JOURNAL OF MATERIALS SCIENCE **21** (1986) 2043-2048

Influence of carbide formation on the strength of carbon fibres on which silicon and titanium have been deposited

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Silicon or titanium was deposited on the filaments of carbon fibres by chemical vapour depositions and the reactions between the deposited silicon or titanium and the carbon fibres were investigated below 1300° C. Between the silicon and the carbon fibres, β-SiC layers formed at rates of 1.5 to 3 nm in 3 h at 1300° C. These rates were 10^{-4} times that of the TiC formation by the reaction of titanium with carbon fibre. Furthermore, the effect of the reaction on fibre strength was investigated. By reaction with silicon, the carbon fibre at a carbonized stage decreased in strength at the beginning of the reaction, but afterwards it recovered to the original level. The carbon fibre at a graphitized stage maintained its original strength after heat treatment for several hours at 1300° C. With the TiC-coated carbon fibres, the carbon fibres decreased in strength following the relation $\sigma_m \propto d^{-1/2}$, where d is the thickness of the TiC layer.

1. Introduction

Much interest has recently been shown in carbon fibre–aluminium composites as high performance structural material with higher thermostability than that of carbon fibre-reinforced plastics. In the fabrication of such composites, in particular by the infiltration of molten aluminium into carbon fibre bundles, however, there are major difficulties such as the lack of wetting of the fibre with molten aluminium and the occurrence of carbon fibre–aluminium reaction causing fibre deterioration. To overcome these difficulties several processes for coating the carbon fibre surface with an appropriate metal or metal compound film have been investigated. The Ti–B coating has been regarded as the most successful for making the carbon fibres wettable with molten aluminium alloys [1]. Silicon coating also seems to be suitable for producing a film with such a property of the carbon fibres, especially in the case of matrices such as silicon-containing alloys. In addition, this coating may also be effective as a layer for inhibiting the reactions between the carbon fibre and the metal matrices by the formation of SiC on the carbon fibre [2]. It is also possible to form SiC film on carbon fibres by a chemical vapour deposition (CVD) process. However, the silicon-carbon reaction in the silicon-coated carbon fibre seems to be advantageous in producing the double-layered coating composed of both an inner layer of SiC and an outer layer of silicon.

The rate of reaction of solid silicon with carbon fibre or graphite, however, has never been investigated systematically, although it has been known that molten silicon can readily react with these materials [3, 4]. On the other hand, the transition metals such as titanium can readily react, even in the solid state, with carbon fibres or graphite to form carbides [5]. In these carbides of transition metals the atoms are combined with bonds of a metallic nature and the carbides have nonstoichiometric compositions, but in silicon carbide the atoms are combined with σ-type covalent bonds and this carbide has a stoichiometric composition [6]. Therefore, the rate of formation of silicon carbide is expected to differ from those of transition metals. Moreover, the silicon layer coated on the carbon fibre and the SiC layer formed by a reaction between them may have different effects on the strength of the carbon fibre.

In this study, silicon film was coated onto carbon fibres by a CVD method, and the reactivity of the silicon with the carbon fibres was investigated, together with the effect of the layer composed of silicon and SiC on the strength of the fibre. Furthermore, the coating of TiC on the carbon fibre was carried out using the reaction of $TiCl_4$ gas with carbon fibre in the presence of H_2, and the effect of the coating layer was investigated to compare with the case of SiC.

2. Experimental procedure

2.1. Carbon fibres

Three kinds of carbon fibre yarns, without surface treatment or sizing treatment, were used as starting materials. These yarns are composed of several hundred to 6000 filaments. Their properties are shown in Table I.

2.2. Film coating on carbon fibres

Silicon or titanium was deposited on the filaments of the carbon fibre yarns using the apparatus shown

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TABLE I Mechanical properties of carbon fibres employed

Fibre type	Commercial designation	Tensile strength, σ_m (GPa)	Modulus of elasticity, E (10^3 GPa)	Number of filaments in a tow
Graphitized, Rayon-based	Thornel 25	1.18	0.172	
Graphitized, PAN-based	TORAYCA M40	1.96	0.363	6000
Carbonized, PAN-based	TORAYCA T300	3.08	0.249	3000

schematically in Fig. 1. The deposited titanium reacts instantly with carbon fibre to form TiC.

In the silicon coating, a mixed gas of $SiCl_4$, hydrogen and argon was made to flow for 60 or 30 min in the alumina tube in which each of the carbon fibre yarns was suspended and heated at 1100° C. Subsequently, changing the gas to a mixture of hydrogen and argon, the coated fibres were heat treated at 1100 or 1300° C for several or 10 h.

In the TiC coating, a gas mixture of $TiCl_4$, hydrogen and argon was made to flow for 5, 10 or 30 min into the tube at a temperature of 900, 1000 or 1100° C. The coated carbon fibre yarn was withdrawn upwards from the tube after heat treatment.

To determine the tensile strengths of the coated carbon fibre yarns, tensile tests were carried out on a gauge length of 20 mm with about 20 single filament specimens per yarn.

3. Results

3.1. Silicon coating

The effect of the hydrogen concentration in the reaction gas on the amount of silicon deposited in 60 min on carbon fibre yarn, TORAYCA T300, was investigated at several flow rates of $SiCl_4$ and at reaction temperatures of 1000 and 1100° C. The flow rate of the mixed gases was 300 ml min^{-1}. The amounts of deposited silicon were determined by weighing the yarn specimens cut off in lengths of 35 mm. The results obtained are shown in Fig. 2. The amount of deposited silicon increases with increasing flow rate of hydrogen and with decreasing flow rate of $SiCl_4$. At 1200° C, no deposition of silicon occurred on the carbon fibre although it occurred in the lower temperature zone. Fig. 3 shows a scanning electron micrograph of the cross section of the carbon fibre yarn coated with silicon for 60 min at 1100° C. Every filament is coated with a film of uniform thickness, ≈ 0.1 μm. On the basis of these results, silicon-coated carbon fibre samples were prepared at 1100° C in a gaseous mixture of $SiCl_4$, hydrogen and argon at flow rates of 3, 60 and 240 ml min^{-1}, respectively.

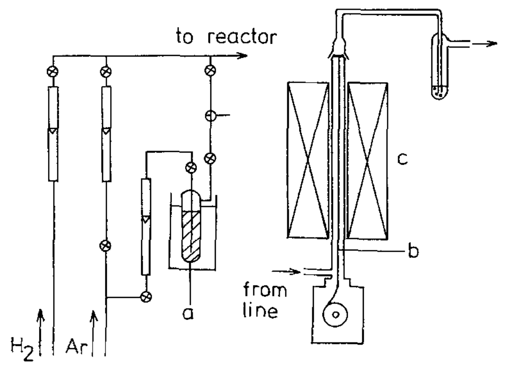

Figure 1 Apparatus for coating and heat treatment. (a) Reservoir of $SiCl_4$ or $TiCl_4$, (b) carbon fibre yarn, (c) furnace.

3.2. Effect of heat treatment of the silicon-coated carbon fibres on their strength

The strengths of the silicon-coated carbon fibres with or without heat treatment at 1100° C are plotted against the sum of the periods of coating and heat treatment in Fig. 4. The strengths of the silicon-coated graphitized fibre, TORAYCA M40, on heat treatment at 1300° C are shown in Fig. 5. The graphitized fibres maintain their strength at the original level in the course of coating and heat treatment, but the strength of the carbonized fibre, TORAYCA T300, initially decreased to 60% of the original, and then increased up to 90% of the original. The second measurements of fibre strength were performed after the silicon coating had been removed with an aqueous mixture of HNO_3, HF and CH_3COOH. The strengths obtained are also shown in the same figures. No practical difference in strength can be seen between the silicon-coated and the silicon-removed fibres. This suggests that the observed change in the strength of the carbonized fibres is not caused by the silicon layer coating.

3.3. Interfacial products in the silicon-coated fibres

The silicon-removed carbon fibres, 5 mm long, were dipped in an aqueous solution of 0.1 N H_2SO_4, and

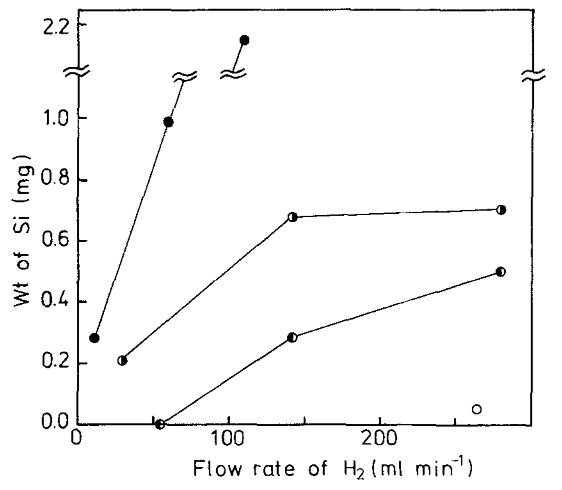

Figure 2 Weight of silicon film coated in 60 min at 1100° C on yarns of fibre TORAYCA T300, 35 mm long. Flow rates of $SiCl_4$: ●, 3; ◑, 7; ◐, 14; ○, 29 ml min^{-1} at 1 atm.

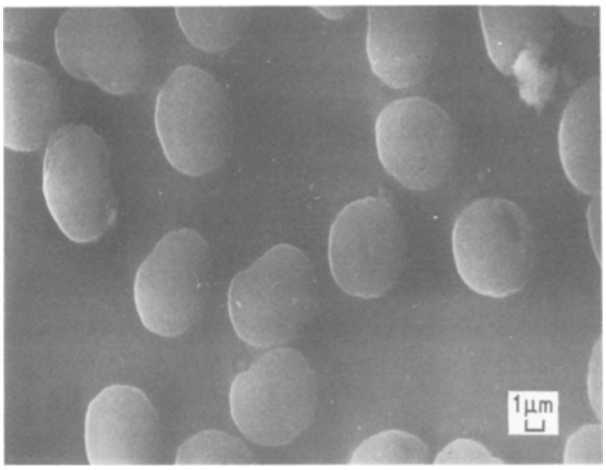

Figure 3 Cross section of the silicon-coated fibre.

oxidized by applying an anodic potential of 5 V. This anodic oxidation left faint brown coloured flake residues. These residues were observed under a transmission electron microscope with an accelerating voltage of 100 kV. The photographs obtained are shown in Figs 6a and 7a. Figs 6b and 7b are the corresponding electron diffraction patterns. The Debye-Scherrer rings in each of these patterns are indexed from inwards as 1 1 1, 2 0 0, 2 2 0 and 3 1 1 of β-SiC. The breadths of the rings in Fig. 6b are narrower than those in Fig. 7b, and discrete diffraction spots due to large crystallites are observed in Fig. 6b.

The basal flake in Fig. 7a, on which the particles assemble two dimentionally, did not show any appreciable diffraction pattern. The flake was proved to be graphite oxide by another study on anodic oxidation of the uncoated carbon fibre [7]. The SiC particles in the interface between carbon fibre and silicon have diameters of 5 to 30 nm in the case of the carbonized fibre T300, and about 5 nm in the case of the graphitized fibre M40. It can be seen from these figures that the amount of SiC is greater in the case of the carbonized fibre T300 than in the case of the graphitized fibre M40, and that the SiC particles on the graphitized fibre are distributed at intervals of several nanometres. The thickness of the SiC layers on the carbonized fibre T300 formed at 1300° C in 1 or 3 h were estimated by chemical analysis. In the analysis, 3 mg of every silicon-removed fibre sample was decomposed in a mixture of molten $NaNO_3$ and NaOH, and analysed for silicon by the molybdenum blue method. The obtained amounts of silicon gave thicknesses between 1.5 and 3 nm for the SiC layers, assuming they are uniform.

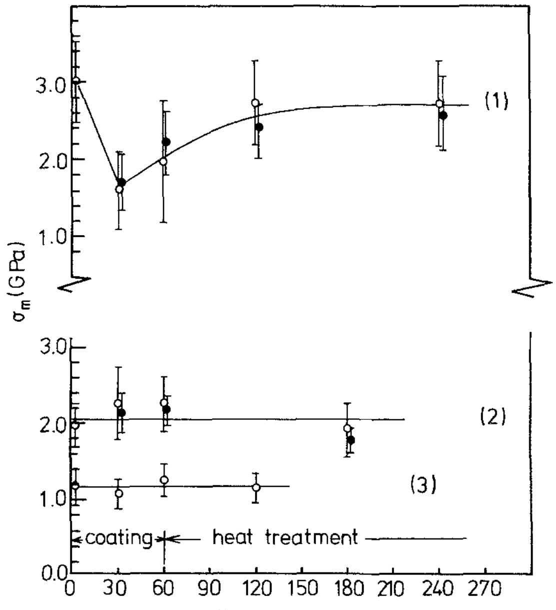

Figure 4 Strength of the carbon fibres silicon film coated for up to 60 min and heat treated for varying periods at 1100° C. ○, with silicon film; ●, silicon film removed. (1) TORAYCA T300 (carbonized), (2) TORAYCA M40 (graphitized), (3) Thornel 25 (graphitized).

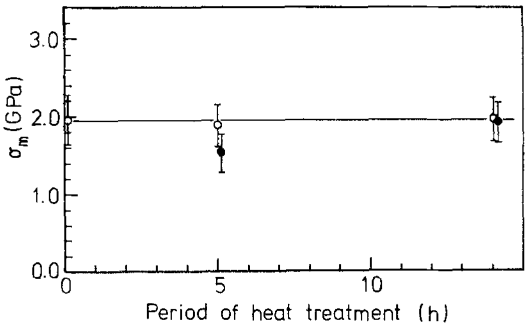

Figure 5 Strength of the graphitized fibre TORAYCA M40 coated with silicon for 60 min at 1100° C and heat treated for varying periods at 1300° C. ○, with silicon film; ●, silicon film removed.

3.4. Rate of formation of TiC layer

Titanium carbide was coated on the carbon fibre yarns from a gaseous mixture of $TiCl_4$, hydrogen and argon at flow rates of 1.4, 100 and 150 ml min^{-1}, respectively, at a temperature of 800, 900 or 1000° C for a period of 5, 10 or 30 min. It is well known that in such cases TiC is formed on the carbon substrate without co-depositing metallic titanium [14, 15]. The thicknesses of the TiC layer on the carbonized fibre TORAYCA T300 were then evaluated from the weight gain due to the titanium deposition, the average diameter of the fibre and the density of TiC crystal, 4.9 g cm^{-3}, and they are plotted against the root of the deposition time in Fig. 8. The thickness of the TiC layer increases linearly with root of the deposition time. From this result, it was considered that the rate of formation of the TiC layer is controlled by the diffusion of atoms through this layer. Then, the apparent diffusion coefficients were calculated by the parabolic rate equation $d = \alpha(Dt)^{1/2}$, where d is the layer thickness, D the diffusion coefficient, t the time, and α a constant which is here assumed to be 1. The coefficients obtained are plotted on a log scale against reciprocal temperature in Fig. 9, and a relation $D = 2.0 \times 10^{-2} \exp(-273\,\mathrm{kJ\,mol^{-1}}/RT)\,\mathrm{cm^2\,sec^{-1}}$ was obtained from this figure.

3.5. Strength of the TiC-coated fibre

Tensile strengths of the TiC-coated carbon fibres are plotted against the thickness of the TiC layer on a log–log scale in Figs 10a and b, together with the strength measured after the TiC layer had been removed with a solution mixture of HNO_3 and HF.

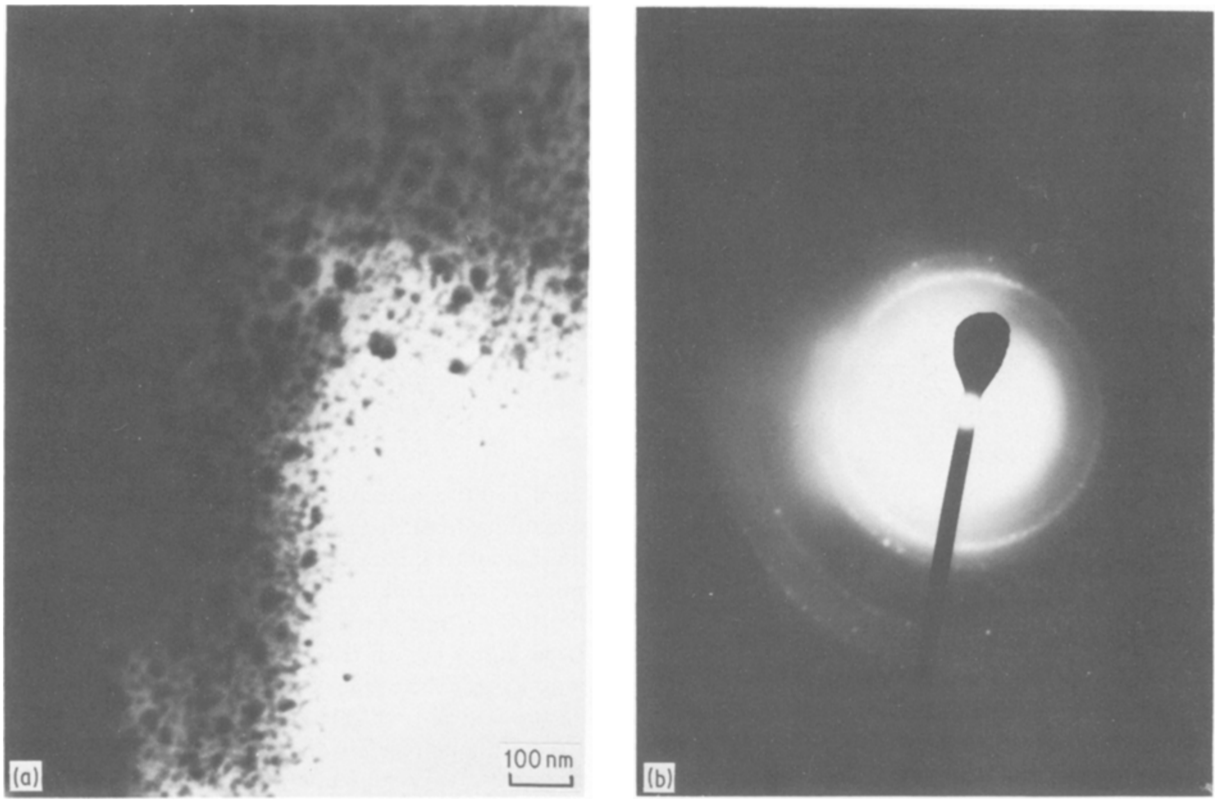

Figure 6 (a) A transmission electron micrograph of the SiC layer formed in the fibre TORAYCA T300 silicon-coated for 60 min at 1100° C. (b) A selected-area diffraction pattern of the SiC in (a).

The tensile strength of the TiC-coated fibre decreases with increasing layer thickness at a slope of $-1/2$, but the TiC-removed fibre regains its original strength. Accordingly, it can be said that this decrease in strength is caused by the TiC layer itself.

4. Discussion

4.1. Strength of the silicon-coated fibres

As the above results show, the strength of the silicon-coated carbon fibres was not degraded by heat treatment at 1100 or 1300° C.

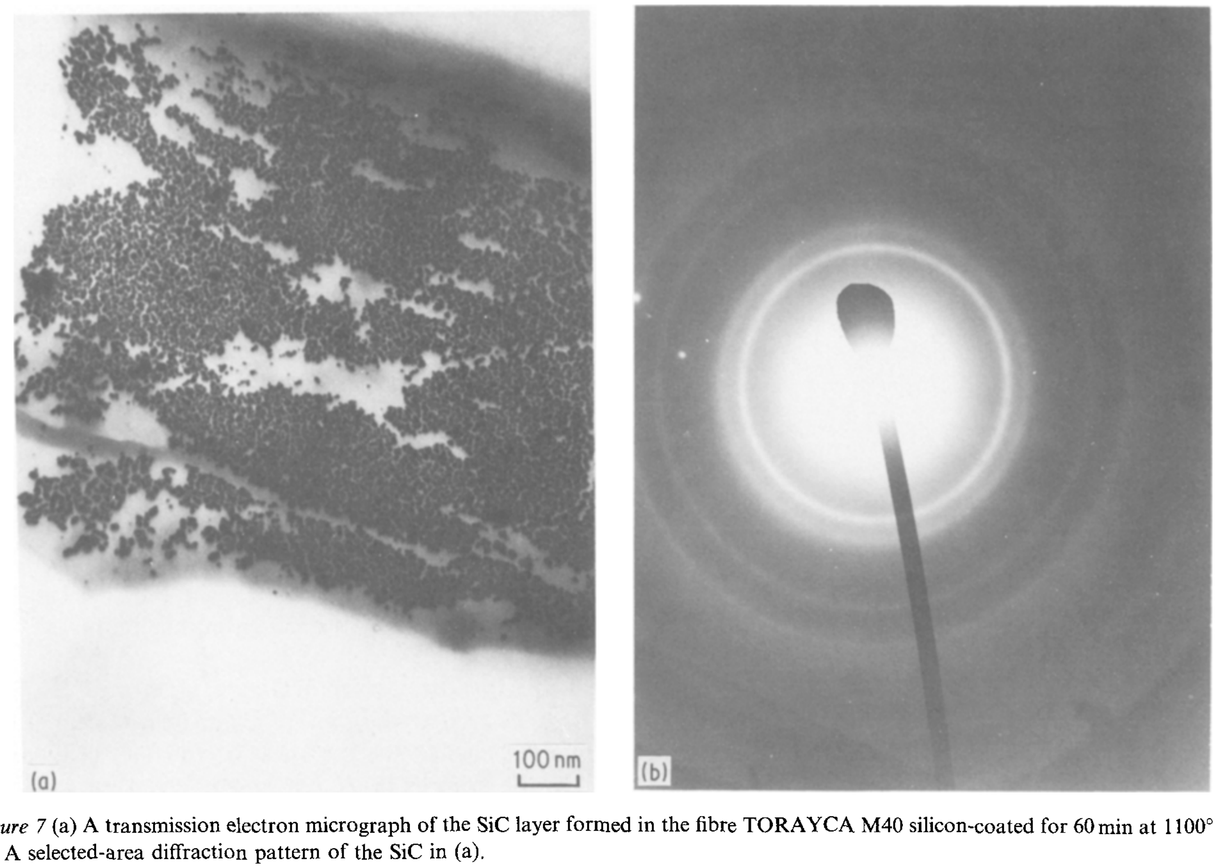

Figure 7 (a) A transmission electron micrograph of the SiC layer formed in the fibre TORAYCA M40 silicon-coated for 60 min at 1100° C. (b) A selected-area diffraction pattern of the SiC in (a).

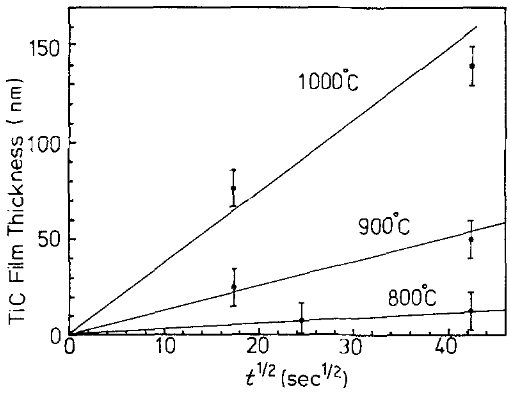

Figure 8 Time dependence of the thickness of the TiC layer formed on the carbon fibre at various temperatures.

The decrease in strength of the carbonized fibre at the beginning of the silicon coating can be attributed to cracks formed on the surface of the carbon fibre itself. They may have originated from an attack with hydrogen in the reaction gas mixture, as well as by thermal stress in the carbon fibre. The recovery of strength in the course of heat treatment will be due to the decrease in surface energy of the crack tip by the reaction with silicon, or to the repairing of the cracks by filling with SiC. The influence of SiC film on the strength of carbon fibres will be discussed again in connection with TiC-coated fibres.

4.2. Reactivity of silicon with carbon fibres

According to the extensive investigations reported on the reaction of silicon with hydrocarbons, methane forms a β-SiC layer with a thickness from several tens to several hundreds of nanometres on solid silicon at a temperature between 950 and 1100° C over a period of 60 min [10–13]. The rate of formation of the SiC layer in these cases has been revealed to be controlled by the diffusion of silicon atoms through the grain boundary in the SiC layer [12, 13].

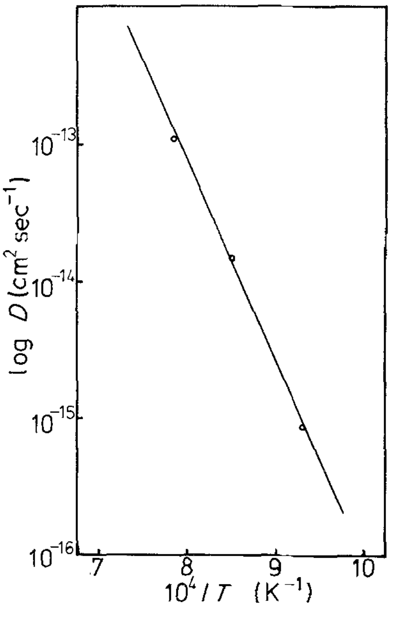

Figure 9 Arrhenius plot of the apparent diffusion coefficient in the TiC layer on the carbon fibre.

The SiC layers formed on the carbon fibres are polycrystalline and island-like, as observed in Fig. 7a. Therefore, we can assume that the diffusion coefficient through this layer is the same order of magnitude as that in the reaction of silicon with methane, 5×10^{-14} cm^2 sec^{-1} at 1200° C [12]. Accordingly, we must attribute the observed slow rate of formation of the SiC layer on the carbon fibre, which is in a range from one-tenth to one-hundredth that of the reaction of silicon with methane, to the slow rate of reaction of silicon atoms with carbon atoms in the fibre surface. It is most probable that the reaction with methane proceeds through reactive intermediates such as free radicals which are easily formed at these temperatures and can readily react with silicon. On the other hand, the surfaces of the carbon fibres are composed of two-dimensional planes of condensed hexagonal aromatic rings, and the carbon atoms on the periphery of these planes are much more active than those in the planes. Silicon atoms are considered to react preferentially with such peripheral carbon atoms. The number of such active sites on the surface can be measured by the chemical adsorption of oxygen gas, and from the result of such measurements it can be said that the lower the heat-treatment temperature of the carbon fibre, the greater is the amount of the peripheral carbon atoms in the cuticle of the carbon fibre. In fact, measurements of oxygen chemical adsorption gave for carbonized fibre T300 a value four times that of the graphitized fibre M40 as the amount of surface active sites [12]. The difference in the amount of the SiC formed on fibres T300 and M40 is thought to be caused by the difference in the number of such active sites on these carbon fibres.

4.3. Strength of TiC-coated fibre

On elongating a brittle fibre coated with a brittle layer having a lower fracture strain than that of the core fibre, a crack is formed initially in the layer, and it will propagate into the core fibre if the bonding between the layer and the core fibre is strong enough to withstand the shear stress at the interface. In such a case, the strength of the coated fibre, $\sigma_m = k(2E\gamma/\pi d)^{1/2}$, where k is a factor related to the shape of the crack given by Ochiai and Murakami [15], E and γ are the modulus of elasticity and the surface energy of the carbon fibre, respectively, and d is the thickness of the layer. Since the strength of the TiC-coated carbon fibre and the layer thickness follow the relation $\sigma_m \propto d^{-1/2}$, this TiC-coated fibre is considered to be fractured by such a mechanism. From Figs. 10a and b, the TiC films with thickness below 10 nm do not decrease the strength of the fibre appreciably. Since the SiC layers in the silicon-coated fibre are 3 nm or less in thickness, it is considered that the SiC layer did not affect the strength of the fibre.

4.4. Rate of TiC formation

In the present study, a value of 273 kJ mol^{-1} was obtained for the activation energy of diffusion by the growth reaction of TiC layer on the carbon fibre.

Aggour *et al.* [8] reported 84 kJ mol^{-1} for the activation energy for the diffusion through the TiC

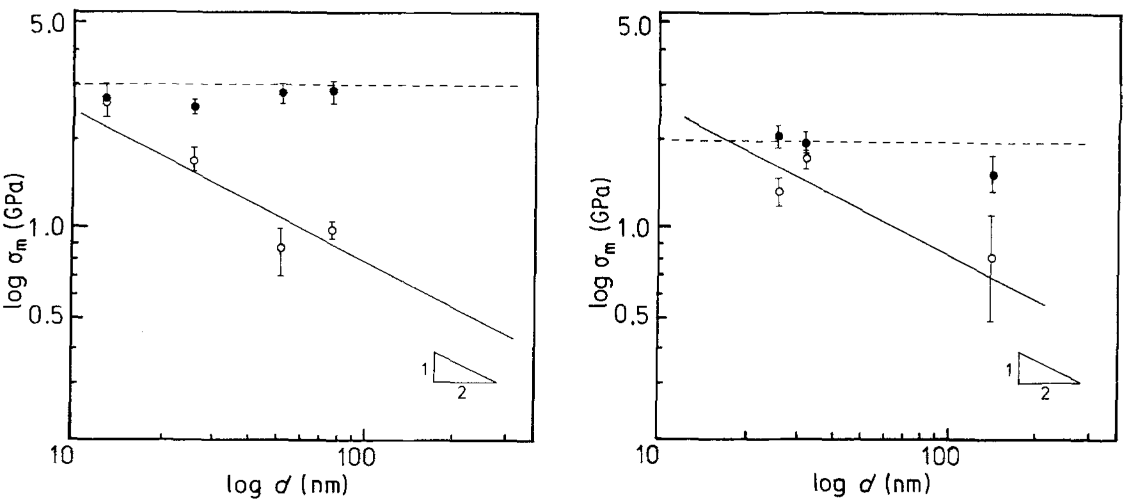

Figure 10 Dependence of the strength of the TiC layer coated carbon fibres on the thickness of the layer. (a) TORAYCA T300 fibre; (b) TORAYCA M40 fibre. ○, with TiC layer; ●, TiC layer removed; ----, level of the original strength of the fibres.

layer on the carbon fibre, which grew to a thickness of half the radius by a reaction with titanium. They attributed this value to the diffusion of titanium atoms, which according to them, is the rate-controlling process in the growth reaction of the TiC layer.

On the other hand, Aggour *et al.* [8], Adelsberg and Cadoff [16] and Vansant and Phelps [5] studied TiC layer growth on flat plates of graphite by the reaction with titanium, and obtained activation energies of 293, 235 and 259 kJ mol^{-1}, respectively, for the diffusion through the TiC layer. These activation energies were attributed by them to the diffusion of carbon atoms.

As the activation energy obtained in the present study agreed with those for the growth on the flat plates, the diffusing species in the present study is suggested to be carbon atoms: the TiC layer in the present study is sufficiently thin relative to the fibre. Accordingly, it is regarded as a layer on a flat plate.

5. Conclusion

1. In the interface between carbon fibre and silicon film, a layer of SiC was formed at temperatures between 1100 and 1300° C. The thicknesses of the layer on carbonized fibre reached 1.5 to 3 nm over 3 h at 1300° C. The thicknesses of the layers on carbonized fibre were thicker than those on the graphitized fibre.

2. The strength of the carbon fibre was not degraded by the formation of the SiC layer. This was attributed to the thinness of the layer. In the case of the carbonized fibre, a recovery in strength during the reaction was observed. This was regarded as a result of the healing of the fine cracks on the surface of the carbon fibre.

3. With the reaction of carbon fibre with a gas composed of $TiCl_4$, hydrogen and argon, a TiC layer was formed at temperatures between 800 to 1000° C, by a mechanism controlled by diffusion of carbon atoms. The thickness of the TiC layer that will be formed over 60 min at 1300° C is estimated to be 10^4 times that of the SiC layer formed under the same conditions.

4. The strength of the TiC-coated fibre decreased following the relation $\sigma_m \propto d^{-1/2}$, where d is the thickness of the TiC layer which is in the range 10 to 100 nm.

5. As the rate of formation of the SiC layer on the carbon fibre surface is much smaller than that expected from the rate of the reaction between solid silicon and hydrocarbons, it is desirable to develop another method by which it is possible to obtain a much thicker layer as a protective layer against attack by aluminium.

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*Received 10 December 1984
and accepted 14 August 1985*