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# CVD Mo, W and Cr oxycarbide, carbide and silicide coatings on SiC yarn

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SiC yarn has been coated with molybdenum oxycarbide and tungsten oxycarbide without degrading the fibre. Conversion of the coatings to the metals has been accomplished by heat treatment in nitrogen. These metal coatings have then been converted to silicide coatings by heating in $SiCl_4$. An SiC/WOC minicomposite has been formed by longer deposition of tungsten oxycarbide on a silicon carbide yarn.

## 1. Introduction

Recently, there has been a renewed interest in developing improved coatings for fibres to control the interface in high-performance composites. This is particularly essential in ceramic matrix composites, where strong fibre–matrix bonding can lead to brittle behaviour [1]. On the other hand, producing a weak carbon interface in SiC yarn–glass–ceramic composites has resulted in tough composite behaviour, and has demonstrated that this brittle problem can be overcome by controlling the interface. In searching for other coatings for SiC yarn, it has become apparent that this yarn, like many of the other high-modulus yarns, is very sensitive to various gases at elevated temperatures [2–4]. Hwan *et al.* [5], of our laboratory, have shown that the amount of degradation of SiC yarn can often be related to the temperature of the coating process. As can be seen in Table I, the higher the processing temperature, the greater is the amount of fibre degradation. Of course, the processing time and reactivity of the coating material are also important, but the importance of low coating processing temperatures on the strength of the fibres has been well recognized. Therefore, it was with considerable interest that we read that a tungsten oxycarbide could be prepared from $Mo(CO)_6$ at temperatures as low as 300 °C [6]. We decided to explore the Mo, W and Cr carbonyl systems. Some preliminary work has been reported [7].

## 2. Experimental procedure

To coat with oxycarbides, Nicalon yarn was first cut into 6.3 cm lengths and rinsed in acetone in order to remove the sizing. Two or four tows were then inserted into a 1 cm long $Al_2O_3$ thermocouple sleeve and placed inside a quartz tube. The tube was evacuated by means of a mechanical pump and a flow of $H_2$, $N_2$ or Ar at 30 $cm^3 min^{-1}$ was passed over reagent grade $Mo(CO)_6$ or $W(CO)_6$ at a pressure of approximately 80 mtorr (1 torr = $1.333 \times 10^2$ Pa) into a quartz tube containing the yarn and exhausted out the other end. The furnace was held at a temperature 350 or 450 °C, then moved over the yarn at the rate of 0.4 cm $min^{-1}$.

To convert the oxycarbide coatings to the metals, MoOC, WOC or CrOC-coated fibres were placed in a clean quartz tube and $N_2$ or $N_2$ then $H_2$ was allowed to flow over the yarn at a flow rate of approximately 30 $cm^3 min^{-1}$. The temperature was raised to 1000 °C at a rate of about 60 °C $min^{-1}$ and then the furnace was cooled.

For the formation of disilicides, $H_2$ was passed through reagent grade $SiCl_4$ at a rate of 20 $cm^3 min^{-1}$ and into the quartz tube containing the metal coated tows held at 1040 °C for 10 min.

Tensile strength measurements were made by first cutting rectangular 6.4 cm × 1.27 cm long strips of cardboard with a 2.5 cm × 0.6 cm rectangular hole in the middle. The yarn was glued to the cardboard and a coat of acrylic was applied to the yarn. The cardboard was then placed into the Instron tester and the cardboard edges cut before testing. The gauge length used was always 2.54 cm because the strength is dependent on gauge length.

The strengths reported were based on yarn tests. Dry yarn tests were made and then tests with acrylic binder. These measurements were lower than those for single filament tests (Table II). As reported by Fareed *et al.* [2], this is what is generally found. Moeller and Worley [8] reported that they also obtained better agreement with single filament tests when they coated the tows with epoxy. The best results were obtained by us when the sizing was removed before the acrylic binder was applied. Therefore, the fibres were cleaned before coating although preheating in the reactor may also remove the sizing. As Moeller *et al.* had done, the cross-sectional area was determined using the fact that the yarn contained 500 fibres which had an average cross-section of 12.5 μm.

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TABLE I Data for coated SiC yarn (yarn tests)

| Coating process | Coating | Processing temp. (°C) | Strength | |
|---|---|---|---|---|
| | | | (MPa) | ($10^3$ p.s.i.) |
| – | None | – | 1587 | 230 |
| Sol–gel | $Al_2O_3$ (hydrous) | 100 | 1635 | 237 |
| Sol–gel | $ZrO_2$ (hydrous) | 100 | 1387 | 201 |
| Sol–gel | $SiO_2$ (hydrous) | 100 | 1283 | 186 |
| CVD | Cr–O–C | 400 | 897 | 130 |
| CVD | Carbon | ~ 1000 | 331 | 48 |
| CVD | Silicon | ~ 1000 | 62 | 9 |

TABLE II Strength of SiC yarn by various testing methods

| Form | Test | Strength | |
|---|---|---|---|
| | | (MPa) | ($10^3$ p.s.i.) |
| Yarn | As received | 1587 | 230 |
| Yarn | Acrylic binder | 2387 | 346 |
| Yarn | Sizing removed w/acetone plus acrylic binder | 2719 | 394 |
| Yarn | Sizing removed w/flame plus acrylic binder | 2394 | 407 |
| Single filament[a] | | 2898 | 420 |

[a] From manufacturer.

## 3. Results

A flow chart showing the coating process for forming all of the coatings is presented in Fig. 1. When $N_2$, $H_2$ or Ar was used to carry the carbonyl into the reaction tube, the coatings formed upon heating were MoOC, WOC or CrOC of variable composition. An MoOC coating on SiC is shown in Fig. 2. The X-ray patterns of MoOC and WOC were similar to those reported in the ASTM card file (see Table III). Ferguson *et al.* [6] indicated that the MoOC forms solid solution phases which vary in composition from $Mo_2C_{0.7}O_{0.6}$ to $Mo_2C_{0.6}O_{0.5}$ and has lattice spacings for an approximately 0.4 nm cubic unit cell. Because CrOC was found to have a similar X-ray pattern it was assumed to also be an oxycarbide. The strength of the tungsten oxycarbider and molybdenum oxycarbide-coated SiC yarn was found to be about 2690 MPa (390 × $10^3$ p.s.i.) which is about the strength measured for the SiC fibres before the coating was applied.

When MoOC-coated SiC yarn was heated in $N_2$ at 800 °C, the coating was converted to $Mo_2C$ and at 1000 °C to Mo metal. Both were identified by their X-ray patterns. The strength of the $Mo_2C$ coated yarn was about 2553 MPa (370 × $10^3$ p.s.i.) while the Mo-coated yarn was 2070 MPa (300 × $10^3$ p.s.i.). When the Mo coating was applied directly from $Mo(CO)_6$ by heating at 900 °C in $N_2$, the strength of the coated yarn was only 1518 MPa (220 × $10^3$ p.s.i.) so there appears to be an advantage in coating with Mo in a stepwise manner (see Table IV). The Mo-coated yarn can then be converted to $MoSi_2$ by heating in $SiCl_4$ carried in $H_2$. However, the strength drops to 1104 MPa (160 × $10^3$ p.s.i.).

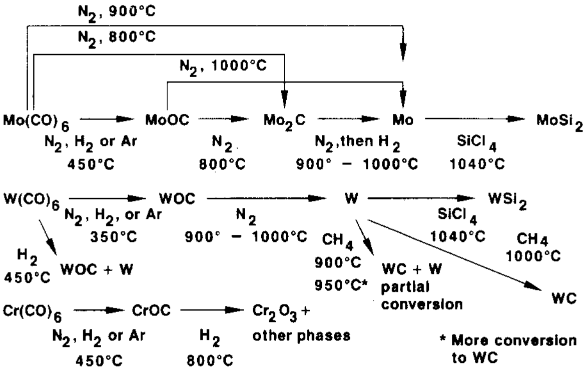

*Figure 1* Fibre coating.

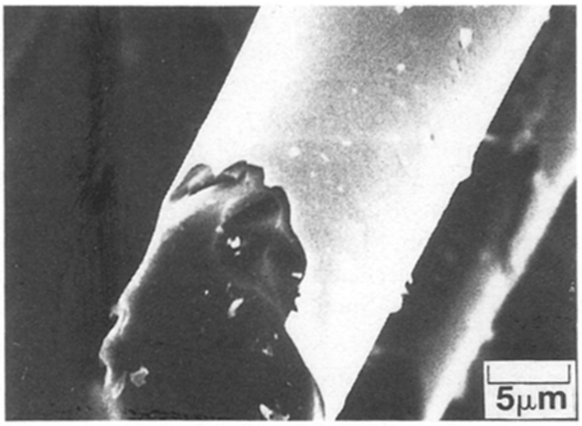

*Figure 2* MoOC coating on SiC yarn.

A similar sequence was observed for $W(CO)_6$ to form a WOC coating and heating in $N_2$ at 900 °C to convert the WOC to W. The tungsten coating can similarly be converted to the disilicide by heating in $H_2/SiCl_4$ at 1040 °C. Unlike the Mo system, the $W_2C$ coating was not observed when the WOC was heated. A mixture of WC and W in the coating was observed when the W-coated yarn was heated in $CH_4$ at 900 or 950 °C and all WC when the temperature was 1000 °C.

TABLE III X-ray data for Mo, W, and Cr oxycarbides

| MoOC | | | WOC | | | CrOC | | |
|---|---|---|---|---|---|---|---|---|
| *hkl* | *d*(nm) | $I/I_0$ | *hkl* | *d*(nm) | $I/I_0$ | *hkl* | *d*(nm) | $I/I_0$ |
| 111 | 0.2417 | 80 | 111 | 0.2423 | 100 | 111 | 0.2393 | 80 |
| 200 | 0.2094 | 100 | 200 | 0.2099 | 92 | 200 | 0.2071 | 100 |
| 220 | 0.1480 | 27 | 220 | 0.1480 | 32 | 220 | 0.1463 | 58 |
| 311 | 0.1222 | 20 | 311 | 0.1209 | 32 | 311 | 0.1248 | 20 |

TABLE IV Strength of coated fibres produced directly from $M(CO)_6$ or in steps

| Temp. (°C) | Atmos. | Phase | Strength | | | |
|---|---|---|---|---|---|---|
| | | | (MPa)[a] | ($10^3$ p.s.i.)[a] | (MPa)[b] | ($10^3$ p.s.i)[b] |
| 450 | $H_2$ | MoOC | 2912 | 422 | | |
| 450 | $N_2$ | MoOC | 2912 | 422 | | |
| 800 | $N_2$ | $Mo_2C$ | 2622 | 380 | 2553 | 370 |
| 850 | $N_2$ | Mo | 2482 | 360 | | |
| 900 | $N_2$ | Mo | 1518 | 220 | | |
| 1000 | $N_2$ | Mo | 1587 | 230 | 2070 | 300 |
| 450 | $H_2$ | WOC | 2415 | 350 | | |
| 1000 | $N_2$ | W | | | 1725 | 250 |
| 450 | $H_2$ | CrOC | 2484 | 360 | | |

[a] Formed directly from $M(CO)_6$.

[b] Formed in steps MoOC → $Mo_2C$ or MoOC → $Mo_2C$ → Mo or WOC → W.

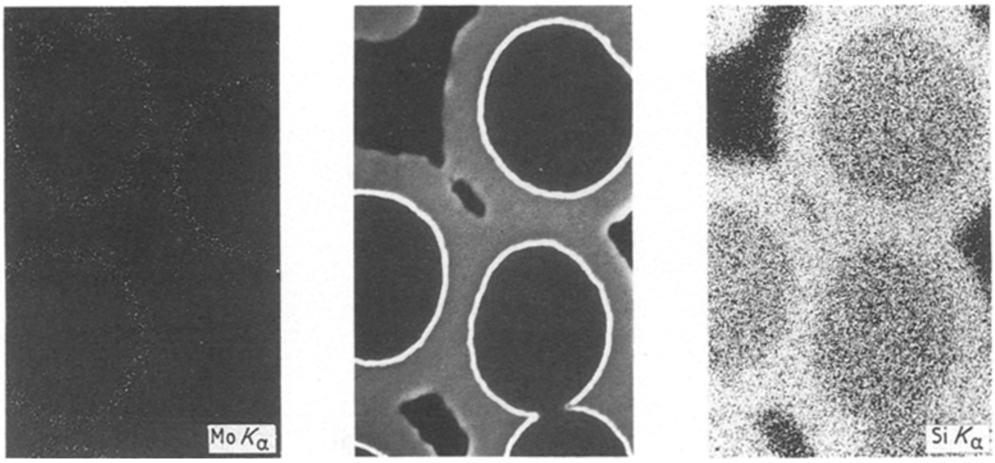

*Figure 3* Scanning electron microprobe analysis of $SiC/MoSi_2/Si$ (composite 2KX).

Only preliminary studies have been conducted with $Cr(CO)_6$. It can be used to form an oxycarbide coating on the yarn by heating in $N_2$ at 450 °C, but heating CrOC at 800 °C in $H_2$ did not produce a Cr coating. Instead it formed a mixture of $Cr_2O_3$ and other phases.

## 4. Discussion

The strength of Nicalon yarn is easily degraded. Therefore, the formation of the molybdenum and tungsten oxycarbide coatings without degrading the fibre is encouraging. This is probably because the formation of the oxycarbides from the carbonyls only requires a temperature of 350 or 450 °C. The coating can be made quite uniform by moving the furnace over the fibres.

The oxycarbides then form a path for producing Wr or Mo-coated fibre with less degradation than occurs when the metal coatings are formed directly from the metal carbonyl. Although this conversion can be conducted in $N_2$, it was found that a purer coating was prepared when $N_2$ heating was followed by heating in $H_2$.

It was also found that the silicides could be formed from the metals but the coated fibres are somewhat degraded. Minicomposites (single yarn) such as $SiC/WSi_2/Si$ and $SiC/WSi_2/SiC$ and others involving $MoSi_2$ were therefore weak. A scanning electron microprobe analysis of $SiC/MoSi_2/Si$ composite is shown in Fig. 3. More work should be conducted on these systems because of their oxidation resistance.

Because the oxycarbide coatings appear not to affect the strength of SiC yarn, attempts were made to form a SiC/WOC composite. The yarn was left in the reactor tube at 450 °C with $N_2/W(CO)_6$ passing over it. The fibre was coated for 36 h and removed for testing. A tensile strength of 193 MPa ($28 \times 10^3$ p.s.i.) was obtained. This is in the range of SiC yarn/CVD SiC composites tested in tension; bend tests gave nearly double the tension values [9].

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