow diamond fibres. For example, for the solid and hollow fibres having the same diameter (Fig. 15), and for a high hollow core volume fraction of $V_v = 50\%$, the hollow fibre would have an effective modulus of $E_f = 446$ GN m⁻² and $E_f/\rho_f = 255$ (Table 4). These values are greater than the corresponding values for commercial solid SiC fibres (by a factor of 2 for E_f/ρ_f) (Table 4).

The dimensions of a hollow fibre having the same mass per unit length, and hence modulus, as a solid fibre, can be calculated by assuming that a core of material diameter d_1 is taken from the centre of the solid fibre of diameter d_2 and distributed on the outside of the fibre to increase the diameter to d_3 , as shown in Fig. 15. Then

$$\frac{\pi(d_3^2 - d_2^2)}{4} = \frac{\pi d_1^2}{4}$$

$$d_3^2 - d_2^2 = d_1^2 \qquad (4)$$
and using k (equation (2a))
$$d_3^2 = d_1^2/1 - k^2 \qquad (5a)$$

$$d_2^2 = k^2 d_1^2/1 - k^2 \qquad (5b)$$



a predicted effective fibre modulus E versus fibre diameter for diamond fibre cores of carbon fibre (10 μm dia.) and tungsten, titanium, quartz (20 μm dia.) compared with commercial monofilament SiC fibres having carbon fibre core or tungsten core; b predicted effective fibre specific modulus E/ρ versus fibre diameter

14 Effect of fibre diameter on Young's modulus for solid fibres

The increase in fibre diameter when a solid fibre is converted to a hollow fibre having the same mass per unit length is given by the ratio d_3/d_2 ; with increase in volume fraction V_v , the modulus decreases and the ratio d_3/d_2 increases (Fig. 16b). Consider the above example of a hollow diamond fibre having half the mass of a solid fibre $(V_v = 50\%)$. If its mass is increased to equal that of the solid fibre then $V_v = 30\%$ and, from Fig. 16b and Table 4, E = 624 GN m⁻² and $E/\rho = 255$, values which are substantially greater than the corresponding values for solid SiC monofilament fibre (Table 4). However, it should be borne in mind that the removal of cores in long fibres has yet to be demonstrated, although this should not present a problem with short fibres of length much longer than the critical length (see following subsection).

In theory, volume fraction of hollow core $V_{\rm v}$ can be tailored to produce a range of hollow diamond fibres having effective moduli substantially greater than the values for solid SiC fibres. For a given volume fraction, the effective hollow fibre modulus is independent of fibre diameter, as shown in Fig. 17a for $V_{\rm v}=30$ and 50%. The fibre specific stiffness $E_{\rm f}/\rho_{\rm f}$ is a constant for hollow fibres, with the same value as for a hypothetical monolithic solid diamond fibre ($E/\rho=255$), compared with values of $E_{\rm f}/\rho_{\rm f}=118-142$ for SiC fibres (Table 4). The dramatic effect of a hollow core is apparent when comparisons of effective fibre specific modulus are made, as can be seen in Fig. 17b and Table 4.

Thin walled hollow fibres may have a further advantage. Under transverse loads the fibre may change shape from circular to oval cross-section and provide greater transverse

Table 4 Stiffness data for commercial SiC fibres and predicted data for diamond fibres having solid or hollow core

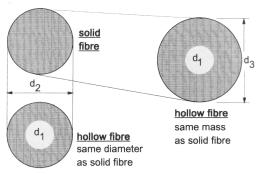
Core	Fibre dia., μm	Fibre core dia., µm	Diamond coating thickness, µm	ρ	<i>E</i> , GN m ⁻²	Ε/ρ
Solid SiC fib	res					
W wire (BP) C fibre	100	20		3.4	400	118
(Textron)	140	37		3	427	142
Solid diamo	nd fibres	S				
W wire	100	20	40	4.13	872	211
	50	20	15	6.03	804	135
Ti wire	100	20	40	3.54	860	243
	50	20	15	3.66	766	209
Silica fibre	100	20	40	3.46	858	248
	50	20	15	3.34	760	228
C fibre	100	20	40	3.48	889	255
	50	20	15	3.45	884	256
Hollow diam	ond fibi	res (V _v =	50%)			
	140	99	20.5	1.75	446	255
	100	70.7	14.7			
	50	35.4	7.3			
Hollow diam	ond fibi	res (V _v =	30%)			
	140	77	31.5	2.45	624	255
	100	55	22.5			
	50	27	11.5			

V_v volume fraction of void.

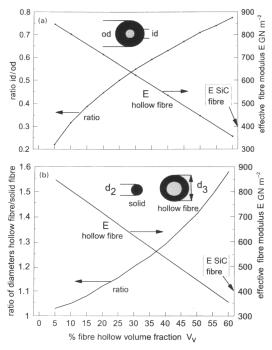
strength than solid fibres.^{58,59} It may therefore be possible by mixing these types of hollow fibre with solid fibres to tailor a composite to have a range of stiffness values or a through thickness stiffness gradient. From the predicted stiffness properties of solid and hollow diamond fibres in Table 4 it can be inferred that, with the exception of the very high modulus pitch based carbon fibres (P100), even hollow fibres may be competitive with the carbon fibre properties given in Table 2.

DISCONTINUOUS FIBRES

In composites continuous fibres provide maximum load transfer between fibre and matrix and maximum strength, but discontinuous or short fibre composites have several important advantages. The cost of composite manufacture is usually much less for discontinuous fibre than for continuous fibre, the discontinuous fibre composite is more easily formed into complex shapes and when the fibres are randomly distributed the composite properties are more isotropic. Although discontinuous fibres can be made by chopping continuous fibres, ideally a lower cost route is



15 Schematic diagram showing formation of hollow fibre with same diameter d_2 as solid fibre, with hollow core diameter d_1 and formation of hollow fibre with larger diameter d_3 with same mass per unit length (i.e. same modulus) as solid fibre



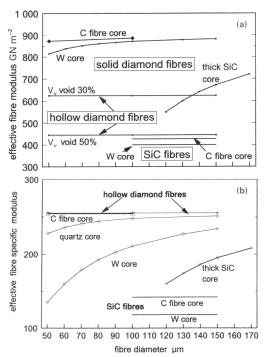
a ratio i.d./o.d. $= d_1/d_2 = k$ and predicted effective fibre Young's modulus versus volume fraction of hollow core V_{ν} for fibre of constant diameter; b ratio d_3/d_2 where $d_2 = d$ iameter of solid fibre converted to hollow fibre of diameter d_3 and same mass per unit length) and effective fibre modulus versus volume fraction of hollow core

16 Diameter ratios for hollow diamond fibres

required. By contrast with aligned continuous fibres, for increasing composite strain the tensile stress in aligned discontinuous fibres is not uniform, but increases with increasing distance from the end of the fibre. A critical fibre length $l_{\rm crit}$ must be exceeded for the maximum stress at the centre of the fibre to reach the fracture stress and for the strength of the fibre to be fully utilised.

The composite strength also increases with increase in l/d, where d is the fibre diameter and the critical fibre aspect ratio becomes l_{crit}/d . Anderson et al.²¹ have used computer modelling data to assess the potential strength of discontinuous diamond fibre composites. The data show $l_{\rm crit}/d$ is minimised for a particular ratio of $E_{\rm d}/E_{\rm m}$ (where $E_{\rm d}$ and $E_{\rm m}$ are the modulus of the diamond fibre and metal matrix respectively). For discontinuous diamond fibre MMCs, $E_{\rm d}/E_{\rm m}$ is in the range 5-14 corresponding to a minimum $l_{\rm crit}/d$ of about 20. For $d = 50 \, \mu \rm m$, $l_{\rm crit} \approx 1 \, \rm mm$. With all discontinuous fibres of length l_{crit} the composite strength would be about half that of a continuous fibre composite containing the same volume fraction of fibre. As shown above, the stiffness of the diamond fibre is about twice that of SiC or carbon fibre typically used in composites and for the same fibre length discontinuous diamond fibre composites are expected to be significantly stiffer. It should also be noted that if $l/l_{\rm crit} > 10$, the discontinuous fibre composite strength can be about 95% of the continuous fibre strength.8 Critical aspect ratios are expected to be much greater for polymer matrixes than for metal matrixes.

Discontinuous fibres may be particularly attractive for hollow diamond fibres since removal of the fibre core by etching may become more viable for fibres about 10 mm in length.



a predicted effective fibre modulus E versus fibre diameter for hollow diamond fibres ($V_{\rm v}=30$ or 50%) compared with solid diamond fibres and commercial SiC fibres; by predicted effective fibre specific modulus E/ρ versus fibre diameter for hollow diamond fibres ($V_{\rm v}=30$ or 50%) compared with solid diamond fibres and commercial SiC fibres.

7 Effective fibre modulus v. fibre diameter for various types of fibre having different cores

Stiffness in compression

Although there have been significant improvements in the tensile strengths of carbon fibre reinforced polymer composites there has been far less improvement in the compressive strengths. ^{39,61} This is largely because in compression the composites are limited by Euler buckling of the fibres. The critical buckling load per unit length for a cylindrical column is given by

$$P_{\rm crit} = EI$$

where I is the second moment of area.

For solid fibre

 $P_{\rm crit} = E d_2^4 \pi / 64$

and for hollow fibre

$$P_{\text{crit}} = E(d_2^4 - d_1^4)\pi/64$$

where d_1 and d_2 are the hollow core diameter and outside fibre diameter respectively.

Some success has been reported in increasing the terms E and I via physical vapour deposition of thin (up to 800 nm) $\mathrm{Al_2O_3}$ films on 20 μ m dia. polymers; large increases in compressive strength were obtained. ⁶² Thus, while recognising that the matrix provides support for embedded fibres in a composite loaded in compression, it is worthwhile comparing the critical buckling loads (P_{crit}) for single unsupported solid and hollow diamond fibres bearing in mind that diamond fibres might be obtained to large diameters and having hollow cores. Comparing large with

small diameter solid fibres

 $P_{\rm crit}$ (100 µm fibre)/ $P_{\rm crit}$ (10 µm fibre) = (100/10)⁴ = 10⁴ Comparing diamond fibres with SiC fibres of the same diameter

 $P_{\rm crit}$ (diamond fibre)/ $P_{\rm crit}$ (SiC fibre) ≈ 2

The ratio of the $P_{\rm crit}$ value for a hollow fibre with $V_{\rm v}=50\%$ relative to a solid diamond fibre of the same mass per unit length is also about 2, with corresponding gains to be made in terms of the specific buckling loads for hollow fibres. Substantial increases in composite compressive properties are therefore expected with diamond fibres.

Cost of diamond fibres

It is too early to state whether diamond fibres are likely to become an 'engineer's best friend', but it will certainly depend on: (i) diamond fibre properties, (ii) fibre cost, (iii) composite manufacturing costs, and (iv) component manufacturing costs.

An estimate of the CVD diamond market for the year 2000 is £4300m (Ref. 63), with 75% of the applications in the wear, abrasives, and electronics fields. The potential increases in diamond fibre and diamond fibre composite stiffness have been demonstrated. There are also possible developments that will exploit hollow diamond fibres and the physical properties of diamond, such as thermal conductivity. Together, these factors will provide a strong driving force for the manufacture of diamond fibres. Nevertheless, the composites are relatively expensive and performance in service to be competitive with alternative composites. 15,64

The manufacturing costs (factors (iii) and (iv) above) are likely to be the same for diamond fibre as for conventional composites. Peel⁶⁵ has emphasised that the cost to achieve the manufactured component is critical in comparing the cost of composites with other materials. In this respect, composites have a major advantage in that they can be manufactured close to form, minimising machining costs and material wastage. With CVD diamond tools, the tool cost is not the most important factor compared with greater product reliability with lower manpower costs.⁶⁶ Benefits obtained by using lower cost precursors for carbon fibre have arisen indirectly from a reduction in the number of fibre defects and an increase in the yield.³⁹

With regard to factor (ii) above, in titanium alloy/continuous SiC fibre monofilament MMCs it was estimated that the SiC fibre accounts for about 12% and the matrix and consolidation costs (plant, labour, profit, etc.) account for about 88% of the composite cost. (As quoted by Cooke, the raw material cost of inorganic fibres is very much less than of superalloys.) Diamond fibre costs will depend on the cost of core material, core pretreatment, diamond deposition, any diamond fibre coating requirements and, as with all fibre production, the yield and cost of fibre quality control. Aftergrowth processing is already an intergral part of the manufacture of bulk polycrystalline diamond for optical and thermal properties. 24

The manufacturing costs for CVD diamond fibres will be associated with the handling of non-toxic low cost hydrogen rich $\rm H_2$ –CH $_4$ gas mixtures, which, though an explosive hazard, are not likely to present such a problem as the handling and retrieval of spent toxic gases required for the CVD of SiC. The processing temperature for the hot filament and microwave plasma CVD diamond processes is lower than for CVD SiC fibre. The up-front plant costs are higher for the latter than for the torch or hot filament CVD diamond methods. Scaling up may be

easier and less expensive for hot filament CVD. This must be balanced against better process control and possibly a higher yield of superior quality fibres using the microwave technique.

It is anticipated that the cost of all diamond deposition processes will be reduced substantially in the future, ⁶⁷ but thin films and higher deposition rates or output will remain critical for lower cost. ⁶⁸ Based upon the selling price per kilogram of polycrystalline CVD diamond heat sinks ⁶⁶ and 100 m length of SiC monofilaments, ⁴⁹ diamond is about 70 times more expensive than SiC fibre, which has been reported ¹⁵ to be £4000–10 000/kg.

For diamond fibres, this indicates a need to increase the number of fibres that can be coated simultaneously in a single reactor. It is shown above (Table 4) that dramatic increases in fibre modulus and specific modulus relative to SiC fibre values are expected with only 15 µm thickness of diamond on small (20 µm) diameter fibres given $V_d = 0.84$. These SiC fibres are supplied as multifilament bundles containing 500-6000 fibres. Taking the current low deposition rate ($\sim 1.5 \,\mu \text{m h}^{-1}$) for high modulus hot filament CVD diamond and a 10 m long reaction chamber, a 10 m fibre length could be CVD coated with 15 µm of diamond in 10 h, an output rate of 1 m h⁻¹. This should be compared with the output of thick CVD SiC monofilament, which is produced at about 1 km h⁻¹, followed by a much slower $\sim 300 \text{ m h}^{-1}$) barrier layer coating stage. The multistage protection treatments for boron fibres lead to a significant increase in cost.40 Thus, a possible target for diamond might be a deposition rate increase by a factor 5 and multiple fibre deposition, say, 50 fibres per reactor, to give a filament output comparable with the slowest stage for SiC.

Much higher diamond deposition rates have been reported. ^{27,69} For example, high quality diamond has been deposited at 50 µm h⁻¹ via the oxyacetylene method and 100–900 µm h⁻¹ using dc and rf plasma torch deposition techniques. The very high plasma temperatures limit the substrates to silicon, molybdenum, and MoS₂ (Ref. 69), but the reported disadvantage of these methods, a limited area that can be coated, may be less limiting for fibre coating.

The greater stiffness indicated for diamond fibres compared with SiC fibres implies that fewer diamond fibres (a smaller volume fraction) may be required to attain a significant increase in composite stiffness. Even lower diamond fibre composite cost might be achieved by placing the diamond fibres only in critical regions in a hybrid fibre composite.³⁹ These advantages of better utilisation of diamond fibres in composites do, of course, require a corresponding increase in the market for diamond fibres, if lower fibre prices are to be obtained by high volume production. However, bearing in mind the advances in diamond processing in recent years and the potential properties of diamond fibres, it is concluded that cost competitive diamond fibre composites might reasonably be expected in the future.

Conclusions

Many properties of chemical vapour deposited (CVD) diamond approach or equal those for natural diamond. The manufacture of solid diamond fibres by deposition on various wire and ceramic cores and the production of hollow diamond fibres by removal of the cores has been demonstrated and there is a reasonable expectation of cost competitive fibre manufacture in the future. The potential Young's modulus values of continuous and discontinuous diamond fibres are predicted to be substantially higher than for current commercial SiC fibres, with corresponding increases in compressive stiffness. Hollow fibres may also allow the use of sensors in smart structures. Inevitably, at

such an early stage in the development of diamond fibres, there are many outstanding problems to be solved associated with deposition rate, substrate—diamond interaction, core removal in long fibres, microstructure and properties of the CVD diamond fibres, and the manufacture of CVD diamond composites. However, there are extensive data covering the manufacture of CVD SiC fibres and SiC and graphite fibre composites, much of which will be directly applicable to diamond fibre processing. Meanwhile, in parallel with fibre and composite development, there is a need to identify applications and potential users capable of exploiting the unique properties of diamond in the form of solid and hollow fibres.

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