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A new criterion for determining the failure of Ti/SiC metal-matrix composites

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The failure of titanium metal-matrix composites (MMCs) strengthened with monofilament carbon-coated sigma SiC fibres has been studied following exposure at a temperature of 900 °C. Statistical analysis of the data shows that the time to penetration of the carbon layer on the as-received carbon-coated sigma monofilament (SiC + C) can be used as a failure criterion for these composites. The same technique can also be used as a measure of the effectiveness of different diffusion barrier coatings.

1. 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 realized because of reaction between the fibre and matrix [1–4], resulting in the production of brittle reaction products which produces 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. However, SiC fibres commonly used in titanium matrices have a coating of carbon (BP sigma monofilament) or a carbon-rich layer on the surface (SCS-6). The production of the brittle reaction zone is related to the consumption of this carbon layer during high-temperature consolidation and subsequent thermal exposure.

The carbon layer ensures that consistent mechanical properties are maintained and reduces 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, 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 carbon-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 strength [8].

Studies of interfacial reactions in SiC/Ti [11, 12] have been inclined to concentrate on the kinetics of reaction-zone formation. These reaction-zone products tend to be relatively non-uniform, making measurements difficult or necessitating long annealing times to produce thicker, easily measurable, reaction zones. It is important to understand the rate of production of the reaction zone, and the consumption of the carbon coating on the sigma fibre can be used as an early indication of formation of this zone and of fibre-strength degradation. Consequently, this may also be used as a method 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 fibre surface.

In this work, a quantitative approach, which uses the consumption of the carbon layer as a failure criterion for the composite, has been proposed and its application to life prediction illustrated.

2. Materials and methods

2.1. Materials

MMCs were produced using commercial purity titanium foils, 0.125 mm thick with the fibres supplied by BP and consisting of (i) uncoated sigma SiC monofilament on a tungsten core, (ii) a carbon-coated SiC sigma monofilament (they were approximately 100 μm diameter having a carbon coating 1 μm thick (SiC + C)). Commercial purity titanium (99.6 + %) was used because the reaction products between SiC and titanium are relatively simple and well known. This makes it an ideal model system for the study of fibre–matrix interaction. Further, the Ti/SiC system represents a very severe 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 CP titanium matrix, is likely to work even better with typical titanium alloy matrices, such as Ti–6Al–4V or Ti–15V–3Al–3Cr–3Sn used in commercial composites.

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2.2. Consolidation of MMCs

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

2.3. Method used to measure the carbon 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 subsequent 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 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 as a calibration 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).

For each condition, two fibres were assessed providing four areas from which six measurements were taken of the remaining carbon thickness to give a set of 24 values from which a normal probability plot was constructed. A typical area for measurement is shown in Fig. 2.

3. Results and discussion

3.1. Variation of the carbon-layer thickness

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 about 1.0–1.6 μm, with a mean of ~1.2 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/200 MPa/0.5 h which shows a reduction in carbon thickness with values varying from about 0.5–1.11 μm with an average value of ~ 0.8 μm. 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 reaction zone varied from 0.23–1.50 μm with a mean of 0.64 μm after the HIP processing.

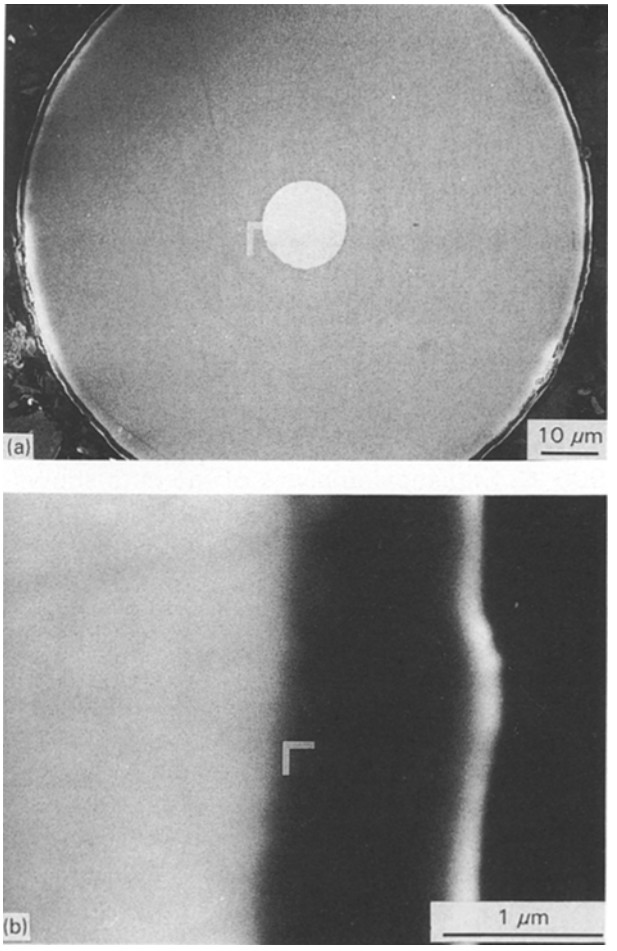

Figure 2 (a) Scanning electron micrograph of a carbon-coated SiC fibre; (b) higher magnification showing the carbon coating/SiC interface used in the thickness measurements.

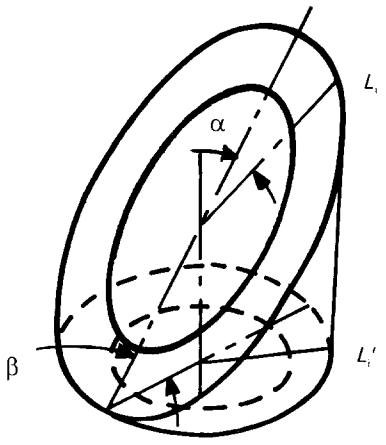

Figure 1 Geometry of the intercepts on the specimen surface and transverse section [13].

3.2. Determination of the amount of carbon layer consumed

The consumption of the carbon layer is controlled by diffusion [10]. The mean thickness of the carbon coating, T_m, retained on the fibres after processing or thermal exposure for a time, t, is given by

$$T_m = T_0 - T_c \quad (2)$$

where T_0 is the minimum thickness of the carbon coating on the as-received fibre, and T_c is the amount of carbon coating consumed at any time t, based on

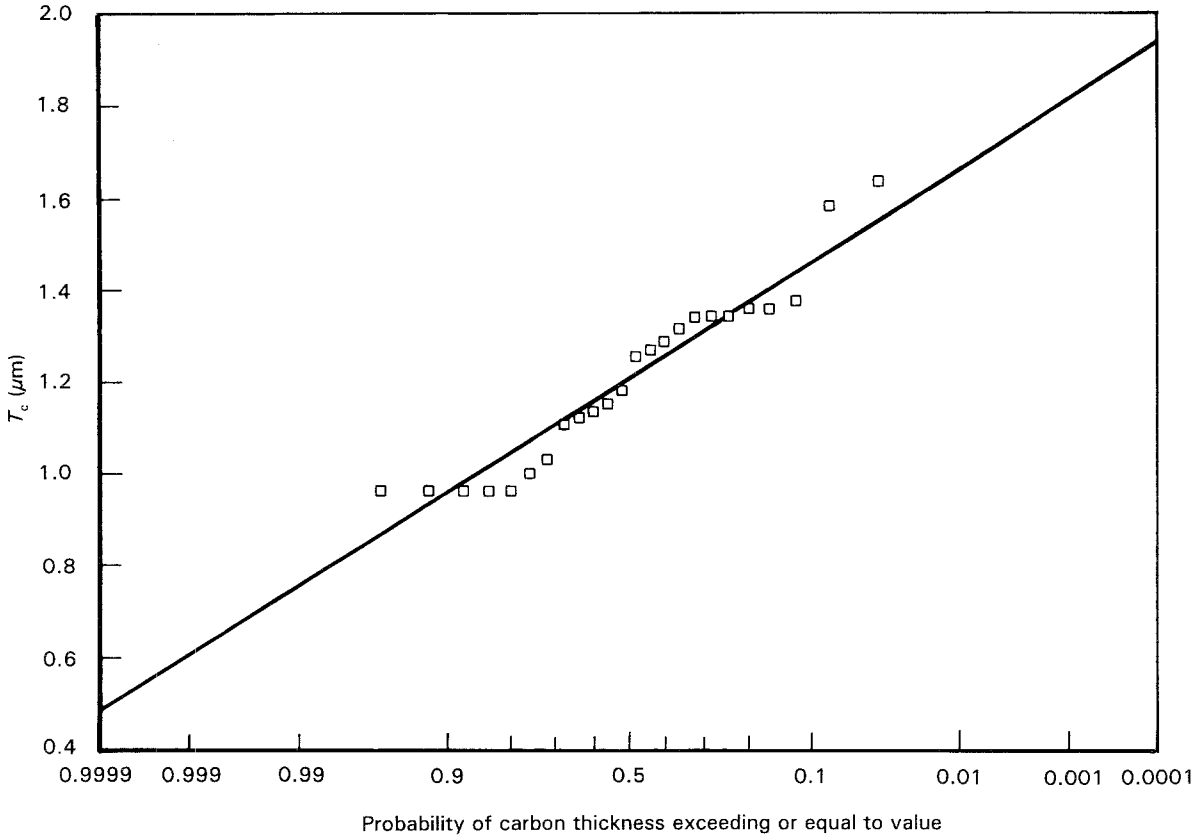

Figure 3 Variation in carbon-coating thickness on as-received fibre. (□) T_c, carbon coating; (——) normal distribution line.

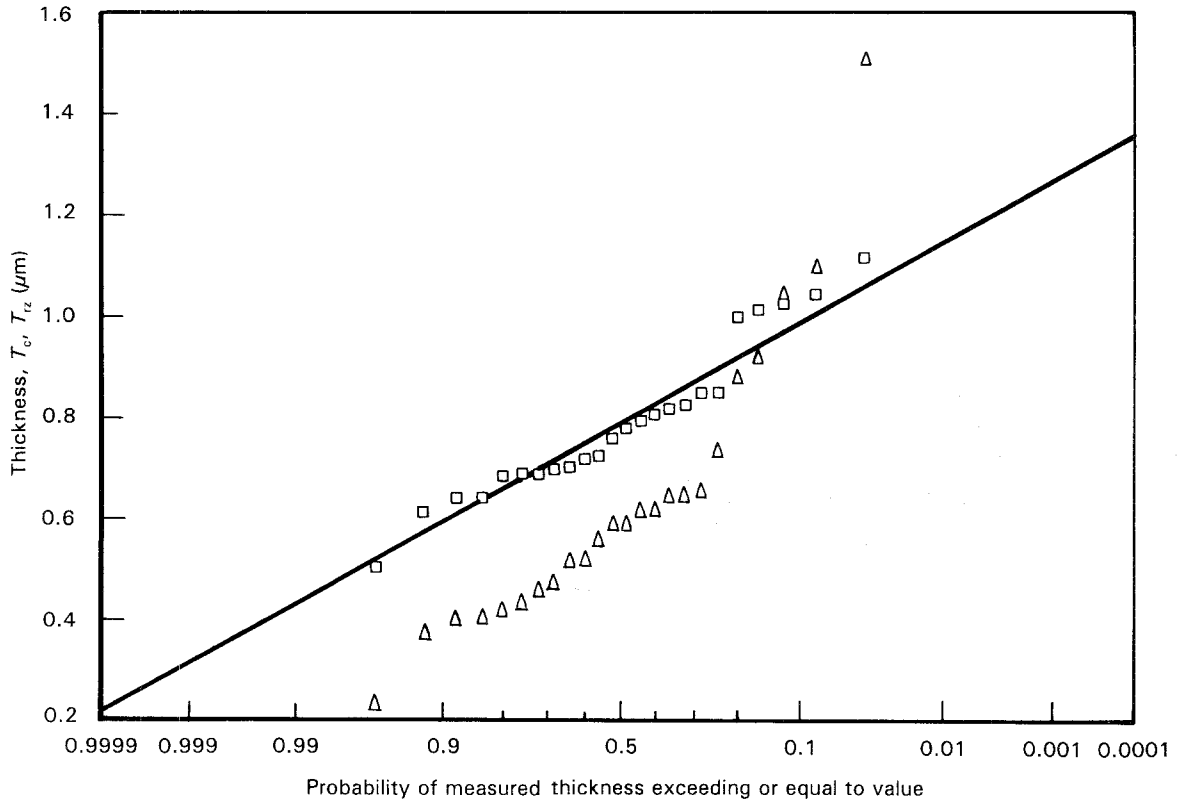

Figure 4 Variation in the thickness of the carbon coating and reaction zone for SiC + C/Ti MMC, HIPped at 900 °C/200 MPa/0.5 h. (□) T_c, carbon-coating thickness; (△) T_{r2}, reaction-zone thickness; (——) normal distribution line.

the assumed minimum carbon-coating thickness of the as-received fibre, T_0. Hence

$$(T_c)^2 = Kt \quad (3)$$

where K is the rate constant ($m^2\ s^{-1}$) and t the time (s), with the Arrhenius relationship

$$K = K_0 \exp\left(\frac{-Q}{RT}\right) \quad (4)$$

being applicable; K_0 and Q (activation energy) are

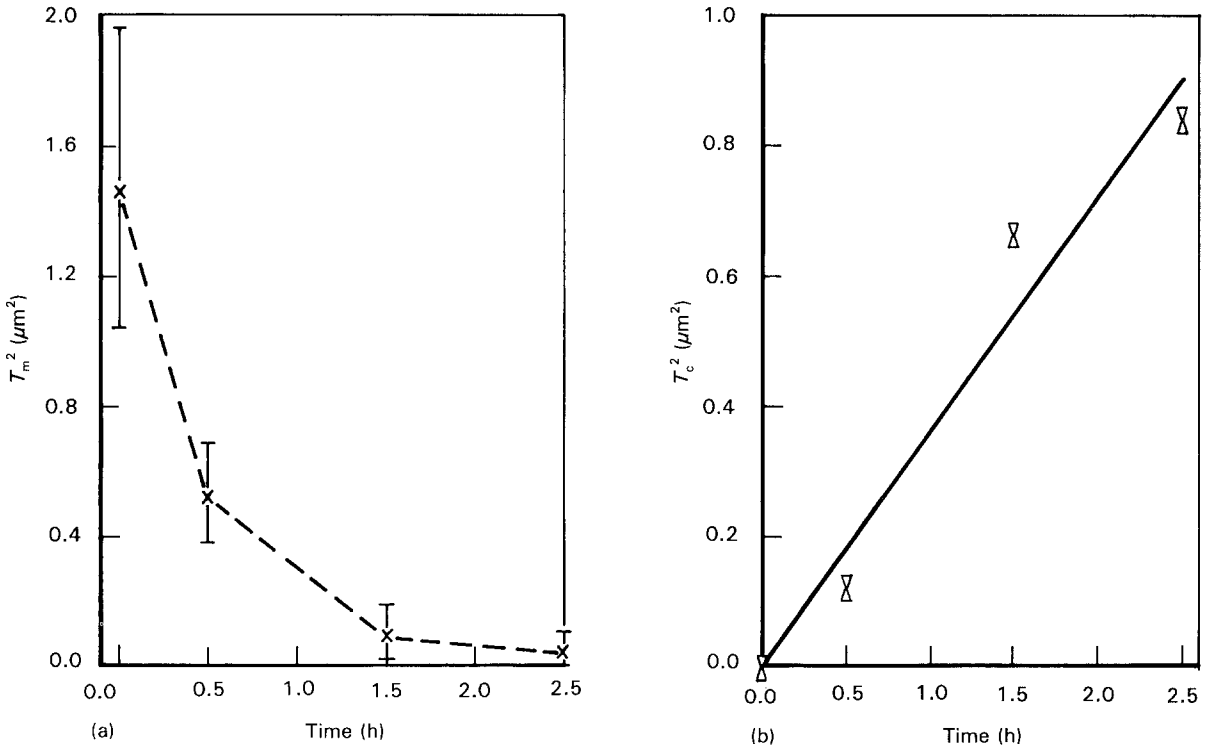

Figure 5 Carbon-coating thickness versus time for a SiC + C/Ti MMC after HIPing and annealing: (a) retained, and (b) consumed carbon layer.

material constants, T the temperature (K) and R is the gas constant.

The values of T_m and T_0 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 to or exceeding this minimum value (95% exceedance probability). The minimum carbon-coating thickness of the as-received SiC + C fibre based on 95% exceedance probability was found to be 0.89 μm.

In this study and in similar studies of this nature, statistical considerations have to be employed due to the observed variations of the as-received carbon-coating thickness and the fact that the consumption of the carbon layer after consolidation is 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, present in the as-supplied fibre, it would fail as a result of larger defects, produced by the non-uniform formation of brittle reaction products. If it is assumed that the thinnest parts of the fibre carbon coating would be the first to be penetrated, this ensures that a worst case scenario is assumed, i.e. a minimum carbon-coating thickness based on a 95% exceedance probability as predicted from the probability plots.

Fig. 5a shows the mean carbon layer retained on the SiC + C fibre after HIPing (900 °C/200 MPa/0.5 h) and thermal annealing for different times at 900 °C. The values are plotted as the square of the carbon coating retained, T_m (μm^2) against time (h) with one standard deviation included as error bars to illustrate the variations in the values.

When the data are plotted as the amount of carbon-coating consumed, T_c, a parabolic consumption relationship becomes evident (Fig. 5b) showing that the consumption is indeed diffusion controlled. The rate of consumption of the carbon coating was found to be 0.36 $\mu m^2 h^{-1}$, from Fig. 5b (regression coefficient 0.96).

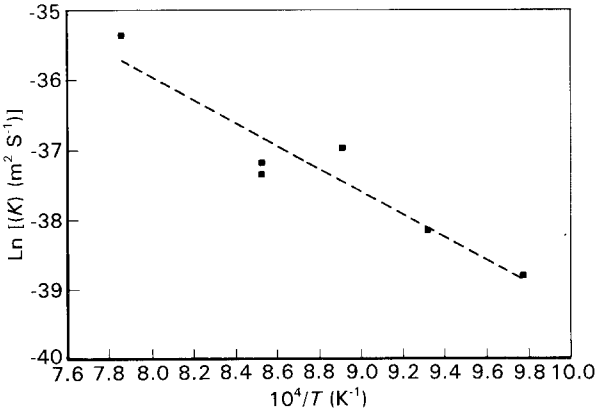

Figure 6 Arrhenius plot of the consumed carbon coating on the SiC + C fibre in a titanium matrix based on 95% exceedance probability.

The rate constant for the consumption of the carbon coating in SiC + C/Ti MMCs also followed the Arrhenius relation in Equation 2 as shown in Fig. 6. The rate constants for the consumption of the carbon coating were obtained after HIP processing at 200 MPa for 0.5 h at different temperatures. An apparent activation energy of 136 kJ mol^{-1} can be calculated from the least squares fit line from Fig. 7 which follows the empirical relationship

$$K(m^2\ s^{-1}) = 1.2 \times 10^{-10} \exp\left(\frac{-16364}{T}\right) \quad (5)$$

where K is the carbon coating consumption rate

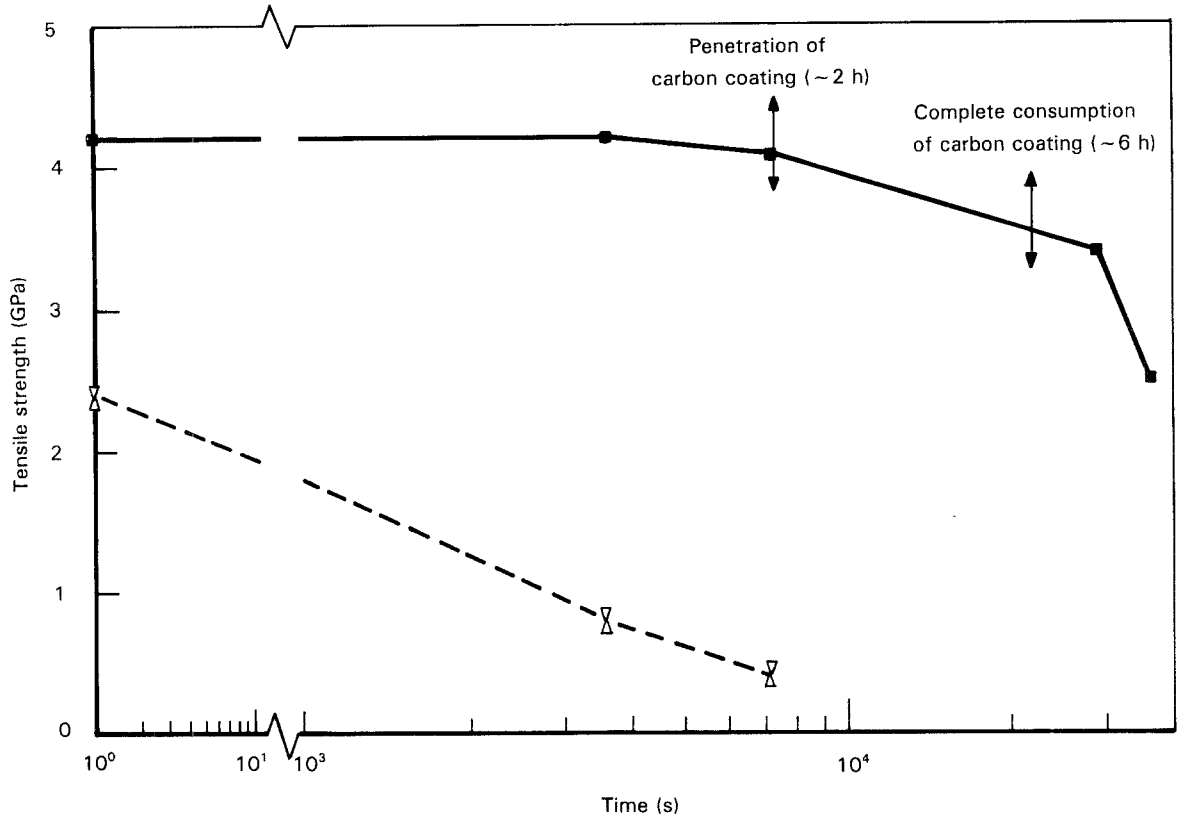

Figure 7 Fracture strength as a function of time for (■) titanium-coated SIC + C fibres in comparison to (X) titanium-coated SiC fibres after thermal exposure at 900 °C showing a drop in strength as soon as the carbon layer is penetrated. Data from [14, 15].

($m^2\ s^{-1}$) and T the temperature (K). From the different rate constants at the different temperatures after HIP processing, the time to first penetration, t_p, of the carbon layer and complete consumption, t_t, can be calculated. The time to first penetration is defined as

$$t_p = \frac{(T_0)^2}{K} \quad (6)$$

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

$$t_t = \frac{(T_{max_0})^2}{K} \quad (9)$$

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

Table I summarizes the time to penetration and total consumption at different temperatures based on the empirical relationship from the Arrhenius plot in Fig. 6 with extrapolation to the envisaged temperature of use (650 °C).

The time required to penetrate the minimum assumed carbon coating at 900 °C on the SiC + C fibre in commercial purity titanium is 2 and about 6 h would be enough to consume the carbon coating. At 650 °C the respective times would be 92 and 271 h. It can, therefore, be concluded that the rate of consumption of the carbon coating on the SiC + C fibre is highly sensitive to temperature as would be expected from a diffusion-controlled reaction.

TABLE I Carbon-coating penetration and total consumption times at different temperatures for a SiC + C/Ti composite based on equations 5–7

Temperature (°C)	First penetration time (h)	Total consumption time (h)
650	92	271
750	16	48
800	7.7	22.8
900	2.1	6.2
1000	1	1.8

3.3. Effect of carbon-coating penetration on fibre strength

Parallel studies by Stephenson *et al.* [15] have shown that the fracture strength of SiC + C fibres coated with titanium starts to drop as soon as the minimum carbon coating is penetrated, as shown in Fig. 7. It should be noted that the strength of a titanium-coated SiC fibre without a carbon coating starts to drop immediately following coating with titanium and before any thermal exposure, as also shown in Fig. 7. This is a consequence of the relatively high surface temperatures which occur during the ion-plating deposition which result in the formation of a significant reaction zone prior to thermal exposure. The strength of the SiC + C fibre coated with titanium is also reduced drastically after the complete consumption of

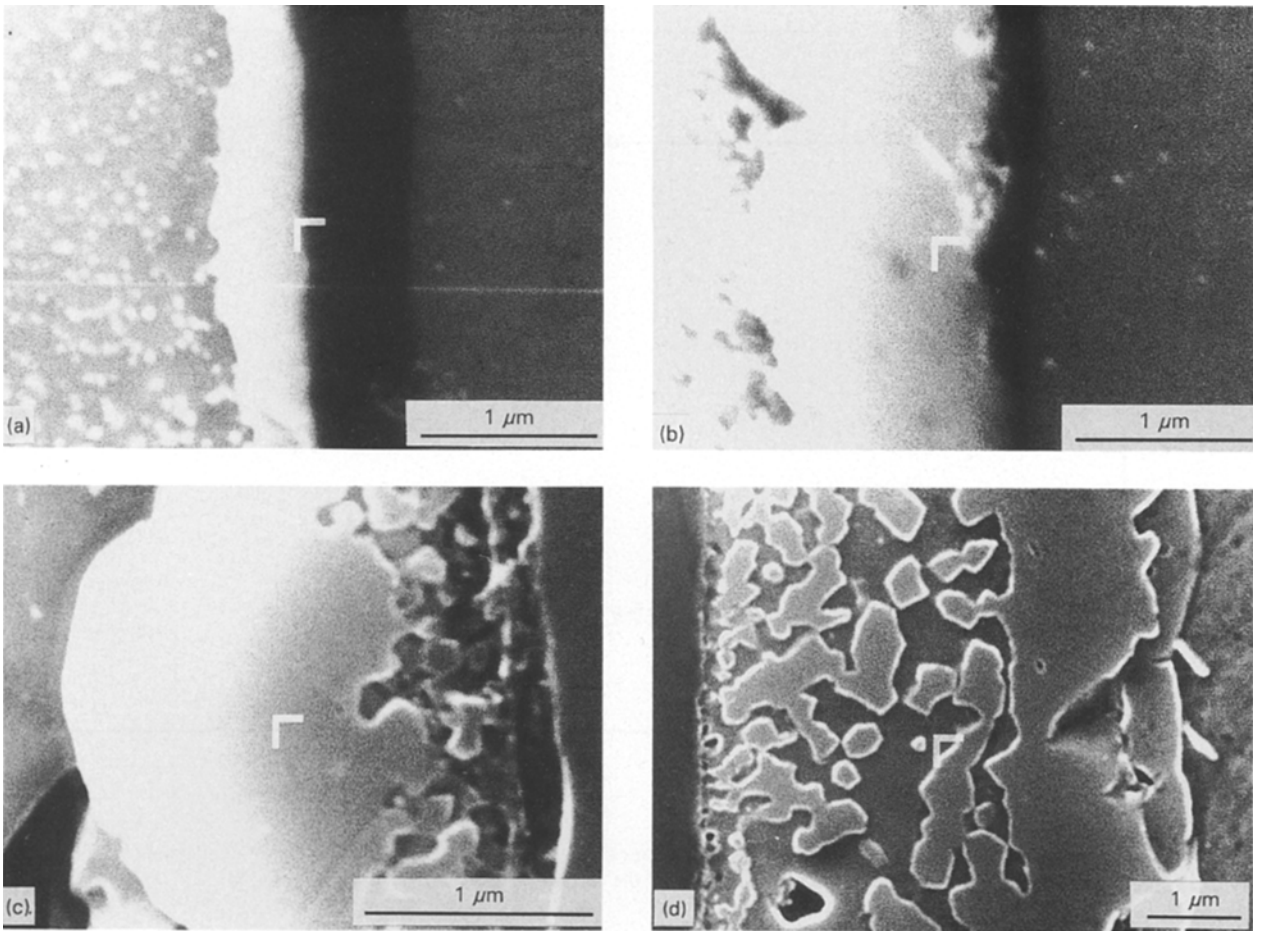

Figure 8 SiC + C/Ti MMCs: fibre–matrix interface after HIPing at 900 °C/200 MPa/0.5 h and annealing at 900 °C for different times: (a) as-HIPed, (b) as-HIPed + VHT 900 °C, 1h; (c) as-HIPed + VHT 900 °C, 2h, (d) as-HIPed + VHT 900 °C, 16 h.

the carbon coating. This behaviour is reflected in the change in the reaction-product morphology shown in Fig. 8, which illustrates the appearance of the fibre–matrix interface after HIPing 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 coating has occurred (Fig. 8d). The morphology of the microstructure changes from a homogeneous thin reaction zone (TiC), between the remaining carbon coating and the titanium matrix after consolidation, into TiC particles in a titanium silicide matrix with the homogeneous TiC formed during the consumption of the carbon coating being displaced outwards into the titanium matrix (Fig. 8d).

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 VHP and single-step HIPing, process cycles of between 20 min and 1 h are normal at temperatures ranging from 850–950 °C for titanium-based MMCs. The penetration times given in Table I, predict that this would cause unacceptable consumption of the carbon layer at 900 °C, with extrapolation to a typical in-service temperature of 650 °C being little better. Penetration of the carbon coating would be predicted to occur after about 92 h at 650 °C and complete consumption in 271 h, which is shorter than the envisaged lifetime for this class of composites. MMCs based on titanium and SiC are expected to be able to withstand at least 2500 h, a typical design lifetime for military aerospace components or 25 000 h, the corresponding design lifetime for civil aircraft components. Obviously, a diffusion barrier is needed to prevent the rapid consumption of the carbon layer from the SiC monofilament. Such barriers like boron-rich TiB_2 coating on the SiC fibre [10, 16] are known to reduce the rate of consumption of the carbon coating. Recently [16], a precious metal intermetallic coating has also shown some promise in delaying the consumption of the carbon coating on the sigma SiC + C fibre. Diffusion/barrier coatings are therefore considered essential to prevent interactions in SiC/Ti MMCs. Measurements of the consumption of the carbon layer following the approach described in this paper can be used to assess their effectiveness [17].

4. Conclusions

1. Consumption of the carbon coating on SiC + C fibres used to reinforce titanium MMCs can be used to predict fibre weakening and hence to predict composite mechanical properties.

2. The statistical approach used is based on a worst case scenario (95% exceedance probability), which takes into consideration the fact that the carbon

coating on the fibre is essential to maintain strength. Penetration of this carbon coating causes the formation of brittle reaction products which impinge on the fibres, resulting in an increase in defect population on their surface.

3. The carbon coating is penetrated relatively quickly at both the processing temperature (900 °C) and the envisaged operating temperature (650 °C). Penetration of the carbon coating would occur after 2 h at 900 °C and complete consumption after 6 h, while at 650 °C the corresponding times would be 92 and 271 h, respectively. These times fall far short of the expected design lifetimes required in the aerospace industry. Thus SiC + C fibres require the use of additional diffusion barriers/coatings if they are to be used successfully in titanium-based MMCs for extended times at high temperatures.

4. 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 carbon layer can be used as a means to assess the effectiveness of these coatings on the SiC + C fibre. This evaluation criterion should be combined with other methods of assessment, e.g. strength measurements, to quantify the overall effectiveness of barriers on SiC fibres in titanium matrices.

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