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Carbon fibres coated with titanium carbide using the liquid metal transfer agent technique

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Protective coatings of titanium carbide were applied to PAN type carbon fibres by a liquid metal transfer agent (LMTA) technique using tin as a transfer agent. The effect of the coating on the strength of the fibres was evaluated by performing single fibre tensile tests. The coatings were examined metallographically, by X-ray diffractometry, and by scanning electron microscopy. Carbide coating thicknesses obtained ranged from approximately 0.05 to 0.5 μm and the coatings were found to be uniform and adherent to the fibres. It was found that wetting of the fibres by the tin alloy is associated with the spontaneous formation of a carbide layer with a thickness dependent upon the melt temperature, after which the carbide layer was found to grow parabolically with time and with an apparent activation energy of 187 kJ mol^{-1}. The strength of the carbon fibres decreased with increasing coating thickness according to a Griffith relation.

1. Introduction

The major drawbacks in the development of carbon fibre–metal matrix composites are that carbon fibres are reactive and/or non-wetting with many matrix metals, thus introducing many difficulties in the fabrication and high temperature application of these composites. One solution to these problems is to apply a suitable protective coating or diffusion barrier to the carbon fibre. This coating should have a low diffusivity for carbon, be stable in the matrix, and not seriously affect the strength of the fibres. Possible coating materials are oxides, nitrides, borides, and carbides, however of these materials, the carbides are generally the most wettable [1] and, by using a liquid metal transfer agent (LMTA) technique, are the easiest to apply to carbon fibres. This method has already been used by several experimenters to obtain smooth and uniform carbide coatings on carbon fibres [2–6]. Recently, the present authors have applied tungsten carbide coatings to carbon fibres using liquid copper as a transfer agent [7] and chromium carbide coatings using liquid tin as a transfer agent [8].

Since carbon is consumed from the fibres to form the carbide layer and cracks in the brittle carbide layer may act as stress concentrators initiating fracture of the fibre, the strength of the fibres is expected to decrease as a result of the coating process. Carbide coatings applied by methods other than the LMTA technique have shown that layer thicknesses in the order of 0.1 μm can significantly reduce the strength of carbon fibres [9–11]. Thus, an evaluation of the strength of fibres coated with thin carbide layers by the LMTA technique should be determined.

The purpose of this paper is to examine the coating of carbon fibres with titanium carbide by the LMTA technique using tin as a transfer medium for titanium. The effect of the coating on the strength of the fibres will then be evaluated by performing single fibre tensile tests of coated and uncoated fibres.

2. Experimental procedure

Fibres used in this study are polyacrylonitrile (PAN) based fibres with a reported strength of 3.4 GPa and a modulus of 400 GPa sold under the trade name of Fortafil 6T from the Great Lakes Corporation. Prior to use, fibre surfaces were cleaned of any organic substances by passing them through a furnace at 800° C containing an argon atmosphere.

The coating of carbon fibres with titanium carbide by the LMTA technique consisted of first attaching the fibres to a carbon frame designed such that a 10 cm length of a fibre bundle containing approximately 150 fibres could be held at both ends for immersion in the coating melt. The coating melt consisted of a Sn–1% Ti alloy contained in a graphite crucible and heated using an induction furnace. Three melt temperatures of 900, 995 and 1055° C were used in the coating process. The immersion of the fibres in the coating melts was done under an argon atmosphere for specific time durations ranging from 15 sec to 10 min. The resulting carbide layer thicknesses were measured by observing the cross-sections of the coated fibres on a scanning electron microscope.

Following the coating procedure the fibres were surrounded in a matrix of the coating bath material. To obtain coated single fibres separate from the matrix for observation and tensile testing, the matrix material was removed by dissolving it in 20% HCl–10% HNO_3 long enough only to remove the tin alloy matrix. Since the carbide is relatively unattacked by the acid, only the carbide coating remains on the fibres. X-ray diffraction analysis of the separated coated fibres was performed in a Debye–Scherrer camera using nickel filtered copper radiation ($\lambda = 0.1542$ nm).

The tensile testing of single fibres was carried out using an Instron tensile testing machine. The specimen preparation and testing procedure was done according to ASTM Standard D3379 [12]. The gauge length of the specimens was about 1 cm and the crosshead speed was 0.005 cm min^{-1}. The cross-sectional area of each specimen was measured by mounting the gauge section in epoxy and magnifying the cross-section to a total magnification of 6700X on an optical microscope.

3. Results and Discussion

3.1. Fibre coating

Carbon fibres were successfully coated with approximately 0.05 to 0.5 μm of carbide identified by X-ray diffraction to be TiC. Fig. 1 shows the cross-section of a fibre bundle after immersion in the Sn–Ti melt at 1055° C for 3 min. The infiltration of the Sn–Ti melt into the fibre bundle was found to be very good and on removal of the fibres from the melt the tin alloy remains on the fibres, thus making up the matrix seen in Fig. 1. In Fig. 1, a continuous coating of titanium carbide having a uniform thickness on all the fibres can be seen.

Fig. 2 shows the surface morphology of the carbide coating formed after 1 min at 1055° C in the Sn–Ti melt. As seen in Fig. 2, the coating is so uniform that the original surface relief of the fibre is preserved and, the coating appears to be adherent to the fibres since no breaking off of the carbide layer from the fibres was observed.

If the growth of the carbide layer is assumed to be controlled by a diffusional parabolic growth mechanism, the thickness of the carbide layer on the fibres can be described by [13]

$$x = (At)^{1/2} \tag{1}$$

where x is the carbide thickness, A the growth constant and t the immersion time in the melt. The carbide thickness formed on the fibres as a function of the square root of the immersion time in the melt is shown in Fig. 3. The data appear to conform to a parabolic growth behaviour with the correlation coefficients of the best fit lines ranging from 0.991 to 0.998. However, a positive thickness intercept at $t = 0$ for the three temperatures studied suggests an equation of the form

$$x - x_0 = (At)^{1/2} \tag{2}$$

should be used, where x_0 is the carbide layer which spontaneously forms on wetting of the alloy with the

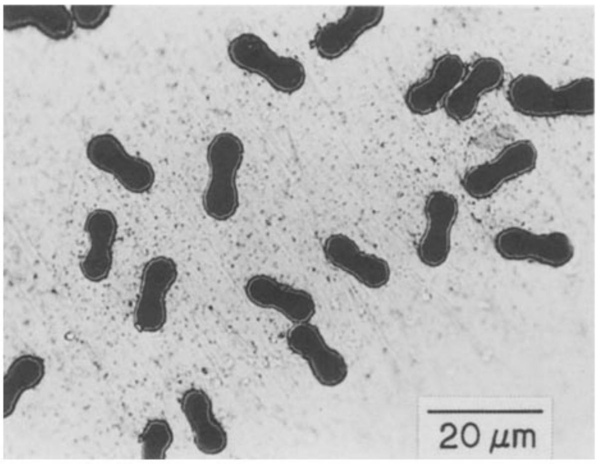

Figure 1 Cross-section of carbide coated fibres after immersion for 3 min in Sn–1% Ti alloy at 1055° C.

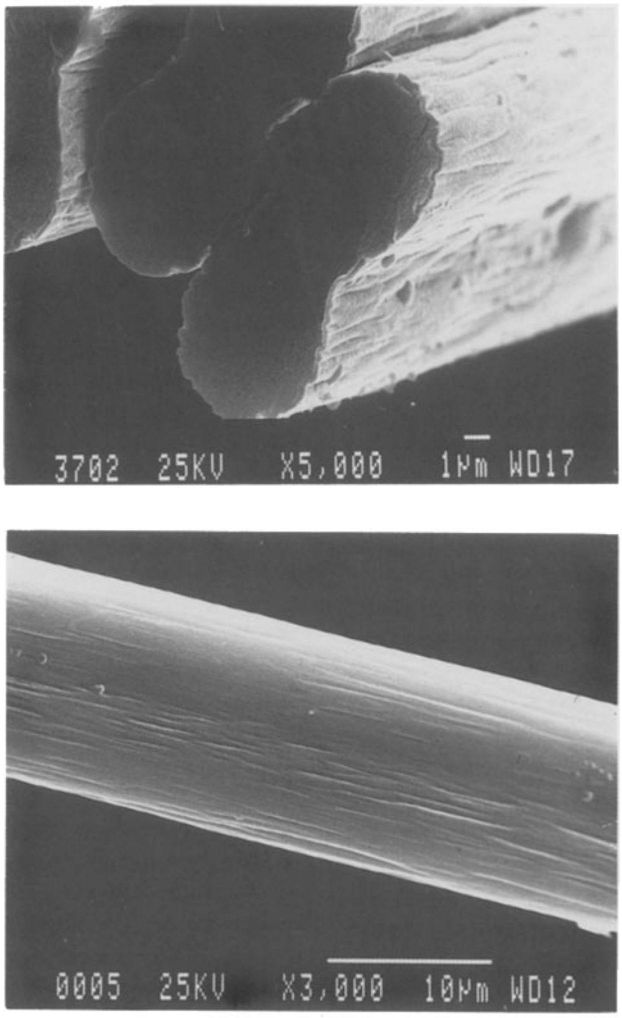

Figure 2 Morphology of the titanium carbide coating formed on carbon fibres after immersion for 1 min in Sn–1% Ti at 1055° C. (a) Fractured end of fibre, (b) surface morphology. (Tin alloy matrix dissolved in acid).

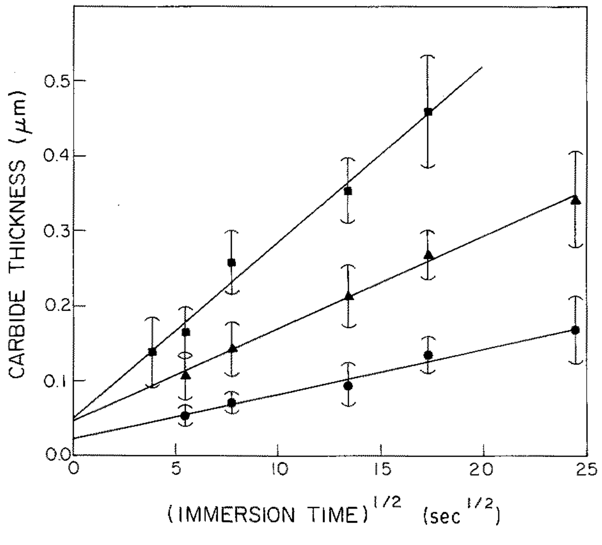

Figure 3 Growth rate of the carbide coating formed from Sn–1% Ti alloy as a function of time and temperature. (Error bars indicate 95% confidence limits) (■ 1055° C, ▲ 995° C, ● 900° C).

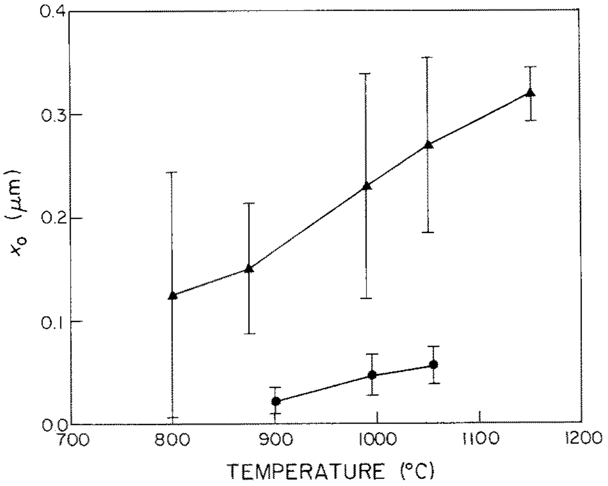

Figure 4 Thickness of the carbide layer, x_0, formed on wetting for titanium (●) and chromium (▲) carbide as a function of temperature. (Error bars indicate 95% confidence limits.)

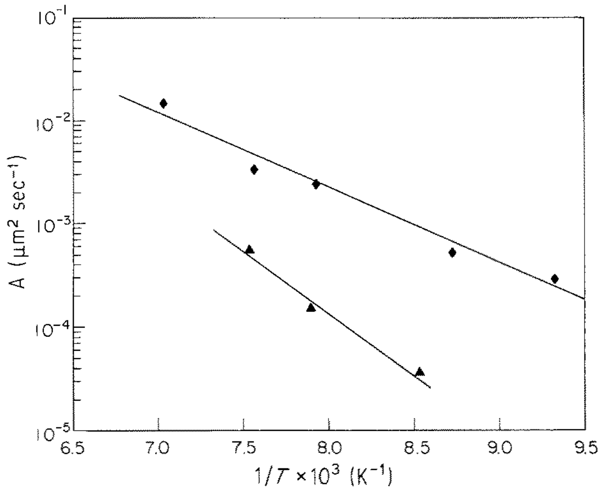

Figure 5 Growth rate constants, A, for the titanium carbide (▲) layer growth from Sn–1% Ti alloy as a function of temperature compared with growth rate constants for chromium carbide (◆) formation from reference [8].

carbon fibres. This carbide layer which forms spontaneously is similar to that observed by Mortimer *et al.* [6] where the wetting of a carbon substrate by Cu–Cr alloy is associated with the formation of a carbide layer of significant thickness. In a previous study by the present authors [8], chromium carbide layers formed on carbon fibres by the LMTA technique also exhibited a spontaneous carbide formation on wetting. In the latter and the present studies, the thickness of the coating formed on wetting was found to be a function of temperature. If the temperature of the alloy melt is decreased the thickness of the carbide layer which forms spontaneously on wetting decreases. It was also observed that the thickness of the coating formed on wetting for the Ti–Sn alloy is smaller than that formed with the Cr–Sn alloy for the same given temperature, as seen in Fig. 4.

The activation energy of the growth rate can be assessed by letting the growth rate constant A be described by the well known equation

$$A = A_0 \exp(-Q/RT) \qquad (3)$$

where Q is the activation energy, T the temperature, A_0 a constant and R the gas constant. Equation 3 is plotted in Fig. 5 and Q was found to be 187 kJ mol^{-1} with a correlation coefficient of 0.991. This value is lower but reasonably close to the activation energy of 225 kJ mol^{-1} obtained by Koyama *et al* [14] for the diffusion of carbon in TiC. The lower activation energy observed in the present study may be attributed to enhanced grain boundary diffusion arising from a different carbide structure than in reference [14]. Also shown in Fig. 5 is the growth constant for chromium carbide formation from reference [8]. The growth rate of titanium carbide is lower than that of chromium carbide for the same temperature. Given the lower growth rate constant for titanium carbide, together with the lower thickness of carbide layer formed on wetting for titanium carbide as compared to chromium carbide, coating fibres with titanium carbide offers more control in the coating process and allows for the formation of thinner coatings than for the case of chromium carbide.

3.2. Fibre strength

The variation of the strength of the carbide coated fibres with coating thickness is shown in Fig. 6. These results are compared with the results of chromium carbide coated fibres coated by the LMTA technique of reference [8]. The fibre strength in both cases is seen to decrease with increasing coating thickness. The strength of TiC coated fibres for carbide thicknesses greater than 0.15 μm appears to be slightly less than that of chromium carbide coated fibres. This may be due to the fact that to achieve a given thickness of carbide coating, more carbon may be consumed to produce a titanium carbide layer than a chromium carbide layer as formed in reference [8]. Thus, titanium may consume more of the carbon fibre resulting in an apparent decrease in the fibre strength over that of chromium carbide coated when the thickness of the titanium carbide layer is greater than approximately 0.15 μm.

Fig. 7 compares the effect of TiC coatings obtained by chemical vapour deposition (CVD) with the coatings obtained in the present study on the strength of

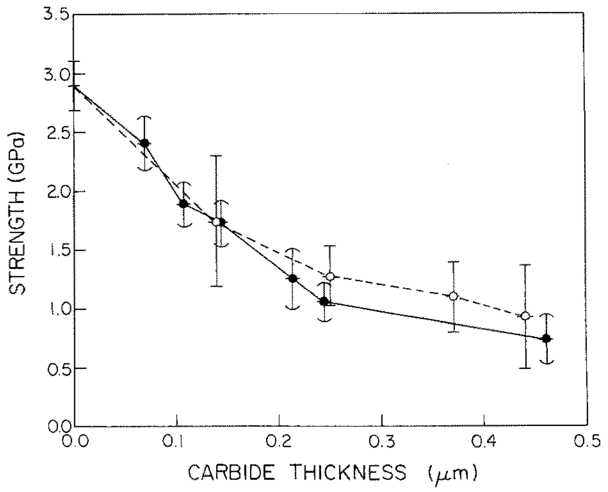

Figure 6 Variation of the strength of the carbon fibres coated by the LMTA technique as a function of the coating thickness. (Error bars indicate 95% confidence limits for the mean) (○ chromium carbide, ● titanium carbide)

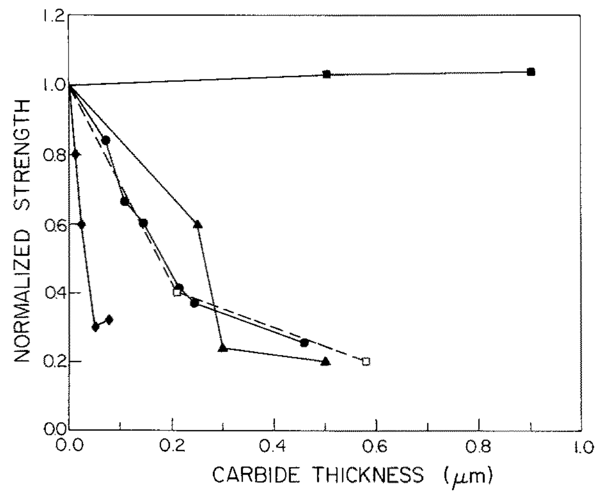

Figure 7 Variation of the strength of carbon fibres coated with TiC by the LMTA technique and by CVD as a function of coating thickness. (● present study, ◆ CVD with no gaseous carbon [9], ▲ CVD with no gaseous carbon [16], □ CVD with gaseous carbon [16], ■ CVD with gaseous carbon [15].)

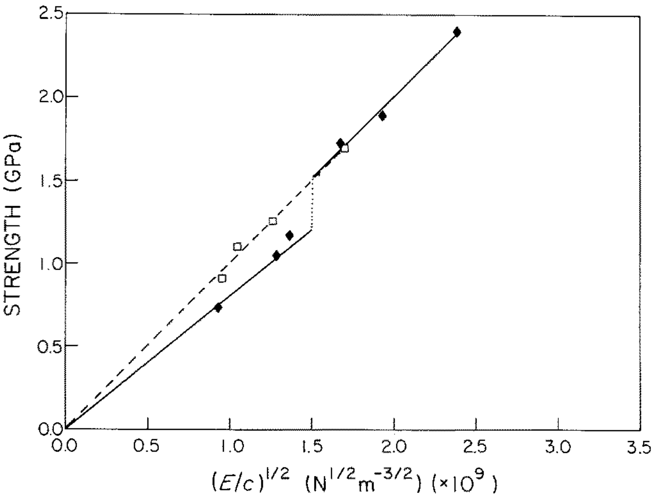

Figure 8 Strength of the coated fibres as a function of $(E/c)^{1/2}$. (□ chromium carbide).

carbon fibres. In almost all cases the decrease in strength with coating thickness in the present study is comparable to or less than that observed with CVD coated fibres even when the original strength of the fibres is taken into account. However, in the study by Kohara *et al.* [15], the fibre strength is not greatly affected by the coating. This difference in strength behaviour is a result of the different methods of depositing TiC on carbon fibres by CVD. Carbon fibres may be coated by the direct deposition of TiC from the vapour phase using carbon supplied from the vapour, by reacting titanium directly with the fibre using carbon from the fibre to form TiC, or by a combination of these methods depending on the amount of gaseous carbon supplied to the feed gas in the CVD process.

It is believed by Aggour *et al.* [17] and Fitzer *et al.* [18] that the strength of the carbon fibres is reduced considerably if carbon from the fibre is consumed in the carbide formation. They found that by increasing the amount of excess carbon in the feed gas used in the CVD process, the loss in strength of the coated fibres was reduced to a point where if the ratio of carbon to titanium exceeds about 4, the original strength of the fibres is maintained. They argue that unless such a high carbon activity in the gas phase is maintained, solid carbon diffuses from the fibre through the carbide layer toward the surface because of the inhibited deposition of carbon from the gaseous hydrocarbons, and thus the strength of the carbon fibres is considerably reduced.

Contrary to the above statement, Honjo *et al.* [9] have shown the decrease in the strength of titanium carbide coated fibres is caused by the carbide layer itself and not by the removal of carbon from the fibres. They found that after removal of the carbide coating formed by the reaction of titanium with carbon from the fibre, the original strength of the fibre is restored. Therefore, another mechanism must be responsible for the weakening of the coated fibres.

It is known that the strength of a fibre coated with a brittle material will be affected by the type of interface which exists between the fibre and the coating. If the interface is strong, cracks form in the coating at small strains and hasten the fracture of the fibres [19]. However, if the interfacial bonding is weak, debonding will occur and the strength of the fibre will not be reduced because debonding will cause blunting of the notch tip [20]. If the use of a large excess of carbon in the gaseous feed results in a weak type of bonding between the TiC layer and the fibre, this may be the reason why no degradation in fibre strength is observed in fibres coated by this method. In support of this argument, fibres coated by the CVD method by Kohara *et al.* [15], in which the strength of the fibres was not affected by the coating (see Fig. 7), showed some debonding of the coating from the fibre in SEM micrographs of the fractured ends of the fibres.

On elongating a brittle fibre coated with a brittle layer having a lower fracture strain than that of the fibre, cracks will initially form in the brittle carbide layer and under further loading will eventually propagate into the fibre if the bonding between the layer and the fibre is strong enough to withstand the shear stress at the interface. With such a behaviour, the strength of a coated fibre, σ, will follow the Griffith equation

$$\sigma = (2E\gamma/\pi c)^{1/2} \tag{4}$$

where E and γ are the modulus of elasticity and the surface energy of the surfaces created by the propagating crack, respectively, and c is the critical crack length i.e. the thickness of the carbide layer. It should be noted that Equation 4 was derived for a homogeneous material and its application to the fracture of titanium carbide coated fibres may be inappropriate given the difference in elastic behaviour of the coating and the fibre. However, the elastic modulus for TiC and the present fibres are quite similar, these being 440 GPa [21] and 400 GPa, respectively. Therefore, the coated fibres may possibly behave as a homogeneous material as concerns the Griffith behaviour.

Equation 4 is assumed to be applicable, and plotted in Fig. 8 for the results obtained here and for the chromium carbide coated fibres of reference [8]. From Fig. 8, the fracture stress of the chromium carbide coated fibres produced by the LMTA technique appears to follow a Griffith behaviour. From the slope of the plot in Fig. 8 for these fibres, the surface energy of the carbon fibres, γ, was calculated to be $1.83\,\mathrm{J\,m^{-2}}$.This value is in good agreement with the value of $2.33\,\mathrm{J\,m^{-2}}$ obtained by Baker *et al.* [22] for high strength fibres. The fracture strength of the titanium carbide coated fibres appears to have two separate regions of fracture behaviour. In the first region where the coatings are thinner than $0.15\,\mu\mathrm{m}$, the fracture behaviour is similar to that of the chromium carbide coated fibres of reference [8]. In the second region where the coatings are thicker, the slope of the line is decreased giving a value of the surface energy of $1.07\,\mathrm{J\,m^{-2}}$. This change in slope may be attributed to the "onion skin" structure of the carbon fibre. There is general agreement [23] that the outer surface of high modulus fibres consists of a sheath of highly ordered crystallites with the basal planes oriented parallel to the fibre surface, beneath which are more random oriented crystallites which make up the core. For a thinly coated fibre, the crack must propagate perpendicular to the basal planes of the graphite which makes up the sheath. For a thicker coated fibre, the sheath may be entirely consumed to form the carbide layer, thus the crack propagates through the more randomly oriented fibre core which may contain basal planes arranged more or less parallel to the crack surface. Since the basal planes have a lower surface energy than those perpendicular to it, the observed value of γ in Equation 4 will be lower for the thicker coated fibres, in which the sheath of the fibre is consumed, than in the thinly coated fibres, in which the sheath of the fibre still remains.

The present single fibre strength tests show that it is desirable to have the thinnest coatings possible so as not to seriously affect the strength of the fibres. As has been shown earlier, the kinetics of the titanium carbide formation allows for the formation of thin carbide coatings which can be applied even more thinly than those of chromium carbide using the LMTA method. For this reason, titanium carbide coatings applied by the LMTA technique using tin as a transfer medium appear very promising in the development of metal matrix composites.

4. Conclusions

The conclusions are as follows.

(1) Titanium carbide coatings of approximately 0.05 to $0.5\,\mu\mathrm{m}$ were successfully applied to carbon fibres by the LMTA technique using tin as a transfer medium. The coatings were found to be smooth, uniform and adherent to the fibres.

(2) The wetting of the carbon fibres by the copper and tin alloys is associated with the spontaneous formation of a carbide layer of a significant thickness. The thickness of the layer was found to decrease with decreasing melt temperature. After the formation of this layer, the carbide coating grows parabolically with time and with an apparent activation energy of $187\,\mathrm{kJ\,mol^{-1}}$.

(3) For the same given temperature, titanium carbide has a lower growth rate and a lower thickness of carbide layer formed on wetting than chromium carbide. This allows for a thinner and more controlled formation of titanium carbide layer on the fibre than for chromium carbide.

(4) The strength of fibres coated with chromium carbide decreases with increasing carbide thickness. A coating of $0.07\,\mu\mathrm{m}$ results in a 15% decrease in the strength of the carbon fibres.

(5) The fracture strength of the coated fibres conforms to a Griffith behaviour.

Acknowledgements

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