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Chemical vapour deposition of tungsten and TiN on SiC fibres

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Handling of uncoated SiC/W (Sigma) fibres resulted in a drop in their strengths. Coating with TiB_2 or boron at about 1000 °C by chemical vapour deposition resulted in a further reduction in strength. Coating with tungsten or TiN by lower temperature chemical vapour deposition processes did not degrade the fibre and the coated fibres also retained their strengths after heating in hydrogen at 1040 °C.

1. Introduction

There has been a great deal of interest in silicon carbide monofilaments for use in ceramic [1, 2] and metal matrix composites [3]. The process for forming the fibres usually involves the decomposition of methyldichlorosilane or methyltrichlorosilane on a tungsten [4] or a carbon fibre substrate [5]. These fibres often exhibit a silicon-rich surface, causing it to react with metals such as titanium in the process of preparing composites. In addition, the fibres are sometimes degraded in the process of unspooling the fibre and handling, especially if abrasion takes place.

One solution to this problem has been to coat the fibres with carbon. In some cases this has involved a complex series of coatings involving carbon-rich surfaces [5]. If it is an in-line coating process, then the problem of handling an uncoated fibre may be eliminated. However, for high-temperature use in an oxidizing atmosphere, carbon is not a desirable coating. In addition, other coatings than carbon would also be of interest to control the fibre–matrix interface for specific matrices.

2. Experimental procedure

2.1. Materials

Two kinds of Sigma fibres (SiC on W) were used to study chemical vapour deposition (CVD) coatings. One was produced by Berghof (BG-Sigma), Germany, and another was obtained from British Petroleum (BP-Sigma). Ultrapure hydrogen, ultrapure argon, 100% anhydrous ammonia and 99.9% $TiCl_4$ were also used.

2.2. Coating processes

The fibres were first cut into 7.5 cm lengths and placed in a 45 cm long, 9 mm diameter quartz reactor. The quartz tube was then attached to the reactant gas lines, as shown in Fig. 1, and the samples were heated in the presence of a hydrogen–argon gas mixture.

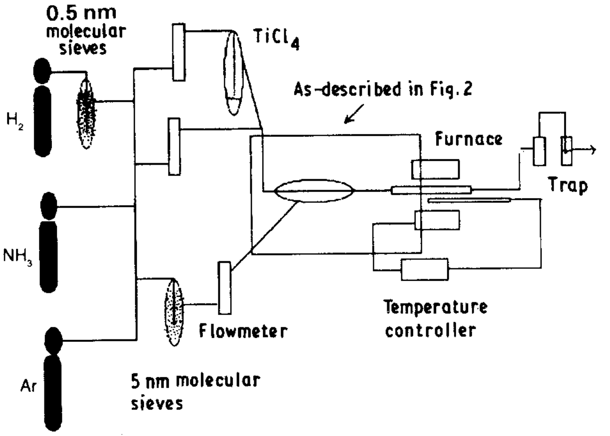

Figure 1 Overall diagram for TiN deposition.

The BP-Sigma fibre was heated at 1000 °C in $TiCl_4$, BCl_3 and hydrogen, the hydrogen being passed through the $TiCl_4$, in an attempt to form a TiB_2 coating. The coated fibre was too weak for further study, probably because of chlorine or HCl attack. The BP-Sigma fibre was also heated in a mixture of BCl_3 and hydrogen producing a weak fibre with crystalline boron on the surface. The boron crystals were large, producing a very uneven coating.

Because these were high-temperature processes for coating and resulted in a reduction in fibre strengths, it was felt that lower temperature processes should be investigated as a means of preventing fibre degradation. Attempts were then made to coat the BG-Sigma fibre with tungsten using $W(CO)_6$ with 60 ml min H_2 carrier gas at a 400 °C deposition temperature. The coated fibre was then heated to 1040 °C in hydrogen for 30 min and X-ray diffraction and tensile strength studies were conducted. Studies by Kmetz *et al.* [6] showed that an oxycarbide coating was formed on SiC yarn at 450 °C and a subsequent heat treatment was required to obtain a conversion to tungsten. The tungsten coating was removed by using an acid before tensile strength measurements were made.

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To produce TiN coatings, after the temperature of the furnace reached 650 °C in a hydrogen–argon gas mixture, the hydrogen carrier gas, which was passed through $TiCl_4$ and ammonia and argon gases were flowed into the reactor. In order to prevent powder formation, H_2–$TiCl_4$ and Ar–NH_3 mixtures were kept separated before the gases were led into the end of the furnace (see Fig. 2), where the temperature was 200 °C. The flow rates used were 75 ml min^{-1} for the hydrogen carrier gas and 280 ml min^{-1} for the diluting hydrogen. The flow rates of ammonia and argon were 140 and 30 ml min^{-1}, respectively. The reaction was stopped after 1 h and samples were cooled in a hydrogen atmosphere. Some of the coated fibres were then heat treated at 1040 °C for 30 min in a hydrogen atmosphere.

2.3. X-ray diffraction studies

A Debye–Scherrer powder camera with a 114.9 mm diameter was used in this study to obtain the diffraction patterns. The tungsten- and the TiN-coated fibres were cut into 1 cm lengths and five pieces of these fibres were wrapped in a parafilm at two ends. The fibres were then loaded in a camera and exposed to CuK_α radiation with a nickel filter for 4 h. The diffraction lines were then analysed and assigned to various phases.

2.4. Tensile strength measurements

In order to try to obtain the strength of unhandled fibre, samples of BP-Sigma fibres were carefully unspooled and the straight fibre was placed between two pieces of weighing paper. The fibre was cut into 7.5 cm lengths using a razor blade, because it was felt that the razor blade would only generate a small area of deformation around the breakage point. In addition, gloves were used in order to avoid touching the fibre. Fibres used for coating were not handled in this manner because it was felt that realistic values should be obtained for fibres which would not be handled so carefully in despooling and coating.

For coated fibres, an acid solution, which was made of 20 vol % H_2O, 30 vol % concentrated HNO_3, and 50 vol % concentrated HF was used to remove the TiN and tungsten coatings from the fibres before tensile strength measurements were made. The diameter of the fibre was also measured before testing.

Tensile strengths were measured using an Instron tester with a 22.7 kg load cell. The ends of the filaments were wrapped in aluminium foil to protect the fibre in the grips. A crosshead speed of 0.01 cm min^{-1} and a gauge length of 2.5 cm were used in the test procedure. Typically, six to ten fibres, except for the carefully handled uncoated fibres (20 fibres) were measured for each run, and the average strength and standard deviation were reported.

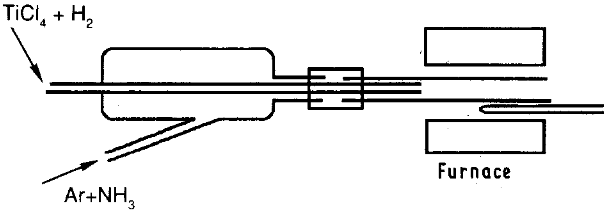

Figure 2 Detailed description of gas flow.

3. Results

The BP-Sigma and BG-Sigma fibres had a similar surface appearance and gave similar X-ray diffraction (XRD) patterns. Fig. 3 shows a scanning electron micrograph of the BP-Sigma fibre. As can be seen, the surface is nodular with approximately 5 μm nodules. The diameter of the fibre is about 100 μm.

The XRD pattern of the Sigma fibre (Table I) shows a beta SiC pattern and a tungsten pattern from the core. In Fig. 4a, it can be seen that the tungsten diffraction lines (2, 3) are broken, typical of a textured drawn wire.

The surface of the boron-coated BG-Sigma fibre is shown in Fig. 5. Note the large crystals on the surface. Table II presents the XRD data which show that the coating is crystalline boron with the SiC and tungsten core lines from the SiC fibre also present. Because the fibre was severely degraded, no further studies were conducted, although lower temperature deposition temperatures may have resulted in a smooth amorphous surface. From studies on amorphous boron fibres, it was expected that the boron coating prepared in this study at 1000 °C would be amorphous [7]. In the boron fibre studies, when the fibres were crystalline rather than amorphous, the fibre strength was much lower.

The TiN coating on the BP-Sigma fibre is shown in Fig. 6. The surface is also nodular but rougher than the uncoated fibre.

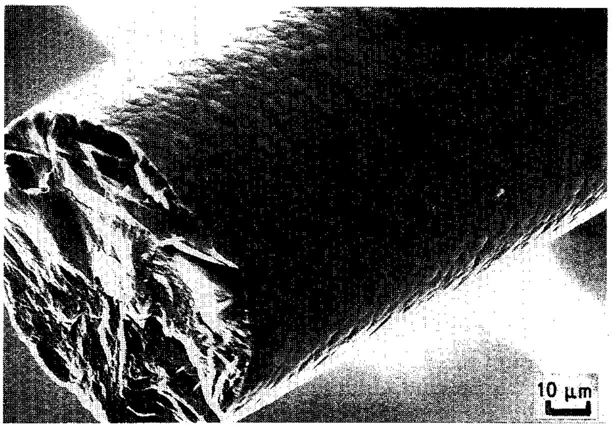

Figure 3 Scanning electron micrograph of as-received Sigma fibre.

TABLE I XRD data for as-received Sigma fibre

Line no.	2θ (deg)	*d*(nm)obs.	*d*(nm)[a]	Phase	*hkl*
1	35.62	0.252	0.251	SiC	111
2	40.32	0.224	0.224	W	110
3	58.35	0.158	0.158	W	200
4	60.08	0.154	0.154	SiC	220
5	71.70	0.132	0.131	SiC	311
6	73.27	0.129	0.129	W	211

[a] ASTM Card: β-SiC, 1-1119, W, 4-08060.

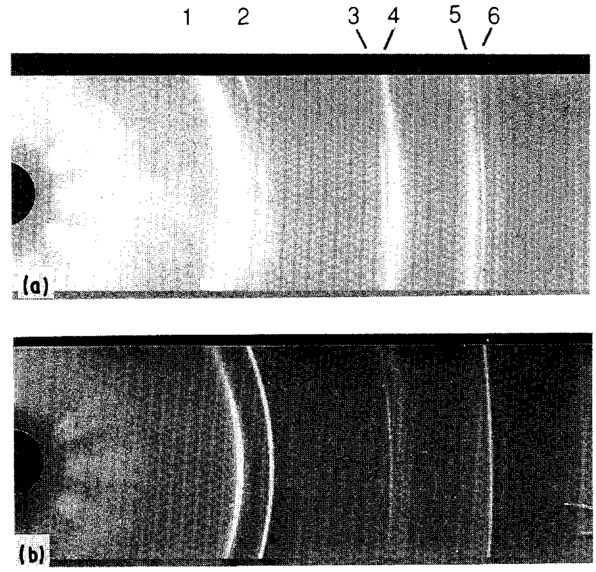

Figure 4 X-ray diffraction pattern for (a) as-received Sigma fibre, and (b) tungsten-coated Sigma fibre.

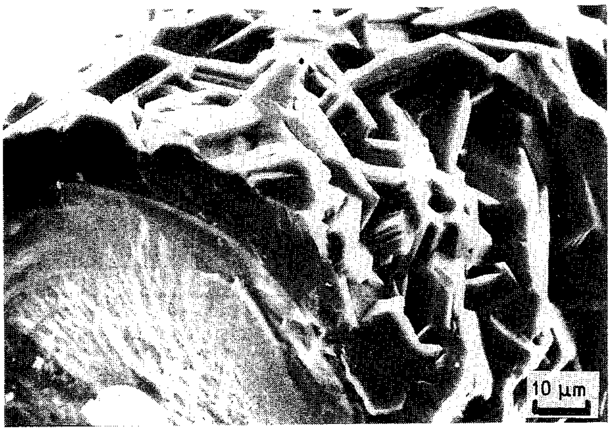

Figure 5 Scanning electron micrograph of the surface and fracture area of a boron-coated BG-Sigma fibre.

TABLE II XRD data for boron-coated Sigma fibre

Line no.	2θ (deg)	*d*(nm)obs.	*d*(nm)[a]	Phase	*h k l*
1	20.27	0.438	0.437	B	2 0 0
2	22.67	0.392	0.392	B	1 1 1
3	35.50	0.253	0.251	SiC	1 1 1
4	37.00	0.243	0.243	B	1 3 1
5	40.19	0.224	0.224	W	1 1 0
6	41.47	0.219	0.219	B	2 3 1
7	58.30	0.158	0.158	W	2 2 0
8	59.95	0.145	0.154	SiC	2 2 0
9	64.63	0.144	0.144	B	1 3 3

[a] ASTM Card: B, 12-469, W, 4-0806, β-SiC, 1-119.

The XRD pattern of the tungsten-coated fibres (Fig. 4b) shows tungsten lines and the SiC fibre lines. By comparing Fig. 4a and b, it can be seen that the lines from the tungsten coating cover the tungsten (core) lines and the lines are complete and not broken. The XRD data for the TiN-coated SiC fibre are presented in Table III. The TiN lines are observed, as well as the SiC and tungsten (core) lines.

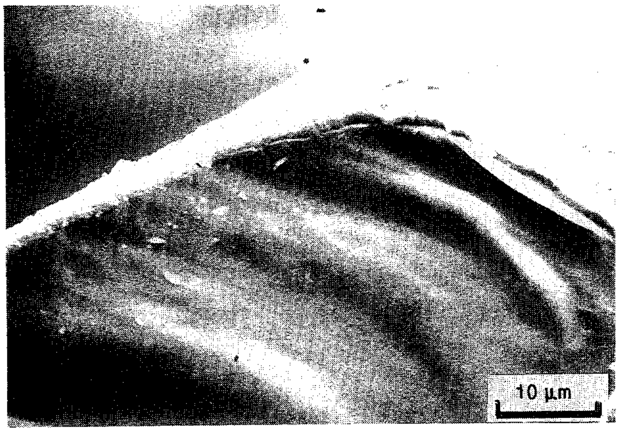

Figure 6 Scanning electron micrograph of TiN-coated fibre.

TABLE III XRD data for TiN-coated Sigma fibre

Line no.	2θ (deg)	*d*(nm)obs.	*d*(nm)[a]	Phase	*h k l*
1	35.60	0.252	0.251	SiC	1 1 1
2	36.85	0.244	0.244	TiN	1 1 1
3	40.37	0.223	0.224	W	1 1 0
4	42.87	0.211	0.212	TiN	2 0 0
5	58.45	0.158	0.158	W	2 0 0
6	59.97	0.154	0.154	SiC	2 2 0
7	62.12	0.149	0.149	TiN	2 2 0
8	71.72	0.131	0.131	SiC	3 1 1
9	73.72	0.129	0.129	W	2 1 1
10	74.40	0.128	0.128	TiN	3 1 1

[a] ASTM Card: TiN, 6-0642, β-SiC, 1-119, W, 4-0608.

The tensile strength of the carefully handled BP-Sigma fibres exhibited two populations, one at 3164 ± 383 MPa (459 ± 45×10^3 p.s.i.) and another at 2056 ± 329 MPa (298 ± 47×10^3 p.s.i.) with an average of 2578 ± 642 MPa (374 ± 93×10^3 p.s.i.).

The tensile strength of as-received BP-Sigma (handled) and as-received BG-Sigma (handled) were 2112 ± 257 MPa (306 ± 37×10^3 p.s.i.) and 1998 ± 434 MPa (290 ± 63×10^3 p.s.i.), respectively. The strength of tungsten-coated BG-Sigma fibre was 2116 ± 276 MPa (308 ± 40×10^3 p.s.i.) after heating to 1040 °C in hydrogen for 30 min. After the TiN coating was applied, the tensile strength of BP-Sigma was 2512 ± 334 MPa (365 ± 48×10^3 p.s.i.) and that of BG-Sigma increased to 2914 ± 546 MPa (423 ± 82×10^3 p.s.i.). Heat treatment of these TiN-coated fibres at 1040 °C in hydrogen for 30 min decreased the tensile strength of BP-Sigma fibre slightly to 2002 ± 153 MPa (290 ± 22×10^3 p.s.i.) and that of BG-Sigma to 2632 ± 158 MPa (382 ± 22×10^3 p.s.i.).

4. Discussion and conclusion

The two tungsten-core SiC fibres, BP-Sigma and BG-Sigma, are basically produced by the same process, but are from different manufacturers. No significant difference was found in these two fibres which were prepared by depositing β-SiC on to a tungsten filament by a CVD technique to form a monofilament. A cross-section and surface of an as-received fibre are shown in Fig. 3. Both fibres have a nodular type appearance.

There was also no difference between the XRD patterns of BP-Sigma and BG-Sigma. The XRD patterns indicated the presence of a β-SiC and a tungsten (core) phase, as shown in Table I. The tungsten coating lines covered the tungsten (core) lines in the pattern of the tungsten-coated fibres. In the XRD pattern of the TiN-coated SiC fibre, the TiN pattern is present with the SiC and tungsten core lines. There were no extra diffraction lines observed, besides the tungsten and TiN diffraction lines, indicating that there was no detectable chemical reaction between tungsten or TiN and SiC. Heat treatment for 30 min of tungsten- and TiN-coated fibres also at 1040 °C did not result in any obvious interaction between tungsten or TiN and SiC.

The tensile strength of the BP-Sigma fibre reported by the manufacturer is 3445 MPa (500×10^3 p.s.i.). However, according to the literature, the average strength of the as-received fibre was 1774 MPa (257×10^3 p.s.i.), which is about half of the manufacturer's value [8]. In our studies, the tensile strengths of the as-received BP-Sigma and BG-Sigma fibres were 2112 ± 257 MPa ($306 \pm 37 \times 10^3$ p.s.i.), and 1998 ± 434 MPa ($290 \pm 63 \times 10^3$ p.s.i.), respectively, which are similar to that reported in the literature. Measuring a lower strength for SiC fibre which is silicon-rich on its surface after handling is often observed [9]. Our tensile strength result on carefully handled BP-Sigma fibre was 2578 ± 642 MPa ($374 \pm 93 \times 10^3$ p.s.i.). Coating with TiB_2 or boron at 1000 °C resulted in severe fibre degradation. However, coating with tungsten or TiN by lower temperature processes and heat treating these coated fibres at 1040 °C in hydrogen did not decrease the fibre strength.

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