

SiC fibre by chemical vapour deposition on tungsten filament

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Abstract. A CVD system for the production of continuous SiC fibre was set up. The process of SiC coating on 19 μm diameter tungsten substrate was studied. Methyl trichloro silane (CH_3SiCl_3) and hydrogen reactants were used. Effect of substrate temperature (1300–1500°C) and concentration of reactants on the formation of SiC coating were studied. SiC coatings of negligible thickness were formed at very low flow rates of hydrogen ($5 \times 10^{-5} \text{ m}^3/\text{min}$) and CH_3SiCl_3 ($1.0 \times 10^{-4} \text{ m}^3/\text{min}$ of Ar). Uneven coatings and brittle fibres were formed at very high concentrations of CH_3SiCl_3 ($6 \times 10^{-4} \text{ m}^3/\text{min}$ of Ar). The flow rates of CH_3SiCl_3 and hydrogen were adjusted to get SiC fibre with smooth surface. The structure and morphology of SiC fibres were evaluated.

Keywords. SiC; CVD; continuous fibre; composite; deposition.

1. Introduction

Ceramic fibres are of great interest as reinforcements for metal matrix and ceramic matrix composites (MMCs and CMCs), in defence and industrial applications. SiC has attractive properties like low density, high temperature strength, and resistance to oxidation and creep. Continuous fibres of SiC are prepared either by polymer pyrolysis or by chemical vapour deposition (CVD).

SiC fibres can be produced by pyrolysis of melt-spun polycarbosilane fibres. These fibres are used extensively to reinforce ceramics. The main disadvantage of this type of fibre is non-stoichiometry and presence of considerable amounts of free carbon and oxygen. At high temperatures the reaction between free carbon and oxygen causes decrease in properties. Stoichiometric chemical vapour deposited (CVD) coatings possess high strength and low porosity along with chemical purity. This is lacking in fibres made by sol-gel (Ling *et al* 1991) or melt-spinning (Edie and Dunham 1989) process. Stoichiometric and high purity SiC fibres have been made since mid 1960s by CVD on to a substrate like tungsten or carbon (Bunsell 1988).

In this process the core fibre (W/C) is fed into a glass reactor through a mercury contact and resistively heated by applying direct current. Mercury acts as gas tight seal and facilitates electrical resistance heating of the fibre. Hydrogen, argon, and silane vapours are fed into the reactor at about 1300°C (Debolt *et al* 1973; Fitzer *et al* 1973, 1975; Randon *et al* 1973; Crane and Kurkonis 1975) to get SiC deposition. Such fibres with different trade names (SCS fibres with C core from Textron Speciality Materi-

als, Lowell, MA, USA; Sigma fibres with W core from Berghof, Germany; Trimarc1 with W core from Amercom, Inc., Atlantic Research Corporation, USA) are commercially available for last 15 years. Microstructure, microanalysis and creep properties of sigma fibres and SCS fibres were studied by Nutt and Wawner (1985), Martineau *et al* (1984), Ning *et al* (1993) and Dicarolo (1986).

Temperatures as high as 800°C have no appreciable effect on the properties, making CVD SiC monofilament a candidate for high temperature applications (Lindley and Jones 1975). The next generation aircraft engines need lighter high performance structural materials with high temperature capabilities (Sorensen 1993). Titanium based MMCs are being developed for use in aircraft turbine engines to operate in the temperature range from 600–800°C. CVD processed SiC fibres with the substrate (either tungsten wire or a carbon monofilament) are used to reinforce these Ti based composites (Mizuhara *et al* 1997; Ellis and Gooch 1997). Some advantages of SiC fibre with tungsten core are: (i) tungsten wire of the appropriate diameter is available in relatively defect free, large spools, unlike carbon monofilament, (ii) the cost of producing W-core SiC fibre is lower than C-core SiC, (iii) the modulus of W-core SiC fibre is generally greater than that of C-core SiC fibre and this may be desirable in stiffness-critical applications (Gambone and Gundel 1997).

Ti–6Al–4V/sigma-1240(SiC) composites exhibit a high elastic stiffness (axial elastic modulus above 200 GPa) and fracture strength (UTS \approx 1.8 GPa) and a 600°C creep rupture life of several thousand hours or more at 1 GPa (Vancheeswaran *et al* 1998). We have recently taken up this work to develop CVD SiC fibre (with tungsten core) to use in Ti alloy SiC composites. Results of the prelimi-

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nary investigation on the chemical vapour deposition of SiC on tungsten filament are presented here.

2. Experimental

Figure 1 shows the schematic diagram of the apparatus used for the preparation of SiC fibre. As shown in figure 2 the glass reactor tube of length 60 cm is fixed with teflon supports on to laboratory stands. Initially a 19 μm dia. tungsten filament was used as a substrate. The tungsten

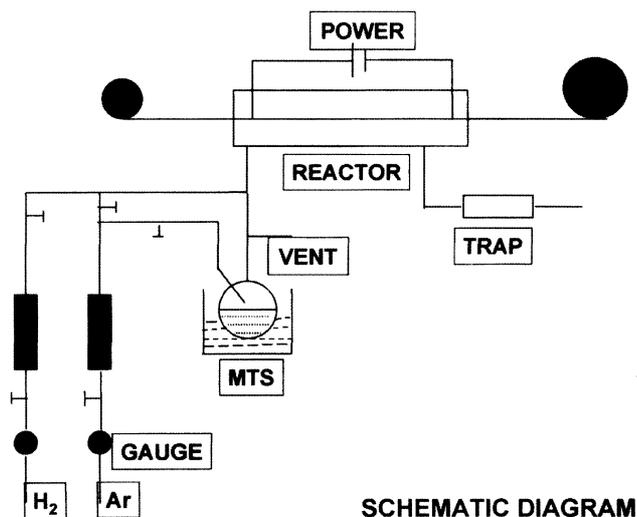
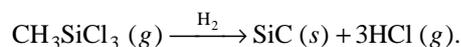


Figure 1. Schematic diagram of the typical CVD apparatus used for SiC coating on tungsten filament.

filament wire from input spool is fed into the reactor from left end. After passing through the reactor for predetermined time, it get wound onto a plastic takeup spool of 25 cm outer diameter. As it becomes brittle after coating with SiC, the fibre has to be wound on to a bigger diameter spool. The W filament wire is resistively heated by applying direct current from power source and through mercury contacts. Mercury acts as gas tight seal and provide electrical contact.

Methyl trichlorosilane (MTS) was used as reactant precursor because it contains silicon and carbon in stoichiometric proportions (Jin Choi *et al* 1997). The MTS bubbler was maintained on a constant temperature bath. As argon bubbles through MTS it carries away silane into the reactor. Hydrogen gas join the silane carrier gas before they enter the reactor. With MTS the basic reaction is expressed as



The exhaust gas mixture containing unspent silane, hydrogen, argon, decomposed products, and HCl was trapped by passing it through NaOH bubbler and water scrubber. The temperature of the W filament was controlled at required temperature by suitably adjusting the power input from d.c. power source. A precision optical pyrometer (Pyrometer Instrument Co., Inc., USA), capable of measuring the temperature of very thin filaments of the order of 0.0005" in diameter was used to monitor the temperature of W substrate.

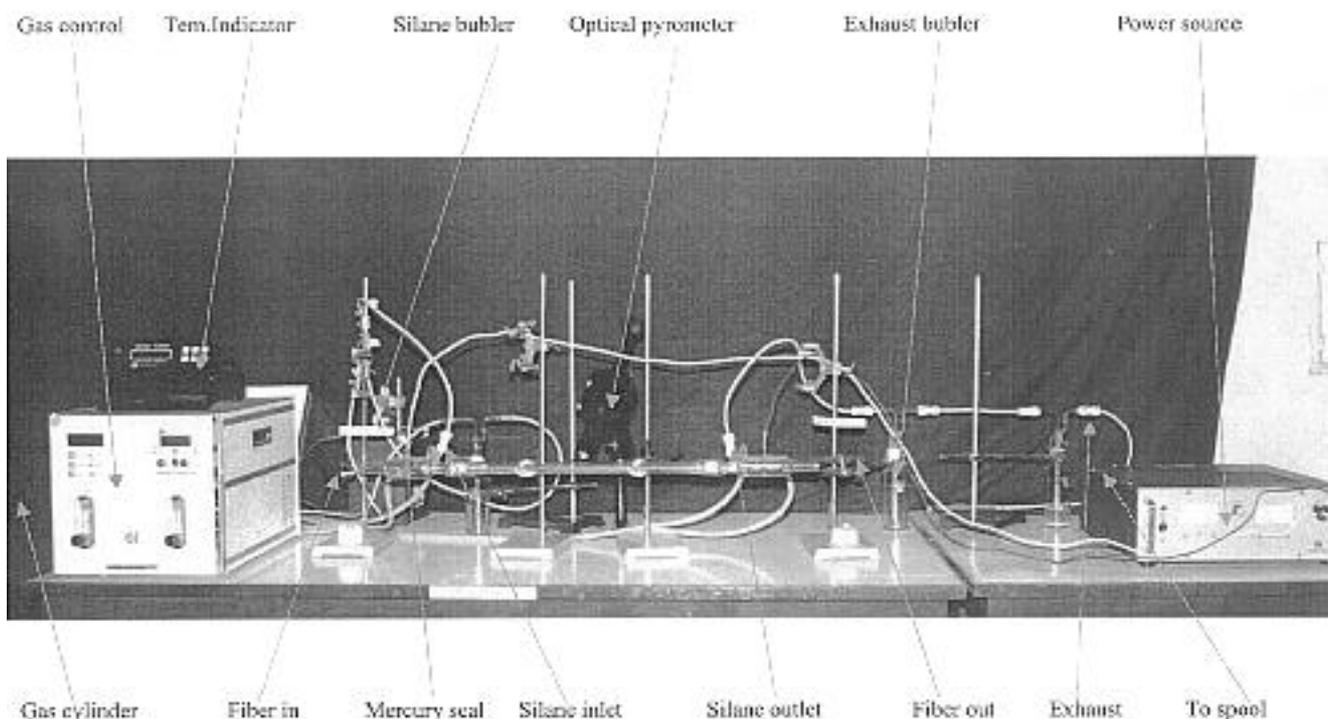


Figure 2. Photograph of CVD assembly with all accessories.

Initially the decomposition of SiC was studied on stationary filaments. The free ends of the W filaments were tied with small weights to keep it straight. After SiC deposition for a residence time of about 20 sec the filament was withdrawn from the reactor. The deposition was studied at different temperatures (1300, 1400 and 1500°C). The effect of concentration of silane (MTS) and hydrogen on coating process was studied by varying the flow rates of hydrogen and argon. The structure and morphology of SiC fibre were studied through Leo scanning electron microscope (SEM). Scanning electron probe microanalysis (SEPMA) was carried out with CAMECA

(model CAMEBAX-MICRO, France) equipment. To study the cross-section of the fibre a small piece of coated fibre was mounted in a steel tube with soldering lead.

3. Results and discussion

We experienced some difficulties during the initial experiments particularly with mercury seals and W filament loading. Pouring the mercury into the water cooled seals is a tough task. Since mercury is very heavy it easily enters into the reactor during pouring into seal and when-

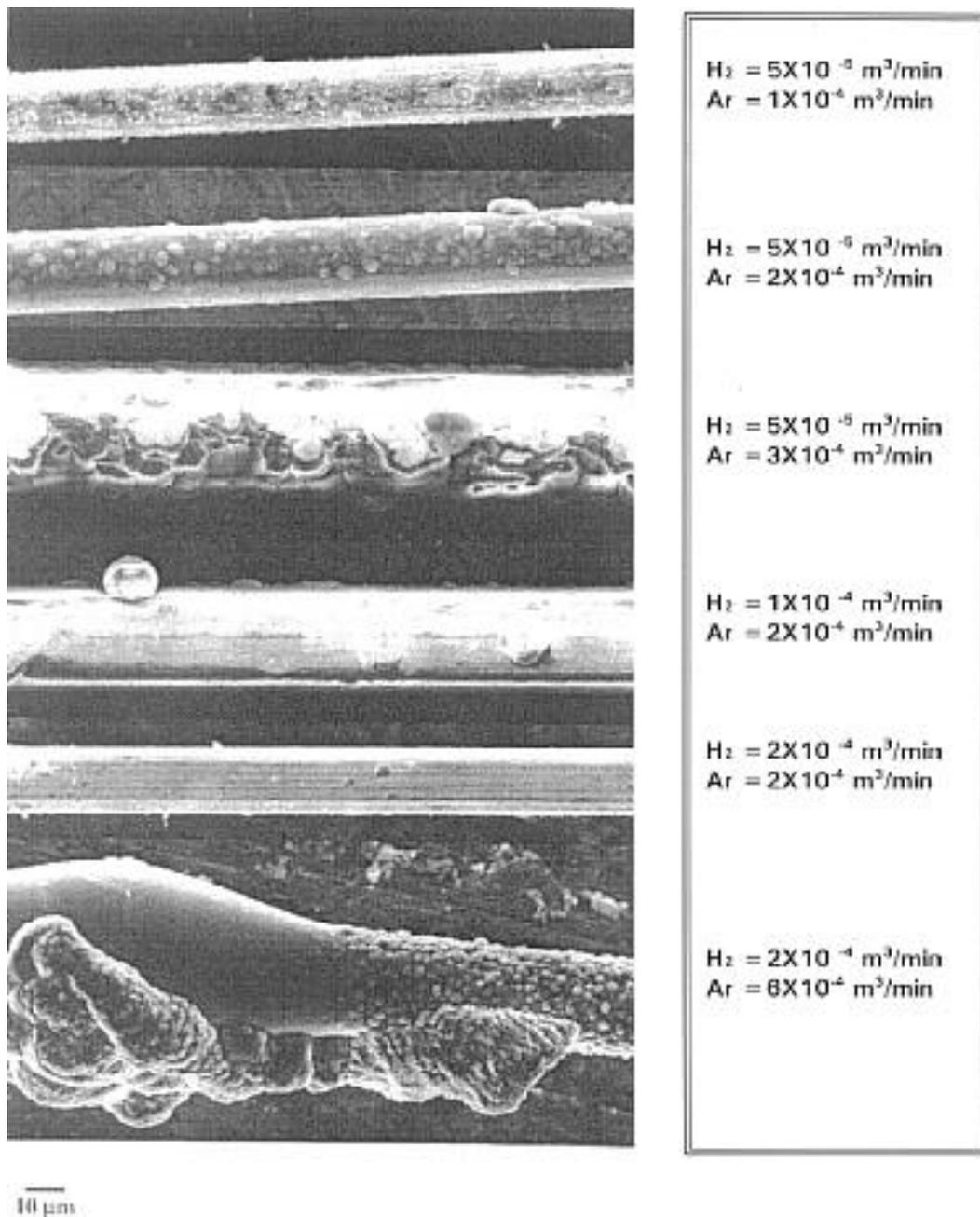


Figure 3. Effect of H_2 and CH_3SiCl_3 concentrations on the formation of SiC coatings.



Figure 4. Uneven and wavy coatings formed at 0.2 Lpm of hydrogen and 0.6 Lpm of argon.

ever there is a slight change in the pressure inside the reactor. Since mercury is very toxic it should be removed from the reactor before starting the coating process. To facilitate easy feeding of mercury into the water cooled seal a special funnel with fine capillary is made. The capillary of the mercury seal is also altered. Loading of W filament through this fine seal capillary of the reactor tube is a difficult task. The initial single piece glass reactor is changed to three-piece reactor. Detachable water cooled mercury seals are attached with ground glass joints to the main reactor glass tube. With this apparatus it became easy to pull the W filament through the reactor. The handling of MTS is another tough job. It is air-sensitive and reacts with all plastic tubes, causes seizing, and galling of corks, lids and exhaust lines. Due to the closure of exhaust lines some time back pressure develops and reactant gasses gush out through mercury seals. Though extreme care is taken, pungent smell is experienced in the vicinity of CVD apparatus during the coating process.

In figure 3, the progress of SiC coating at 1300°C is shown. Initially the flow of hydrogen was kept constant at $5 \times 10^{-5} \text{ m}^3/\text{min}$ to study the effect of concentration of silane. At $1 \times 10^{-4} \text{ m}^3/\text{min}$ flow of argon, very negligible amount of deposition was observed. This was due to very low concentration of MTS in argon carrier gas. When argon flow was increased to $2 \times 10^{-4} \text{ m}^3/\text{min}$ considerable increase in coating thickness was observed. Further increase in argon flow to $3 \times 10^{-4} \text{ m}^3/\text{min}$ resulted in thick and coarse grain coatings. The coarse grained surface of the fibre is detrimental to mechanical properties because the grain boundary of coarse grain acts as stress concentrator. In order to produce thicker coating, MTS concentration in $3 \times 10^{-4} \text{ m}^3/\text{min}$ argon is compensated by increasing the hydrogen flow from $5 \times 10^{-5} \text{ m}^3/\text{min}$ to $1 \times 10^{-4} \text{ m}^3/\text{min}$. Interestingly this combination has produced thicker and smooth surface coatings as can be seen in figure 3.

Further rise in hydrogen flow from $1 \times 10^{-4} \text{ m}^3/\text{min}$ to $2 \times 10^{-4} \text{ m}^3/\text{min}$ caused no coating. As the hydrogen flow is doubled it takes away the silane concentration so that no coating is formed on W substrate. To undo this effect further the flow of argon is increased to 0.6 Lpm to provide more silane. Very thick and uneven (wavy) coatings were formed (figure 4) at high flow rates of hydrogen and argon (MTS). This fibre unlike other fibres is very brittle and became powder during handling. With high concentrations of hydrogen and MTS, hot spots were observed on W filament during the initial stages of coating. During

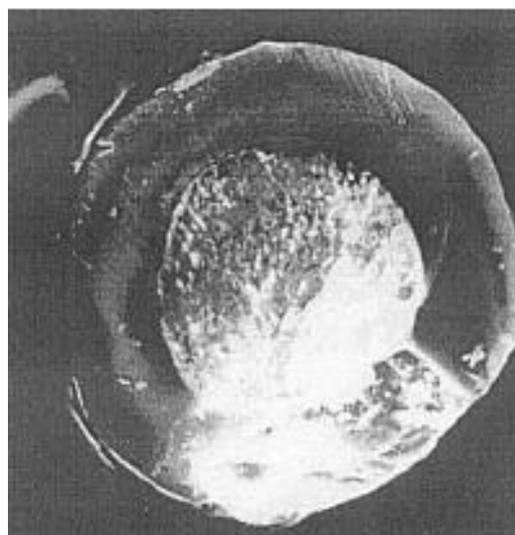
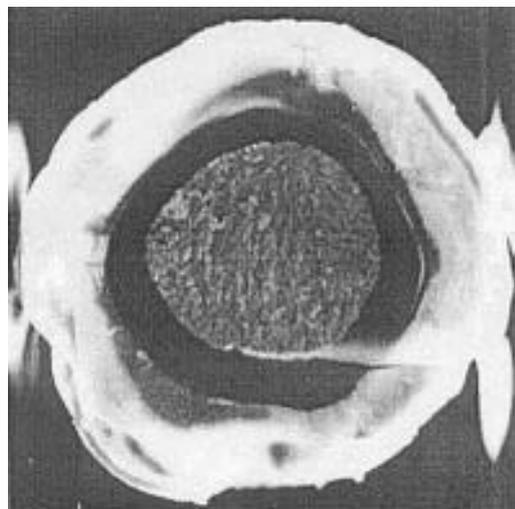


Figure 5. Cross-section of the fibre coated at 0.1 Lpm of hydrogen and 0.2 Lpm of argon.

initial stages of coating if thick coatings were formed at random places on substrate, the resistivity at those spots increased. This caused rise in temperature and fast build up of coating at such spots. This continued till the filament broke at some hot spot. Once hot spots were formed, the temperature of the remaining length of the filament decreased. Thick and fast growing coatings were formed at hot spots only causing uneven wavy coatings. This continued till the filament was broken at some hot spot.

The fibre formed at 1×10^{-4} m³/min hydrogen flow and 2×10^{-4} m³/min argon flow was cut with a sharp blade. The cross-section of the broken fibre is shown in figure 5. Since the surface is not polished it appeared like a cup and cone type fracture of a ductile fibre. Further 5 mm long fibre pieces were mounted by casting in a steel tube with solder lead. After polishing, the cross-section was examined by EPMA. Back scattered electron (BSE) image of the fibre cross-section is shown in figure 6. Tungsten in the substrate and silicon in the SiC coating were identified by X-ray mapping (figures 6b–c). From the clean interface between SiC coating and W it appears that there is no reaction between Si and W. However, there has been some difficulty in detecting the carbon in SiC coating. This could be due to the combined carbon and it is surrounded by heavy metal tungsten. However, carbon in the SiC coating was detected by auger electron spectroscopy

(figure 7). Similarly no carbon was shown by Petitcorps *et al* (1988) in the X-ray microprobe analysis. They studied the structure and composition of *s* and SCS fibres. They have only shown silicon and tungsten lines scans for sigma SiC fibre. To confirm this we studied the structure of sigma fibre reinforced Ti alloy received from a commercial source. In this sample, free carbon from protective coating on the fibre only was detected but not the carbon from SiC deposition.

Further to confirm the presence of SiC in the CVD coating on W filament, a small piece of the coated fibre was treated with HF acid. No effect of HF acid on the coating was observed. If it was oxide of Si it must have dissolved in HF acid. HF treated and untreated fibres appeared similar. In figure 8 HF treated SiC fibre is shown. No sign of reaction with HF acid was noticed. This along with EPMA and AES analyses confirmed that

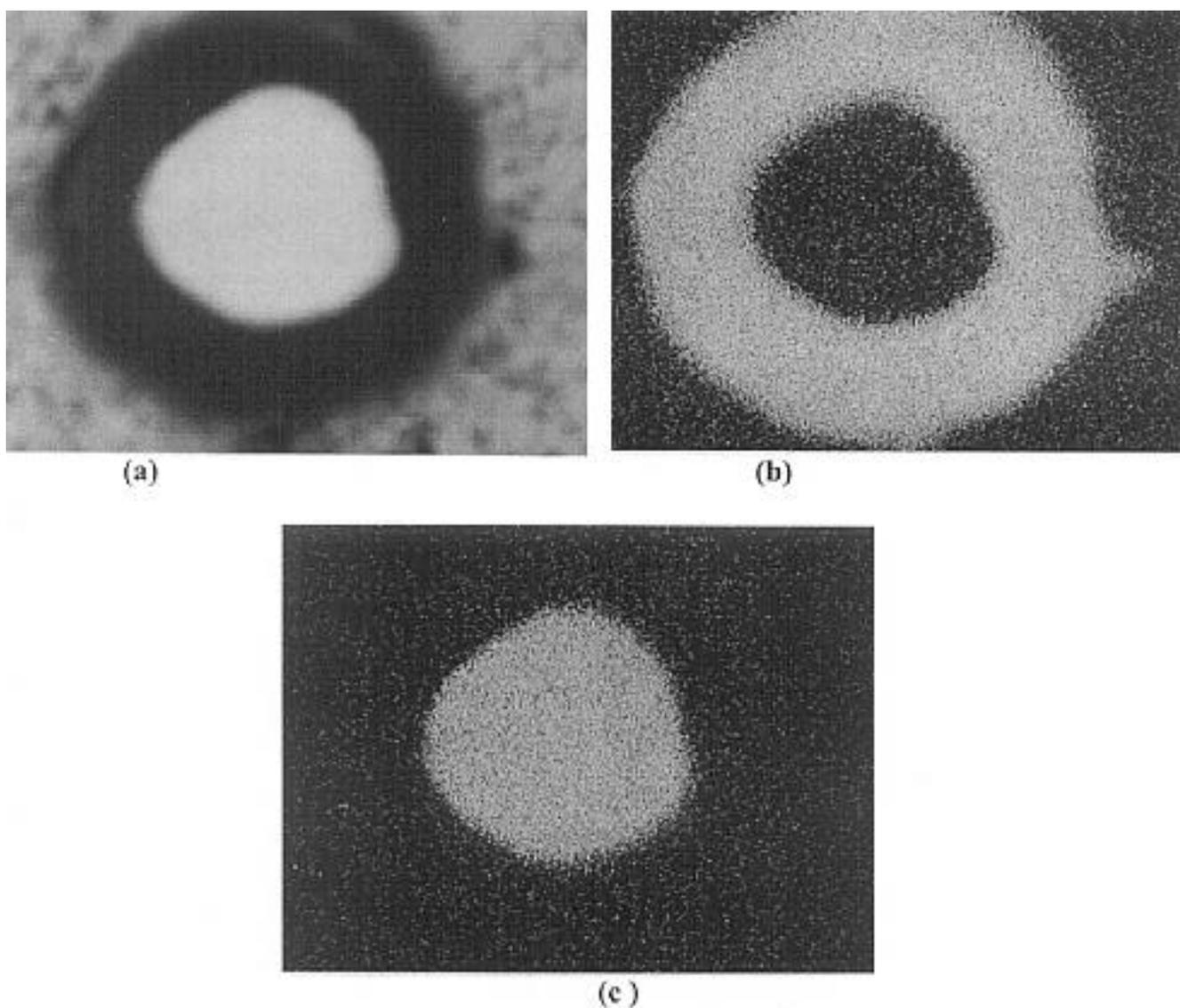


Figure 6. EPMA analysis of polished cross-section of SiC fibre: (a) BSE image, (b) Si X-ray map and (c) W X-ray map.

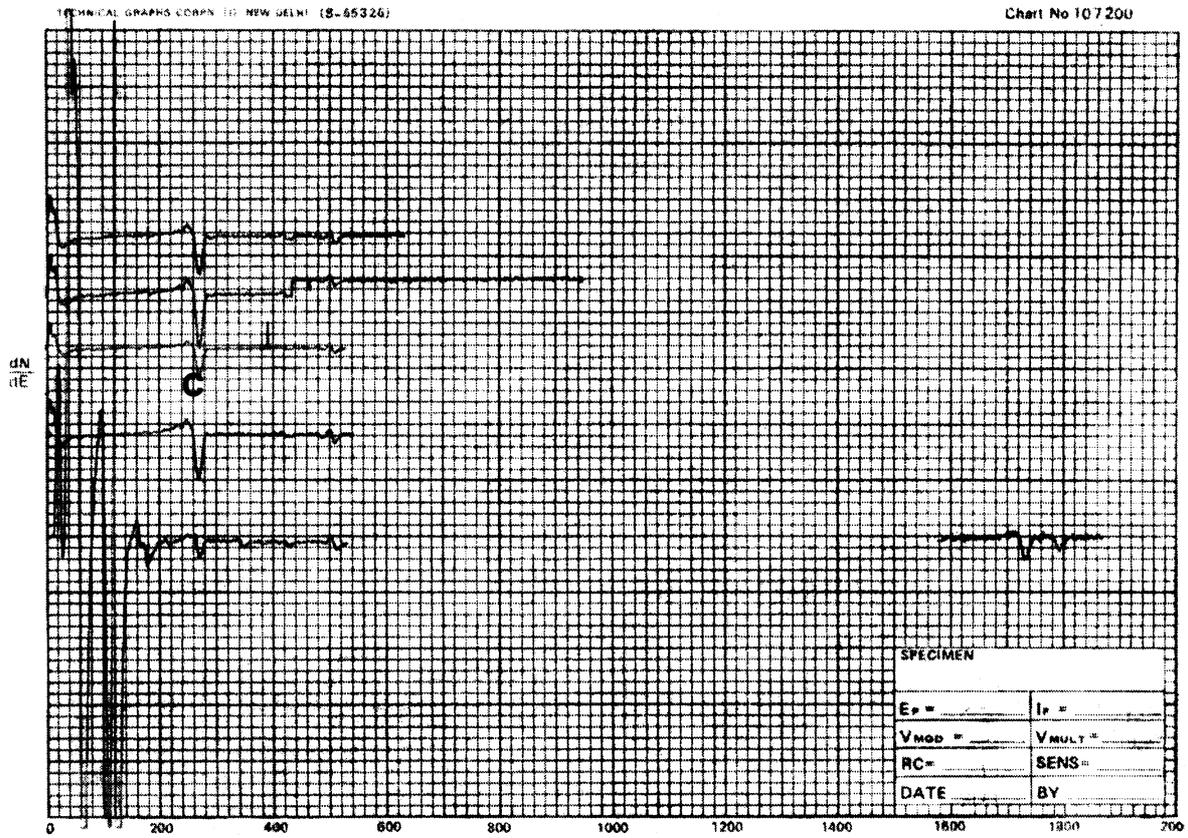


Figure 7. AES analysis identifying the carbon in SiC coating of the fibre.

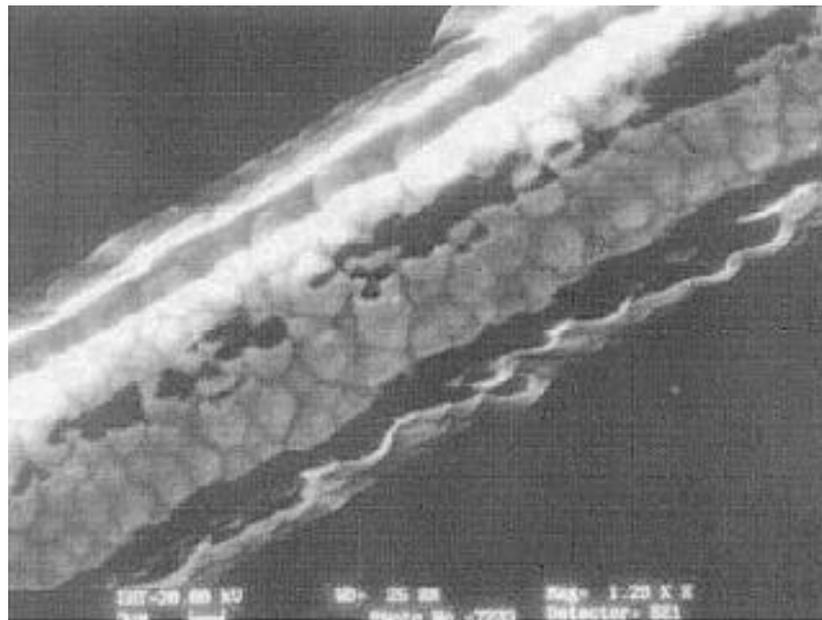


Figure 8. SiC fibre after treatment with HF acid.

the coating formed was SiC. Further rise in coating temperature to 1400 and 1500°C caused breaking of the filament during coating, and formation of brittle and uneven coatings.

4. Conclusions

A reactor for the formation of continuous SiC fibre by chemical vapour deposition on tungsten core filament has been successfully set up. To get smooth and evenly coated CVD SiC fibre, hydrogen flow and argon (carrying MTS) flow was found to be in the ratio of 1 : 2. High flow rates of hydrogen (2×10^{-4} m³/min) and argon (6×10^{-4} m³/min) lead to the isolated and uneven SiC coatings. Such wavy coatings are formed due to hot spots on the tungsten core filament. The cross-section of the fibre can be polished for analysis by mounting (casting) in solder lead. The analysis of carbon in CVD SiC with tungsten core is found to be difficult.

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