

# Evaluation of the efficiency of $TiB_2$ and $TiC$ as protective coatings for $SiC$ monofilament in titanium-based composites

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The vigorous interfacial reactions in  $SiC/Ti-6Al-4V$  composites at elevated temperatures lead to the deterioration of the mechanical properties of the composites.  $TiB_2$  and  $TiC$  were selected as potential protective coatings for  $SiC$  fibres in titanium-based composites. These coatings were deposited on to fibres by the chemical vapour deposition technique. Comparisons and evaluations have been made of the effectiveness of these ceramics as protective coatings for  $SiC$  fibres by incorporating the coated fibres into a  $Ti-6Al-4V$  matrix using the diffusion bonding method. Emphasis has been placed on the chemical compatibility of the candidate coating with  $SiC$  and  $Ti-6Al-4V$  by examining the interfaces of the fibre/coating/matrix using microscopic methods and chemical analysis. A stoichiometric  $TiB_2$  coating was found to be stable with  $SiC$  and has proved an effective barrier to prevent the  $SiC$  fibre from reacting with the  $Ti-6Al-4V$ . The  $TiC$  coating showed no apparent reaction with a titanium-alloy matrix under the conditions studied, but was found to react with the  $SiC$  fibre substrate.

## 1. Introduction

Titanium is a very reactive metal. Currently one of the most attractive fibre reinforcements that is available for titanium-based composites is monofilament  $SiC$  fibre. The high strength, high stiffness, low density and high temperature capabilities of  $SiC$  fibres combined with the toughness and resistance to impact damage of titanium-based alloys has produced titanium matrix composites, which have applications in aerospace as structural materials for aerojet components and compressor blades. However, the development of titanium-based composites for high-temperature applications has been hindered, largely because of the interfacial reaction between  $SiC$  and titanium matrices at elevated temperatures (700 °C and above), which leads to the formation of a brittle reaction zone consisting of titanium carbide and titanium silicides which weakens the mechanical properties of the composites [1, 2]. The chemical compatibility between  $SiC$  fibres and titanium-based alloy matrices is not sufficient to prevent this deleterious fibre–matrix interfacial reaction at elevated temperatures. Therefore,  $SiC$  filament-reinforced titanium matrix composites must be regarded as non-equilibrium systems at high temperatures. Although efforts have been made to deposit a layer of pyrocarbon which is considered particularly efficient for retaining the high mechanical performance of  $SiC$  monofilaments (such as the SCS-6 fibre produced by Textron Speciality Materials), the carbon coating is not sufficiently stable to prevent any significant fibre–matrix reaction and is progressively

consumed by interfacial reaction with the titanium alloy matrix [1, 3].

Various approaches can be adopted to inhibit or reduce the fibre–matrix interfacial reaction: the use of high speed and lower processing temperature during composite fabrication; the selection of fibre and matrix materials that are more compatible; however, this approach is limited in high-temperature applications; the development of less reactive matrices by the addition of alloys such as niobium, aluminium, chromium, vanadium, tin, zirconium and molybdenum, to the titanium matrix to decrease the diffusivity of active elements, and hence slow the reaction kinetics, however, this approach cannot fully eliminate the fibre–matrix interfacial reaction.  $SiC$  is still found to react with titanium-alloy matrices (e.g.  $Ti-6Al-4V$ , and  $Ti_3Al-20Nb$ ,  $Ti-15Mo$ ,  $Ti-13Cr-11V-3Al$ ,  $Ti-1100$ ) [2, 4, 5]. Therefore, the development of a layer of protective coating on the fibres to modify the fibre–matrix interface is necessary to prevent the deleterious interfacial reaction. The selected potential protecting coating must not only be capable of preventing the deleterious fibre–matrix interfacial reaction, but must also not react severely with the fibre through interdiffusion or grain-boundary penetration.

The work here describes the study of  $TiB_2$  and  $TiC$  as potential protective coatings for  $SiC$  fibre-reinforced titanium-based composites. These two coatings have a high chemical stability (Gibbs free energy of formation,  $\Delta G \ll 0$ ).  $TiC$  is in equilibrium with titanium; however,  $TiC$  is non-stoichiometric (Fig. 1a) and

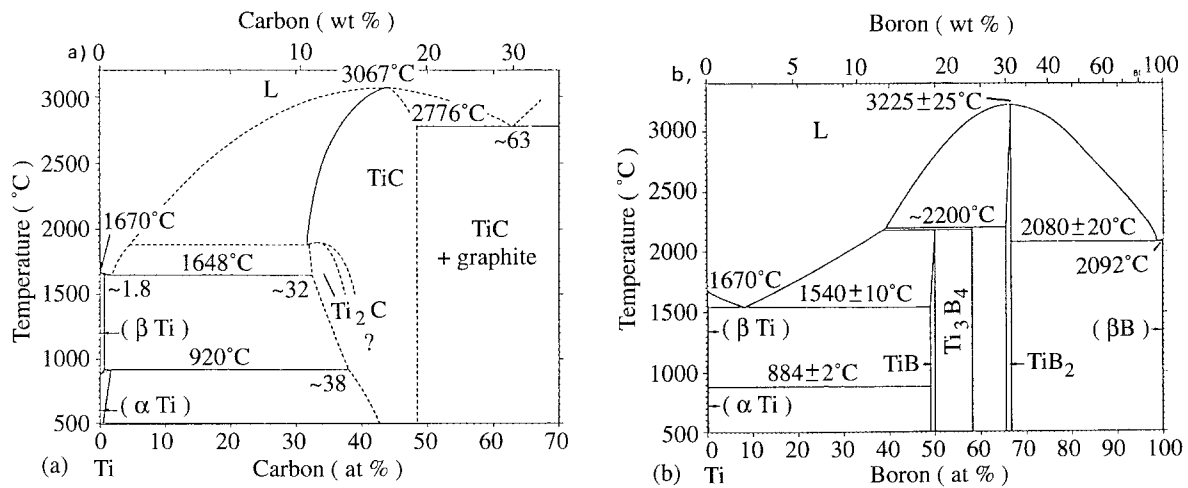


Figure 1 Binary phase diagram of (a) Ti-C and (b) Ti-B. (Adapted from Massalski [6]).

is better represented as  $TiC_x$  ( $x < 1$ ), where  $x$  is a function of temperature when in contact with titanium. This could lead to some chemical degradation and penetration of the protective coating at elevated temperatures.  $TiB_2$  is more stoichiometric (Fig. 1b) but under certain conditions, in contact with titanium,  $TiB$  can form. However, refractory  $TiB_2$  is known to be very stable kinetically and it is believed that  $TiB_2$  may prove to be a sufficient barrier against any chemical reaction with the titanium matrix. In addition, titanium has a lower solubility for the boron in  $TiB_2$  than the carbon in  $TiC$ , and boron has a lower rate of diffusion in titanium and  $TiB_2$  than carbon in titanium and  $TiC$  [7]. The thermal expansion coefficient of  $TiB_2$  is also more closely matched to that of  $SiC$  than is  $TiC$ . Based on these physical and chemical compatibility considerations,  $TiB_2$  should provide better protection than  $TiC$  for  $SiC$  fibres in titanium-based composites. It should be noted that the Ti-6Al-4V (Ti-6-4) was chosen as the matrix in this study because this is the most common and readily available alloy in foil form and not because it is viewed as the most compatible matrix.

The protective coatings were deposited on  $SiC$  monofilaments by the chemical vapour deposition (CVD) technique. Compared with other coating methods such as sputtering, physical vapour deposition (PVD) or ion implantation, this technique has the ability to produce a dense, uniform coating with well-controlled surface morphology and composition without relying on line-of-sight between the source material and the substrate. In addition, this technique offers the potential for rapid and continuous processing that would be desirable for a large-scale composites programme [8, 9].

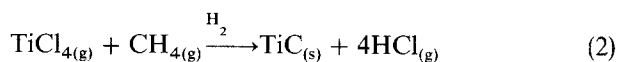
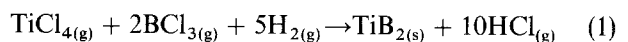
$SiC$  fibre-reinforced titanium-based composites are normally fabricated by solid-phase fabrication methods, e.g. diffusion bonding, which utilizes press forming to achieve consolidation of the fibre and matrix through the application of pressure and temperature. Other methods such as liquid-phase processing are not suitable because titanium is a very reactive metal and has a high melting point (1662 °C). The compatibility and efficiency of the selected material as a protective coating for fibre-reinforced com-

posites can be determined by various methods such as mechanical testing, chemical analysis (e.g. electron probe microanalysis (EPMA), scanning Auger microscopy), and microscopic examination to characterize the fibre-matrix interface.

## 2. Experimental procedure

### 2.1. CVD of protective coatings

The  $SiC$  fibres used in this study were BP Sigma  $SiC$  monofilaments ( $\sim 100 \mu m$  diameter with a tungsten core). The  $TiB_2$  and  $TiC$  protective coatings were deposited individually on to  $SiC$  monofilaments at Oxford by CVD. The experimental apparatus used for the fabrication of these coatings and the details of the coating procedures, and deposition conditions (temperature, pressure, input gas ratio) used to optimize the morphology, microstructure and composition of the  $TiB_2$  and  $TiC$  coatings have been described elsewhere [10, 11]. The coating process was carried out in a cold-wall reactor under reduced pressure through the following reactions



The morphology, microstructure, and composition of the coating-substrate interface were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and EPMA.

### 2.2. Fabrication of the composite

The compatibility of the  $TiB_2$  and  $TiC$  coatings with  $SiC$  fibres and the titanium-alloy matrix was evaluated by incorporating the coated fibres into a Ti-6Al-4V matrix using diffusion bonding. The  $TiB_2$ -coated  $SiC$  fibres used in this evaluation were deposited at a temperature of 1150 °C, a pressure of 15 kPa and a hydrogen flow rate of  $300 \text{ cm}^3 \text{ min}^{-1}$ , but at different  $BCl_3:TiCl_4$  gas ratios of 1:1, 3:1 and 8:1. Uncoated BP Sigma  $SiC$  monofilaments were also used in this study as control specimens. Almost stoichiometric  $TiC$ -coated  $SiC$  fibres were used in this study, which

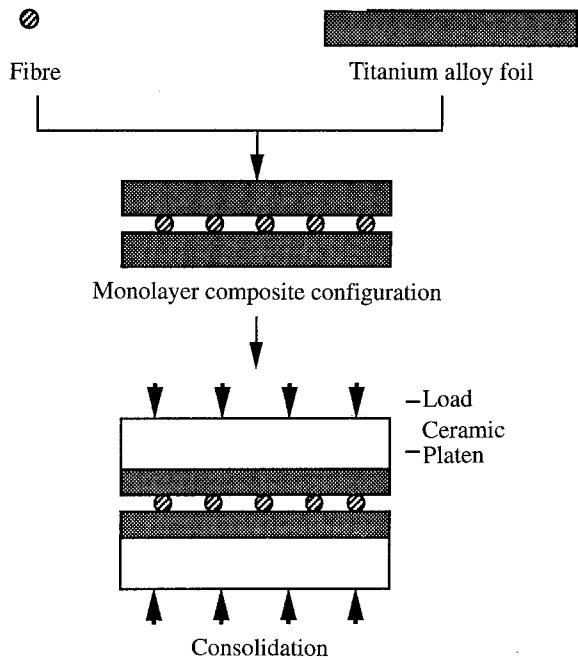


Figure 2 Schematic illustration of the composite fabrication process via the diffusion bonding method.

were fabricated at 1000 °C, 15 kPa, hydrogen flow rate 300 cm<sup>3</sup> min<sup>-1</sup> and CH<sub>4</sub>:TiCl<sub>4</sub> = 2.5:1.

The composite fabrication process is illustrated schematically in Fig. 2. Coated and uncoated fibres were aligned and sandwiched between two sheets of titanium-alloy foil (10 mm × 10 mm × 1 mm) and were consolidated using diffusion bonding under a contact pressure of 10 MPa, at 1100 °C for 1 h in vacuum (10<sup>-3</sup> Pa) to form a monolayer composite.

### 2.3. Characterization of the diffusion-bonded specimen interface

The bonded composites were sectioned, mounted and polished using diamond paste on metal lapping plates, working from 14 μm down to 1 μm paste, finishing with syton (added with 1/4 μm diamond paste) on cloth to remove any residual stress and damage. Subsequently the interfacial composition and microstructures of the SiC/TiB<sub>2</sub>/Ti-6Al-4V and SiC/TiC/Ti-6Al-4V interfaces were examined using SEM, TEM and EPMA. The TEM preparation method used has been described elsewhere [12]. EPMA was performed using a Cameca SEMPROBE (SU30) equipped with a wavelength-dispersive spectrometer. Qualitative microprobe elemental mapping, quantitative line scans and point analyses were performed to investigate the composition of the fibre-coating-matrix interface.

## 3. Results and discussion

### 3.1. SiC/TiB<sub>2</sub>/Ti-6Al-4V

The properties of the TiB<sub>2</sub>-coated SiC fibres produced by CVD in this study and their compatibility in titanium-alloy composites have been presented elsewhere [10–12] and a summary of our findings is

presented here. The morphology of the TiB<sub>2</sub>-coated SiC fibres (deposited under different input gas ratio) used to reinforce titanium-alloy matrices are shown in Fig. 3. All these coatings are dense and uniformly distributed around the circumference of the fibres. The adhesion of the TiB<sub>2</sub> coating on the SiC fibre seems to be good, no cracking or spalling of the coating was observed, as shown in Fig. 4. The adhesion of the TiB<sub>2</sub> coating to the titanium-alloy matrix as shown in Fig. 5 also seems to be good. Therefore, the coating is able to provide load transfer, and can also act as a barrier against chemical interactions with the fibre.

Both TEM and quantitative electron probe microanalysis showed that there was no interfacial reaction between the TiB<sub>2</sub> coatings and SiC substrates.

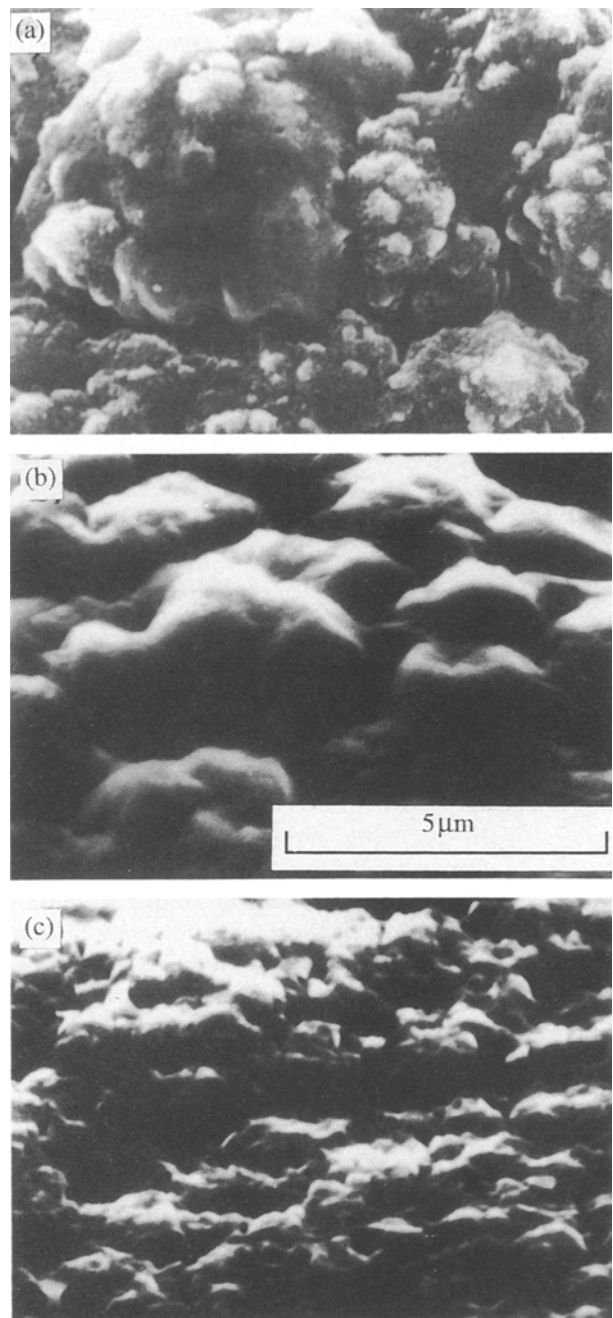


Figure 3 Scanning electron micrograph of the surface morphology of TiB<sub>2</sub> coatings deposited at different TiCl<sub>4</sub>:BCl<sub>3</sub> ratios: (a) 1:8, (b) 1:3, and (c) 1:1.

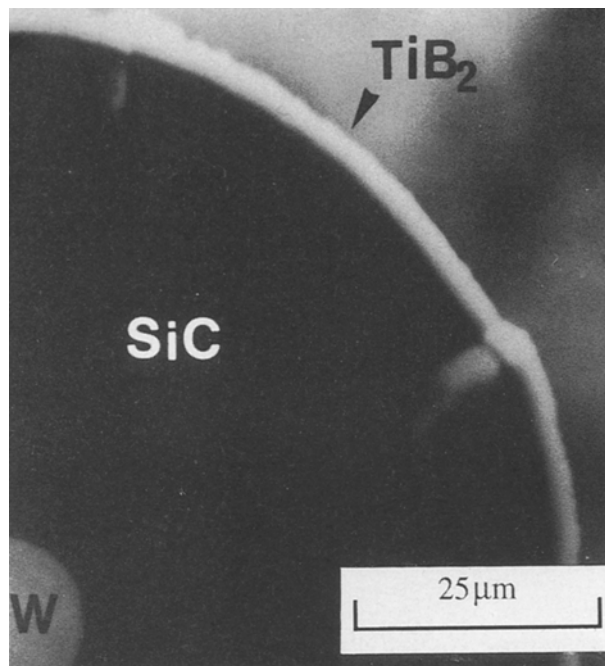


Figure 4 A typical cross-section of the  $\text{TiB}_2$ -coated SiC monofilament. The  $\text{TiB}_2$  coating is uniformly distributed around the circumference of the fibre. The coatings adhere well to the fibre, no cracking or spalling of the coating was observed.

A typical microstructure of the  $\text{TiB}_2/\text{SiC}$  interface is shown in Fig. 6. This indicates that the  $\text{TiB}_2$  coating is stable when in contact with SiC. The quantitative electron probe microanalysis showed that there is also no apparent interfacial reaction between the  $\text{TiB}_2$  coating (deposited at  $\text{BCl}_3:\text{TiCl}_4 = 1:1$  and  $3:1$ ) and the titanium-alloy matrix. Fig. 7 shows a typical quantitative wavelength dispersive spectrum (WDS) obtained across the interfaces of  $\text{SiC}/\text{TiB}_2/\text{Ti-6Al-4V}$  for  $\text{TiB}_2$  coatings deposited under the above input gas ratios, indicating that the  $\text{TiB}_2$  coating is stable on the SiC fibre and with the Ti-6Al-4V matrix. The atomic percentage of silicon and carbon is reduced abruptly at the  $\text{SiC}/\text{TiB}_2$  interface. The corresponding ele-

mental ratio, shows that there is only the  $\text{TiB}_2$  layer between SiC fibre and titanium-alloy matrix. Other reaction products were absent at the fibre-matrix interface. Therefore, the  $\text{TiB}_2$  interlayer has successfully inhibited the deleterious fibre-matrix interaction as compared with the uncoated SiC fibres (fabricated under similar conditions). The WDS profile line-scan across the  $\text{SiC}/\text{Ti-6Al-4V}$  in Fig. 8 shows that the uncoated SiC fibre reacts with titanium-alloy matrix forming a mixture of titanium carbide and silicides in the reaction product at the interface. This reaction layer is approximately  $6\ \mu\text{m}$  thick.

Normally,  $\text{TiB}_2$  is believed to react with titanium ( $\text{Ti} + \text{TiB}_2 \rightarrow 2\text{TiB}$ ). The absence of such reaction between the  $\text{TiB}_2$  and the matrix in this work may be due to the following reasons.

(a)  $\text{TiB}_2$  is kinetically stable in general.

(b) The addition of alloying elements such as aluminium and vanadium in titanium stabilizes the presence of  $\text{TiB}_2$ . Hence further work needs to be carried out to establish an understanding of the reaction mechanisms in  $\text{TiB}_2$  with pure titanium, and in  $\text{TiB}_2$  with titanium-based alloy.

The  $\text{TiB}_2$  coating deposited under high  $\text{BCl}_3:\text{TiCl}_4 = 8:1$  was also capable of retarding the SiC/titanium-alloy interfacial reaction. However this  $\text{TiB}_2$  contains co-deposited free boron [13], which leads to the formation of a needle-like phase adjacent to the  $\text{TiB}_2$  as shown in Fig. 9. This needle-like phase has been identified by quantitative WDS analysis as TiB. The free boron may react with the titanium matrix, forming TiB. This needle-like TiB phase has also been observed at the interface between BP commercial boron-rich  $\text{TiB}_2$ -coated SiC fibres and titanium-alloy matrix at temperatures above  $770^\circ\text{C}$  [14, 15]. The coatings deposited under input gas ratio of  $\text{BCl}_3:\text{TiCl}_4 = 3:1-1:3$  were almost stoichiometric, and did not exhibit any formation of a needle-like TiB second phase when incorporated into the titanium-alloy matrix (fabricated under similar composite processing conditions). This finding shows that the control of the  $\text{BCl}_3:\text{TiCl}_4$  input gas ratio during the chemical vapour deposition of  $\text{TiB}_2$  coatings is very

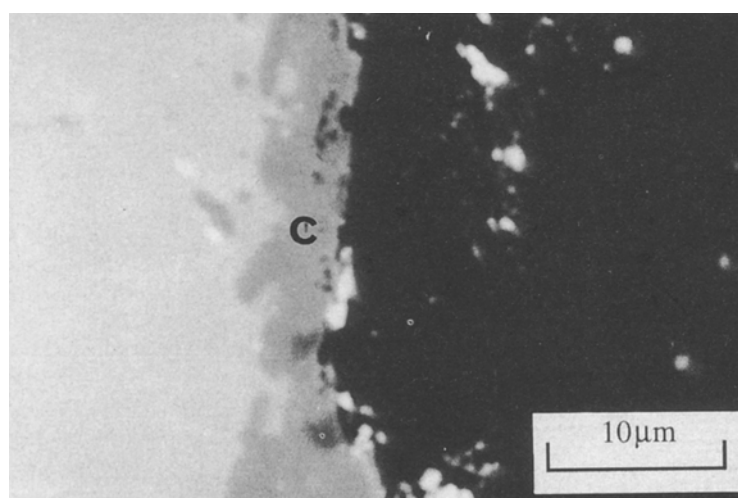


Figure 5 A back-scattered image of the  $\text{SiC}/\text{TiB}_2/\text{Ti-6Al-4V}$  composite. The adhesion of  $\text{TiB}_2$  coating (marked "C") to the titanium-alloy matrix seems to be good.

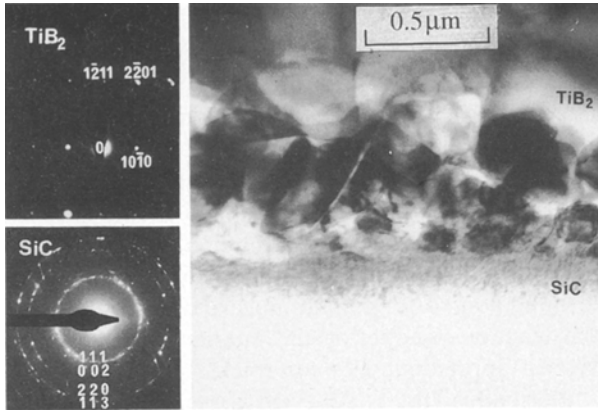


Figure 6 Typical transmission electron micrograph of the interface of  $\text{TiB}_2/\text{SiC}$  showing a clear interface with no apparent interfacial reaction.

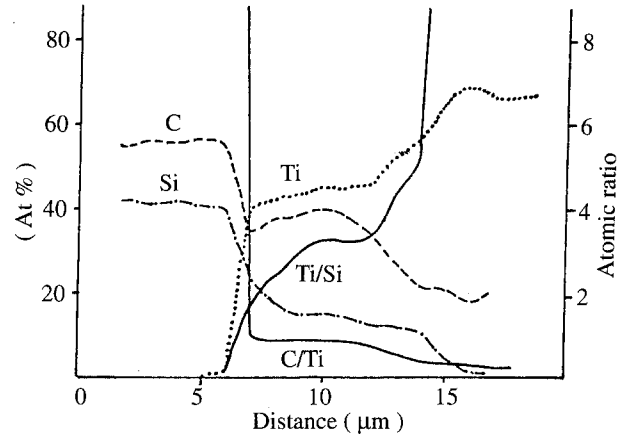


Figure 8 The WDS line scan profile across the interface of  $\text{SiC}/\text{Ti-6Al-4V}$  shows that the uncoated  $\text{SiC}$  fibre reacts with titanium-alloy matrix forming a mixture of titanium carbide and silicides reaction product at the interface.

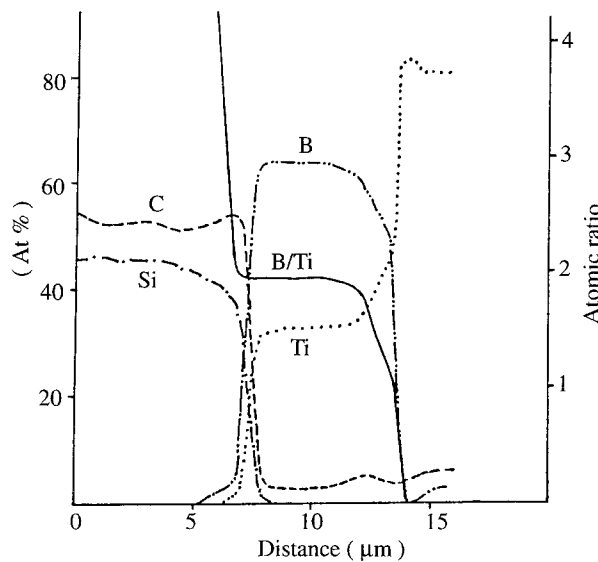


Figure 7 A typical quantitative WDS line scan of  $\text{SiC}/\text{TiB}_2/\text{Ti-6Al-4V}$  ( $\text{TiB}_2$  coatings were deposited at the input gas ratio of  $\text{BCl}_3:\text{TiCl}_4 = 1:1$  and  $3:1$ ) showing the composition distribution and elemental ratio across the interfaces.

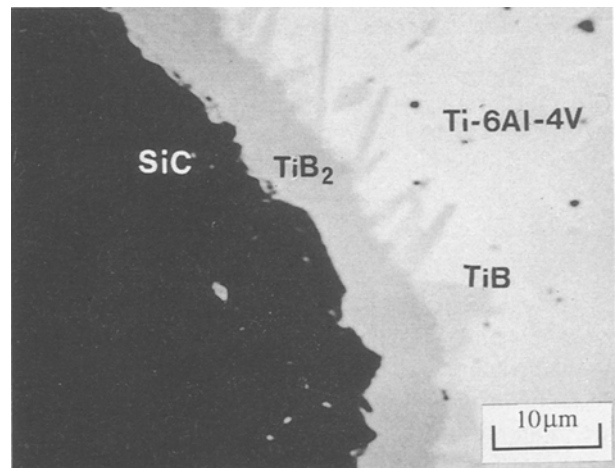


Figure 9 Back-scattered image of the  $\text{TiB}_2$  (deposited under high input gas ratio of  $\text{BCl}_3:\text{TiCl}_4 = 8:1$ ) coated  $\text{SiC}$  fibre-reinforced  $\text{Ti-6Al-4V}$ . Note the formation of a needle-like second phase adjacent to the  $\text{TiB}_2$  coating.

important to produce a stable coating for effective protection in titanium-based composites.

### 3.2. $\text{SiC}/\text{TiC}/\text{Ti-6Al-4V}$

The morphology and nature of the CVD  $\text{TiC}$  coatings on  $\text{SiC}$  monofilaments have been presented elsewhere [11]. Cracks were easily observed in  $\text{TiC}$  coatings that were deposited at high temperature (above  $1200^\circ\text{C}$ ) which would not provide effective protection for  $\text{SiC}$  in titanium-based composites. In order to obtain more adherent  $\text{TiC}$  coatings to  $\text{SiC}$  fibre substrates, a lower deposition temperature should be used. The morphology of this  $\text{TiC}$  coating is shown in Fig. 10.

EPMA revealed that the  $\text{TiC}$  coating reacted with the  $\text{SiC}$  fibres during the diffusion bonding. This is shown in the back-scattered electron image and elemental mappings of  $\text{SiC}/\text{TiC}/\text{Ti-6Al-4V}$  (Fig. 11), where silicon is seen to have diffused into the  $\text{TiC}$  coating. This diffusion leads to a reaction between the  $\text{SiC}$  fibre (substrate) and the  $\text{TiC}$  coating, forming a

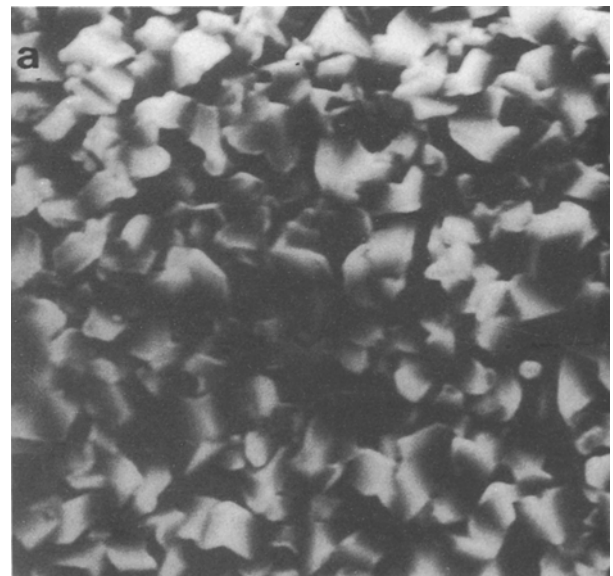


Figure 10 Scanning electron micrograph of the surface morphology of  $\text{TiC}$  coating deposited on  $\text{SiC}$  fibre at  $1000^\circ\text{C}$ , 15 kPa, hydrogen flow rate  $300\text{ cm}^3\text{ min}^{-1}$  and  $\text{CH}_4:\text{TiCl}_4 = 2.5:1$ .

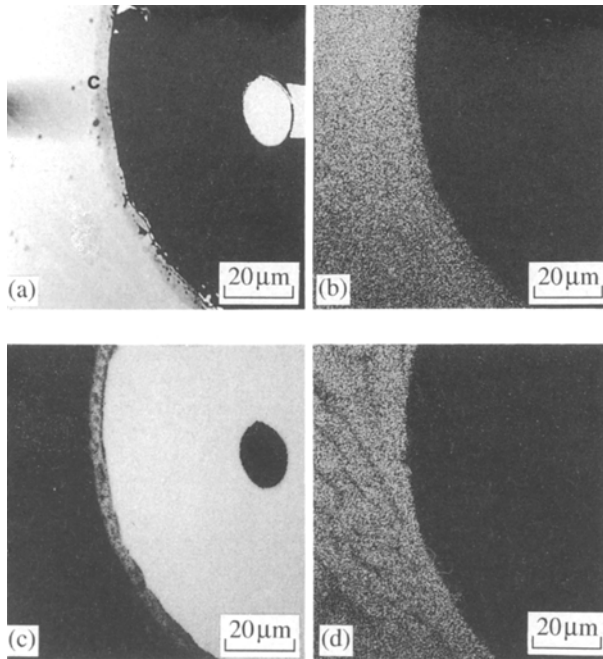


Figure 11 (a) The back-scattered image and elemental mappings of (b) titanium, (c) silicon, and (d) carbon in the SiC/TiC/Ti-6Al-4V composite. The TiC coating is marked "C".

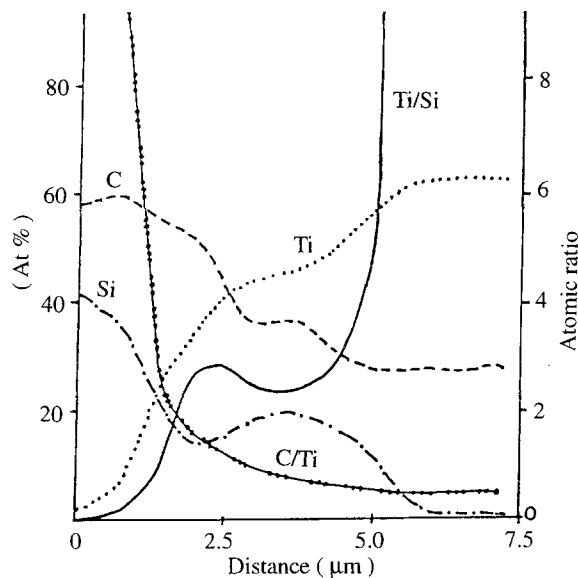


Figure 12 Quantitative WDS analysis of SiC/TiC/Ti-6Al-4V showing the composition distribution and elemental ratio across the interfaces. TiC coating was found to react with the SiC forming a possible mixture of Ti-Si-C and/or titanium silicides.

possible mixture of Ti-Si-C and/or titanium silicides as shown in the composition distribution across the interfaces in Fig. 12. The precise composition requires further analysis. Similar observations were reported by Boss and Yang [16] and Mattingley [17], where silicon had diffused into TiC coatings and was likely to form a mixture of Ti-Si-C compounds.

However, both the optical microscopy and SEM show there is no significant reaction between the TiC coating and the titanium-alloy matrix, as can be seen

in Fig. 11, and there is no apparent change of composition at the TiC and Ti-6Al-4V interface, Fig. 12. This observation is in accordance with the work by Konitzer and Loretto [18]. They reported no chemical reaction between TiC particulates and a Ti-6Al-4V matrix even after heat treatment for 50 h at 1050 °C, though using analytical TEM the diffusion of carbon was found to alter the stoichiometry of TiC (i.e. the carbon concentration, 50%, was reduced to 30% at the interface).

Although the TiC coating cannot completely eliminate the deleterious interfacial reactions, it helps to retard the reaction layer that forms when uncoated SiC fibre is used to reinforce Ti-6Al-4V. Therefore, TiC is still a promising protective coating if the diffusion of silicon is controlled. One way to stop the diffusion may be by depositing TiC coatings on a carbon rich SiC fibre, where the carbon might act as a barrier to diffusion. Therefore, TiC still has positive aspects for use as a protective coating to inhibit the SiC and titanium-matrix interaction.

#### 4. Conclusion

Uncoated SiC fibres react vigorously with Ti-6Al-4V under the conditions studied forming a reaction layer 6 μm thick. Both stoichiometric TiB<sub>2</sub> and TiC coatings show effectiveness in inhibiting the SiC/titanium-alloy interfacial reactions. These two coatings show good adhesion to the fibre and matrix, therefore these coatings are able to provide load transfer, and also act as a barrier against chemical interaction between the matrix and the SiC fibre. However, the TiC coating was found to react with the SiC fibre. Silicon from the SiC fibres diffuses into the TiC coating possibly forming Ti-Si-C and/or titanium silicide compounds. Such a fibre-coating interface reaction was not observed in the TiB<sub>2</sub>-coated SiC fibres. Based on this chemical compatibility assessment, TiB<sub>2</sub> is found to be a more effective protective coating for SiC fibres in titanium-based composites than TiC. However, TiC can still be a promising protective coating if the fibre-coating reaction can be overcome by precoating a layer of diffusion barrier between the fibre substrates and TiC. That is, multiple protective coatings should be used if TiC were to be used as one of the protective coatings.

The control of the BCl<sub>3</sub>:TiCl<sub>4</sub> input ratio during the chemical vapour deposition is very important to avoid non-stoichiometry on the TiB<sub>2</sub> coating. Boron-rich TiB<sub>2</sub>-coated fibres tend to form needle-like TiB phase between the TiB<sub>2</sub> and the titanium-alloy matrix in the composites. This needle-like phase may cause stress concentrations and microcracking, which affects the performance of TiB<sub>2</sub> as a protective coating in SiC/Ti-alloy metal matrix composites.

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