JOURNAL OF MATERIALS SCIENCE **25** (1990) 2839–2845

Studies on nickel coated carbon fibres and their composites

SUSAN ABRAHAM*, B. C. PAI*, K. G. SATYANARAYANA*, V. K. VAIDYAN†
**Regional Research Laboratory, Trivandrum 695019, India.*
†Dept. of Physics, University of Kerala, Trivandrum 695581, India.

Uniform and continuous coating of nickel was given to the carbon fibres by cementation, electroless or electroplating techniques. The coating thickness was ranged between 0.2 and 0.6 μm for all the three methods used. Coating thickness less than 0.2 μm showed discontinuous coating of nickel over the fibre surface. Beyond 0.6 μm thickness, nickel deposited in dendrite form over the continuous coating. For continuously coated fibres, the ultimate tensile properties of electroless coated fibres were near to uncoated carbon fibres suggesting adherent and defect free coating; while fibres coated by electrolytic and cementation process exhibited lower ultimate tensile strength (UTS) properties. The tensile fracture of the cementation coated fibres suggested degradation of the fibres. In composites, prepared by dispersing the coated fibres in pure aluminium matrix, no appreciable fibre-metal interaction was observed. $NiAl_3$ intermetallics were observed around and adjacent to the carbon fibres. Sometimes carbon fibres were found embedded in massive $NiAl_3$ intermetallics suggesting that fibre surface can also act as nucleating centre for these precipitates.

1. Introduction

In metal matrix composites (MMC) interface between the dispersoids and the matrix largely controls their performance. The chemical reaction between the dispersoids and the matrix at the interface during synthesis of the composite or during service conditions affects its performance irrespective of synthesising route adopted. Similarly the non-wetting of the dispersoids with the matrix can also lower the performance of the composite as a result of discontinuity at the interface [1]. To overcome these problems, the surface of the dispersoids is coated by a refractory material which is non-reactive both with dispersoid and the matrix, e.g. Titanium boride coatings or SiC coatings over carbon fibres [2]. This prevents chemical reaction and simultaneously improves wetting with the matrix. However, these types of coatings are very expensive. The metallic coatings to the surface of dispersoids such as nickel [3] and copper [4] are also found to be effective in improving the wetting with the matrix aluminium alloys. In these cases the coatings dissolve in the matrix alloy during synthesis to give precipitation of brittle intermetallics e.g. $NiAl_3$, $CuAl_2$ adjacent to the carbon fibre. It is reported [5] that $NiAl_3$ precipitate linked the fibre surface with the matrix. During secondary processing such linkages are found to break, thus lowering the mechanical properties. It is also possible that metallic coatings which form intermetallic with the matrix alloy can also form intermetallics with the alloying elements present in the matrix alloy, depending upon the energetics [6], giving both beneficial or deleterious effects. In all cases the morphology of the coating structure, thickness of the coating and nature of the coating namely adhesion and bonding with the dispersoid surface, are likely to play a significant role.

In this paper an attempt has been made to understand some of the above factors in the carbon fibre – aluminium system with nickel coating. Carbon fibres were coated with nickel using cementation [7, 8] electroless [9] and electro-plating [10] techniques. The morphology of the coatings structures and nature of the bonding between the fibres and coating are evaluated observing the tensile fracture of the fibres under the scanning electron microscope (SEM). The coated fibres were dispersed in pure aluminium matrix and the microstructure of the composites were evaluated by optical metallographic technique.

2. Experimental details

Grafil XA-S standard grade carbon fibres both in chopped and continuous form were used in the present investigations. First, the fibres were heat cleaned at about 973 K for 10 min. This step removes finish and sizing treatment [8]. The fibres were then coated with nickel using cementation, electroless or the electroplating techniques described below.

2.1. Cementation method

The detailed procedures used for this process are described earlier [7, 8]. The heat cleaned fibres were first treated with ≈ 4 vol % glacial acetic acid for activating the surface prior to coating. Nickel was deposited over the fibres from a $NiSO_4$ bath using magnesium as a displacing agent. Experimental conditions were adjusted to get continuous, uniform coating of Ni over the fibres.

0022-2461/90 $03.00 + .12

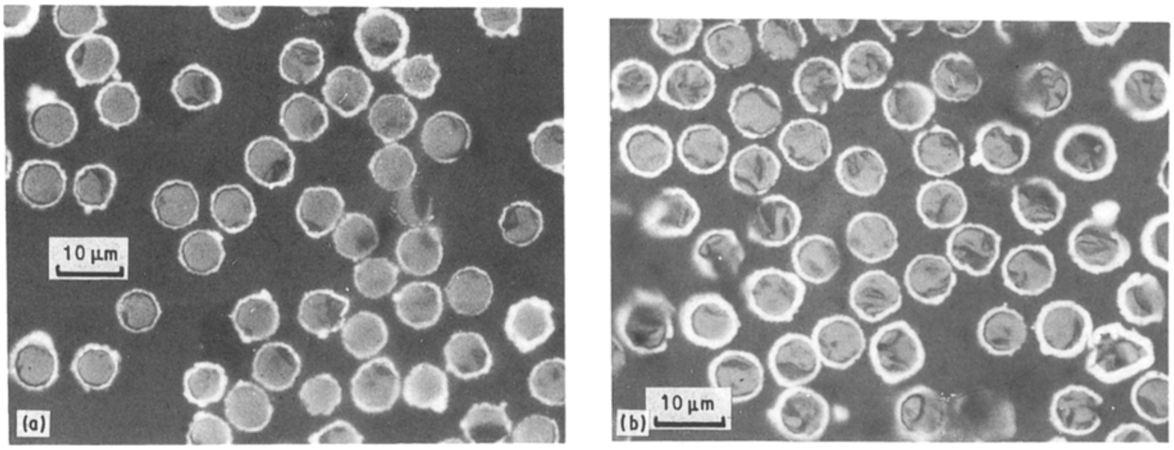

Figure 1 Cross section of nickel coated carbon fibres by (*a*) cementation method, (*b*) Electroless method.

2.2. Electroless depositions [9]

The heat cleaned fibres were subjected to ultrasonic vibration to activate the surface. The fibres were dipped in nickel chloride solution with sodium hypophosphite as a reducing agent. Ammonium chloride and sodium citrate were used as buffering agents to maintain the pH between 9 and 10. The bath temperature was kept between 358 K and 363 K. Experimental conditions were adjusted to get continuous thin coating of nickel over the fibre surface.

2.3. Electrolytic coating [10]

Nickel coating was obtained over heat cleaned carbon fibres from $NiSO_4$ bath at pH 1. The coating temperature used was about 328 K. In order to get a continuous thin coating of nickel over the fibre the coating was carried out for 15 min at 9 V and 9 A current levels.

The coated fibres were mounted in cold setting resin and cross-sectioned. Under the optical microscope the continuity and thickness of the coatings were determined. The morphology of the coating structure was evaluated observing the fibres under SEM.

Individual fibres under different conditions were pulled under universal testing machine (INSTRON) to measure the tensile properties. All tensile properties were measured at 50 mm gauge length of the fibres. The tensile fracture of the fibres was observed under the scanning electron microscope. About 5 wt % both coated and uncoated fibres were dispersed in pure aluminium metal matrix by stirring the molten metal at around 1013 ± 10 K using a mechanical impeller and then introducing the fibre into the vortex. After the completion of dispersions the composite melt was stirred for another 10 min and then solidified. The microstructure of the composite were examined.

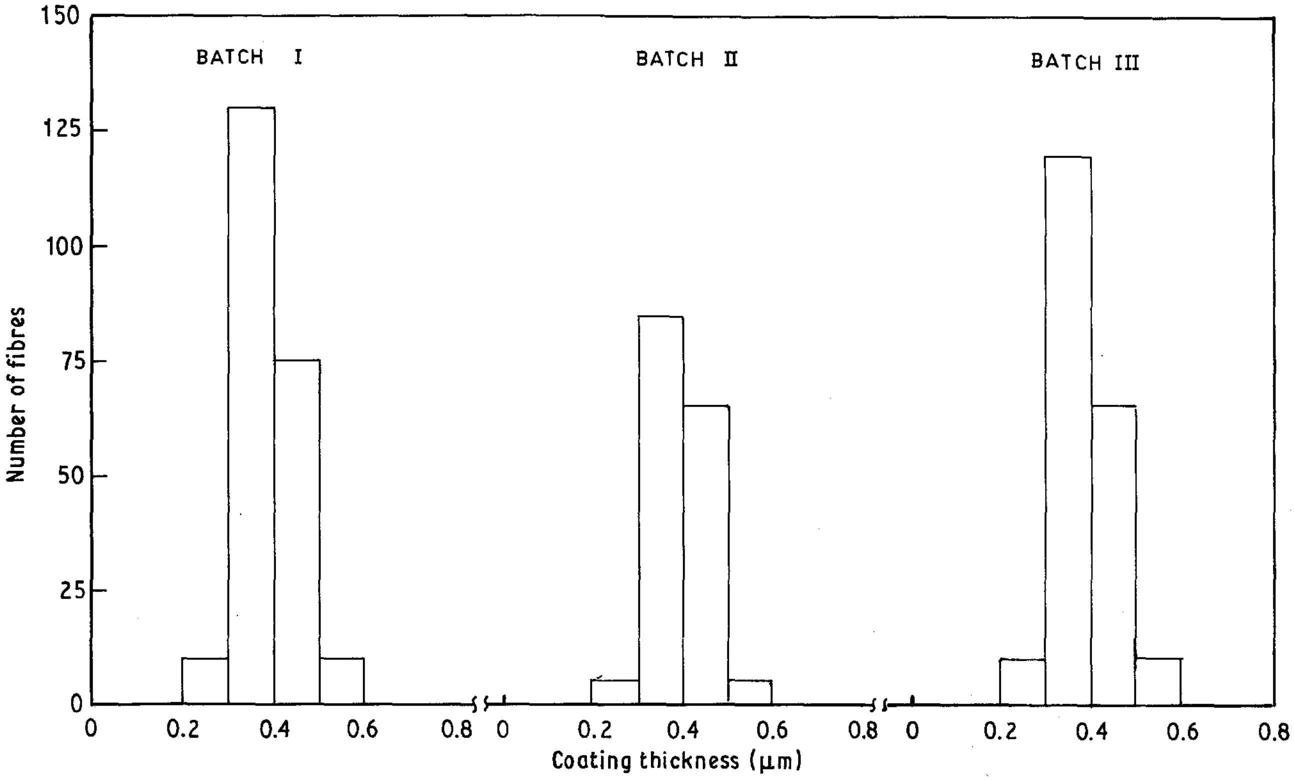

Figure 2 Typical variation in the coating thickness as a function of number of fibres for three batches of fibres coated by cementation method.

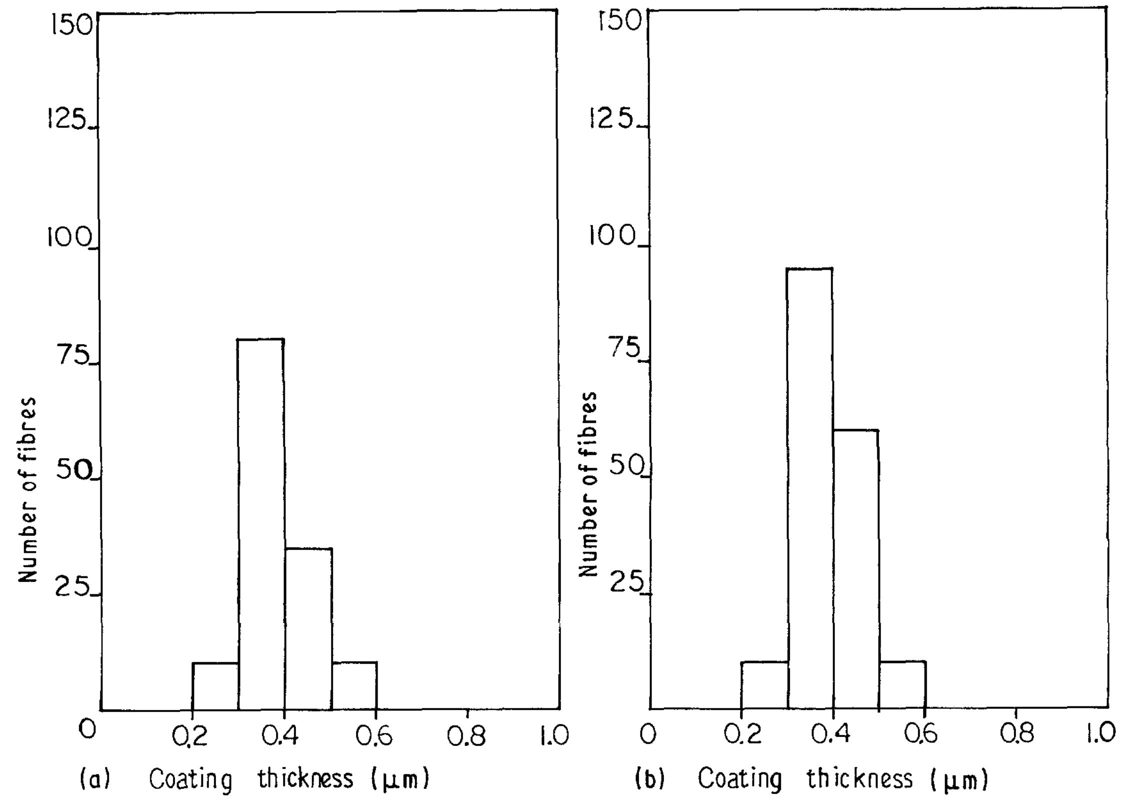

Figure 3 Variation in the coating thickness as a function of number of fibres coated by (a) electroless method, (b) electroplating technique.

3. Results and discussion

3.1. Coating thickness distribution and mechanism

Typical cross-sections of nickel coated carbon fibres by cementation and electroless methods, mounted in resin are shown in Figs 1a and b. Electroplated fibres have also showed similar coating behaviour. In all the three methods, the coating thickness is uniform throughout the circumferences of the fibres. In a tow of 6 000 fibres more than 95% of them were uniformly coated. The typical histograms in Fig. 2 show the variation in the coating thicknesses as a function of number of fibres for three batches in cementation process. Similarly Figs 3a and b are histograms obtained for electroless and electro-plating methods respectively. These results also indicate in all the three coating processes the coating thickness was ranged between 0.2 to 0.6 μm. Majority of the fibres ($\approx 60\%$ of the total) had coating thickness between 0.30 to 0.40 μm followed by ($\approx 30\%$ of the fibres) the coating thickness ranged between 0.40 to 0.50 μm. It is found at lower coating thicknesses, $< 0.2\,\mu$m the coatings were partial (Fig. 4) and at higher coating thicknesses, $> 0.6\,\mu$m dendrite type nickel growth over already continuous coated surface (Fig. 5) was observed.

The microscopic examinations of the coatings suggests that nickel first deposits on the fibre surface at energetically favoured sites to a thickness of about 0.2 μm. Then coating spreads over the fibre surface without appreciably increasing its thickness. By the time the entire surface of the fibre gets covered by nickel, the thickness was marginally increased to about 0.30 to 0.60 μm max (Fig. 6). Dendritic type growth normally seems to take place after entire coating of the fibre surface. The dendritic type growth (Fig. 5) contains only nickel confirmed by EDAX analysis. These results clearly suggest that for all the three coating processes investigated it is not possible to coat the entire fibre surface with less than 0.2 μm thickness of nickel, and above 0.6 μm coating

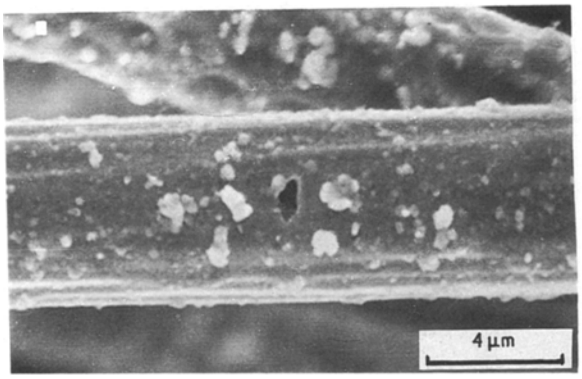

Figure 4 Partially coated carbon fibre, thickness of the Ni coating about 0.2 μm.

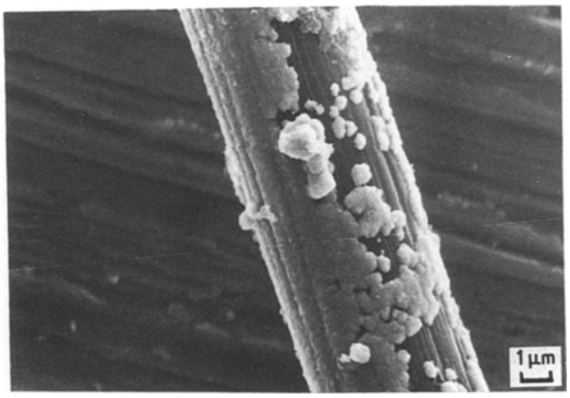

Figure 5 Fully coated carbon fibre thickness of the Ni coating about 0.6 μm. Dendritic type precipitations are seen.

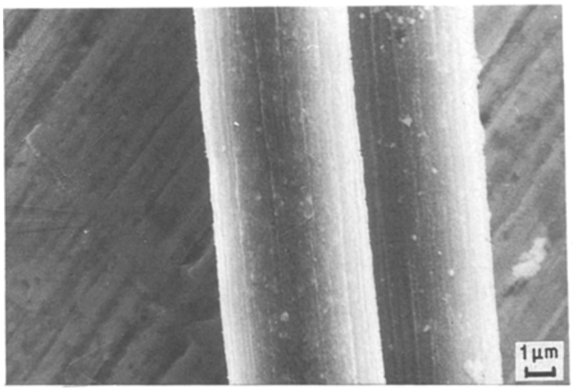

Figure 6 Completely coated carbon fibre, thickness of the coating about 0.4 μm.

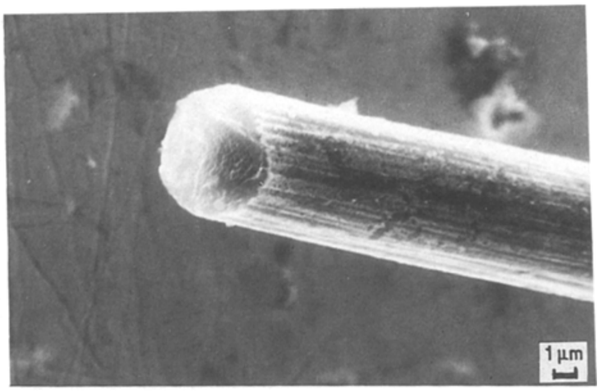

Figure 8 Fractured tip of nickel coated carbon fibre by cementation process.

thickness stray deposit in the form of dendrites build-ups.

Thus the mechanism of coating is first, deposition of nickel over energetically favoured sites, followed by the bridging of these sites covering the entire surface of the fibre.

3.2. Mechanical properties

Thus ultimate tensile properties of the fibres uncoated, treated and coated were evaluated by conducting single fibre tests. The UTS of the carbon fibre in the as received condition was found to be between 2.6–3.2 GPa against 3.00 GPa given by the manufacturers. (Hysol-Grafil). The heat treated carbon fibres (973 K for 10 min in air) did not show any deterioration in the mechanical properties. Fibres coated by cementation process gave UTS properties between 1.5–1.81 GPa for coating thickness ranged between 0.2–0.4 μm. For electrolytically coated fibres the UTS was ranged between 1.5–2.25 GPa for coating thicknesses ranged between 0.30–0.4 μm. For electroless method the UTS was ranged between 2.4 GPa–3.00 GPa for the coating thicknesses ranged between 0.29–0.34 μm. These results suggest that in the electroless method defects in coating are less compared to other two methods. The microstructure examination also confirms this. The mechanical properties are lower because the coatings have increased the cross-section but not contributed to the strength.

3.2.1. Fracture mode

The uncoated carbon fibres exhibited brittle fracture (Fig. 7) under tension. Fibres coated by cementation process exhibited cup and cone type fracture (Fig. 8) consistently. Electrolytic coated fibres exhibited brittle type fracture (Fig. 9) like uncoated fibres. Electroless coated fibres also exhibited brittle fracture but the fracture mode is slightly different from the uncoated fibre (Fig. 10). From the studies on the fracture modes and mechanical property evaluation of coated fibres it is clearly seen that during cementation process the coating has interacted with the fibre surface reducing its strength. In the electrolytic coated fibres, surface defects are evident (Fig. 9), hence the coating probably does not contribute to the strength. At the same time fibre surface is not affected by the coating. Similar observations are made with electroless coated fibres also. However in electroless coated fibres no defects are seen over the coatings (Fig. 10). Hence higher strength properties are observed with these.

3.3. Composites

A typical microsection of composite (≈ 5 wt % uncoated carbon fibre dispersed in aluminium) Figs 11a and b shows uniform distribution of carbon fibre in the matrix. The carbon fibre seems to have undergone chemical reaction (Fig. 11b) with the matrix. The traces of Si and Fe present in the matrix have randomly precipitated in the matrix. The composite prepared using nickel coated carbon fibre by cementation process (Fig. 12a) showed well the distribution of the carbon fibres. $NiAl_3$ and Si are precipitated adjacent to the carbon fibres and the fibre surface seemed to act

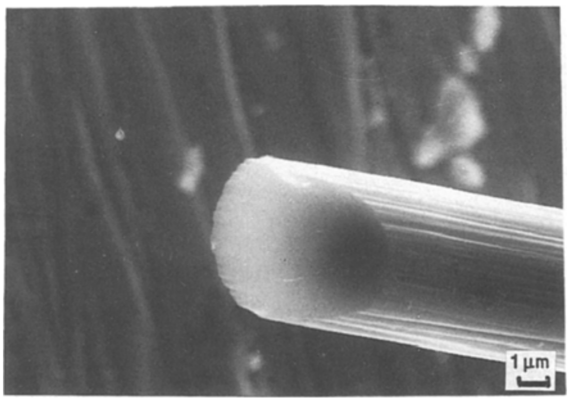

Figure 7 Fracture tip of uncoated carbon fibre.

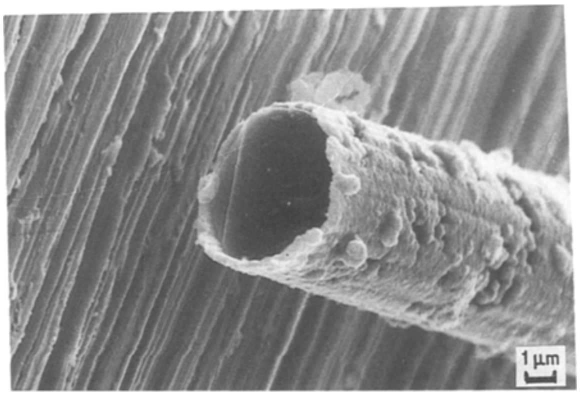

Figure 9 Fractured tip of nickel coated carbon fibre by electroplating technique.

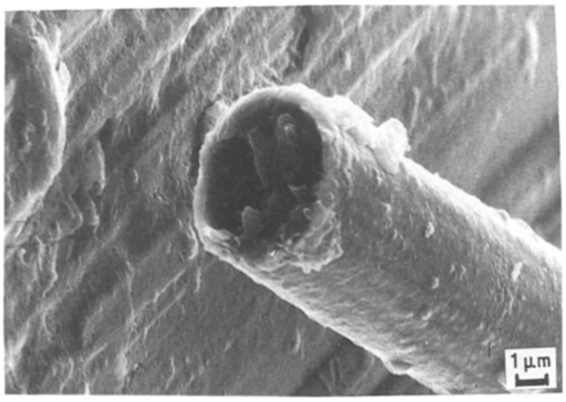

Figure 10 Fractured tip of nickel coated carbon fibre by electroless plating technique.

as nucleation centres for these phases. The composites made out of carbon fibres with electrolytic nickel coating also showed similar distribution of carbon fibres (Fig. 13). However the carbon fibres are linked with massive $NiAl_3$ precipitates. The composite made with electroless nickel coated carbon fibres (Fig. 14) also showed fairly equal distribution of carbon fibres in the matrix with massive $NiAl_3$, Si and iron aluminium intermetallics. The intermetallics have well covered the carbon fibres (Fig. 14), suggesting that the fibre surface might have been acting as nucleating centre.

In all cases the important microstructural feature of these composites are carbon fibres which are well distributed in the aluminium matrix. With uncoated carbon fibres (heat treated prior to dispersion), matrix/fibre interaction (Fig. 11b) is clearly visible. But with cases of nickel coated carbon fibres no fibre matrix interaction is visible under the used magnifications (1000 ×). The formation of $NiAl_3$ intermetallics with the matrix during introduction probably prevents the interaction between fibre and the matrix. After complete addition of the fibres the melt has been stirred for about 10 min. During this period the formed $NiAl_3$ has every chance to get detached from the fibre surface and to get dispersed in the matrix because of the strong fluid flow conditions. These separated intermetallics can reprecipitate during solidification into massive phases. Besides, during coating, nickel must have been interacted with the carbon fibre surface, probably forming some kind of chemical bond which could not have been disrupted by the fluid flow. This probably can give localised $NiAl_3$ bonding with the fibre surface and these isolated $NiAl_3$ phases can be a nucleation centre for $NiAl_3$ phases during solidification of the composites. Thus the observed massive precipitation of $NiAl_3$ embedding the carbon fibres as well as isolated precipitation of $NiAl_3$ at carbon fibre surface can be explained.

The results also suggest that Ni coating over the carbon fibre can play a dual role, first it can prevent the molten aluminium coming into direct contact with carbon thus the fibre matrix interaction can be eliminated. Secondly, if the formation of $NiAl_3$ is controlled a coherent interface bonding should be possible between the matrix and the fibre. However, it is essential to reduce the free precipitation of $NiAl_3$ in the matrix which normally gives brittleness to the composite. A very thin layer (monolayer) of nickel over the fibre surface will be ideal, but, using the present three methods of coating it may not be possible to coat less than 0.2 μm thick nickel. The morphology of the coating is likely to play an important role on the interface and mechanical properties of the composites which are being investigated now.

4. Conclusion

1. Uniform and continuous coating of nickel was given to carbon fibres using cementation, electroless or electroplating techniques. Irrespective of

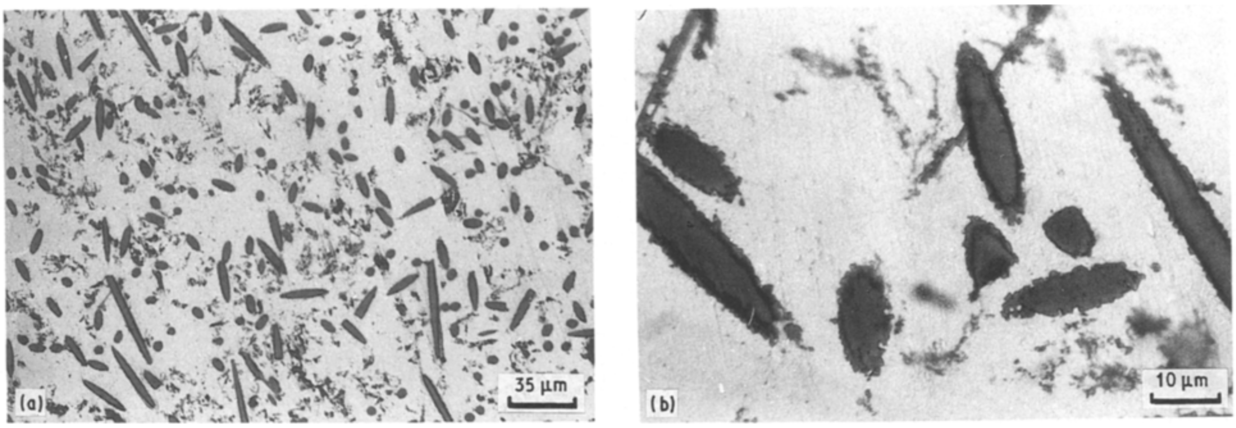

Figure 11 Microstructure of composite, uncoated carbon fibres dispersed in aluminium matrix, (*a*) showing the fibre distribution, (*b*) the interaction between the fibre and the matrix is evident.

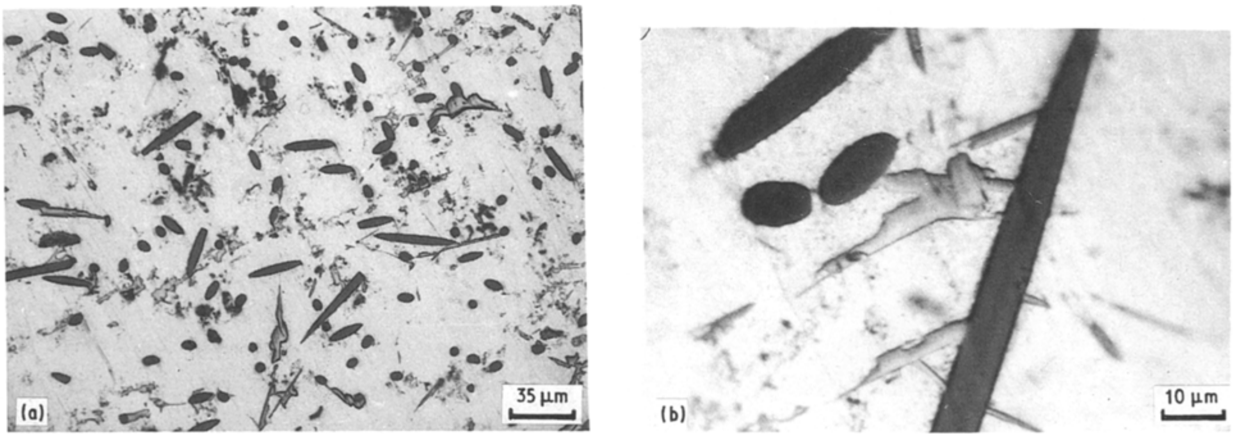

Figure 12 Microstructure of the composite, nickel coated carbon fibre by cementation process dispersed in aluminium, (*a*) showing the fibre distribution, (*b*) interaction of $NiAl_3$ with the carbon fibre.

the methods used the coating thickness was ranged between 0.2–0.6 μm. Thickness below 0.2 μm coating was discontinuous and above 0.6 μm dendrite type growth was observed over the continuously coated fibre surface. The mechanism of coating seems to be first deposition of nickel at energetically favoured sites at a thickness in the order of 0.2 μm and a subsequent bridging of these deposits to cover the entire surface of the fibre.

Figure 13 Microstructure of the composite, nickel coated carbon fibres by electrolytic method dispersed in aluminium matrix.

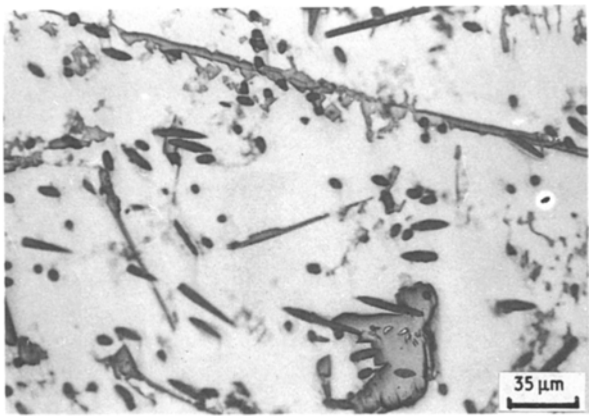

Figure 14 Microstructure of the composite, nickel coated carbon fibres by electroless method dispersed in aluminium matrix.

2. Among the coating methods investigated electroless method gave best results, giving ultimate tensile properties of coated fibres near to that of uncoated fibres, whereas fibres coated by electrolytic and cementation process exhibited lower tensile properties compared to uncoated fibres.

3. Under tension loads, cementation process coated fibres exhibited cup and cone type fracture, whereas uncoated, electroplated and electroless plated fibres exhibited brittle fracture.

4. The composite prepared using uncoated carbon fibres showed fibre/matrix interaction at the interface, whereas with nickel coated carbon fibre composites fibre matrix interaction was not observed. The formation of $NiAl_3$ intermetallic seemed to prevent the interaction. At some places the carbon fibres were found embedded in massive $NiAl_3$ phase and $NiAl_3$ was also found to be surrounding the fibre, suggesting that the fibre surface is nucleation centre to $NiAl_3$ precipitates.

Acknowledgement

The authors wish to acknowledge the help of Mr. S. G. K. Pillai for optical metallography work, Mr. Peter Koshy and Mr. Prabhakar Rao for SEM work, Mr. P. Vijayakumar for photography, Mr. K. Sukumaran and Mr. K. K. Ravikumar for mechanical testing of fibres, members of the composite group for their help during experimental work, Dr. A. D. Damodaran, Director, Regional Research Laboratory, Trivandrum, for his encouragement and AR & DB for funding the project at initial stages of the work.

References

1. A. G. METCALFE, in "Composite Materials – Vol. 1, Interfaces in metal matrix composites", edited by L. J. Broutman and R. H. Krock, (Academic Press, New York, London, 1974) pp. 1–30.
2. E. A. FEEST, M. J. BALL, A. R. BEGG and A. A. BIGGS, Metal matrix composites developments in Japan – Report on OSTEM Visit to Japan, Oct. 1986, Harwell Technology for Industry.
3. F. A. BADIA and P. K. ROHATGI, *AFS Transactions*, **77** (1969) 402–406.
4. B. C. PAI and P. K. ROHATGI, *Trans. IIM* **27** (1974) 97–101.

5. I. W. HALL, *Metallography* **20** (2) (1987) 237–246.
6. F. DELANNAY, L. FROYEN and A. DERUY HERE, *J. Mater. Sci.,* **22** (1987) 1.
7. B. C. PAI and P. K. ROHATGI, *Mater. Sci. & Engng* **21** (1975) 161.
8. B. C. PAI, A. G. KULKARNI and N. BALASUBRAMANIAN, *J. Mater. Sci.* **14** (1979) 592–598.
9. S. F. SMITH, *Metal Finishing* **77** No. 5 (1979), 60–62.
10. A. M. POSKANZER, *Plating* **67** No. 4 (1980), 38–40.

Received 20 March
and accepted 13 September 1989