CARBON LAYER PENETRATION AS A FAILURE CRITERION FOR TITANIUM METAL MATRIX COMPOSITES REINFORCED WITH CARBON COATED SiC FIBRES.

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ABSTRACT

A study of the consumption of the C-layer in carbon coated sigma SiC monofilament/Ti metal matrix composites (MMCs) after hot isostatic pressing (HIP) consolidation and subsequent thermal exposure has been undertaken. Statistical analysis of the data shows that the time to penetration of the assumed minimum thickness of the C-layer on the as received carbon coated sigma monofilament (SiC+C) can be used as a criterion to judge the effectiveness of different diffusion barrier coatings and indirectly as a failure criterion for the SiC+C/Ti MMCs. The minimum carbon layer coating as well as the carbon remaining after a given time were based on an exceedance probability of 95%.

INTRODUCTION

SiC/Ti based MMCs are being considered for advanced material applications because of their specific strength, high modulus and higher temperature capabilities compared to monolithic materials. The potential for this class of composite has not been fully realised because of the reaction between the fibre and the matrix [1-4] resulting in the production of brittle reaction products which result in lower composite strengths than are expected theoretically.

Several studies [5-8] have attempted to correlate the size of the brittle reaction zone and the fracture of fibres/MMCs by assuming the presence of an elliptical crack equal to the thickness of the reaction zone. SiC fibres used in titanium matrices have typically a coating of carbon (BP sigma monofiiament) or a carbon rich layer on the surface (SCS-6). The production of the brittle reaction zone is related to the consumption of the C-layer

during high temperature consolidation and subsequent thermal exposure.

The carbon layer ensures that consistent mechanical properties are maintained and reduce the rate of interaction between the fibre and matrix [9]. The carbon layer also increases the damage tolerance of the fibres enabling them to be handled without suffering strength degradation due to self abrasion and handling, while acting as a compliant layer in composites, isolating the SiC from brittle reaction products [10]. Clearly it is important that the carbon layer is maintained during processing and subsequent thermal exposure as well as during the deposition of any additional barrier coatings on the surface of the SiC+C fibre. Any reduction of the C-layer thickness due to fibre/matrix interaction will result in the production of brittle reaction products(mainly TiC and titanium silicides), leading to a reduction in the strength of the fibre and hence the composite [8].

Studies of interfacial reactions in SiC/Ti [11 12] have tended to concentrate on the kinetics of reaction zone formation and especially long term performance after consolidation. The reaction zone products tend to be relatively non uniform, making measurements difficult or necessitating long annealing times to produce thicker easily measurable reaction zones. While it is important to understand the rate of production of the reaction zone, especially with the need to predict long term performance at typical service temperatures, the consumption of the C-coating on the sigma fibre can be used as an early indication of fibre strength degradation and consequently as a measure of assessing the expected change in composite properties as a result of processing and subsequent high temperature exposure. This approach has been undertaken by Warwick and Smith [10], who proposed that the carbon layer continues to be beneficial until the brittle reaction zone product(TiC) reaches the SiC.

In this paper an approach which uses the consumption of the C-layer as a failure criterion for the composite is proposed and its application to life prediction illustrated.

MATERIALS AND METHODS

Materials

MMCs were produced using commercial titanium foils, 0.125 mm thick with the fibres being supplied by BP and consisting of: (i) uncoated sigma SiC monofilament on a W core, (ii) a carbon coated SiC sigma monofilament, approximately 100 μm in diameter having a carbon coating of 1 μm thickness (SiC+C). Commercial purity titanium (99.6%Ti) was used since the reaction products between SiC and Ti are relatively simple and well known, making it an ideal model system for the study of fibre matrix interaction and the Ti/SiC system represents the severest test for barrier coatings due to the high reactivity of titanium. A diffusion barrier that would succeed in reducing the rate of reaction between SiC fibres and a commercial purity Ti matrix, would probably work even better with the typical titanium alloy matrices, such as Ti-6Al-4V or Ti-15V-3Al-3Cr-3Sn used in actual composites.

Consolidation of MMCs

The MMCs were consolidated by hot isostatic pressing (hereafter HIP) of foil-fibre-foil lay ups in a stainless steel can at temperatures from 750-1000 °C, at 200 MPa for 30 minutes. A small amount of organic binder was used to hold the fibres in place. Following consolidation further thermal exposure of the specimen HIPped at 900°C, was carried out in a vacuum furnace ($<10^{-7}$mbar) at 900 °C for up to 16 hours.

Method used to measure the C-layer thickness

Specimens for scanning electron microscopy (SEM) were sectioned perpendicular to the fibre axis, ground and polished to 0.25 μm, with light etching and repolishing as the last step. Backscattered electron images were used to study the fibre matrix interface and measure the change in carbon coating thickness and formation of the reaction zone. Measurements were made at the tangents to the smallest diameter of the fibre when fibre sections were not precisely normal to the fibre length. The diameter of the tungsten core was used to calibrate the SEM and as a means of

checking that the measurements were being made on the minor axis of the sectioned fibre. Measurements taken on other than the minor axis were corrected using the relationship [13]

$$L_i' = L_i[E^2 + (1 - E^2)\sin^2 \alpha]^2 \quad (1)$$

where E is the ratio of the minor axis to major axis, α is the angle between the test line and the major axis, L_i is the thickness measured on the elliptical section of the fibre and L'_i is the corrected thickness (Fig. 1).

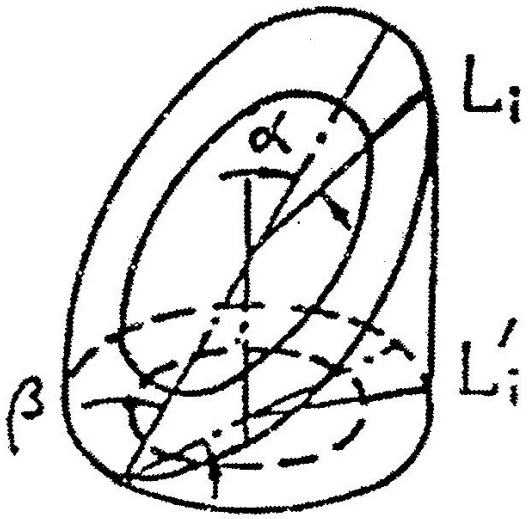


Fig. 1 Geometry of the intercepts on the specimen surface and transverse section[13]

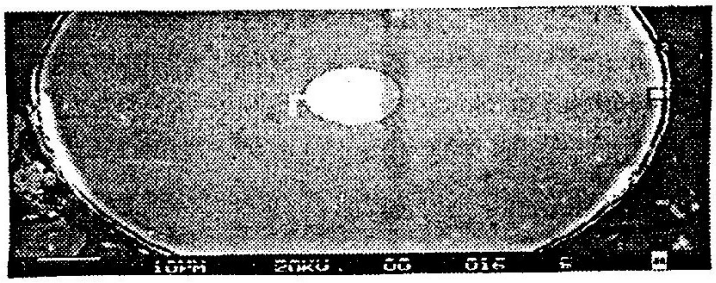
For each condition two fibres were assessed providing four areas from which measurements were taken. Each area was divided into six sections by line intercepts in the horizontal direction on which the thickness of the remaining carbon layer was measured (Fig. 2). This gave a set of 24 values from which a normal probability plot was constructed.

RESULTS AND DISCUSSIONS

Variation of the C-layer

Fig. 3 is a normal probability plot that illustrates the variation of the carbon coating thickness on the as received SiC+C fibre. The coating thickness was found to vary from 1.0 to 1.6 μm, with a mean of 1.2±0.2 μm. This can be compared to the variation of the carbon coating thickness in Fig. 4 for the SiC+C/Ti MMC after HIP processing at 900°C/200MPa/

(a)



(b)

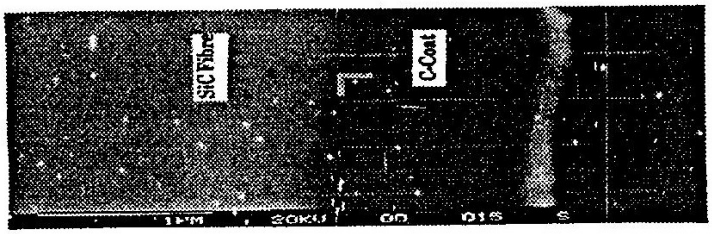


Fig. 2 SEM micrograph of a SiC+C fibre (a) overall (b) close up micrograph of the C-coating/SiC interface used in the thickness measurements

0.5h.. The variation in reaction zone thickness is also presented for comparison. It can be observed from Fig. 4 that, while there is a considerable scatter in the carbon coating thickness values, the values of the reaction zone thickness exhibit even greater scatter. The carbon coating thickness varied from 0.50 to 1.11 μm with a mean of 0.79±0.15 μm, while the reaction zone varied from 0.23 to 1.50 μm with a mean of 0.64±0.27 μm after the HIP processing.

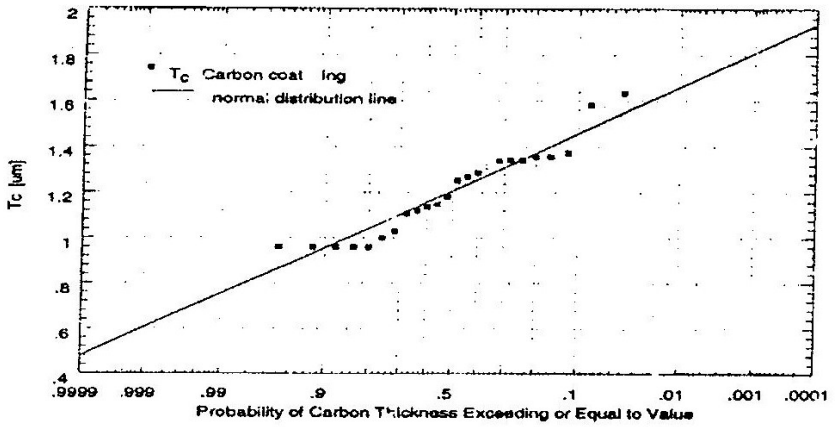


Fig. 3 Variation of the thickness of the carbon coats: SiC+C: as received

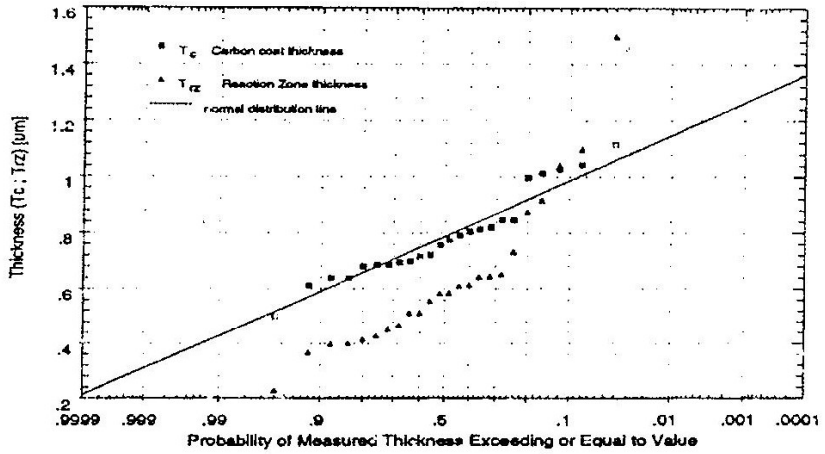


Fig. 4 Variation of the thickness of the C-coat and reaction zone for SiC+C/Ti MMC, HIPped at 900°C/200MPa/0.5h

Determination of the amount of C-layer consumed

The consumption of the C-layer is controlled by diffusion [10]. The mean thickness of the carbon coating, $T_{crest\,t}$, retained on the fibres after processing or thermal exposure for a time t is given by :

$$T_{crest.t} = T_{crest.o} - T_{ccons.t} \qquad (2)$$

where $T_{crest\,o}$ is the minimum thickness of the carbon coating on the as received fibre, and $T_{ccons\,t}$ is the amount of carbon coating consumed at any time t based on the assumed minimum C-coating thickness of the as received fibre ($T_{crest\,o}$). Hence,

$$(T_{ccons.t})^2 = Kt \qquad (3)$$

where K is the rate constant in m^2/s and t the time in seconds, with the Arrhenius relationship:

$$K = K_o \exp(\frac{Q}{RT}) \qquad (4)$$

being applicable; K_o and Q (activation energy) are material constants, T the temperature in Kelvin degrees and R is the gas constant.

The values of $T_{crest\,t}$ and $T_{crest\,o}$ were derived from normal probability plots of the measured thickness values, based on a probability of survival of 95% of all thickness values measured being equal or exceeding this minimum value (95% exceedance probability). The minimum C-coating

thickness of the as received SiC+C fibre based on 95% exceedance probability was found to be 0.89μm.

In this study statistical considerations were employed due to the observed variations of the as received C-coating thickness and the fact that the consumption of the C-layer after consolidation was highly non-uniform. Considering the fracture strength of the fibre, non uniform consumption of the carbon layer would increase the defect population such that instead of the fibre failing due to intrinsic surface defects, it would fail as a result of larger defects produced by the non uniform formation of brittle reaction products. The thinnest parts of the fibre C-coating would be the first to be penetrated. Therefore the worst case scenario was assumed, i.e. a minimum C-coating thickness based on a 95% exceedance probability as predicted from the probability plots.

Fig. 5 illustrates schematically the concept of penetration of the carbon layer, and its consumption based on statistical considerations (95% exceedance probability). The arrow labelled P in the figure shows the advancement of the reaction zone front due to the consumption of the C-layer and its interaction with titanium. As soon as the minimum layer is penetrated the SiC is no longer isolated from the effect of the reaction products and the strength of the fibre is reducced.

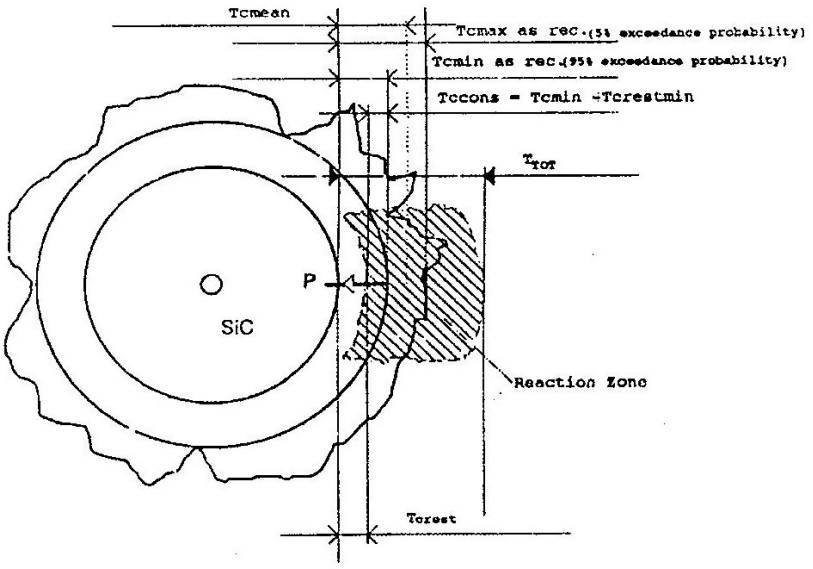


Fig. 5 Schematic illustration of the basis for the penetration of the C-coat

Fig. 6a shows the mean carbon layer retained on the SiC+C fibre after HIP processing (900°C/200MPa/0.5h) and thermal annealing for different times at 900°C. The values are plotted as the square of the carbon coating retained ($T_{crest\ t}$) in μm^2 against time in hours with one standard deviation included as error bars to illustrate the large variations in the values.

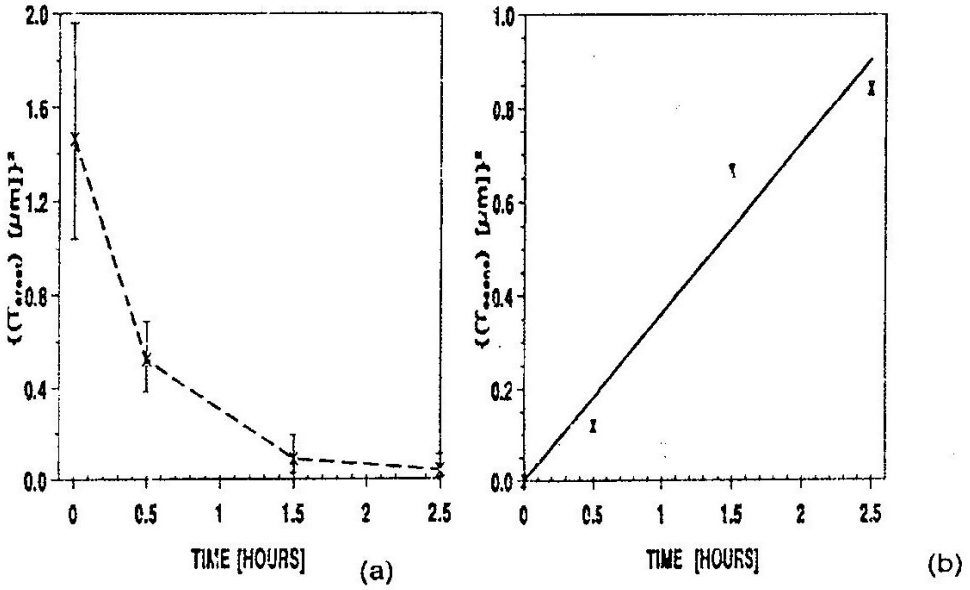


Fig. 6 C-coat thickness vs time for a SiC+C/Ti MMC after HIPping and annealing: (a) retained and (b) consumed-C layer

When the data are plotted as the amount of carbon-coating consumed ($T_{ccons\ t}$), a parabolic consumption relationship becomes evident (Fig. 6b) showing that the consumption is indeed diffusion controlled. The rate of consumption of the C-coat (K_{ccons}) was found to be 0.36μm^2/h, from Fig. 6b (regression coefficient 0.96).

The rate constant for the consumption of the C-coating in SiC+C/Ti MMCs also followed the Arrhenius relation in equation (2) as shown in Fig. 7. The rate constants for the consumption of the C-coating were obtained after HIP processing at 200MPa for 0.5h at different temperatures. An apparent activation energy of 136KJ/mole can be calculated from the least squares fit line from Fig. 7 which follows the empirical relationship:

$$K_{ccons}[m^2/s] = 1.2x10^{-10}\exp(\frac{-16364}{T}) \qquad (5)$$

where K_{ccons} is the C-coat consumption rate in m^2/s and T the temperature

in degrees Kelvin. From the different rate constants at the different temperatures after HIP processing, the time to penetration of the C-layer and complete consumption can be calculated. The time to penetration (t_{pen}) is defined as:

$$t_{pen} = \left[\frac{(T_{crest.o})^2}{K_{ccons}} \right] \tag{6}$$

The complete consumption of the C-layer is based on the maximum value (5% exceedance probability) of the C-layer thickness ($T_{cmax\ o}$) on the as received SiC+C, therefore:

$$t_{pen} = \left[\frac{(T_{c\,max.o})^2}{K_{ccons}} \right] \tag{7}$$

The likelihood of penetration of the C-layer depends on the local environment(matrix material, coating on fibre), time, temperature and the original C-layer variation [14]; thus the use of statistics in determining the minimum C-layer.

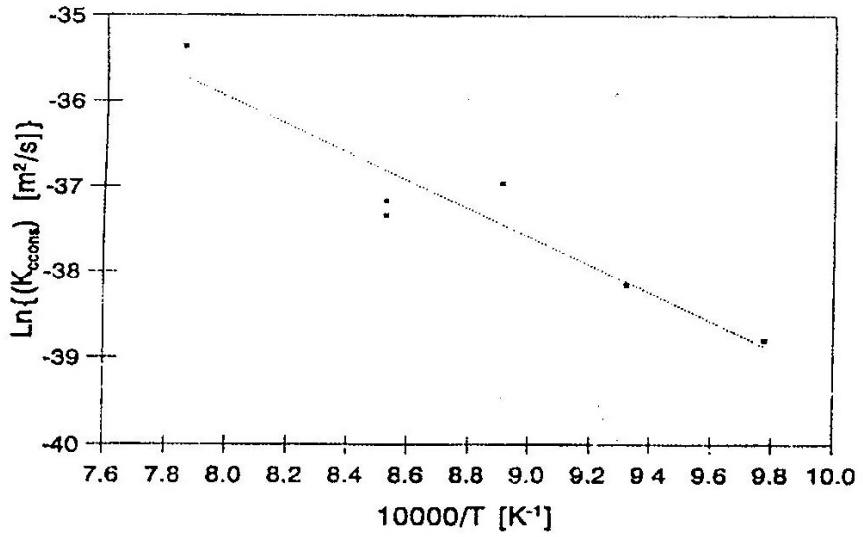


Fig. 7 Arrhenius plot of the consumed C-coat on the SiC+C fibre in a Ti matrix based on 95% exceedance probability

Table 1 summarizes the time to penetration and total consumption at different temperatures based on the empirical relationship from the Arrhenius plot in Fig. 7 with extrapolation to the envisaged temperature of use (650°C).

Table 1 **Carbon coat penetration and total consumption times at different temperatures for a SiC+C/Ti composite based on equations (5-7)**

Specimen	Temperature oC	Penetration Time [h]	Consumption Time [h]
	650	92	271
	750	16	48
SiC+C/Ti	800	7.7	22.8
	900	2.1	6.2
	1000	1	1.8

The time required to penetrate the minimum assumed C-coating at 900°C on the SiC+C fibre in commercial purity titanium is 2 hours and about 6 hours were enough to consume the C-coat. At 650°C the respective times would be 92 and 271 hours. It can therefore be concluded that the rate of consumption of the C-coat on the SiC+C fibre is highly sensitive to temperature.

Effect of C-coat penetration on fibre strength

Parallel studies [15] have shown that the fracture strength of SiC+C fibres coated with titanium start to drop as soon as the minimum C-coating is penetrated as Fig. 8 shows. For comparison the strength of a titanium coated SiC fibre without a carbon coating starts to drop immediately. The strength of the SiC+C fibre coated with titanium also drops drastically after the complete consumption of the carbon coating. This fact is also reflected in the change in the reaction product morphology in Fig. 9, which shows the appearance of the fibre-matrix interface after HIP processing at 900°C, 200 MPa, 0.5 h and annealing in a vacuum furnace at 900°C for different times. A change in the reaction zone morphology can be observed as the exposure time increases and complete consumption of the carbon coat has occurred (Fig. 9d). The morphology of the microstructure changes from a homogeneous thin reaction zone (TiC), between the remaining C-coat and the titanium matrix after consolidation, into TiC particles in a titanium silicide matrix with the homogeneous TiC formed during the con-

sumption of the C-coat being displaced outwards into the titanium matrix(Fig. 9d).

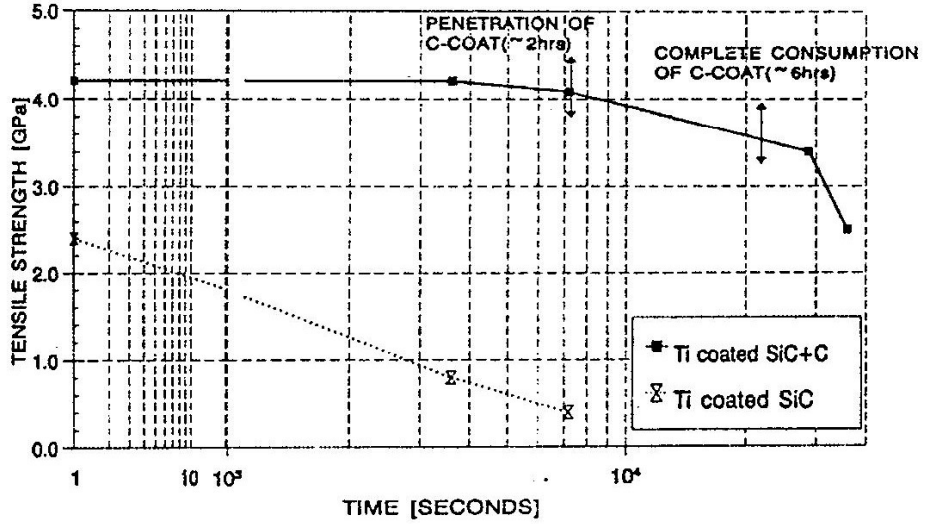


Fig. 8 Fracture strength as a function of time for titanium coated SiC+C fibres in comparison to titanium coated SiC fibres after thermal exposure at 900 °C, showing a drop in strength as soon as the C-layer is penetrated[15]

Titanium based MMCs using SiC as the reinforcement are normally processed by vacuum hot pressing (VHP), hot isostatic pressing (HIP) or a combination of diffusion bonding and superplastic forming. For VHT and single step HIP, durations of between 20 minutes and 1 hour are normally the norm at temperatures ranging form 850-950 °C for titanium based MMCs. Going by the penetration times given in Table 1, at 900°C for example, this would cause unacceptable consumption of the C-layer, with extrapolation to the typical use temperature 650°C not being better. Penetration of the carbon coat which would be expected to occur at about 92 hours at 650°C and complete consumption in 271 hours, indicates a shorter than envisaged lifetime for this class of composites. MMCs based on Ti and SiC are expected to be able to withstand at least 2500 hours, the design lifetime for military aerospace components or 25000 hours, the corresponding design lifetime for civil aircraft components. Obviously a diffusion barrier is needed to prevent the fast consumption of the C-layer from the sigma monofilament. Such barriers like the boron rich TiB_2 coating on the sigma SiC fibre [10, 16] are known to reduce the rate of consumption of the C-coat. Recently [16] a precious metal intermetallic coating has

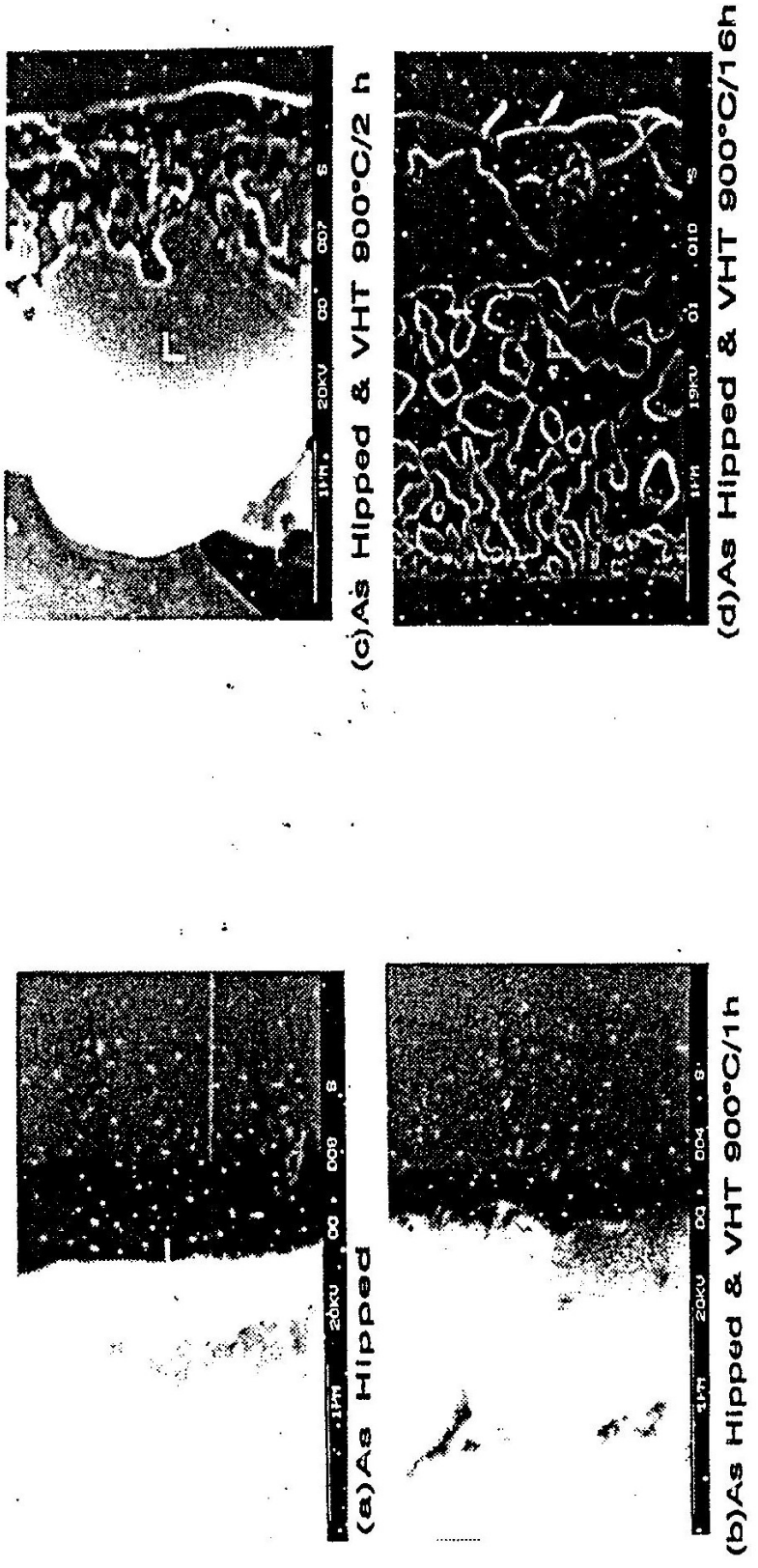


Figure 9 SiC+C/Ti MMCs: Fibre-matrix interface after Hipping at 900°C/200MPa/0.5h and annealing at 900°C for different times.

also shown some promise in delaying the consumption of the C-coat on the sigma SiC+C fibre. In using these diffusion/barrier coatings to prevent interactions in SiC/Ti MMCs, consumption of the C-layer following the approach described in this paper can be used to assess their effectiveness [16].

CONCLUSIONS

i Consumption of the C-coat on titanium MMCs reinforced with SiC+C fibres can be used as an indication for composite failure as well as a tool to judge the effectiveness of diffusion barrier/ layers on the fibre.

ii This approach which is based on worst case scenario employing statistics(95% exceedance probability), takes into consideration the fact that the carbon coat on the fibre is essential in maintaining its strength with penetration causing the formation of brittle reaction products resulting in an increase in defect population on the surface of the SiC.

iii It has been illustrated that the carbon coat on its own, does not last long at both the processing temperature (900 °C) and the envisaged use temperature (650 °C). Penetration of the C-coat would occur after 2 hours at 900 °C and complete consumption after 6 hours, while at 650 °C the corresponding times would 92 and 271 hours respectively. These times fall far short of the expected design lifetimes used in the aerospace industry. Thus the SiC+C fibre cannot be used without diffusion barriers/coatings in Ti based MMCs.

iv With the need for a diffusion barrier/coating to protect the carbon on the fibre, the approach described in this paper based on the consumption of the C-layer can be used as a means to assess the effectiveness of these coatings on the SiC+C fibre. This would only be one evaluation criteria and must be combined with other means eg. strength measurements, to assess the overall effectiveness of barriers on SiC fibres in titanium matrices.

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