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Thermal stability of interfaces in Ti–6Al–4V reinforced by SiC Sigma fibres

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Interfacial reactions in Ti–6Al–4V/SiC Sigma fibres (coated with carbon and TiB_2) were studied at different temperatures (600, 700 and 1000 °C). Interface microstructure was investigated by scanning electron microscopy and Auger electron spectroscopy. A simulation of the chemical phenomena occurring at the interfaces was carried out using powders of pure titanium, carbon and TiB_2; the reaction products were identified by X-ray diffraction. The double coating of Sigma fibres is effective in delaying detrimental reactions with the matrix. At the interfaces matrix/TiB_2 and TiB_2/C, the TiB and TiC_x phases form, respectively. The protective coating of fibres shows a lifetime greater than 1000 and 750 h at 600 and 700 °C, respectively.

1. Introduction

Titanium/SiC composites exhibit strengths well below those expected on the basis of fibre and matrix properties. This loss of strength is chiefly attributed to detrimental fibre–matrix reactions. The SiC fibres are the most stable of the ceramic fibres commonly used to reinforce the titanium matrix. However, the following reaction can occur, with a free energy change at 1000 K of $-294\ (\pm 30)\ \mathrm{kJ\,mol^{-1}}$ [1]

$$8/3\ \mathrm{Ti} + \mathrm{SiC} \rightarrow \mathrm{TiC} + 1/3\ \mathrm{Ti_5Si_3} \qquad (1)$$

Because titanium/SiC composites can be used for high-temperature applications, an appropriate stability of interfaces between matrix and ceramic reinforcement is required.

It is well known that during composite preparation, as well as during the course of a subsequent annealing treatment at high temperature, a complex reaction layer develops at the interface between fibre and matrix. Several authors [2–5] agree that the middle part of the reaction zone, between uncoated SiC and titanium alloys, is constituted of a mixture of TiC_x (with x ranging between 0.14 and 0.44) and Ti_5Si_3(C) containing carbon in solid solution. In the outermost part of the layer, near the metal matrix, a Ti_5Si_3(C) phase was detected [3–5]. Close to the SiC fibre, a very thin and complex zone containing silicon, carbon and titanium was observed. According to Martineau *et al.* [3], this part of the reaction zone is probably constituted of Ti_3SiC_2, while according to Onzawa *et al.* [5] it contains TiC, $TiSi_2$ and Ti_5Si_3. On the contrary, Dudek *et al.* [4], observed in this area the formation of just TiC. Dudek *et al.* also suggested a formation mechanism for the reaction layer, according to which SiC first reacts with titanium giving a two-phase zone consisting of titanium carbide and silicide, then, titanium diffuses through this layer from the matrix towards the fibre. As there is a deficiency of diffused titanium, only TiC forms and, in the meantime, free silicon is obtained. The free silicon diffuses towards the matrix giving rise to the more external silicide layer.

The presence of alloying elements in the matrix does not appreciably affect the composition of the reaction layer, in fact most of the alloying elements (e.g. aluminium and many β stabilizers) are rejected from the reaction front [3, 5]. On the contrary, the metal matrix composition seems to influence the reaction kinetics [3, 5]. Anyway, the reaction occurs rapidly at the beginning, afterwards the carbide and silicide layer slows down the degradation process. It is thought that the growth of the reaction zone decreases the strength of the composite when the reaction layer becomes thicker than about 1 μm [5, 6]. In order to slow down detrimental reactions, several fibre coatings were studied. Protective layers of $Y + Y_2O_3$ [1], aluminium or Ti_3Al [7] and carbon or carbon plus silicon were tested [3, 8–13]. The carbon-based coatings can be obtained at the end of the fibre production process (carried out by chemical vapour deposition), by changing the composition of the gaseous atmosphere. In particular, it is possible to obtain the deposition of stoichiometric SiC, pure carbon or a mixture of carbon and silicon [9]. Furthermore, by varying the composition of the gaseous mixture, it is also possible to obtain coatings with a tailored concentration profile of the layer-components (SiC, carbon, silicon). First, coatings about 4 μm thick (referred to as SCS-2) made of pyrocarbon with an external part rich in silicon were studied [3, 10]. More recently, AVCO and Textron developed SCS-6 fibres which show a

0022-2461

complex coating. Inside this coating, moving from the SiC fibre-core towards the surface, different zones are encountered: a mixture of SiC and carbon (with a decreasing content of silicon), pure pyrocarbon, an outermost part made of carbon and silicon with an increasing content of silicon, and a surface constituted of stoichiometric SiC [3, 12].

All the SCS coatings are able to delay reactions between the two components of the composite; on the other hand, the coatings react with the matrix because of the hot-pressing consolidation of the material and during annealing at high temperatures as well. The growth of the reaction layer takes place in the direction of both SiC fibre and matrix with a kinetics controlled by diffusion [3, 5, 6, 8]. It is thought that a continuous external layer of SiC is essential to protect the fibre from detrimental reactions, even if about 60% of the SCS-6 coating is already destroyed during the consolidation of the composite [12]. Furthermore, some authors [8] found a better behaviour of SCS-2 with respect to SCS-6, when these fibres were coupled with a titanium alloy having a β structure.

The stability of the coatings were tested during isothermal annealing at temperatures generally above 700 °C [3, 6, 8, 10, 11]: the best durability was assigned to SCS-6/Ti–6Al–4V composite which seems to have an almost indefinite lifetime below 700 °C [6]. On the contrary, in SCS-2/Ti–6Al–4V, the strength is strongly affected by interfacial reactions occurring during hot pressing (30 min at 800–900 °C). This material shows an ultimate tensile strength of about 1400 MPa, if consolidated at 816 °C, and of only 860 MPa, if the production temperature is 927 °C [7]. The consolidated SCS-6/Ti–6Al–4V composite shows an ultimate tensile strength of 1450 MPa. Its strength decreases to 830 MPa after a 5 h annealing at 900 °C and to 674 MPa after 16 h at 870 °C [14]. The reaction zone for the carbon-rich coatings (SCS-2) is basically constituted of TiC [3, 8, 10]; for long annealing times, the formation of a two-phase area containing TiC + Ti_5Si_3 was also observed in the central part of the reaction layer, and the presence of a thin layer of titanium silicide was found close to the SiC fibre [3, 10]. In the case of SCS-6 fibres, there is not always agreement about the composition of the reaction zone. Differences in the fibre coating from batch to batch can be inferred in order to explain disagreements found in literature. It is well known that the outermost part of the reaction layer is made of Ti_5Si_3 and that the inner part of it, close to the fibre, contains a mixture of titanium carbide and silicide [5, 11, 12]. According to Rhodes and Spurling [11], the middle part of the reaction layer is constituted of TiC, while according to Onzawa *et al.* [5] it contains a mixture of TiC and Ti_5Si_3; Jones *et al.* also detected the presence of SiC [12]. Recently, B.P. Metal Composites has developed a new coating for SiC fibres. These coated fibres, referred to as Sigma fibres, are protected by an internal layer of pure carbon (1 μm) and a more external one of TiB_2 (1 μm). The external TiB_2 acts as a barrier which prevents the damage of the carbon layer of SiC fibre. It is well established that TiB_2 reacts with titanium matrices [15]. Owing to interfacial reactions, the strength of Sigma-fibre/Ti–6Al–4V composite (35 vol % fibres) decreases from about 1700 MPa to 1400 MPa, after a 3.5 h annealing at 865 °C. A lifetime longer than 1500 h at 700 °C was predicted on the basis of the reaction activation energy [15]. At present, the reaction mechanism at the Sigma fibre/titanium alloy interface has not been well investigated. In a previous paper [16] we reported an Auger characterization of fibre-coating microstructure, carried out after the composite consolidation. During the production process, TiB_2 reacts giving elongated TiB crystals embedded in the matrix. Between the boride and the carbon layers, a zone containing titanium, boron and carbon was detected. Probably titanium diffuses through the boride sub-layer and reaches the TiB_2/C interface, where it reacts to form a carbide or a boron carbide. A TEM study on the composition of the coating, after annealing of the composite at high temperature (770–970 °C), was carried out by Guo *et al.* [17]. Several sub-layers involving alternate distributions of titanium carbide and silicide, were detected at 970 °C. Because this reaction layer appears to be like that observed in the case of uncoated SiC/Ti composite [3], it can be inferred that, under these conditions, the reactions involve not only the coating, but also the SiC fibre.

With the purpose of gaining a better understanding of the mechanism of the first steps of the reactions, and in order to adopt annealing conditions closer to the projected temperature of use, the stability of the interface at 600 and 700 °C has been studied.

2. Experimental procedure

Panels of the composite Sigma fibre/Ti–6Al–4V were supplied by B. P. Metal Composites Ltd. Sigma fibres consist of a TiB_2/C-coated SiC monofilament with a diameter of 100 μm and a tungsten core of 12 μm diameter. The six-ply unidirectional panels were prepared by hot pressing (180 MPa) carried out at 900 °C for 20–30 min. Small samples (about 1 cm^2 area) were cut from the panels, sealed under vacuum in silica tubes and annealed at 600, 700 and 1000 °C for times ranging between 100 and 1000 h (Table I).

Cross-sections of the as-received and annealed materials were obtained by cutting the specimens with a low-speed diamond saw perpendicular to the fibre direction. After polishing, sample sections were observed by metallographic and scanning electron

TABLE I

Sample	Annealing conditions	
	Temperature (°C)	Time (h)
C-1	As-received	
A6-1	600	100
A6-2		200
A6-3		1000
A7-1	700	200
A7-2		750
A10-1	1000	120

microscopes (SEM Philips 525M). Energy dispersive X-ray analyses (EDX) were carried out on these sections (Philips-EDAX 9100). The EDX analysis was suitable to the study of fibre–matrix interaction zone only in the case of samples annealed at 1000 °C for 120 h, owing to the broadness of the reaction layer. On the contrary, in order to characterize the reaction zone in samples annealed at lower temperatures, Auger electron spectroscopy (AES) was used because of its better spatial resolution. A Thin Film Analyser–Physical Electronics Model 4200 was employed, with a beam diameter of about 4 μm. A progressive sputtering was performed on the sample surface parallel to the fibre axes, using an ion gun generating Ar^+ ions. Depth profiles of titanium, boron, carbon and silicon were obtained by repeating Auger analysis after each sputtering step. The peak-to-peak ratio heights of each signal, obtained from the derivative spectrum, were normalized to the maximum value measured on the depth profile. The Auger experimental conditions and analysis of results were detailed in a previous paper [16]. The interactions possibly occurring in the composite between titanium and the components of the coating were also simulated by solid state reactions involving titanium, carbon and pure TiB_2. To this purpose, powders of titanium, carbon and TiB_2 were mixed, cold pressed and sealed under vacuum in silica tubes. After annealing 300 h at 1000 °C, the obtained phases were identified by X-ray diffraction (Philips PW1710 equipped with a monochromator).

3. Results

3.1. SEM analysis

Fig. 1 shows the fibre/matrix interface for the as-received composite. It is evident that the TiB_2 coating reacted with titanium giving rise to elongated crystals within the metal matrix. Between the white TiB_2 coating and the SiC fibre, a dark layer (mainly consisting of carbon) can be observed. It seems to be divided in two sub-layers, the more internal one being darker. The white TiB_2 and the black carbon-based layers show a thickness of about 500 and 800 nm, respectively. Furthermore, their thickness is not constant around the fibre because of the irregularity of the interfaces between the zones with different composition: in particular, at several points the dark layer thickness is appreciably reduced.

In Figs 2–4 the evolution of the coating morphology during annealing at 600 °C is shown for treatment times of 100, 200 and 1000 h, respectively.

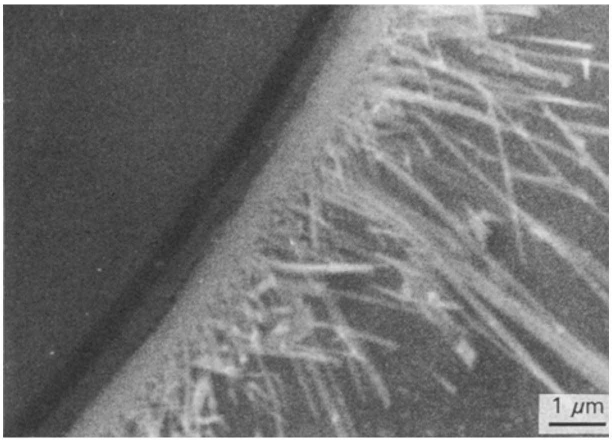

Figure 2 Sample A6-1: interface morphology after 100 h annealing at 600 °C.

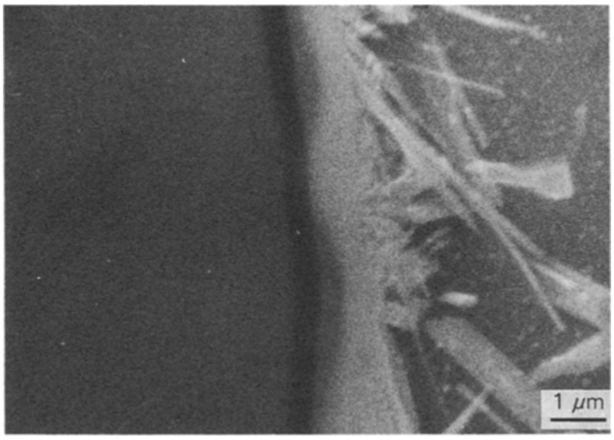

Figure 3 Sample A6-2: interface morphology after 200 h annealing at 600 °C.

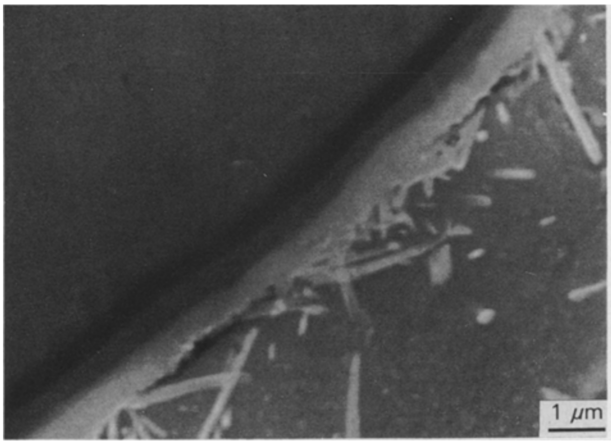

Figure 1 As-received Ti–6Al–4V/SiC composite.

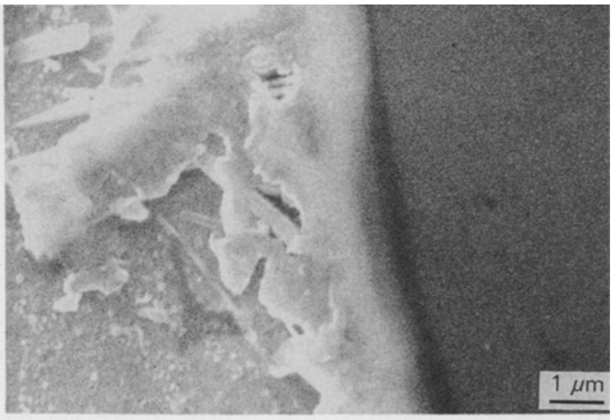

Figure 4 Sample A6-3: interface morphology after 1000 h annealing at 600 °C.

During annealing the white layer greatly broadens, the thickness of the carbon layer progressively decreases, and the acicular crystals in the matrix become less elongated. In particular, the innermost darker part of the coating is greatly reduced and it almost disappears in some zones after 1000 h.

After annealing at 700 °C the morphology of the interphase layer changes in the same way. Fig. 5 shows that the result of the isothermal treatment for 750 h at this temperature is equivalent to the annealing at 600 °C, 1000 h.

During an exposure of 120 h at 1000 °C, about 50% of each fibre reacts; in addition, diffusion of elements from the fibre to the matrix occurs as long as precipitates are present in the whole matrix between the fibres (Fig. 6). On the contrary, precipitation inside the matrix does not occur after thermal treatment at 700 °C for 750 h (Fig. 7).

3.2. Auger analysis

The features of the interfacial zones in the as-received composite were previously investigated [16]. In Fig. 8a, the Auger concentration curves are reported for this material in order to compare them with those obtained for annealed samples.

The concentration profiles in Fig. 8a show that during composite fabrication, a complex interaction zone forms. The carbon layer contains a small amount of silicon which increases moving from the central part of this coating to the SiC fibre core. The middle part of the carbon layer shows an almost constant composition (100% C). Between the pure carbon and the subsequent TiB_2 coating, a zone containing boron, carbon and titanium is present. In this area, the titanium concentration curve has a maximum, owing to an accumulation of titanium.

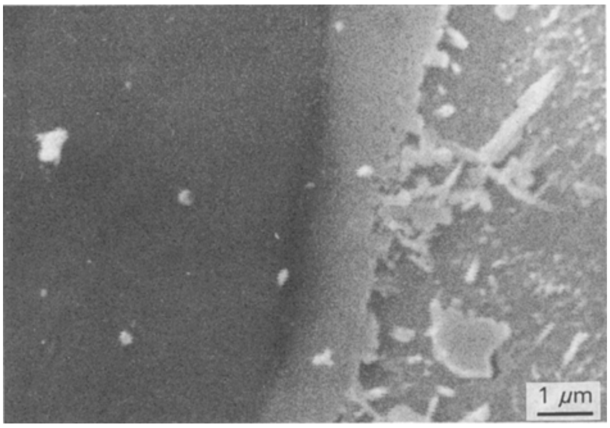

Figure 5 Sample A7-2: interface morphology after 750 h annealing at 700 °C.

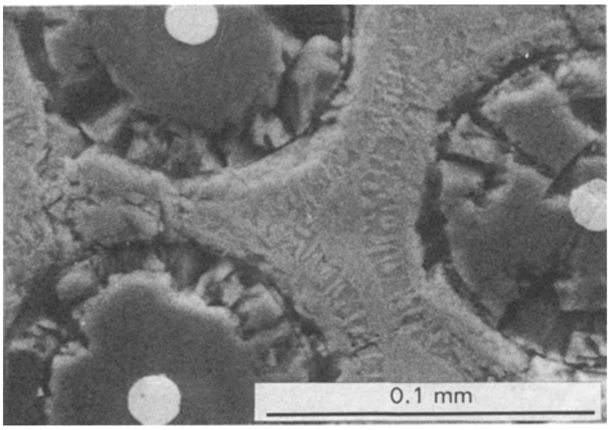

Figure 6 Sample A10-1: interface morphology and precipitation within the matrix after 120 h annealing at 1000 °C.

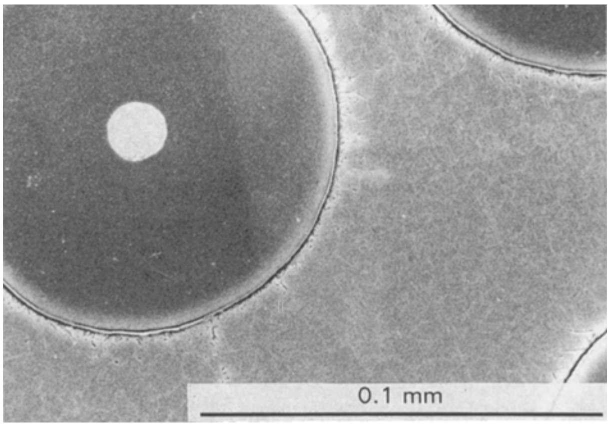

Figure 7 Sample A7-2: composite matrix free of precipitates after 750 h annealing at 700 °C.

In the subsequent zone, encountered moving towards the matrix, both boron and titanium maintain a constant level, and no other elements were detected. Here the presence of stoichiometric TiB_2 can be assumed.

Moving from the TiB_2 towards the matrix, the boron concentration decreases while the titanium content increases. It is worthy of note that both these two concentration profiles show shoulders corresponding to 120–150 min sputtering. This feature suggests the presence of a stoichiometric boride with a lower content of boron with respect to TiB_2.

Concentration profiles progressively modify during annealing at 600 °C. Fig. 8b shows the Auger results for a sample annealed for 1000 h. The composition of the coating containing carbon and silicon, placed close to the SiC fibre, is unchanged with respect to the as-received composite. On the other hand, silicon diffuses from this zone and its concentration curve broadens. The zone containing only carbon disappears, while the neighbouring part of the layer containing boron, carbon and titanium grows at the same time. In the subsequent more external layer, boron shows a constant level and, in correspondence with this step, the titanium curve has a shoulder. However, owing to the presence of an appreciable amount of carbon, the formation of more than one phase should be expected here. The curves of titanium and boron are strongly overlapped, showing that diffusion of titanium towards the fibre and of boron in the opposite direction occurred during annealing.

In Fig. 8c the concentration profiles after 750 h at 700 °C are shown. The microstructure of the interphase layer develops further on, with the trend described above for the samples annealed at 600 °C. Titanium and boron profiles becomes broader, but

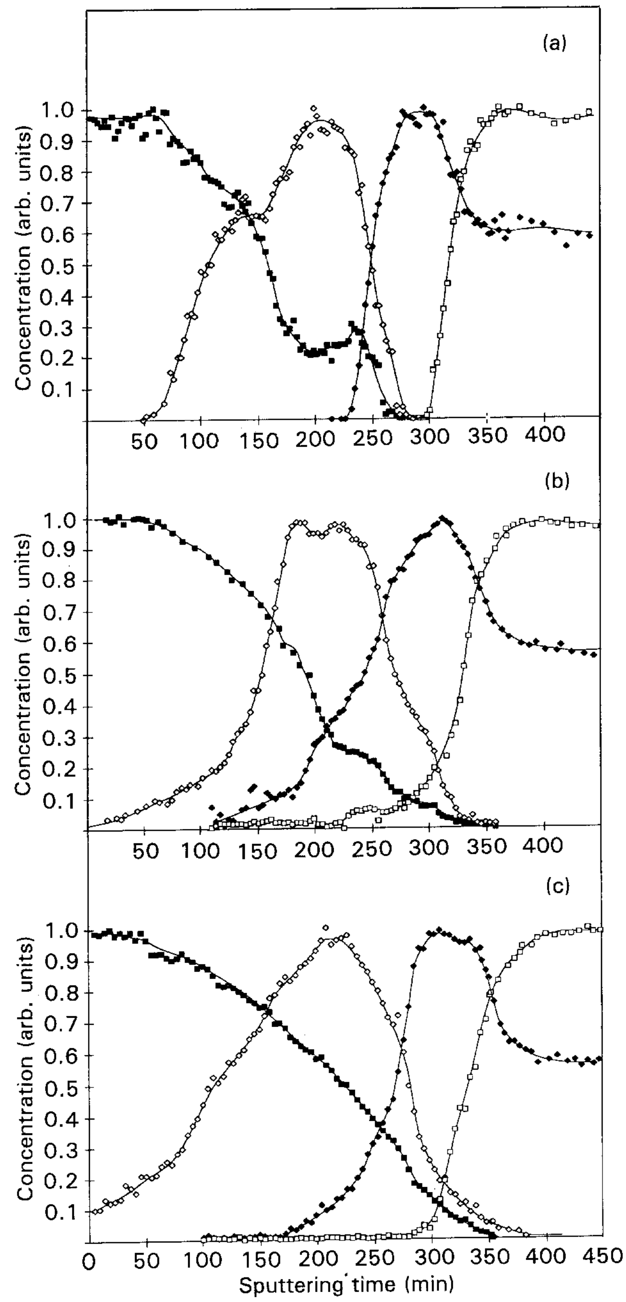

Figure 8 Auger concentration profiles of (■) Ti, (◇) B, (◆) C and (□) Si at the matrix/fibre interface; (a) as-received (sample C-1), (b) after 1000 h at 600 °C (sample A6-3), (c) after 750 h at 700 °C (sample A7-2).

titanium does not reach the SiC fibre. The presence of a surviving carbon layer (containing silicon) close to the SiC fibre is doubtful. On the contrary, carbon and silicon curves are very similar to those of Fig. 8b. Then these two elements do not seem to diffuse deeply in the matrix, but they stay within the reaction zone (mainly containing boron and titanium) next to the fibre.

A strong penetration of silicon in the metal matrix needs higher annealing temperatures. For instance, after 120 h at 1000 °C, EDS analysis shows that silicon can be detected in the matrix 60–70 μm away from the tungsten fibre core. At the same time, titanium diffuses within the SiC fibre (Fig. 9). The Auger concentration curves of this last sample greatly broaden and show a very irregular trend, with a series of maximum and minimum points. Probably this trend is due to the precipitation of large crystals pertaining to several different reaction products. Annealing at 1000 °C causes the formation of a very thick polyphasic reaction zone which develops because the protective coating is completely destroyed and the SiC fibre is consumed by chemical reactions.

3.3. X-ray diffraction (XRD)

In order to investigate the phases present in the layer containing titanium, boron and carbon, which develops at the TiB_2/C interface, experiments involving reactions between powders of these pure substances were performed. In a previous paper [16] we referred to the solid state reaction between carbon and TiB_2. After 20 days at 1000 °C, any new compound forms, even if, on the basis of the slight decrease of the carbon peak intensities in the XRD patterns, the development of $Ti(B, C)_2$ solid solution could be supposed.

TiB_2, titanium and carbon were mixed in the stoichiometric proportion suitable to obtain solid solutions of formulas $TiC_{0.7}B_{0.3}$ and $TiC_{0.5}B_{0.5}$. The solid state reaction (at 1000 °C) results basically in the formation of a TiC-type phase. After isothermal treatment, the intensities of titanium and carbon peaks greatly decrease, while those of TiB_2 peaks are practically unchanged. In addition, a new TiC_x phase forms. The peaks of this phase are shifted towards higher angles with respect to those of stoichiometric TiC, showing that TiC_x has a lower carbon content ($x < 1$) (Fig. 10). Efforts were also made to prepare solid solutions derived from TiB. To this purpose TiB_2, titanium and carbon were mixed in suitable stoichiometric proportions for the formation of TiB and $TiB_{0.8}C_{0.2}$, then the samples were annealed at 1000 °C. Titanium and TiB_2 always react to give TiB; furthermore, the annealing of the TiB_2–Ti–C mixture with the lower carbon content gives rise to the formation of both TiB and TiC_x.

4. Discussion

Interfaces in titanium alloy matrix reinforced by Sigma SiC fibres have to be regarded as non-equilib-

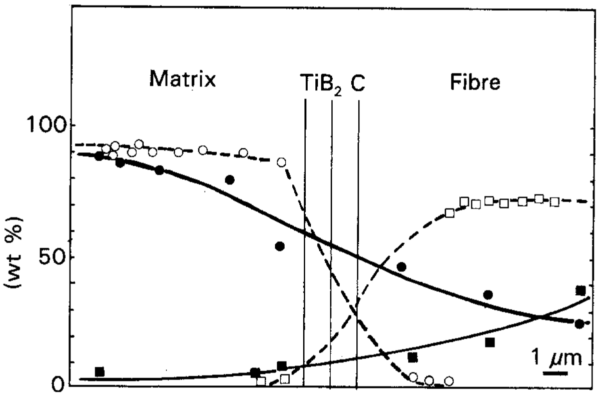

Figure 9 EDS concentration profiles of (○, ●) Ti and (□, ■) Si, (○, □) as-received at the matrix/fibre interface after (●, ■) 120 h at 1000 °C (sample A10-1).

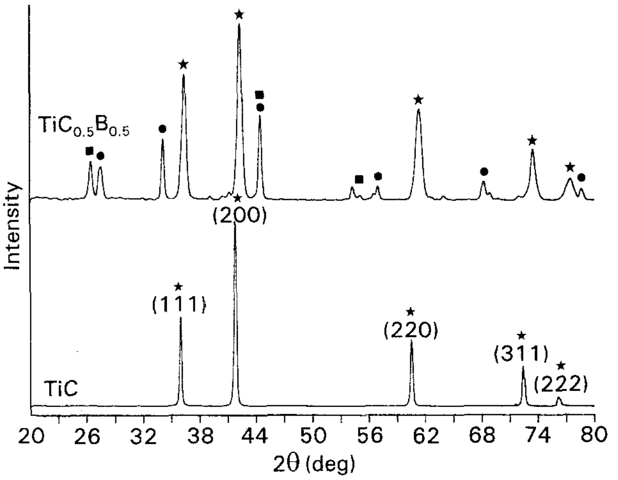

Figure 10 TiC_x formation after solid state reaction of a TiB_2–Ti–C mixture. (★) Ti(C, B), (●) TiB_2, (■) C.

rium systems. During composite fabrication and also isothermal annealing, the Ti–6Al–4V matrix and the protective coating react. Some reactions occur both at the TiB_2/matrix and at the TiB_2/C interfaces.

4.1. TiB_2/matrix interface

According to the Ti–B phase diagram, TiB_2 can react with titanium giving borides with a lower boron content (Ti_3B_4 and TiB). It is well known that a reaction between titanium matrix and boron filament or many other reinforcements containing boron, gives rise to the titanium monoboride formation [18–20]. As expected, this boride forms also by reaction of TiB_2 fibre coating with titanium matrix [16, 17].

As acicular crystals of TiB were observed within the matrix far from the continuous boride coating, diffusion of boron towards the matrix occurs. Owing to the low solubility [21] of boron in both α-titanium (less than 1.7 at % at 882 °C) and β-titanium (less than 1 at % at 1540 °C), boride precipitation easily occurs. The particular morphology of these precipitates could probably be attributed to preferential boron diffusion paths or to the different solubility of boron in the two crystallographic modifications (α and β) of titanium.

4.2. TiB_2/C interface

Different hypotheses can be advanced in order to justify the reaction observed at this interface. For instance, it can be inferred that carbon reacts with TiB_2 to form a solid solution. The TiB_2 compound is not stoichiometric, showing a boron content ranging from 65.5–67 at % [21]. Despite this, the solubility of carbon in TiB_2 is very low; it reaches a value of 2% at 2507 °C and rapidly decreases below 2000 °C [22]. Previous solid state reaction experiments [16] also demonstrated that the amount of carbon which can be inserted in the TiB_2 crystal lattice is very low; in fact, after reaction with carbon, the TiB_2 lattice parameters were practically unchanged.

On the other hand, Auger analysis clearly shows an interaction zone between TiB_2 and carbon. The thickness of this zone and its morphological features, observed by SEM, cannot be satisfactorily explained only with the formation of the $Ti(B, C)_2$ solid solution.

As the Auger analysis of the as-received composite shows an accumulation of titanium in this zone, diffusion of titanium from the matrix (through the TiB_2 layer) to the TiB_2/C interface should be supposed. As a consequence of titanium diffusion, here TiC_x could form. In addition, the TiC_x carbide displays a homogeneity range between 32 and 48.8 at % C [21] and can accept variable amounts of TiB_2 in solid solution. The solubility of TiB_2 in TiC_x depends on x, increasing up to 7%–8% as x decreases from 0.95 to 0.68. However, below 2000 °C no mutual solubility was observed [22, 23]. Also, another reaction could be proposed

$$x/2\,TiB_2 + (1 - x/2)\,Ti + (1 - x)\,C \rightarrow TiB_xC_{1-x} \qquad (2)$$

Unfortunately, the literature data about the solubility between TiC and TiB do not agree. In fact, according to Samsonov [24], a complete mutual solubility exists (at 600–1600 °C), while, according to more recent papers [22], this is not possible, owing to the different crystal lattices of TiB (orthorhombic) and TiC (cubic). On the other hand, the existence of a face centred cubic TiB was also assessed [25]. Because of this uncertainty, we carried out experiments of solid-state reaction at 1000 °C. These experiments show that, when a high concentration of carbon is present in the reactive mixture of TiB_2–Ti–C, titanium reacts with carbon to produce TiC_x ($x < 1$), while, if the carbon concentration is lower, a mixture of TiC_x and TiB is obtained. On the contrary, our results do not agree with the formation of a Ti(B, C) solid solution. Then, at the TiB_2/C interface, titanium coming from the matrix, at the beginning, reacts with carbon giving TiC_x. Soon afterwards, the diffusion of titanium and of carbon in opposite directions causes the formation of a polyphasic (multicomponent) reaction zone (probably containing $TiB_2(C)$, TiB and TiC_x).

4.3. Composite thermal stability

Annealing treatments at 600 and 700 °C for 1000 and 750 h, respectively, do not cause the complete destruction of the protective coating of Sigma fibres. In fact, during these treatments, two reaction zones grow at the TiB_2/matrix and TiB_2/C interfaces, but silicon does not diffuse from the coating until the metal matrix and titanium no longer reaches the SiC fibres. The SiC fibres are affected by reactions with titanium only after annealing at the highest temperatures. For instance, at 1000 °C the Sigma fibres, after a rapid and complete consumption of the protective coating, react in the same way as uncoated SiC fibres.

5. Conclusions

1. The double coating of Sigma fibres delays the reactions of SiC fibre core with the matrix of Ti–6Al–4V.

2. During annealing at high temperatures, first TiB and TiC_x form at the matrix/TiB_2 and TiB_2/C interfaces, respectively.

3. The protective coating of Sigma fibres is effective when the composite is annealed at temperatures up to 600 °C.

In order to evaluate correctly the efficiency of Sigma fibres, further studies will be performed to understand how the new phases formed at the interfaces affect the mechanical behaviour of the composite.

Acknowledgement

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