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Plasma-assisted chemical vapour deposition of tin oxide coatings

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A feasibility study was performed to assess the potential of plasma-assisted chemical vapour deposition as a method for the coating of carbon fibre bundles. Rayon-based carbon filaments, in 2000-filament tows, were coated with SnO_2. Direct-current and hollow-cathode discharges generated in an $SnCl_4$–O_2 medium helped to deposit the SnO_2 coatings on fibres that were heated to approximately 800 °C, by plasma bombardment, and kept in the plasma for 15 min. Both routes were shown to produce uniform and well adhered coatings, and also to offer advantages in terms of processing temperature and the possibility of continuous processing.

1. Introduction

Coating of fibres for high-temperature metal-matrix composite (MMC) and/or ceramic-matrix composite (CMC) applications is predicated on the provision of a diffusion barrier that obviates strong chemical bonding between the fibre and the matrix. The coating is expected to provide a weak interface between the coating and matrix to promote crack deflection, fibre debonding and/or fibre pull-out, all of which are considered to contribute greatly to the toughness of the composites [1, 2].

The coatings, approximately 1 μm thick, are generally deposited through chemical vapour deposition (CVD), sol–gel or polymer–precursor deposition processing. CVD affords an easy process for high rates of deposition and better control of stoichiometry, composition and structure, by control of the deposition parameters. These parameters include the pressure of the gases, the deposition temperature, and the partial pressure of the reactants [3, 4].

Plasma-activated CVD is also a vapour deposition process in which a partially ionized and quasi-neutral gas (plasma) is used to produce and to activate the required chemical reactants. The main features of the plasma-activated CVD process are: [5, 6]

(a) relatively low substrate temperatures are required;

(b) reasonably high deposition rates are achieved;

(c) good adhesion between coating and fibre is obtained due to sputter cleaning of the substrate surface impurities;

(d) control of film properties is rendered straight forward by the easy control of deposition parameters; and

(e) this low-pressure CVD (5 to 20 m torr in the case of direct-current and 200 to 400 m torr in the case of the hollow-cathode-generated discharges) also affords higher uniformity in the deposited coatings, because of the increase in the mean free path of gas molecules.

The intent of the present undertaking was to utilize direct-current and hollow-cathode-generated discharges in the deposition of tin-oxide coatings on carbon fibres.

2. Experimental procedure

2.1. Plasma-assisted CVD apparatus

The direct-current discharge apparatus is shown schematically in Fig. 1. In this arrangement, the fibre to be coated is made the cathode of the d.c. cell and thus the ionized chemical species are deposited on it. Heating of the fibre is achieved from the inherent ion bombardment. Thus, this assembly is appropriate for plasma-assisted CVD coating of conducting fibres such as carbon, silicon carbide, etc. Partial pressures of the plasma gases are adjusted to achieve the desired substrate (fibre) temperatures [6].

The hollow-cathode discharge (HCD) arrangement is shown in Fig. 2. The electron bombardment experienced by an axially located substance in this arrangement [7] is used to heat the substrate carbon fibre to the desired temperature. The electron bombardment is expected not only to dissociate the plasma gases more efficiently but also to help in the ready formation of well adhered and dense coatings. This geometry is suited for plasma-assisted CVD coating of both conducting and non-conducting (such as Al_2O_3) fibres.

2.2. Carbon fibres

The carbon fibres used for this feasibility study were old stock of unknown history, but the tensile-strength data of Table I, X-ray diffraction (XRD) information of Table II and scanning electron micrographs of

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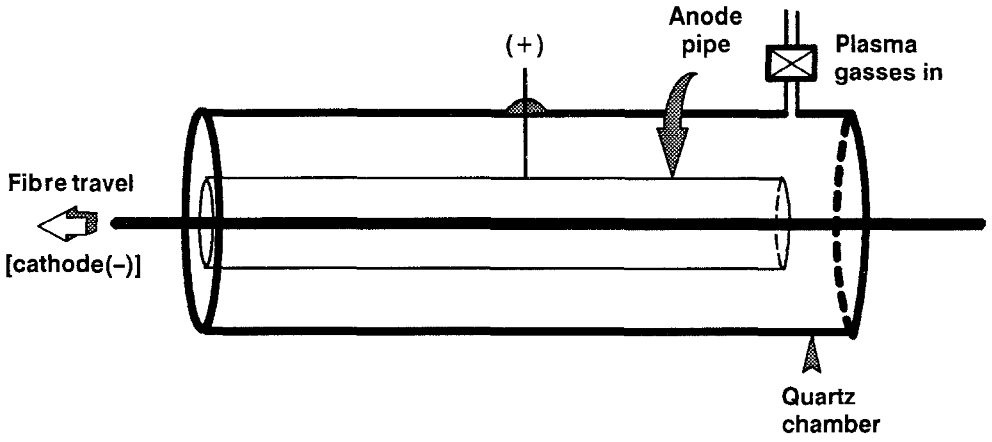

Figure 1 Direct-current glow discharge apparatus.

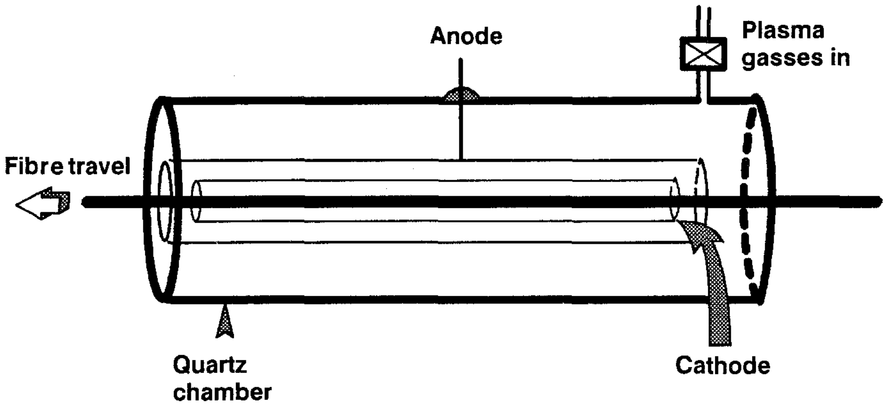

Figure 2 Hollow-cathode discharge apparatus.

TABLE I Tensile strength of rayon-based carbon fibres[a] before and after plasma-assisted CVD

Fibre description	Tensile strength (GPa)
Carbonized rayon-based fibres [10]	0.3–0.8
As-received carbonized rayon-based fibres	0.70
HCD plasma-assisted CVD-coated fibres	0.63
d.c. plasma-assisted CVD-coated fibres	0.47

[a] Average of 20 tests.

TABLE II X-ray diffraction data of carbonized rayon fibres

d(nm)	I/I_1	Matching peaks to (C) 8H
0.365	100	–
0.332	70	3.35_x
0.234	28	–
0.203	44	2.03_1
0.166	17	1.67_1
0.143	17	–
0.122	27	1.23_1

Fig. 3 all suggest they were rayon-based filaments that had been carbonized. The energy-dispersive spectrum of the uncoated fibres (Fig. 4) shows peaks associated with the machine chamber and no peaks related to tin; this spectra was taken as a standard. The fibres were then coated in the form of 2000-filament tows.

2.3. Plasma-assisted CVD

Direct-current plasma coating, in an $SnCl_4$–O_2 medium, was done with the application of 500 V d.c. at 20–50 m torr pressure for an exposure time of approximately 15 min.

Hollow-cathode discharge coating of the carbon-fibre tows was done with a similar plasma composition, but at a higher pressure (100–105 m torr), and with the application of 400 V d.c. for approximately 15 min. In both cases of plasma generation, the 1 m length of the tubular assemblies (Figs 1 and 2) contained a uniform plasma that was quite visible. Each coating procedure was initiated following a 20 min argon-ion sputtering of the fibre tows for cleansing purposes.

The temperature of the fibres during coating was read optically to be $\approx$ 800 °C, corrected for the presence of the plasma.

2.4. Characterization of the fibres

X-ray diffraction (Phillips X-ray generator, CuK_α radiation, 40 kV, 20 mA) was used to characterize the uncoated fibres. Surface details of the coated and uncoated fibres, and fracture surfaces of coated fibres, were scrutinized through scanning electron microscopy (Hitachi, model HHS-2R, operated at 20 kV).

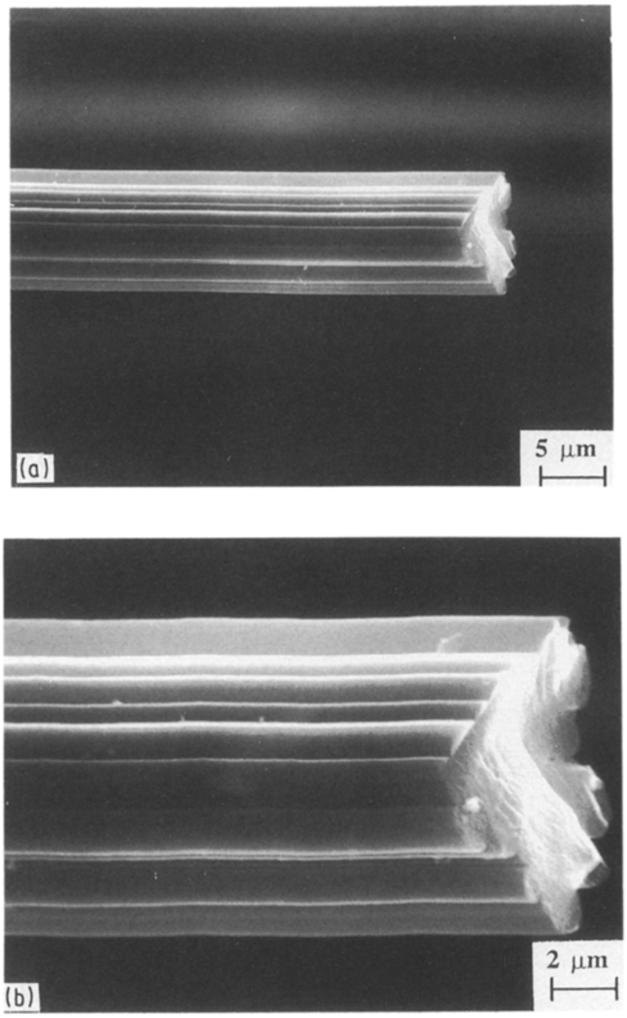

Figure 3 (a, b) Rayon-based carbon fibres.

The associated energy-dispersive X-ray unit was used to obtain energy-dispersive spectra and dot maps in each case.

Tensile testing was done with a 500 g load cell (Instron model 1122) at a crosshead speed of 0.008 mm s^{-1}, and samples of 17 mm gauge length. Fibres were individually mounted on paper frames and their diameters measured with an optical microscope.

3. Results and discussion

Fig. 5 shows a fibre that had a d.c. plasma-assisted coating of SnO_2, at two magnifications. The energy-dispersive X-ray spectrum (Fig. 6) shows the coating to contain Sn, and Fig. 7 shows the Sn dot map of this fibre. Charging, characteristic of the substrate carbon, as well as sputtering of the coating in the electron beam in this case, have made the dot map appear less than specific to the fibre, but this, we believe, is a common problem with carbon substrates and SnO_2 coatings. The profile of the fibre is evident in the micrograph.

Fig. 8 shows the SnO_2 coating deposited by hollow-cathode discharge-assisted CVD, at two magnifications. Fig. 9 shows the energy-dispersive X-ray spectrum of the coating surface, verifying the presence of the Sn, and Fig. 10 is the Sn dot map of the area. Once again, charging of the substrate and sputtering of the coating are evident in this micrograph, but the presence of the coating and its consistency are verified.

Fig. 11 shows the fractured end of a coated fibre. The added transparency of the broken edge indicates this to be coating only, and the broken fibre obviously pulled out of it. One could thus surmise that the broken fibre pieces were briefly held together by the coating, and thus that fibre fracture was not enhanced by any irregularities in the coating (as has been observed [8] with direct CVD coatings). This claim, though, is not fully supported by the tensile-test data shown in Table I; tensile strengths obtained for the

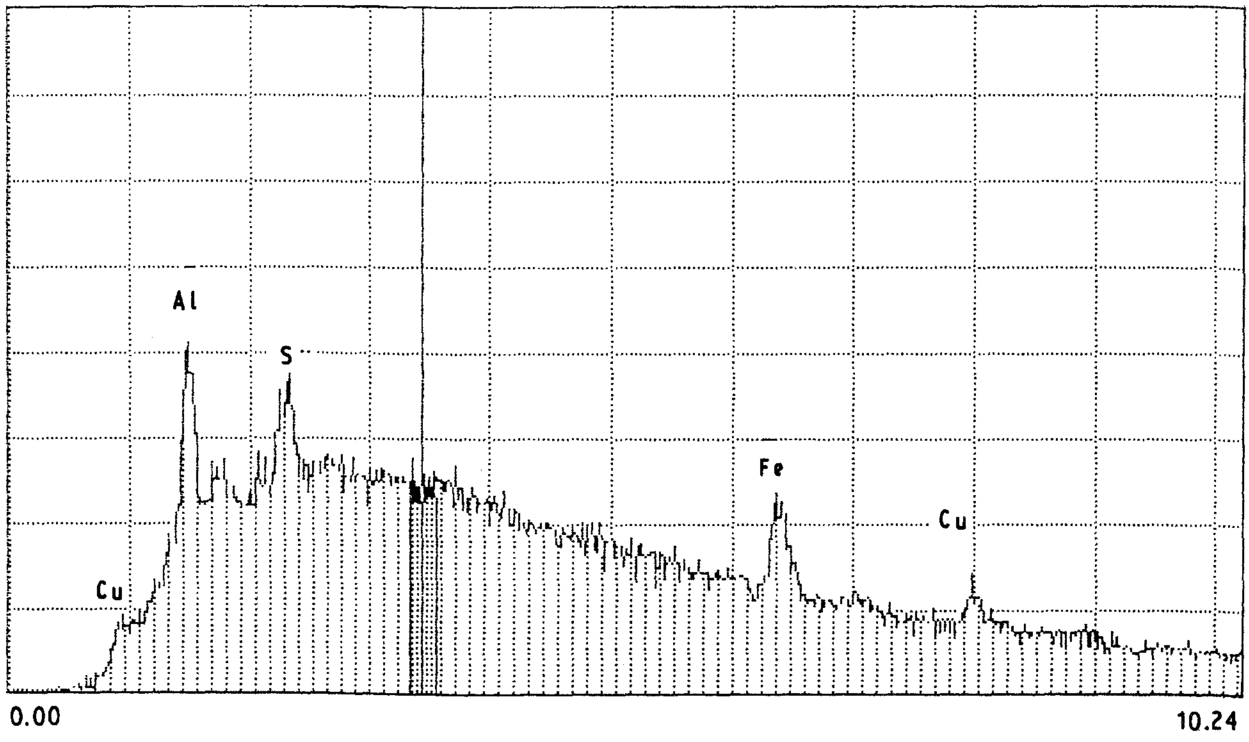

Figure 4 Energy-dispersive X-ray spectrum of the carbon fibres; peaks are those of the instrument-associated components.

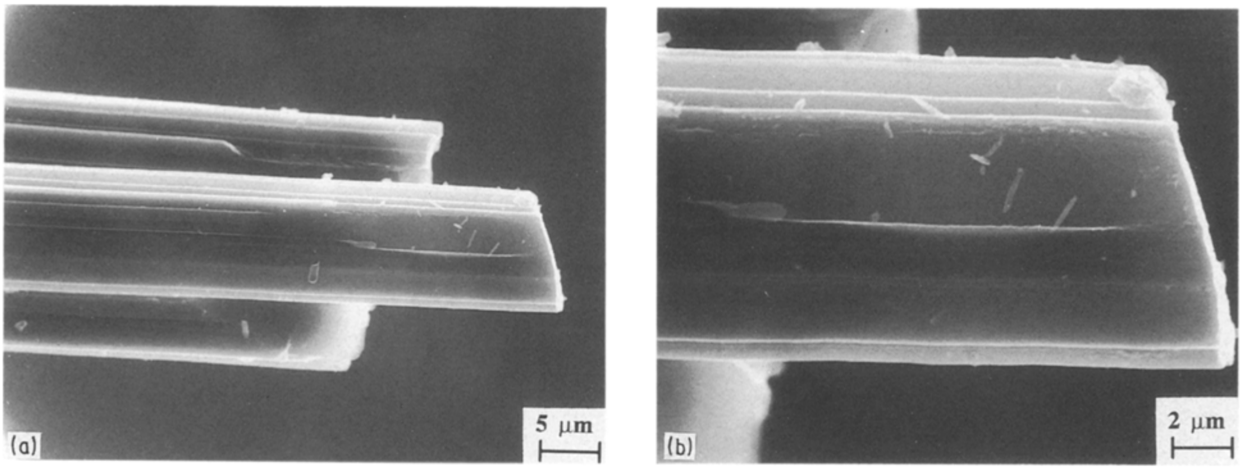

Figure 5 (a, b) Carbon fibre coated with direct-current plasma-assisted CVD.

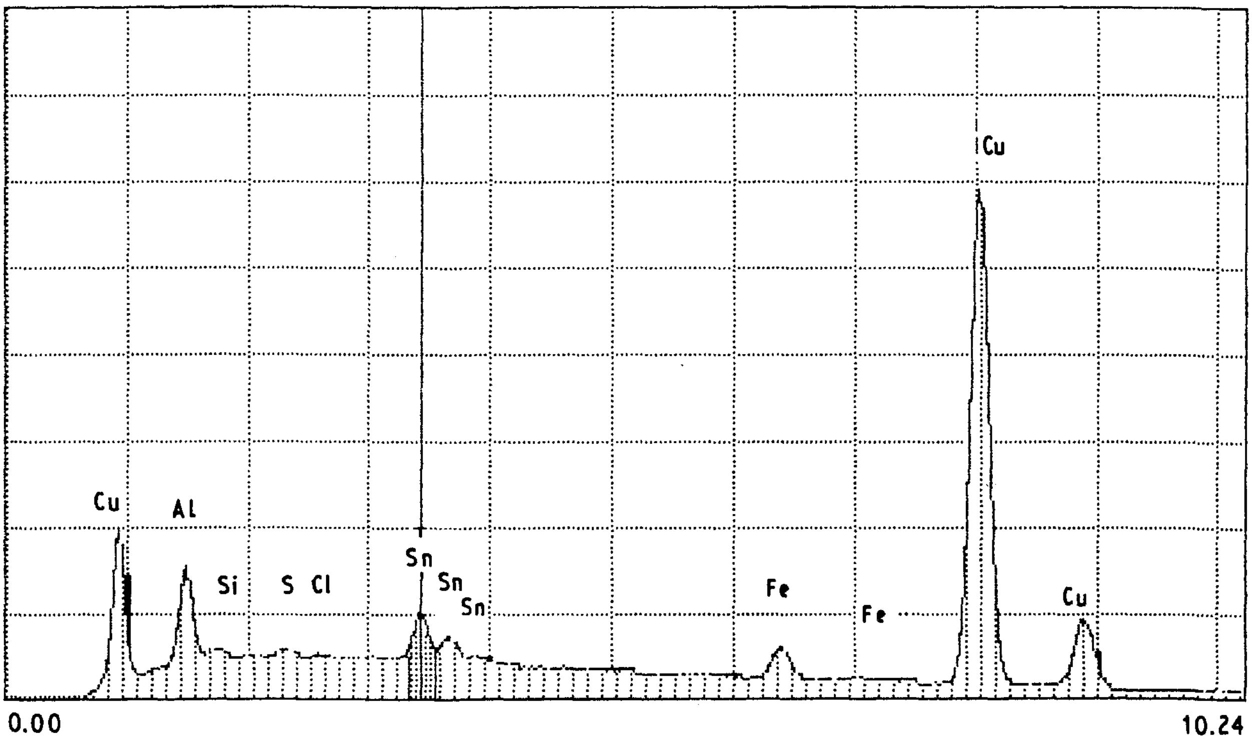

Figure 6 Energy-dispersive X-ray spectrum of fibre in Fig. 5; Sn of SnO_2 is present.

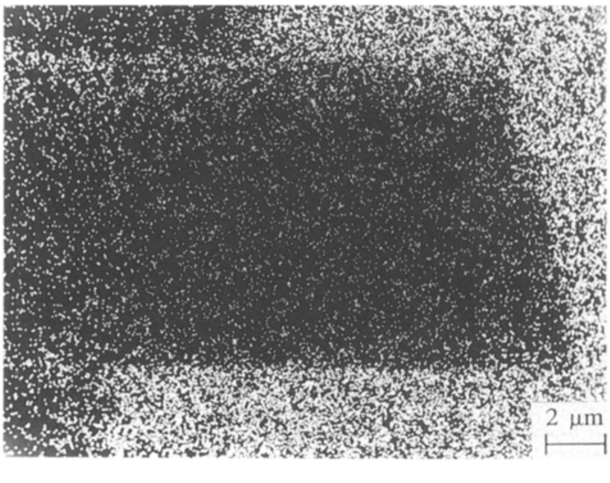

Figure 7 Dot map of fibre in Fig. 5; X-rays specific to Sn.

coated fibres were lower than those of the uncoated ones. This latter fact could also emanate from the presence of oxygen with the carbon fibres at 800 °C during coating; such degradation following CVD coating has also been observed in previous work [8, 9] although for different reasons.

The coatings, shown in Figs. 5 and 8, are quite uniform and smooth. The fact that complete coverage is obtained throughout the 1 m length of the plasma-generating unit suggests that the 15 min residence time in the plasma is quite sufficient for coating of the fibres. There is thus the possibility of direct application to continuous processing.

Finally, the temperature of the fibres was optically read to be around 800°C (corrected for the presence of the plasma), which is considerably lower than those

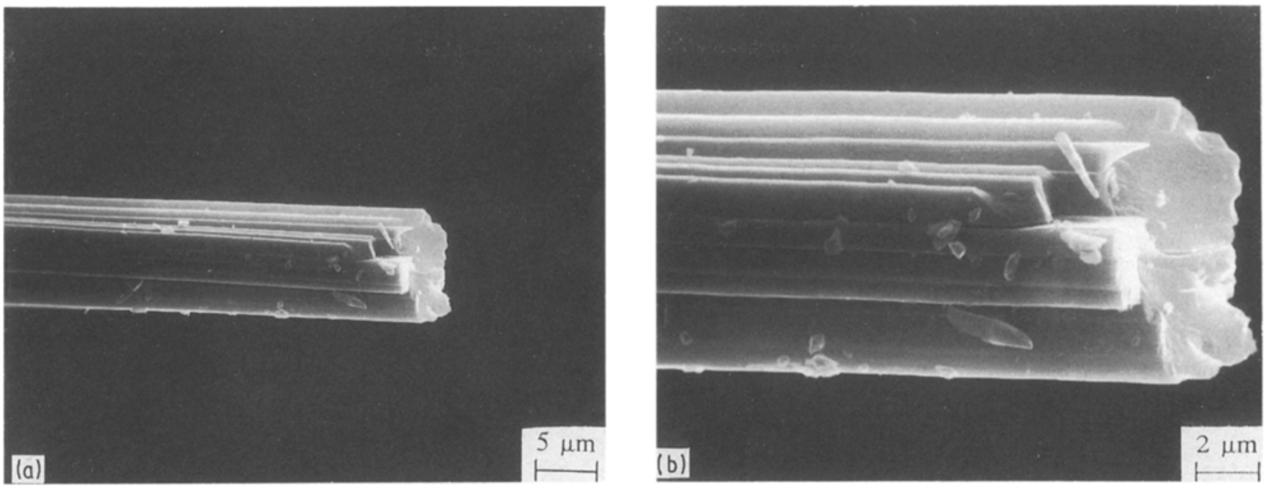

Figure 8 (a, b) Carbon fibre coated with hollow-cathode discharge assisted CVD.

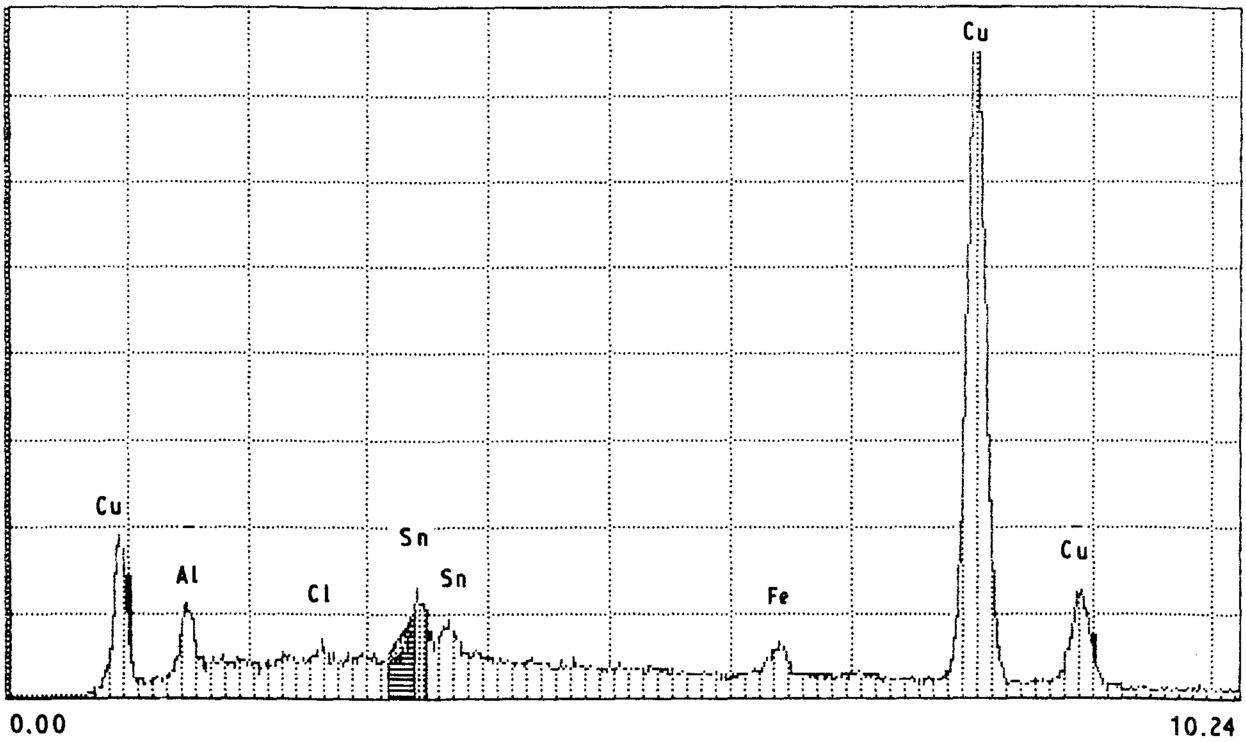

Figure 9 Energy-dispersive X-ray spectrum of fibre in Fig. 8; Sn of SnO_2 is present.

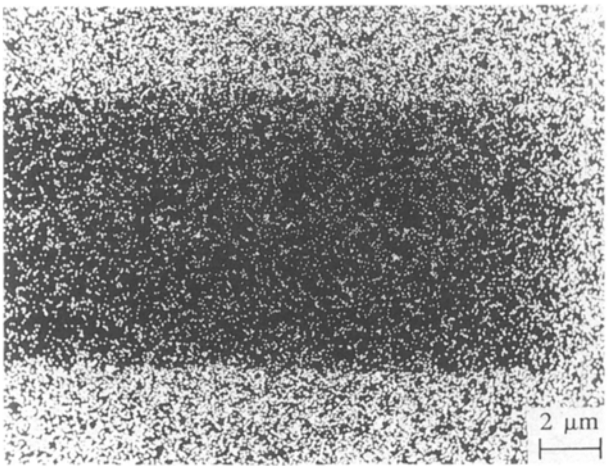

Figure 10 Dot map of fibre in Figure 8; X-rays specific to Sn.

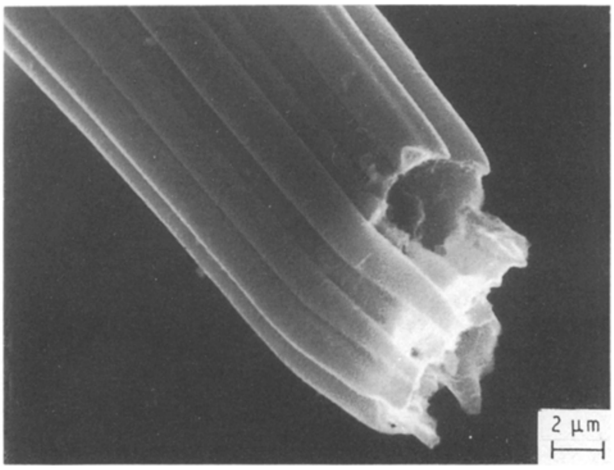

Figure 11 Fractured end of SnO_2-coated fibre.

used in other CVD processing. This should greatly facilitate the maintenance of fibre properties when exposed to the various plasma compositions associated with coatings to be used on fibres for high-temperature composite applications.

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