2. P. H. HERMANS, "Physics and Chemistry of Cellulose fibres" (Elsevier, New York, 1949).
3. E. OTT, M. SPURLIN and W. GRAFFLIN, "Cellulose and Cellulose derivatives" (Interscience, New York, London, 1954).
4. P. S. MUKHERJEE, A. K. DE and S. BATTACHERJEE *J. Mater. Sci.* **13** (1978) 1329.
5. P. S. MUKHERJEE and G. B. MITRA.

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Coating structure of metal-coated carbon fibres

Applications of coated fibres in preparation of metal matrix composites are growing at an increasing rate. To obtain a good composite the fibre should be wetted by the matrix to ensure good bonding. A coating on carbon fibre can promote this wetting by the matrix material and also helps in preventing surface damage during composite fabrication. Details of the coating of Cu, Ni and Co on to carbon fibres by the cementation process were described earlier [1, 2]. A tow of 1000 filaments, 20 cm long carbon fibres (PAN base) were heat treated in vacuum (10^{-5} Torr) at 700° C for 15 min to remove any coupling agents and adsorbed layer of gases. Heat-treated carbon fibres were then treated in glacial acetic acid to activate the fibre surface.

These surface activated fibres were immersed in metal salt solutions of known amount and concentration. Displacing agents Zn for Cu coating and Mg for Co and Ni coating were added in the form of granules to displace the respective metals from their salt solutions by the cementation process. Coated fibres were tested individually in a universal testing machine (Instron). In each batch, 25 to 30 fibres were tested and average strength was computed. The present note reports the effect of the concentration of glacial acetic acid during coating on the structure of the coating formed on heat-treated carbon fibre as determined by scanning electron microscopy, and its effect on the strength of the coated fibre.

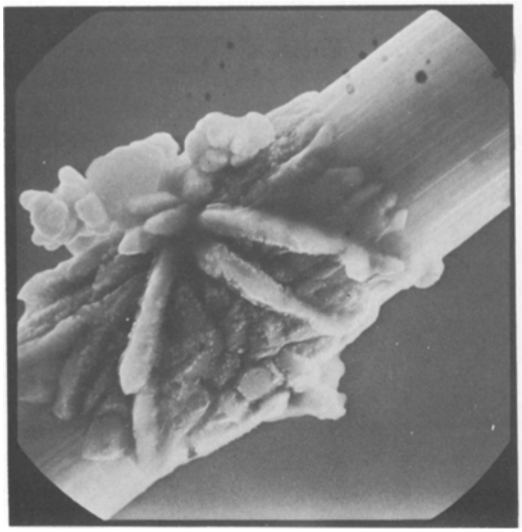

Figure 1 Isolated dendritic copper coating on non-heat-treated unactivated carbon fibre, × 4800.

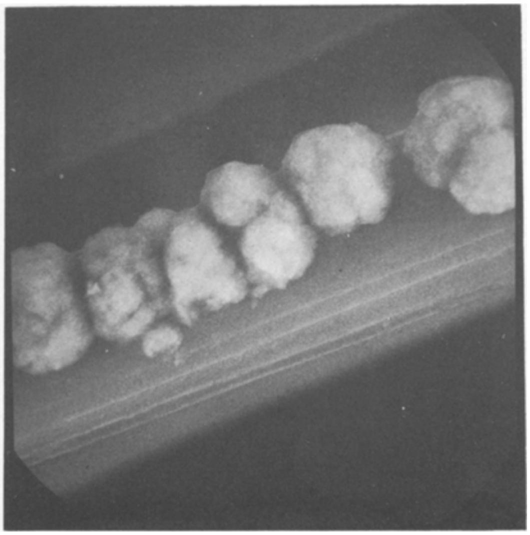

Figure 2 Isolated massive crystallite copper coating on carbon fibre, acetic acid concentration 2 vol%, × 4800.

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The observations show that copper coating takes place by bridging the isolated precipitates, but for Ni and Co the coating spreads uniformly over the fibre.

Copper coating: isolated patches of copper were deposited on non-heat-treated and unactivated carbon fibre. These patches were dendritic in structure (Fig. 1). Less than 2 vol% acetic acid in the coating bath gave isolated patches of copper coating on heat-treated carbon fibre, but the coating then comprised massive crystallites (bulbous or botriyords) (Fig. 2). Increasing the acetic acid concentration to 3.5 vol%, however, coated almost the entire surface of the fibres with these crystallites (Fig. 3). Additions of 5 vol.% acetic acid ensured that the crystallites grew fully (Fig. 4). No further build up of the coating was found to be possible under the experimental conditions. Increasing the acetic acid concentration to 6 to 7 vol% changed the massive crystallite structure to a dendritic form (Fig. 5). Further increases in concentration to 10 vol% gave finer and finer dendrites (Fig. 6). In the transition range (5 to 7 vol% acetic acid) both massive crystallites and dendrites formed simultaneously but on different individual fibres (Fig. 7).

It was reported earlier [3] that increasing the concentration of Cl^- ions in the bath during cementation of copper on aluminium discs changed the morphology of copper deposition from massive crystallites to dendritic. This transition was attributed to a change in the rate constant for the cementation reaction. In the present investigation, it is probable that up to 5 vol% acetic acid acts as a surface activator. The excess acid at higher concentration may change the rate constant of the cementation reaction. Generally the crystallite form was more adherent than the dendritic deposit.

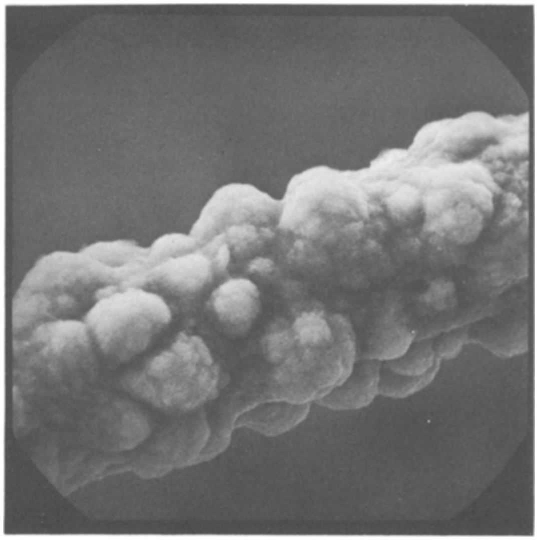

Figure 3 Massive crystallite copper coating on carbon fibre. Crystallites were not fully grown. Acetic acid concentration 3.5 vol%, × 4800.

Nickel and cobalt coating: cobalt and nickel behaved identically during coating. Untreated and unactivated carbon fibre would not take a nickel or cobalt coating. Small additions of glacial acetic acid (less than 1 vol%) resulted in isolated patches of coating. At sufficient [1] concentration of acetic acid (4 vol% for Ni and 2 vol% for Co), however, the coating was very thin, smooth and adherent. A coating of the order of 0.1 μm thick (Fig. 8) was obtained by controlling the time and other parameters as described earlier [1]. Further increase in acid concentration (greater than 4 vol% for Ni and greater than 2 vol% for Co) resulted in consumption of reducing agent (Mg) by the acetic acid. No noticeable change in deposition characteristics were observed by such an increase in acid concentration. Thick coatings of cobalt and nickel can be obtained simply by coating for a long interval of time.

Strength of the coated fibres: Fig. 9 shows the

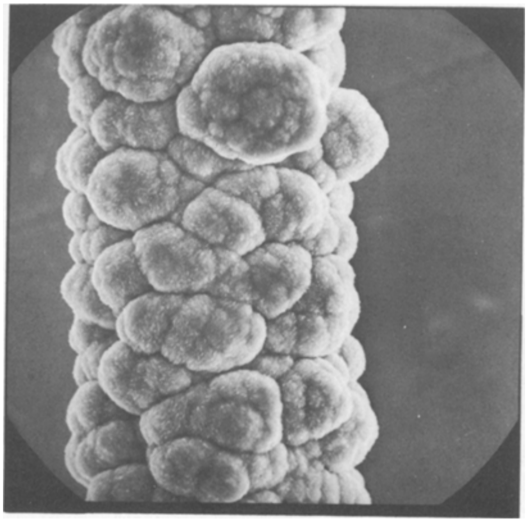

Figure 4 Fully grown massive crystallites of copper. Acetic acid concentration 4.5 vol%, × 2000.

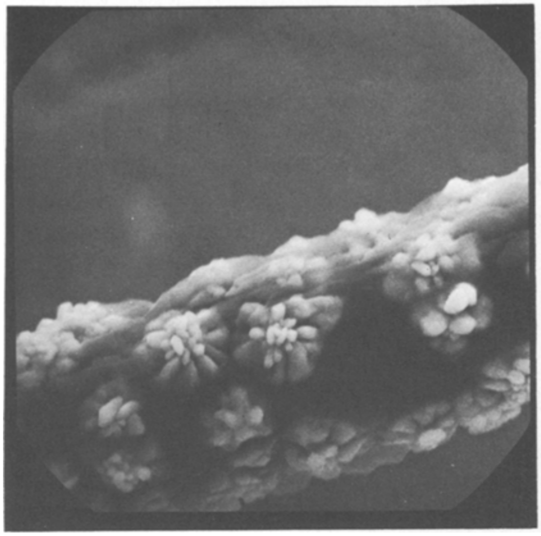

Figure 5 Dentritic-type copper coating on carbon fibres. Acetic acid concentration 6.5 vol%, × 4800.

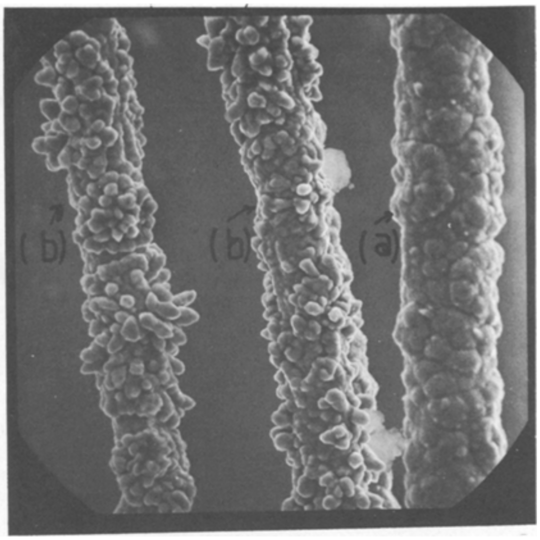

Figure 7 Crystalline- (a) and dendritic- (b) type coatings formed simultaneously on different fibres. Acetic acid concentration 6 vol%, × 1100.

ultimate strength of copper- (crystallite form), nickel- and cobalt-coated fibres as a function of coated carbon fibre diameter. For copper coating, the strength continuously decreased with increase in coated fibre diameter. It was obvious from the structure that copper coating took place by (i) nucleation of crystallites at isolated places on the fibre surface, (ii) growth of these nuclei bridging gaps in coverage to eventually cover the entire fibre surface. The copper coating is thus essentially an aggregate of many particles precipitated over the fibre surface. Bonding between particles may be poor so that the interface between them may separate very easily in tension and therefore the coating does not increase the strength. However, the coating did not reduce the virgin strength of the carbon fibre, since the breaking load remained practically the same in spite of the increase in diameter of the fibre by coating, which was thus quite suitable for composite preparation in the coated form.

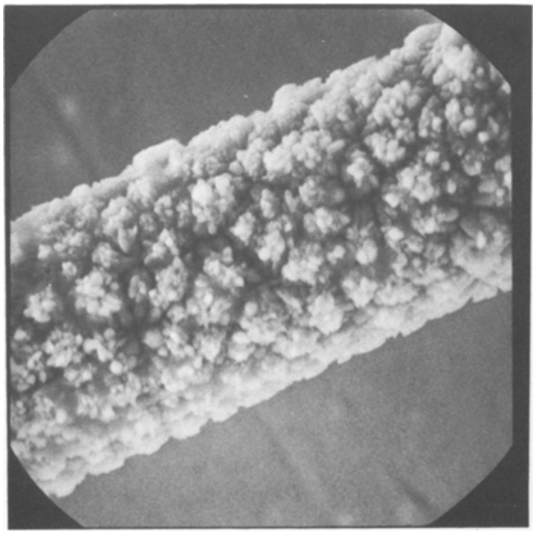

Figure 6 Fine dendritic-type copper coating on carbon fibres. Acetic acid concentration 8.0 vol%, × 4800.

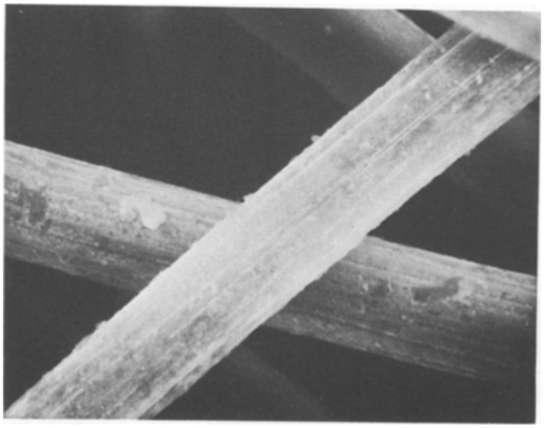

Figure 8 Cobalt-coated carbon fibre. Acetic acid concentration 2.5 vol%, × 2000.

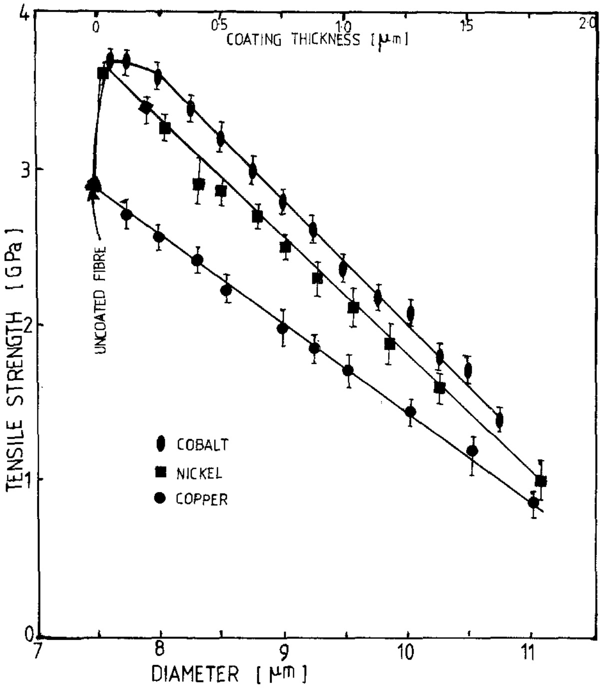

Figure 9 Plot of diameter of the coated carbon fibres versus ultimate tensile strength for copper, cobalt and nickel.

Nickel and cobalt coatings in contrast increased the coated fibre strength at small thickness of coating (Fig. 9). This may be due to the uniform nature of these coatings. At this stage the thin metal film may cover the surface defects of fibres, resulting in increased strength. However, further increase in the thickness of the coating might have developed internal stresses in the deposits. Hence the coating does not contribute to the strength. Thus the ultimate tensile strength of the Ni- and Co-coated fibres decreased (Fig. 9). However, Ni-coated carbon fibres were successfully introduced into an Al matrix and composites were prepared [1], thus showing the suitability of these coatings on carbon fibres in preparation of composites.

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References

1. A. G. KULKARNI, B. C. PAI and N. BALASUBRAMANIAN, *J. Mater. Sci.* **14** (1979) 592.
2. B. C. PAI and P. K. ROHATGI, *Mater. Sci. Eng.* **21** (1975) 161.
3. V. ANNAMALI, J. B. HISKEY and L. E. MURR, *Hydrometallurgy* 3 (1978) 163.

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