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Copper coating on carbon fibres and their composites with aluminium matrix

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A uniform and continuous coating of copper was given to carbon fibres by cementation or electroless techniques. In both cases, when coating thicknesses were less than 0.2 μm, copper deposition was discontinuous over the fibres, and above 0.2 μm, coatings were continuous. In electroless coating, about 75% of the continuously coated fibres had a coating thickness range 0.2–0.5 μm and above this showed isolated dendrite deposits of copper. In the cementation process, about 75% of the continuously coated fibres had a coating thickness range 0.2–0.6 μm, and above this thickness, fine crystallite-type copper deposition was found over smoothly coated copper. The ultimate tensile strength of continuously electroless-coated fibres were nearer to the uncoated fibres, suggesting defect-free coating, while fibres coated by the cementation process exhibited lower ultimate tensile strength values. The tensile fracture of both electroless- and cementation-coated fibres showed delamination of the coating, suggesting poor bonding between coating and the fibre. In composites, prepared by dispersing the coated chopped fibres in a pure aluminium matrix, uniform and random distribution of the fibres were observed without appreciable fibre–metal interaction. The $CuAl_2$ intermetallics were largely found in the matrix and only very small amounts were observed at fibre/matrix interfaces. Additions of about 2 wt% Mg to the matrix prior to the fibre dispersion did not appreciably change the distribution pattern of the fibres, but in addition to $CuAl_2$ phase, Mg_2Si phases were observed in the matrix as well as at the interface.

1. Introduction

The interface plays a most vital role in the overall performance of a composite material. Improper wetting and chemical reaction occurring between the dispersoid surface and the matrix at the interface during synthesis or under service conditions, can degrade the mechanical properties of the composites [1]. Special alloying additions to the matrix and refractory material coatings on the dispersoids can effectively reduce the chemical reaction between the matrix and the dispersoid surface [2]. Copper and nickel coatings on carbon fibres prior to dispersion enhanced the wettability of the carbon fibre with molten aluminium [3, 4]. In both cases, the coating materials, i.e. copper and nickel were dissolved in the matrix aluminium to give brittle intermetallics and, at the same time, the intensity of the possible interfacial reaction between molten aluminium and the carbon fibre was also reduced [4]. In an earlier paper [5] we reported the structure and morphology of nickel-coated carbon fibres and their composites with a pure aluminium matrix. It was observed that $NiAl_3$ intermetallics were found adjacent to the carbon fibres and, in some cases, carbon fibres were embedded in $NiAl_3$ phase. This was mainly attributed to the chemical interaction between the nickel coating and the carbon fibre in the coating stage, and such interactions act as nucleating centres for $NiAl_3$ intermetallic precipitate during composite synthesis. In this paper, similar to nickel [5], studies were carried out on copper-coated carbon fibres and their composites with pure aluminium. Carbon fibres were coated with copper using cementation [3] and electroless techniques. The morphology of the coating structure and the nature of the bonding between the fibre and coating were evaluated by tensile property measurements, as well as by observing the tensile fractured fibres under the scanning electron microscope (SEM). The coated fibres were dispersed in a pure aluminium matrix and the microstructure of the composites was evaluated by an optical metallographic technique.

2. Experimental procedure

Carbon fibres XA-S grade (Grafil) both in continuous and chopped form were used in the present investigation. The sizing and finish treatments from the surface of the fibres, prior to coating, were removed by heating them to about 970 K for 10 min in air. Subsequently they were coated with copper using cementation and the electroless process, as described below.

Cementation method. Details and mechanism of the

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coatings have been described earlier [3, 6]. Heat-cleaned fibres were first treated with glacial acetic acid to activate the surface, and the copper deposition was made over the fibre surface using copper sulphate solution with zinc as displacing agent. Conditions were adjusted to obtain continuous coatings of copper over the fibre surface.

Electroless method [7]. Heat-cleaned fibres were activated using stannous chloride (0.1 $\mathrm{g\,l^{-1}}$) followed by palladium chloride (0.01 $\mathrm{g\,l^{-1}}$) treatment. Ultrasonic vibrations were applied during the activation treatment to facilitate uniform activation throughout the entire surface of the carbon fibres. The fibres were coated in copper sulphate both with sodium potassium tartarate as chelating agent and NaOH as buffering agent to maintain the pH between 10 and 11, and formaldehyde as the reducing agent. Experimental conditions were adjusted to obtain a continuous coating of copper over the fibre.

For mechanical property and coating structure evaluation, carbon fibres in continuous form were used. For dispersing in the aluminium matrix, the same grade of fibres in chopped form were coated. No appreciable changes in coating structure were observed with continuous or chopped fibres when coated under similar conditions for both types of coating. The coated fibres were mounted in cold-setting epoxy resin and transverse cross-sections were examined under the optical microscope to ascertain the thickness, uniformity and continuity of the coatings. Single-fibre tests (50 mm gauze length) were carried out in a universal testing machine (Instron). The tensile fracture and coating morphology were studied by SEM.

About 5 wt % of the both coated and uncoated chopped fibres were dispersed in pure aluminium matrix by stirring the liquid metal using a mechanical impeller and introducing the fibres in the vortex at 990 ± 10 K in 250 g level melts. The microstructure of the cast composites was examined with the help of an optical microscope.

3. Results and discussion

3.1. Coating thickness, distribution and mechanism

Typical transverse cross-sections of copper-coated carbon fibres by the cementation and electroless methods, mounted in resin are shown in Fig. 1a and b. In both cases, the coating thickness is uniform throughout the circumferences of the fibres and more than 98% of the fibre surface was found to have been covered. Fig. 2a and b are typical histograms showing the variation in the coating thickness as a function of the number of fibres coated by the electroless method for two separate batches. Fig. 3a and b are typical histograms comparing the variation in the coating thickness as a function of the number of fibres coated by electroless and cementation process, respectively. The numbers inside the histograms indicate the percentage of coated fibres in that thickness range in that batch. From Figs 2a, b and 3a it is seen that in electroless-coated copper, the coating thickness ranges between 0.1 and 0.9 μm with above 75% of them having a coating thickness between 0.2 and 0.5 μm. In this 40% alone was the coating thickness between 0.3 and 0.4 μm. In the cementation process the spread in coating (Fig. 3b) thickness lies between 0.1 and 1.1 μm. Here about 50% of the coatings had a thickness of 0.2–0.5 μm and only 25% were in the 0.5–0.6 μm thickness range.

The SEM examination of the coated fibres showed that when the coating thickness was less than 0.2 μm, isolated patches of copper were formed at the fibre surface [8] in both types of coating method. When the coating thickness exceeded 0.2 μm, a continuous metal spread was seen (Fig. 4). Further increase in the coating thickness takes place by fine crystallite growth over continuously coated copper in the cementation process (Fig. 5), whereas in the electroless process, few massive crystallite growths are observed at isolated places (Fig. 6) over smooth and continuously coated copper.

The mechanism of copper-coating on the carbon fibre in these cases seems to be similar to that observed in the case of nickel-coating [5], i.e. during coating, the copper deposits over energetically favoured sites followed by bridging of these sites covering the entire surface of the fibre. However, the growth of copper coating over continuously coated fibres in the cementation process seem to be different from that observed in the case of nickel by all three processes [5], or with copper coated by the electroless process. The observed

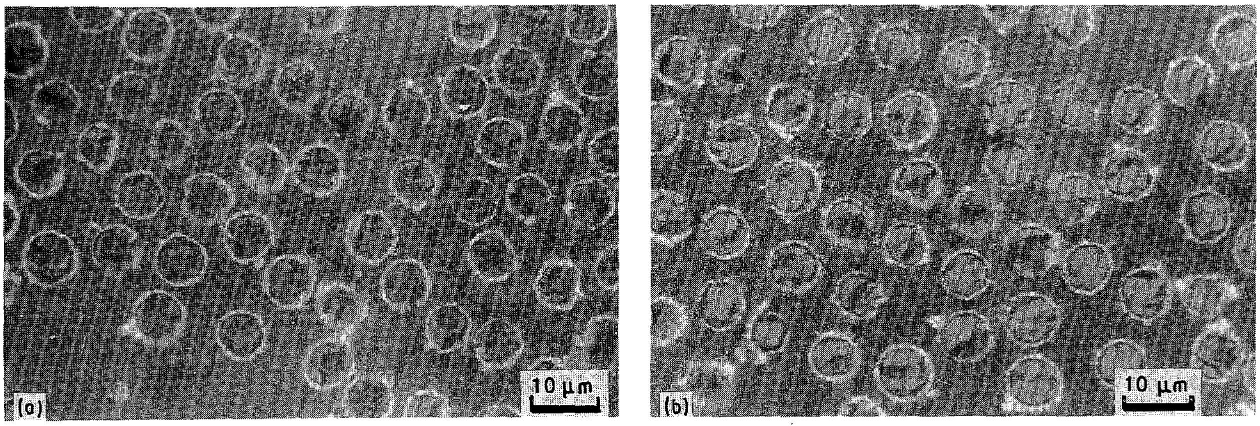

Figure 1 Transverse section of copper-coated carbon fibre mounted in cold-set resin: (a) cementation method, (b) electroless method.

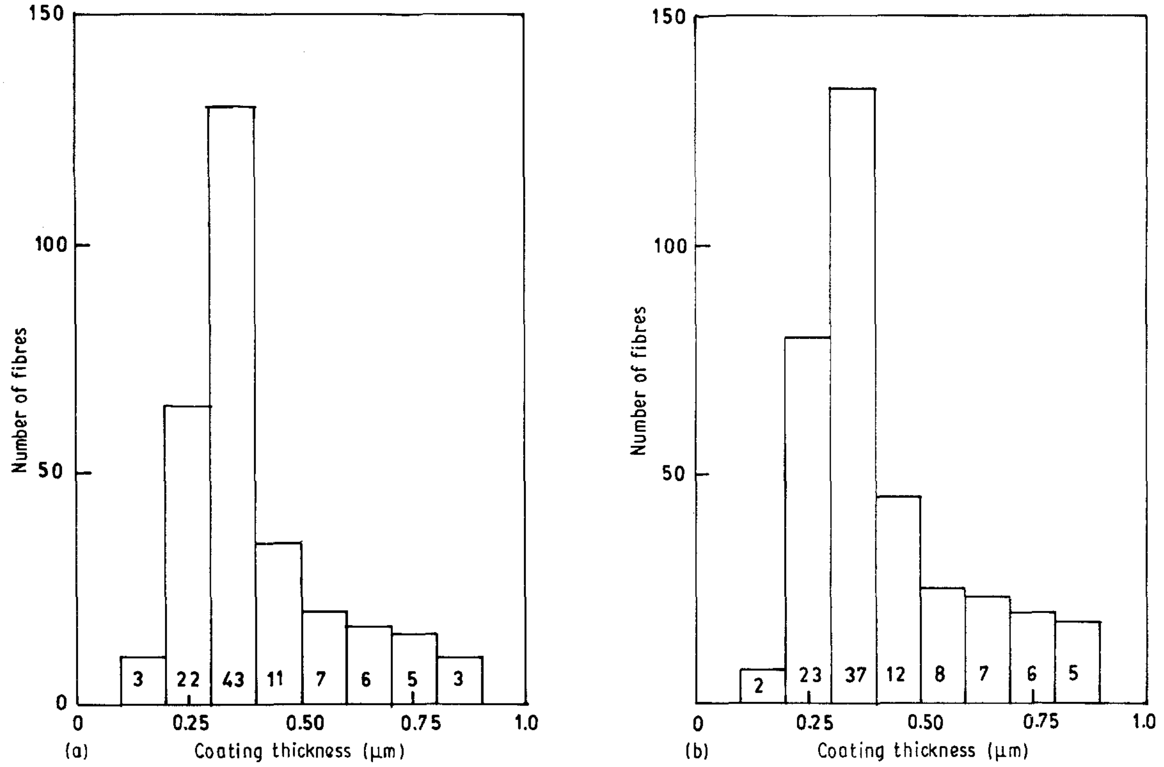

Figure 2 Variations in the coating thickness as a function of the number of coated fibres for two batches, by the electroless method. (a) 300 fibres, (b) 370 fibres.

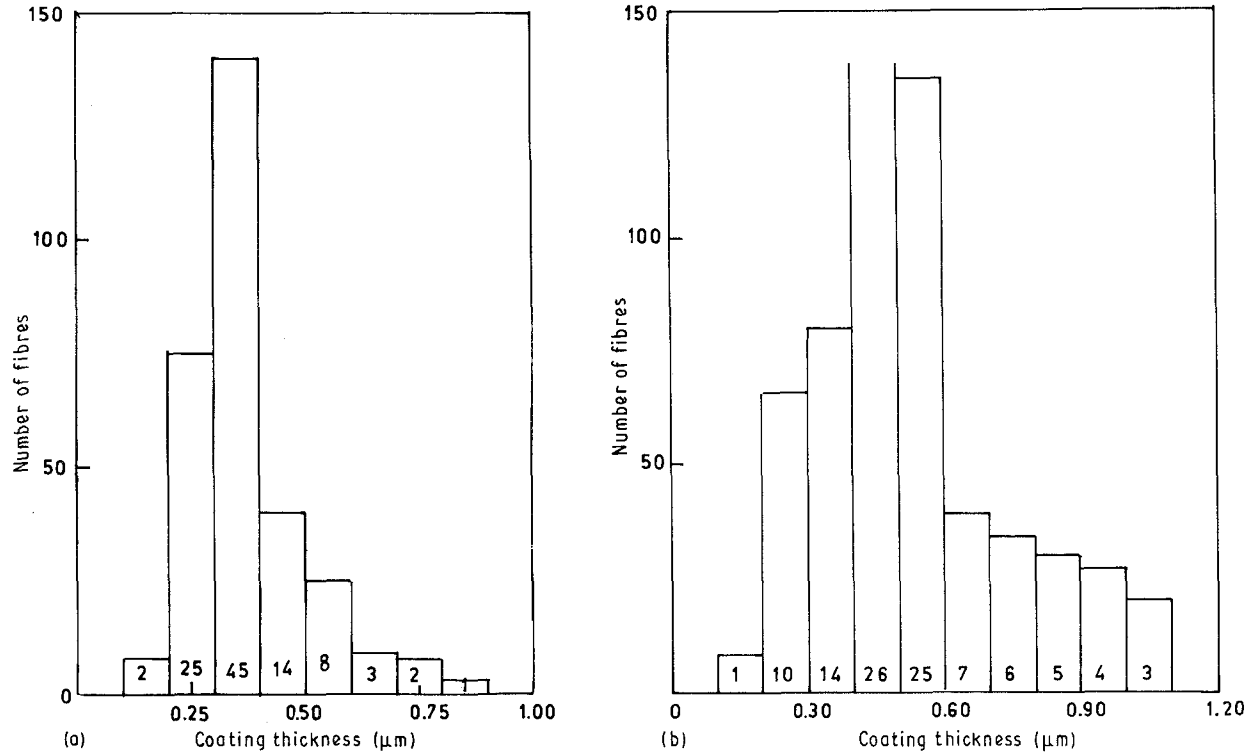

Figure 3 Variations in the coating thickness as a function of the number of coated fibres: (a) electroless method, 305 fibres; (b) cementation method, 550 fibres.

variation in the coating thickness in a batch (Figs 2a, b, 3a, b) could be mainly due to non-uniform activation of the surface of the fibres prior to deposition. When the total amount of metal ions available in the coating bath is much lower than the amount required for coating about 0.5 μm thick layer over all the fibres in the bath, most of the fibres are found to be partially coated but few fibres are found to be completely coated. This was also observed when the total metal ion concentration was much higher than the optimal amount – for 0.5 μm thickness coating, a small percentage (~ 2%–3%) of fibres were found to be still

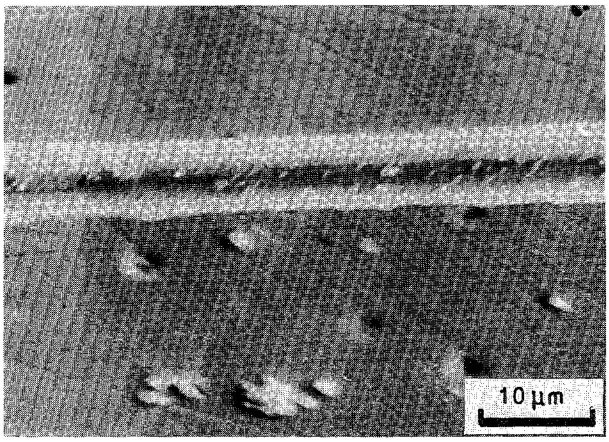

Figure 4 Surface of a carbon fibre copper-coated by the cementation method; coating thickness about 0.3 µm.

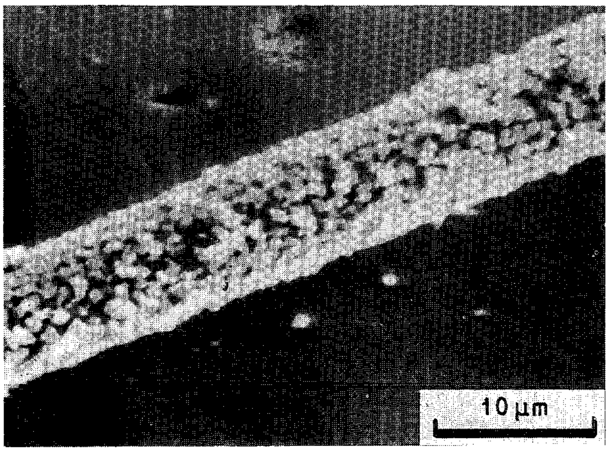

Figure 5 Surface of a carbon fibre copper coated by the cementation method; coating thickness about 0.8 µm.

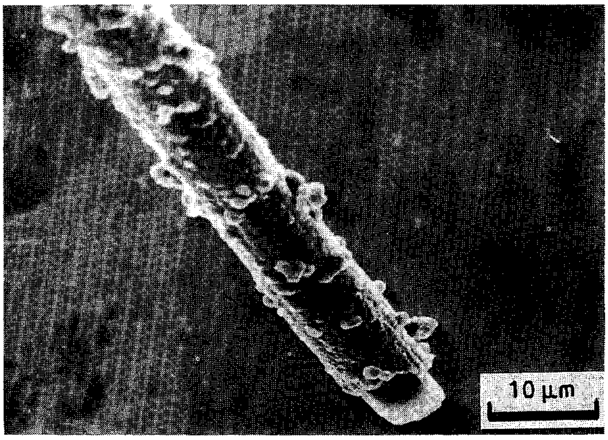

Figure 6 Surface of a carbon fibre copper-coated by the electroless method; coating thickness 0.6 µm.

partially coated, others fully coated, and excess metal was precipitated in free form giving a distribution in coating thicknesses as described earlier. These results suggest that by these coating methods it may not be possible to produce a continuous coating of copper over carbon fibre less than 0.2–0.3 µm thick and a variation in the coating thickness is also inevitable.

3.2. Tensile property evaluation

The average tensile properties of carbon fibres after different treatments determined by single-fibre pull-out tests are given in Table I. As seen from the table, the ultimate tensile strength (UTS) values in the as-received condition, after heat-cleaning treatment, and after acetic acid treatment, did not significantly change from the data sheet values supplied by the manufacturer of the fibre. However, a small reduction in the percentage elongation values were observed. It is assumed for all practical purposes that the pre-treatments have not affected the strength properties. The typical measured UTS values of the coated fibres, as a function of coating thickness for both electroless and cementation process coated fibres, determined by single-fibre pull-out tests are plotted in Fig. 7. In the electroless process for one value of coating thickness of 0.1 µm, the UTS was found to be low, 1.8 GPa, and at the same time for two coating thicknesses, in the range 0.2–0.3 µm, the UTS values were high, 3.5 GPa. Otherwise, in all cases for the coating thicknesses between 0.2 and 0.4 µm the UTS values ranged between 2.8 and 3.1 GPa, suggesting that coating had not deteriorated the UTS of the fibres. The microstructural examination of the surfaces of the electroless-coated fibre (Fig. 6) has shown a smooth defect-free coated surface. In cementation-coated fibres the UTS values (Fig. 7) were much lower, 1.8–2.2 GPa, for the coating thickness range 0.4–0.9 µm. The lower observed strength in these can be explained by the morphology of the coating structure. In cementation-coated fibres the copper spread is not smooth and uniform, as in the electroless process (Fig. 5). Owing to the gap and the microdiscontinuities between the precipitated crystallites, the coating does not contribute to the strength properties. In these cases it was observed that the breaking load of the coated fibres was of similar value to that of uncoated fibres and the lower strengths of the fibres were due to the increased cross-sectional area of the fibre, contributed by the coating thickness, which practically does not contribute to the strength. This also proves that the cementation coating process does not damage the fibre or lower its tensile properties.

3.3. Fracture studies

The uncoated carbon fibres exhibited brittle fracture under tension (Fig. 8). The electroless copper-coated fibre (Fig. 6) showed delamination during fracture. The percentage elongation in this case was about 1.8. Probably the fibre fractured first when its breaking load was reached and subsequently delamination and failure of the coating took place. Fracture does not indicate any strong physical or chemical bond with the coating. In cementation-coated fibres (Fig. 9) the mode of fracture is different. The coating has fractured at many places probably due to the surface defects, as described earlier. In this case the coating fractured first followed by the fibre. The observed percentage elongation in this case was about 1.3. There is no evidence for any chemical/physical interaction between the fibre and the matrix. The delaminated fracture in both cases

TABLE I The average tensile properties of carbon fibres under different treatment and coating conditions determined by the single-fibre pull-out test

Serial no.	Condition	Coating thickness (µm)	Ultimate tensile strength (GPa)	Elongation (%)
1	Data sheet value	–	3.00	1.5
2	Tested in as-received condition	–	2.6–3.2	1.5
3	After heat cleaning (970 K, 10 min)	–	2.5–3.1	1.2
4	Heat cleaned + acetic acid treatment (4.5 vol %, 5 min)	–	2.9–3.0	1.4
5	Copper-coated cementation process	0.4–1.1	2.1–1.8	1.1–1.4
6	Copper-coated electroless process	0.1–0.7	1.8–3.6	1.4–1.8

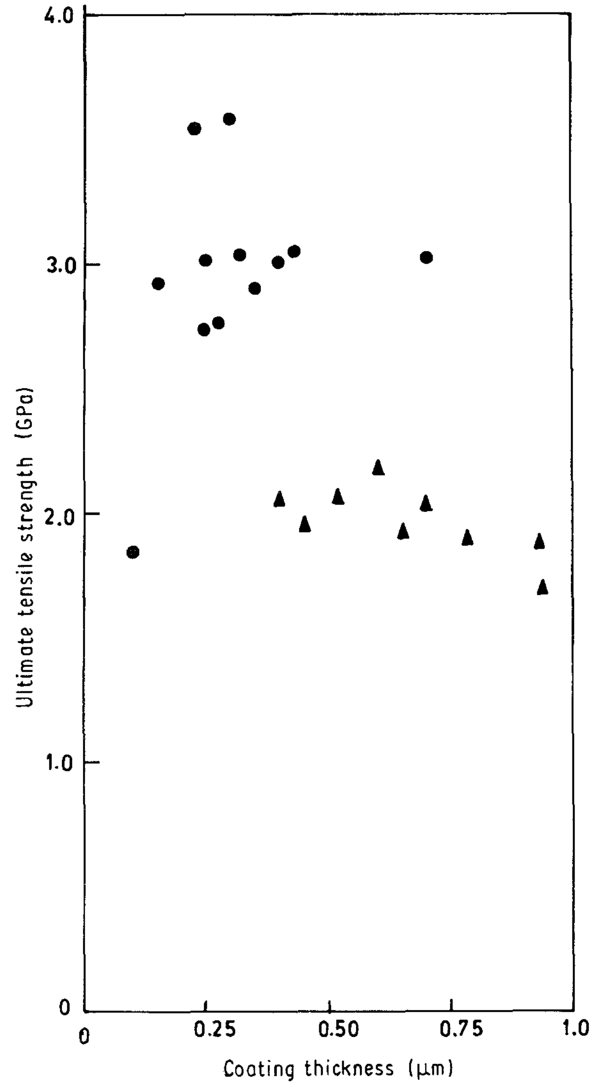

Figure 7 Variation in the ultimate tensile values of the coated fibre as a function of coating thickness for (●) electroless- and (▲) cementation-coated fibres determined by the single-fibre pull-out test.

indicates poor bonding between the coating and the fibre in the present context.

3.4. Composites microstructure

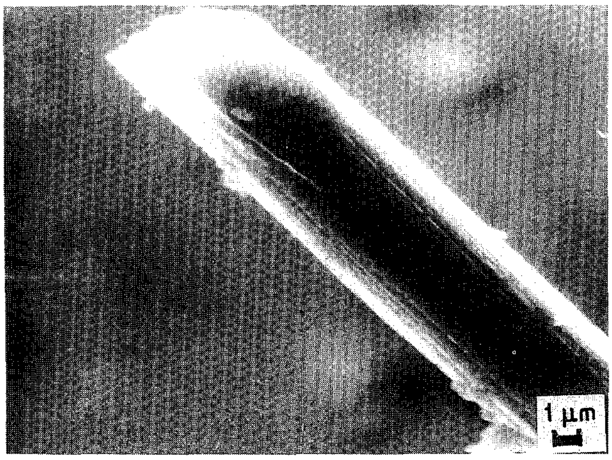

Figure 8 Fracture tip of an uncoated carbon fibre.

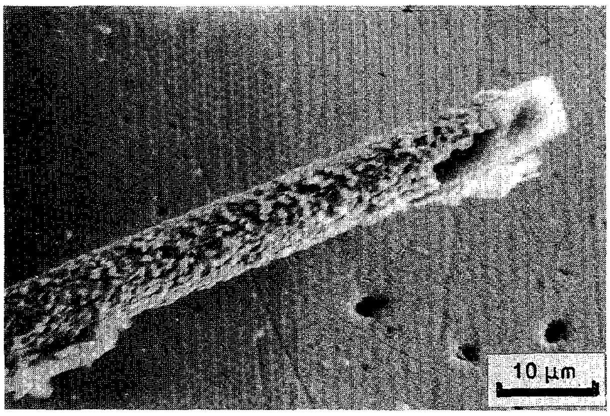

Figure 9 Fracture tip of a cementation copper-coated carbon fibre.

Typical microsections of the composite prepared with uncoated carbon fibres dispersed in aluminium (Fig. 10) showed fibre matrix interactions. Reaction products were observed almost at the entire interface. To facilitate wetting and to reduce the agglomeration, about 2 wt % Mg was added to the melt prior to dispersion of the fibres. In addition to the reaction products at the interface, Mg_2Si and silicon precipitates were found at the interface. The microsection of the composites prepared by electroless copper-coated carbon fibres (Fig. 11a) showed agglomerate-free random

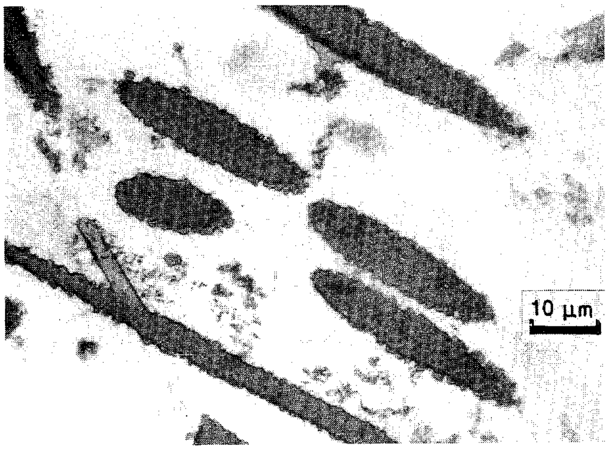

Figure 10 Microstructure of an uncoated carbon fibre dispersed in an aluminium matrix composite. Fibre–matrix interaction is seen.

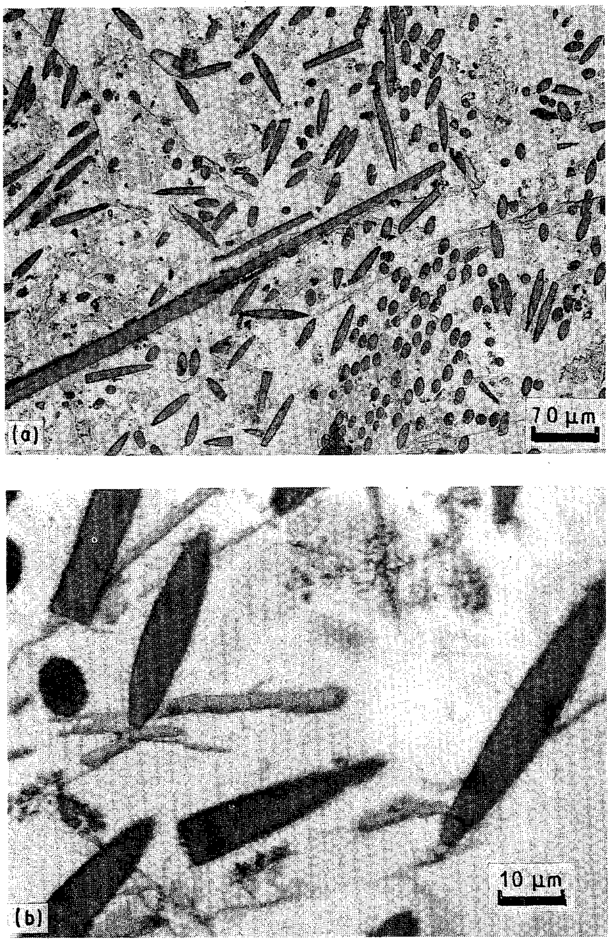

Figure 11 Microstructure of electroless copper-coated carbon fibre dispersed in an aluminium matrix: (a) distribution of carbon fibre and $CuAl_2$ phase in the matrix, (b) typical fibre/matrix interface.

distribution of the fibres in the matrix with fine $CuAl_2$ precipitate in the matrix. The interface did not show (Fig. 11b) appreciable amounts of the reaction products or significant amounts of $CuAl_2$ phase. The addition of 2 wt% Mg to the matrix did not appreciably change the distribution pattern of the carbon fibres (Fig. 12a) or overall microstructure. At higher magnifications, the concentration of Mg_2Si phase is seen at the fibre matrix interface (Fig. 12b). The morphology of the silicon phase has also not been affected much. The silicon is an impurity (up to 0.2 wt %) in the matrix aluminium. The microstructure of the composites prepared using cementation copper-coated carbon fibres (Fig. 13a and b) is similar to that of the composite prepared using electroless-coated fibres with and without magnesium addition. Uniform and random distribution of the carbon fibres in the matrix are observed (Fig. 13a). At higher magnifications, $CuAl_2$ and Mg_2Si phases are observed at the fibre/matrix interface (Fig. 13b). In some places, silicon needles in coarse form are observed.

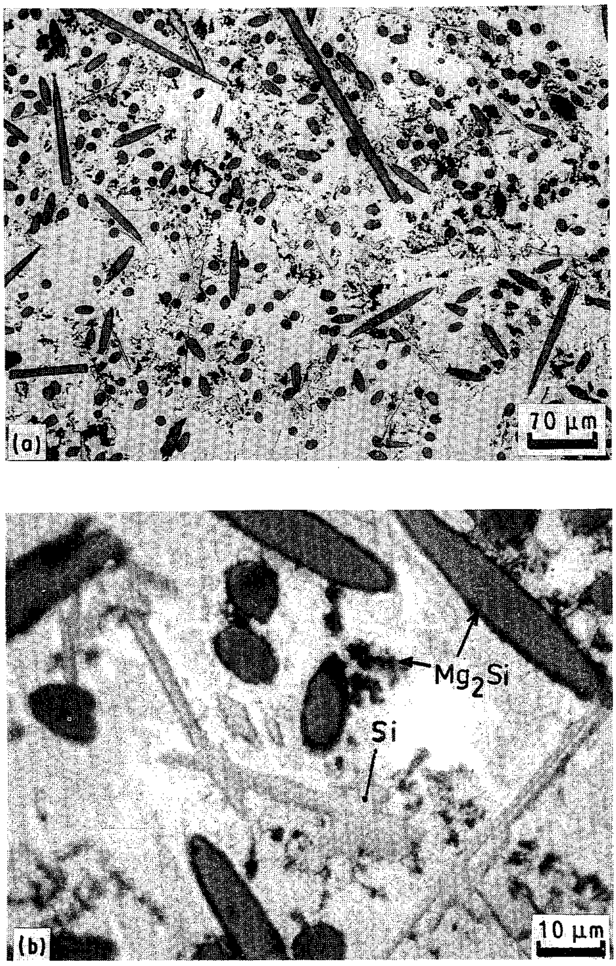

Figure 12 Microstructure of electroless copper-coated carbon fibre dispersed in an aluminium + 2 wt % Mg matrix: (a) distribution of the carbon fibre, $CuAl_2$ and Mg_2Si phases in the matrix, (b) typical fibre/matrix interface at higher magnifications.

The semiqualitative analysis of the distribution of $CuAl_2$ phase and Mg_2Si phases in the composites showed that their concentration was higher in the matrix (Figs 11a, 12a and 13a) than near the fibre/matrix interface. The coating process does not seem to have any effect on the morphology of $CuAl_2$ precipitation in the composites in the present investigation. From the overall comparison of the microstructures of the composites prepared using nickel-coated [5] carbon fibres and copper-coated carbon fibres in the present investigation, it can be said that in copper-coated fibre-dispersed composites, the majority of the $CuAl_2$ phase formed is distributed in the matrix and a very small amount is found near the fibre/matrix

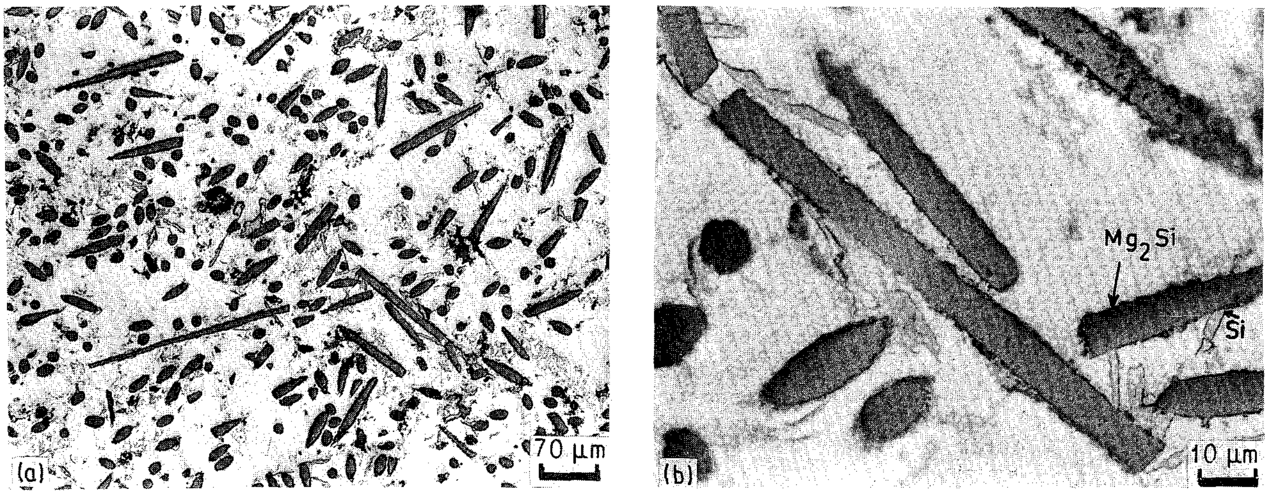

Figure 13 Microstructure of cementation copper-coated carbon fibre dispersed in an aluminium + 2 wt % Mg matrix: (a) distribution of the carbon fibre and other phases in the matrix, (b) typical fibre/matrix interface at higher magnifications.

interface. In nickel-coated fibres [5] the reverse observations are made. The $NiAl_3$ phase seems to embed carbon fibre in many places and such structures are not observed with $CuAl_2$ phase. This was attributed to the bonding between the fibre and nickel deposited [5]. The fluid flow present during synthesis plays a dominant role on the distribution of the intermetallics in the composites. On the other hand, the viscosity of the composite melt reduces the fluid flow in between the fibres, and higher thermal conductivity of the fibres compared to the matrix metal; the interface will be the last part to solidify. In the process, the concentration of the last eutectic phase to be solidified will be greater near the interface.

The present results indicate that the copper coating over the fibres prior to dispersion facilitates easy dispersion of the fibres in molten aluminium. The copper coating reduces the interaction between the fibre and the matrix. The $CuAl_2$ intermetallics formed become dispersed in the matrix readily, due to the high fluid flow. A small percentage of the $CuAl_2$ phase present at the fibre/matrix interface could be due to the high viscosity of the composite melt, especially in the interfibre regions and also due to the lower thermal diffusivity of the carbon fibres which makes the last solidifying region approach the interface and in the process the intermetallics will be pushed into that region. The addition of magnesium to the melt give rise to Mg_2Si phase precipitate which is found to behave like the silicon phase.

To prepare high-strength composites, generally 15–20 wt % carbon fibre addition is required. Under the present experimental observations, the addition of copper-coated fibres to aluminium may not be practically very attractive to obtain high carbon content composites because the copper metal introduced into the matrix through the coating is in a similar amount to that of the weight per cent of the carbon fibre introduced. The weight of an 0.4 μm thick copper coating over 7 μm diameter fibre is almost equal to the weight of equivalent fibre. Hence it is essential to have much thinner coating of copper over the carbon fibre to take advantage of effective coating during introduction, and at the same time the copper content in the matrix should be within a specific range so that the alloy can be made heat treatable for further improving the mechanical properties. Continuous coatings less than 0.2 μm thick do not seem to be possible using the present techniques.

4. Conclusions

1. A uniform and continuous coating of copper was given to carbon fibres using cementation or electroless plating techniques. The coating thickness ranged between 0.2 and 0.9 μm, in electroless coating and between 0.2 and 1.1 μm in cementation coating. For thicknesses below 0.2 μm, the coatings were discontinuous in both cases. In the electroless process, 75% of the fibres had a continuous coating of thickness between 0.2 and 0.5 μm, above which isolated dendritic growth was observed. In the cementation process, about 75% of the coated fibres were in the 0.2–0.6 μm coating thickness range and above this thickness, a fine crystallite-type deposition of copper was found over the continuously coated copper.

2. In electroless-coated fibres, the ultimate tensile strength properties were not reduced after coating, suggesting that the coating has a strength equivalent to that of the fibre, whereas in the cementation process, the coated fibres exhibited lower UTS values. In these cases coatings were microscopically discontinuous and were defective.

3. Under tension, load delamination of the coating from the fibre surface was observed, suggesting poor interfacial bonding between the fibre and coating in both processes.

4. In composites prepared using the coated fibres, fibre–matrix interaction was reduced to a greater extent. The precipitation of $CuAl_2$ phase was largely observed in the matrix and only small amounts were seen precipitated at the fibre/matrix interface. Additions of 2 wt % Mg metal to the matrix prior to dispersion did not affect the distribution of the coated

fibre, but Mg_2Si phase precipitation at the matrix, as well as at the fibre/matrix interface along with $CuAl_2$, was observed.

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