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The effect of varying deposition conditions on the Young's modulus of diamond coated wires

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Abstract

Diamond Coated Tungsten (W) fibres/wires have been produced by hot filament chemical vapour deposition (HFCVD), and their Young's modulus measured using a resonance test. Changing the diamond deposition conditions results in changes in morphology, grainsize, film thickness, and quality, which in turn affects the composite fibre modulus and other mechanical properties (e.g. strength and fracture toughness). The aim of this investigation was to see the effect of varying the methane (CH_4) concentration and the deposition time on fibre modulus. © 1997 Elsevier Science S.A.

Keywords: Young's modulus; Diamond; Fibres; Composite

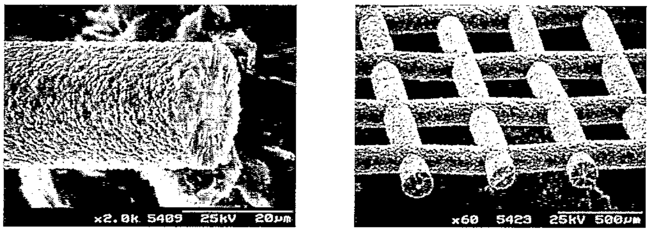
1. Introduction

The idea of diamond coating fibre/wire cores, in order to exploit diamond's extreme properties (e.g. Young's modulus, thermal conductivity and strength) in fibre form, was introduced in the early 1990s [1]. Since then, various research groups [2–7] have taken on the challenge, and applications have emerged in the areas of fibre reinforcement [8], thermal management [6,7] and grinding technology [9]. Diamond coated fibres can yield modulus values up to 900 GPa, depending on deposition conditions and diamond volume fraction [10]. These values are substantially greater than those of existing fibre reinforcements (~400 GPa, SiC and W).

Single fibres and wires of diameters as small as 10 μm have been diamond coated (Fig. 1(a)). In addition, several other configurations have been coated; including parallel arrays of fibres [10], mesh (Fig. 1(b)) and fine coils to produce tubes [11]. Recent work on coating steel wires has resulted in magnetic fibres [12]. Copper, titanium, magnesium and polymer matrix composites containing both diamond coated fibres and tubes have been produced [13].

2. Growth of diamond on wires

The substrate wires, W (125 μm diameter), were diamond coated by hot filament chemical vapour deposition (HFCVD) [10]. The filament temperature (2150–2180 °C), pressure (20 Torr) and gas flow rate (200 sccm) were kept constant, while the CH_4 concentration and the time were varied (Table 1). Three or four samples from each batch were modulus tested. Unfortunately, it was not possible to test sample TS117 or those prepared at a 1.25% CH_4 concentration. An estimated value for the Young's modulus of TS117 was calculated from tensile test data [14] which yielded a modulus 80% of that of TS116.



(a) (b)

Fig. 1. A 10 μm diameter Tyrano (SiC based) fibre coated with ~7 μm of diamond. (b) A 20 μm diameter tungsten mesh (wire separation ~0.5 mm) coated with 70–80 μm of diamond.

Factors that affect growth include: CH_4 concentration, growth rate, temperature, pressure and flow rate [15–18]. A high CH_4 concentration leads to a high nucleation density as it aids carburisation of the substrate surface. The crystalline quality of diamond decreases with increasing growth rate, due to incorporation of non-

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Table 1
Growth and Raman details: (a) Diamond (doublet or triplet), (b) Crystalline graphite (c) Amorphous carbon, (d)Disordered graphite, or amorphous carbon

Sample	Methane Concentration (%)	Deposition time (h)	Raman Peak Position (cm^{-1})
TS117	0.5	24	1334,1336 (a); 1580-1600 (b); 1400 (c).
TS94		48	1334,1336 (a); ~1500 (d).
TS99		72	1334,1336,1339 (a); ~1500 (d).
TS112	0.75	24	1334,1337 (a); 1530 (d);
TS85		48	1334,1337 (a); 1530 (d);1400 (c)
TS88		72	1334,1337,1339 (a); 1530 (d);~1390 (c)
TS116	1	24	1334,1337(a); 1530 (d);1380 (c)
TS82		48	1334,1337,1339 (a); 1525 (d); 1400 (c)
TS98		72	1334,1337,1339 (a); 1525 (d); 1380 (c)
TS118	1.25	24	1334,1336,1338 (a); 1500 (d)
TS83		48	1334,1337,1339 (a); ~1570 (d)

diamond carbon, morphological twins and other defects. Film density decreases gradually with increased CH_4 concentration. Morphology and texture depend both on the substrate temperature and the CH_4 concentration, and hence on the growth rate. Low gas pressure and/or high gas flow rates lead to high nucleation densities. It is thought that high gas flow rate may increase the movement of gas species to the substrate surface, and results in an increased growth rate.

3. Young's modulus measurement

Resonance methods of measuring the Young's modulus are among the most accurate. The resonance test used here is described in detail elsewhere [10,19]. The technique allows the diamond modulus to be calculated using the following equation [15],

$$E_d = \frac{1}{(D^4 - d^4)} [1.28868 f^2 L^4 (\rho_c d^2 + \rho_d (D^2 - d^2)) - E_c d^4], \quad (1)$$

where f is the resonant frequency, L is the sample length, D and d are the total diameter and core diameters respectively and E_d, E_c, ρ_d, ρ_c are the Young's modulus and density of the diamond and the core respectively. The composite fibre modulus was calculated using the rule of mixtures.

Factors that may affect the Young's modulus and other mechanical properties include: the percentage of non-diamond carbon in the film, grainsize and morphology, growth defects and voids, film adhesion and internal film stress [15,20,21]. Increasing the amount of non-diamond carbon in the film will reduce the Young's modulus. As non-diamond carbon is thought to reside primarily in grain boundaries, the greater the grain boundary area, the lower the modulus should be. Therefore, small grainsize material should yield lower modulus values. The fracture toughness, however, should be greater due to the extra ductility afforded by the grain boundary material [22]. Theoretical calculations of Young's modulus as a function of orientation show slight differences, with the $\langle 111 \rangle$ and $\langle 100 \rangle$ orientation showing the highest and lowest values of modulus respectively [23].

Defects and voids of grainsize proportions can be incorporated into the diamond microstructure, especially in more rapidly grown films [16,18,20]. These voids may contain non-diamond carbon or poorly crystallised material, which would reduce the density and also the Young's modulus. Fracture properties would be expected to fall due to a greater possibility of finding a strength limiting flaw. The internal stress in the film should change with changing grainsize, film thickness and growth rate. Defects and void incorporation in the film cause changes in density resulting in growth strains. The stress induced may be inhomogeneous. Grain boundaries are thought to be the primary cause of stress [20]. Therefore, stress should be greater in small grainsize material.

4. Results and discussion

4.1. Growth

The growth rate appears to increase with CH_4 concentration up to 1%, but then drops off (Fig. 2(a)). The 0.5% CH_4 samples show the steadiest growth rate with time. As expected from the columnar nature of diamond growth, all samples (except those deposited with 1.25% CH_4) showed an increased grainsize with thickness. As mentioned previously, nucleation density increases with methane concentration. Therefore, for films of equal thickness, the higher the methane concentration, the smaller the grainsize. After 24 h (Fig. 2(b)), the 1%

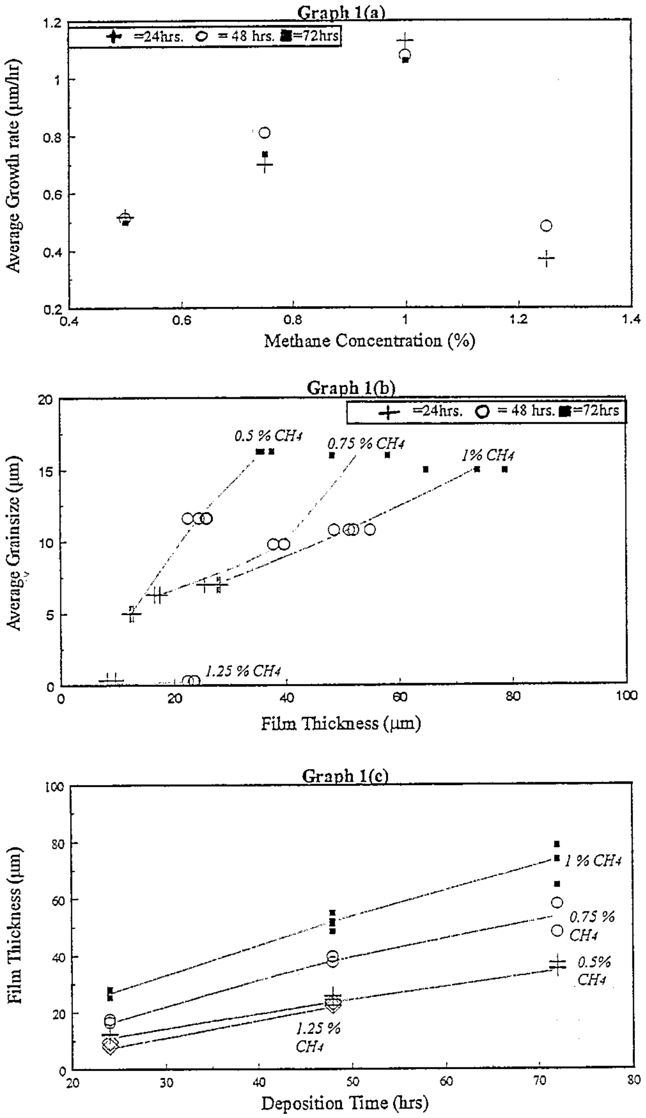


Fig. 2. Plots showing (a) average growth rate of CVD diamond film on W wire as a function of methane concentration determined from deposition of 24(+), 48 (O) and 72 (■) hours duration. (b) Average grain size as a function of film thickness. (c) Variation of film thickness with deposition time for four different CH_4/H_2 mixing ratios.

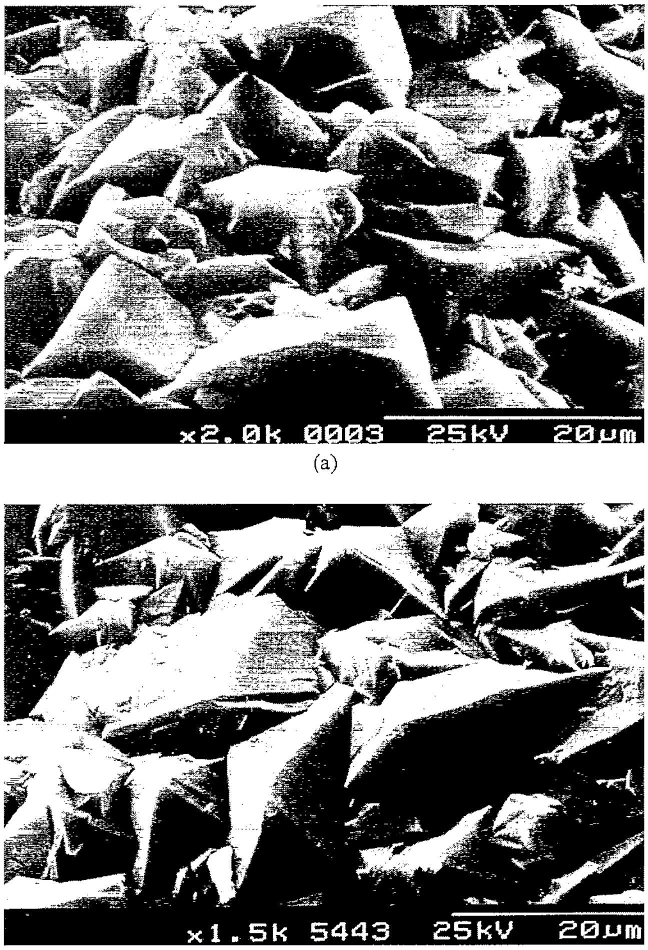
CH_4 sample shows the largest surface grainsize. The reason for this is the higher growth rate and greater film thickness.

A film grown at 0.5% CH_4, of the same thickness (27 µm), has almost twice the average grainsize. The rate of grain growth with film thickness can be seen to increase with decreasing methane concentration. As a result, the 72 h 0.5% CH_4 sample has the greatest surface grainsize. Also, due to the lower nucleation density of this sample, the grainsize throughout the film thickness will be larger than films grown at higher CH_4 concentrations. As the grainsize has been shown to be related to modulus, an increase in modulus with film thickness and/or reduction in CH_4 concentration would be expected.

As expected, film thickness increases with deposition time for all concentrations (Fig. 2(c)). The film thickness increases with CH_4 concentration up to 1% and decreases thereafter. The 1.25% CH_4 samples showed the lowest thickness. A similar relationship exists between average grainsize and deposition time.

4.2. Morphology and Raman spectra

The 0.5% CH_4 samples showed predominately ⟨111⟩ orientation (Fig. 3(a)), while the 1% CH_4 samples appear to be predominately of ⟨110⟩ orientation (Fig. 3(b)) Those deposited at 0.75% CH_4 show mixed ⟨111⟩ and ⟨110⟩ morphology. All showed a fairly rough surface. Overall there appears to be a change from ⟨111⟩ to ⟨110⟩ orientation with increasing methane concentration up to 1%. The 1.25% CH_4 sample showed a fine grained floret-like structure with some evidence



(a)

(b)

Fig. 3. (a) Sample TS99, 0.5% methane, grown for 72 h. (b) Sample TS98, 1% methane, grown for 72 h.

of crystal planes (Fig. 4(a)), and a smooth surface (Fig. 4(b)).

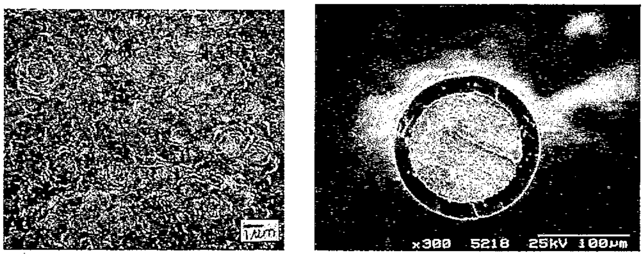
Raman peak shifting to higher frequencies is caused by compressive stress [18] and was similar for all the films tested. All samples showed multiple peaks (Table 1) which may be the result of stress inhomogeneity [21]. The thicker films and those deposited with greater %CH_4 showed a higher degree of peak splitting. Triplet peaks suggest differing stress components in the three principal directions. Further examination of the doublet peaks exhibited by some samples would be required to determine their stress state. Raman showed the diamond quality of the 1.25% sample to be the lowest. Differences in quality between the other samples were less evident.

4.3. Modulus measurement

The samples deposited at 0.5% CH_4 (Fig. 5(a)) showed expected behaviour (i.e. an increase in Young's modulus with increased grainsize). Their growth rate was low and therefore a low level of defect and non-diamond incorporation is expected. The films grown at 0.75% CH_4 showed a decrease in modulus with increasing grainsize. An explanation for this could lie in grainsize length voids, which have been reported to occur in more rapidly grown films [20]. These voids would reduce the film density and also the modulus. Another contributing factor may be internal film stress. At 1% CH_4 the modulus initially decreases with increased grainsize and then flattens out.

Comparing films grown for the same time but with different methane concentrations (Fig. 5(a)) shows that after 24 h, the 1% CH_4 sample had the largest surface grainsize and the highest modulus. After 72 h, the 0.5% sample had the greatest grainsize and the highest modulus, with the modulus decreasing with decreasing grainsize. A similar relationship exists between modulus and film thickness.

When comparing the composite modulus with the growth rate (Fig. 5(b)), there appears to be very little difference in modulus by varying the CH_4 concentration. The reason is that with increasing CH_4 concentration (up to 1%), there is an increase in the film thickness, and therefore an increased volume fraction diamond and hence an increased composite modulus. The differences lie in the geometry of the fibre. Those produced at lower CH_4 concentrations have thinner, higher quality films, yielding finer diameter fibres, which may be preferential in some composite applications. Other factors to be taken into account are surface finish and morphology as these will affect adhesion to the matrix material, as well as affecting strength.



(a) (b)

Fig. 4. (a) Floret type structure of sample TS83 and TS118. (b) Smooth fibre surface.

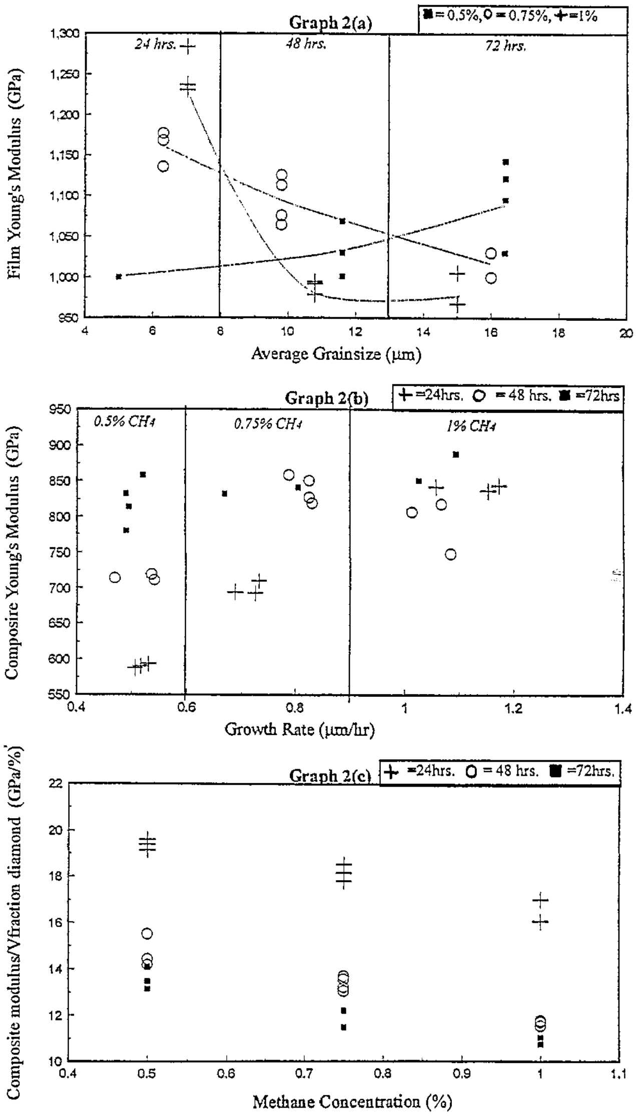


Fig. 5. Plots showing (a) the way in which the Young's modulus of the CVD diamond film varies with grain size, (b) the variation of the composite Young's modulus with growth rate, and (c) this same data normalised according to the volume fraction of diamond in the coated wire sample.

Fig. 5(c) is a measure of diamond quality as a function of the volume of the film. It can be seen that, as expected, the higher the methane concentration the lower the overall fibre quality.

5. Conclusions and future work

This investigation gives an insight into the degree of variation in geometry and properties that diamond coated fibres can possess. Hopefully it will provide a guide to composite manufacturers, who wish to tailor fibre properties and dimensions to give the required level of reinforcement. Further work is required to substantiate these trends.

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