THE CVD OF TiB_2 PROTECTIVE COATING ON SiC MONOFILAMENT FIBRES

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Abstract - TiB_2 protective coatings have been deposited on SiC monofilament by a CVD technique. The CVD coating process studied involved the formation of TiB_2 on resistively heated SiC fibres from the chemical reaction of TiCl_4 , BCl_3 , H_2 at reduced pressure in a cold wall reactor. The effects of temperature, pressure and input reactant gas ratio on the morphology and nature of the coatings were investigated. The efficiency of chemically vapour deposited TiB_2 as protective coating to inhibit the fibre-matrix interaction in titanium metal matrix composites was also evaluated by incorporating coated fibres in Ti-6Al-4V using diffusion bonding.

1. - Introduction.

SiC fibre reinforced Ti metal matrix composites have applications in the manufacture of aerojet fan blades and compressor blades [1,2]. However, detrimental reactions at the metal/ceramic interface during fabrication or in service, lead to the formation of titanium carbide and titanium silicides which cause a deterioration in the mechanical properties of the composites [2,3]. This interaction can be minimized by developing chemically inert ceramic coatings on SiC fibre. TiB_2 is of particular interest as a protective coating because thermodynamically it is expected to be stable in contact with titanium matrices and SiC . This protective coating can be deposited on SiC monofilament by CVD technique because it does not require line-of-sight between the source material and substrate as needed by PVD, sputtering or ion implantation techniques. Therefore it is able to produce uniform coatings on fibres [4].

2. - Experimental.

A schematic diagram of the CVD apparatus used for the coating process is shown in Fig. 1. A SiC monofilament (BP Sigma with a 100 μm diameter SiC fibre on a 12 μm tungsten core) of effective length 270 mm was drawn into a cold wall reactor consisting of a quartz tube 420 mm in diameter and 310 mm long, and gas sealed by mercury at the upper and lower portions of the deposition tube and supported by its own surface tension. The mercury also served as an electrical contact with the filament to permit resistive heating of the fibre. The system was then evacuated and flushed with Ar. The fibre was cleaned by preheating at 950°C for 5 minutes. Subsequently it was heated to the deposition temperature. Then a gaseous mixture of TiCl_4 , BCl_3 and H_2 was fed into the reactor. The deposition occurs through the following reactions:

Fig. 1. - A schematic diagram of the experimental apparatus used for CVD of TiB_2 on SiC monofilament.

The TiCl_4 which is a liquid at room temperature was evaporated from a vaporizer at a constant rate in order to maintain a constant equilibrium vaporizing pressure. The TiCl_4 flow rate was calculated from the change of TiCl_4 weight in the vaporiser. The TiCl_4 gas line was heated to prevent condensation. BCl_3 and H_2 were individually metered into the reactor through Tylan mass flowmeters. Each deposition run was for 10 minutes with constant monitoring and occasional adjustment of temperature and pressure.

The coating process variables chosen for the study were substrate temperature, deposition pressure and $\text{TiCl}_4:\text{BCl}_3$ gas ratio. The morphology and microstructure of the deposited layer would be of extreme importance if they were to be used as protective coatings. These experimental parameters were systematically varied to investigate the effects of these parameters on the surface morphology, growth rates and microstructures of the TiB_2 coating. The coated fibres were characterized by optical microscopy, SEM, X-ray diffraction and chemical analysis.

3. - Results and discussion.

A typical X-ray diffraction pattern is shown in Fig. 2. X-ray diffraction analysis showed that in all cases, the dominant phase that deposited was TiB_2 . The presence of other thermodynamically possible phases such as B [5] or TiB [6] were not detected by the X-ray analysis.

The typical cross-section of the coated fibres is shown in Fig. 3. All the coatings are shown to adhere well to the fibre. After the coated fibres had been subjected to ultrasonic cleaning for 30 minutes, no cracking or spalling of the coatings was observed. Chemical microanalysis by EPMA showed a constant titanium to boron ratio across the coating thickness.

Due to the effects of reactor geometry, the deposition rate and morphology of the coated fibres were found to vary along the deposition tube. Therefore all the coating measurements and samples were taken at the same position for comparison.

The deposition rate of the coating was a strong function of deposition temperature as is shown in Table 1.

Fig. 2. - The typical X-ray diffraction pattern of TiB_2 coatings on SiC fibres.

Fig. 3. - The typical cross section of the coated SiC fibre.

The surface morphology of the TiB_2 coating was very sensitive to the substrate temperature. This is illustrated in Fig. 4. As the substrate temperature increased, deposits consisting of randomly oriented fine-grained polycrystals grew into more dense and coherent dome-like columnar grains and then grew into larger faceted grains at even higher temperature. If the temperature was further increased, the faceted morphology grew into even larger and more strongly faceted grains with the grain surfaces revealing many steps.

This growth pattern is as a result of the fact that high surface temperature increases thermally activated reactions. This induces a higher growth rate and increases surface mobility of the atomic species and higher surface diffusion. The Arrhenius plot of $\ln$ of deposition rate versus reciprocal temperature, Fig. 5, indicates two different rate controlling mechanisms that are operating within the temperature range studied. When temperature increases from 1050°C to 1350°C , deposition rate increases rapidly. This indicates that the rate-limiting mechanism is chemical kinetics. From the slope, the activation energy is found to be 144kJ/mol . At temperatures above 1350°C , the slope is markedly smaller and the mechanism has an activation energy of 30kJ/mol . This value is significantly lower than the previous value. Therefore at temperature above 1350°C , the deposition rate weakly depends on temperature and depends more on the rate of diffusion of the active gaseous species through a boundary layer to the deposition surface. Therefore it is mass transport limited.

Table 1. - Effect of substrate temperature on deposition rate. Other parameters were maintained at pressure 15 kPa, flow rates ($\text{cm}^3 \text{min}^{-1}$): TiCl_4 , 24; BCl_3 , 72; and H_2 , 300.

Substrate Temperature ($^\circ\text{C}$)	Deposition rate ($\mu\text{m min}^{-1}$)
1050	0.19
1100	0.35
1150	0.55
1250	1.20
1300	1.60
1350	2.30
1400	2.45
1450	2.55

Fig. 4. - Scanning electron micrograph of the surface morphology of the TiB₂ coatings deposited at various temperatures. a) 1050°C. b) 1100°C. c) 1150°C. d) 1250°C. e) 1400°C.

Fig. 5. - An Arrhenius plot of ln of deposition rate versus reciprocal temperatures.

Table 2. - Effects of deposition pressure on deposition rate. Other parameters were maintained at temperature 1150°, flow rates (cm³ min⁻¹): TiCl₄, 24; BCl₃, 72; and H₂, 300.

Pressure (kPa)	Deposition rate (µm min ⁻¹)
6	0.10
15	0.55
23	0.84

As the pressure increased from 6 kPa to 15 kPa, the shape of the crystallites became more clearly defined and the surfaces smoother, with rounded growth features. This is due the fact that increase in pressure, increases the concentration of the reactants (higher supersaturation). Hence the nucleation rate increases. As a result, finer and smoother polycrystals were deposited at high pressure. If the pressure was increased further to 23 kPa, even smaller and finer grains were obtained. However due to even higher nucleation rate at increasing pressure, these grains deposited on top of each other forming clusters of grains as seen in Fig. 6 (c). The deposition rate was also found to increase as the pressure increased within the pressure range studied (Table 2).

Table 3. - The effects of TiCl₄ : BCl₃ gas mole ratio on deposition rate. Other parameters were maintained at temperature 1150°C, pressure 15 kPa and H₂ flow rate 300 cm³ min⁻¹.

TiCl ₄ : BCl ₃	Deposition rate (µm min ⁻¹)
1 : 3	0.55
1 : 1	0.25
3 : 1	0.12

The variation of TiCl₄ : BCl₃ input gas ratio has less significant effects on the deposition rate within the range studied. However, there was an observed trend of decrease in deposition rate as the TiCl₄ : BCl₃ input ratio was increased (Table 3). As the TiCl₄ : BCl₃ input ratio increased, smaller grains were deposited (Fig. 7). This may be due to the fact that an increase in TiCl₄ concentration, increases the nucleation rate. Although nucleation rate is high at high concentration of TiCl₄, the growth rate is low, resulting in a low deposition rate. The reason for this slow growth rate is not yet known.

4. - TiB₂ as a protective coating.

The evaluation of the efficiency of chemical vapour deposited TiB₂ on SiC fibres as a protective coating used for inhibiting the interfacial reaction between the fibre-matrix was carried out by incorporating the coated SiC fibre in Ti-6Al-4V using diffusion bonding under 10 MPa at 1100°C for 1 hour. It was found that the TiB₂ coating deposited by CVD successfully inhibited the interfacial reaction between the SiC fibres and titanium matrix. The detailed information on the chemical behaviour of the chemically vapour deposited TiB₂ on SiC filament in titanium alloy will be published later.

Fig. 6. - Scanning electron micrograph of the surface morphology of TiB₂ coatings deposited at various pressures. a) 6 kPa. b) 15 kPa. c) 23 kPa.

Fig. 7. - Scanning electron micrograph of the surface morphology of the TiB₂ coatings deposited at different TiCl₄ : BCl₃ ratios. a) 1 : 3. b) 1 : 1. c) 3 : 1

5. - Conclusion.

Titanium diboride coatings have been successfully deposited on SiC monofilament by CVD technique. From the deposition conditions studied, coatings consisting of fine grains and smooth surfaces can be obtained at lower temperature (1100°C) and higher pressure (15 kPa). This chemically vapour deposited TiB₂ coating has successfully acted as a protective coating to inhibit the fibre-matrix interaction.

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