WETTABILITY OF COPPER COATED CARBON FIBERS

G. Carotenuto, A. Gallo, L. Nicolais, Department of Materials and Production Engineering.
University of Naples, Piazzale Tecchio - 80125 Napoli (Italy)

The wetting kinetics of a solid surface by a molten metal decrease with increase of its roughness. The topography of the growing copper coating, produced on carbon fiber surface by electroplating from a sulphat bath, has been studied by scanning electron microscopy. The smoothes surface is produced after 200÷300 milliampere-hour of plating.

1. INTRODUCTION

When aluminum reinforced with continuous carbon fibers is fabricated by liquid-phase methods a gradient of chemical potential exists at the ceramic/metal interface, which provides a driving force for a chemical reaction (1,2). This interaction influences the mechanical properties of the composites in a very obvious appearance (3,4), which is attributed to the formation of a brittle layer of aluminum carbide at interface between the metal and the carbon. In addition, the carbon fibers resist wetting when immersed in molten aluminum. Several methods have been investigated in order to fabricate metal-matrix composites to improve the bonding between the fiber and matrix, and to provide a diffusion barrier on the reinforcement surface. In 1976 Amateau (5) has suggested that CVD Ti-B coating is a very good method. However this method is complex, the efficiency is low, and the fabrication of composite parts is difficult. Improvement in the wettability between fiber and matrix without introducing the interfacial chemical reaction, can be obtained through the metal coating of fibers. This facilitates the penetration of molten metal into the fiber rows and prevents the interfacial reaction. Surface treatments for non-conductive fibers are usually complicate and with high cost; however with carbon fibers an easily way for the surface modification is the electrodeposition of a metal higher melting than aluminum, e.g. copper. The electroplating avoids mechanical damage of the fibers and results less expensive than other technologies. The copper can be used as metallic coating for carbon fibers in the fabrication of aluminum-carbon composites because it is non-reactive with carbon, scarcely soluble in molten aluminum, and moreover, interfacial phenomena, such as the intermetallics crystallizations, are negligible. The roughness of the surface of coating layer produced during the plating changes with the process time; this property influences significantly the wettability of the resulting modified fibers (6), and consequently it must be minimized. In the present communication the results of a topographic study on the growth behaviour of copper coatings on the surface of carbon fibers, from sulphate bath, is described. This analysis allows the individuation of the plating conditions necessary to produce the less rough surface that causes the best wettability of the fibers.

2. EXPERIMENTAL

For the present investigation, the reinforcement material used is a continuous 9μm diameter filament of carbon fiber, type EHNS (Grafil Courtaulds Carbon Reinforcement). Prior to use, fiber surfaces were cleaned of any organic substances by passing them through a furnace at 800°C containing a nitrogen atmosphere. The solution was prepared by adding copper sulphate to the water, at room temperature, under stirring, followed by sulphoric acid. All the chemicals were analytical grade and the solutions were prepared from distilled water. After each plating run the solution was filtred through glass wool, the anode was removed and tank and anode were thoroughly washed in water and acetone, and then dryed. The elecrolytic cell consisted of a 1000ml glass tanks placed in a thermostatic bath. High purity copper sheets (99.99%Cu) were used as anode material. The cathode used was a plexiglass frame (8cmx14cm) with two horizontal clampings to tighten the fibers. The upper clamping was in copper and it was keeped outside the solution during the plating run. The cathode surface was a 1cmx7cm plane roving with 200 carbon filaments. Each experiment was carried out with a freshly prepared cathode. All the plating experiments were performed at constant anodic current density of 90 Am^{-2}, obtained by a current generator (Mod. Stab-AR30), and the resulting voltages was low (0.6V). The morphology of the deposit was examined with the aid of a scanning electron microscope (HITACHI S-2300). The examinations, carried out at 25kV, were performed directly on the surface of samples produced at various stages of the bath life.

3. RESULTS

The results shown here were obtained from a set of copper deposits produced by one plating bath to which no further additions of chemicals were made throughout the bath life. The copper plating bath which was selected for this work was the bath developed for high penetrating electroplating, this for a complete coating of the fibers at the center of the tows. It consisted essentially of an acidic solution of copper sulphate. The nature of the growth process was investigated using a scanning electron microscope (SEM) to discover whether any change in morphology takes place with increasing of the bath life. Figures 1÷5 illustrate the growth morphology from the initial plating run and after 4, 20, 50, 300 and 600 milliampere-hour of plating, at a magnification of 1,000÷6,000x. In the initial stages, a high density of spherical crystals were growing on the surface of carbon fibers.

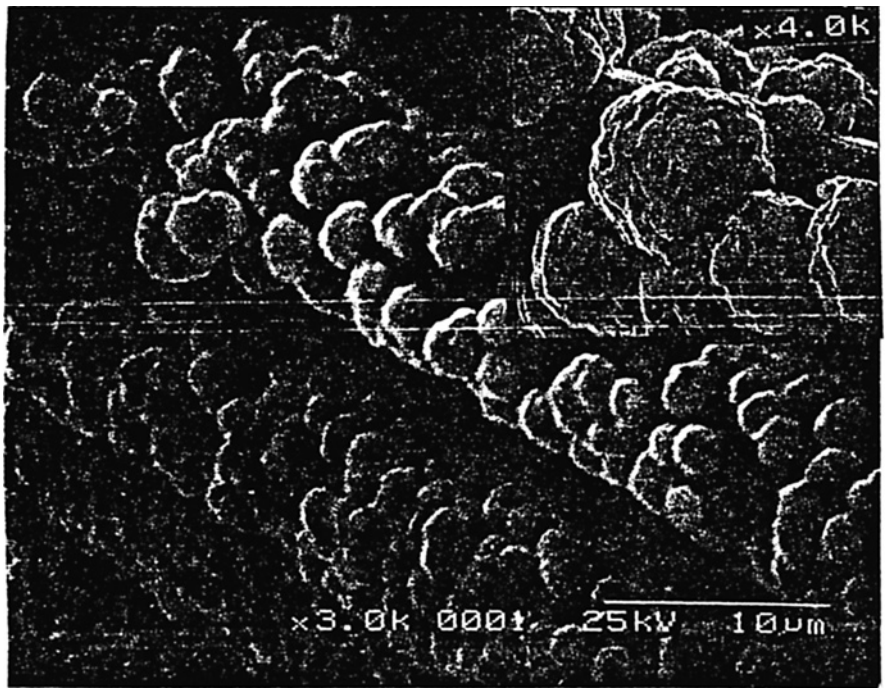

Fig. 1 - SEM photomicrograph showing the nature of the growth during the initial run of the bath (4 milliamper-hour).

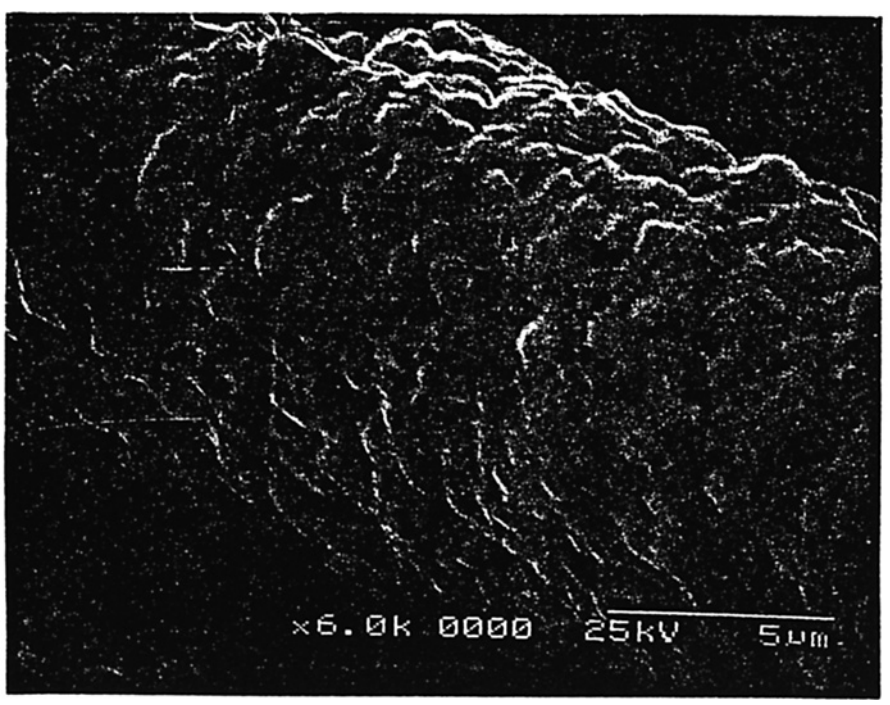

Fig. 2 - SEM photomicrograph of the growing copper layer on the carbon fiber surface after 20 milliampere-hour.

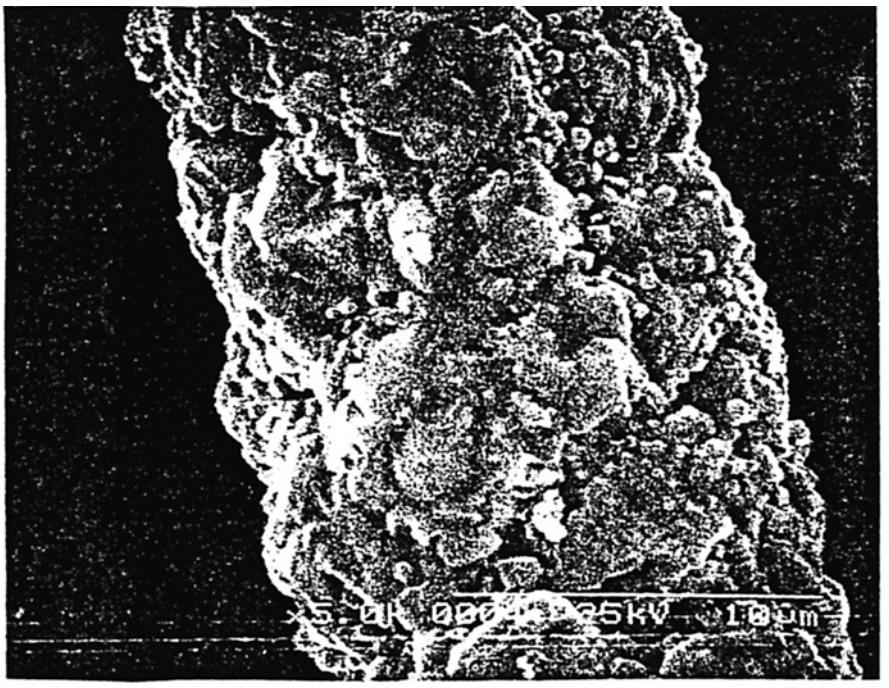

Fig. 3 - Secondary electron SEM micrograph of the fiber surface during the deposition (50 milliampere-hours). Pyramid and fine spherical crystals are visible.

Such a growth form changes within the first 50÷100 milliampere-hour of plating; for istance at 300 milliampere-hour a coarse pyramidal growth is taking place, and spherical crystals are not observed on the metal surface, see Figure 4. It is to be noted that there is a hint of hexagonal symmetry about the growing crystal facets.

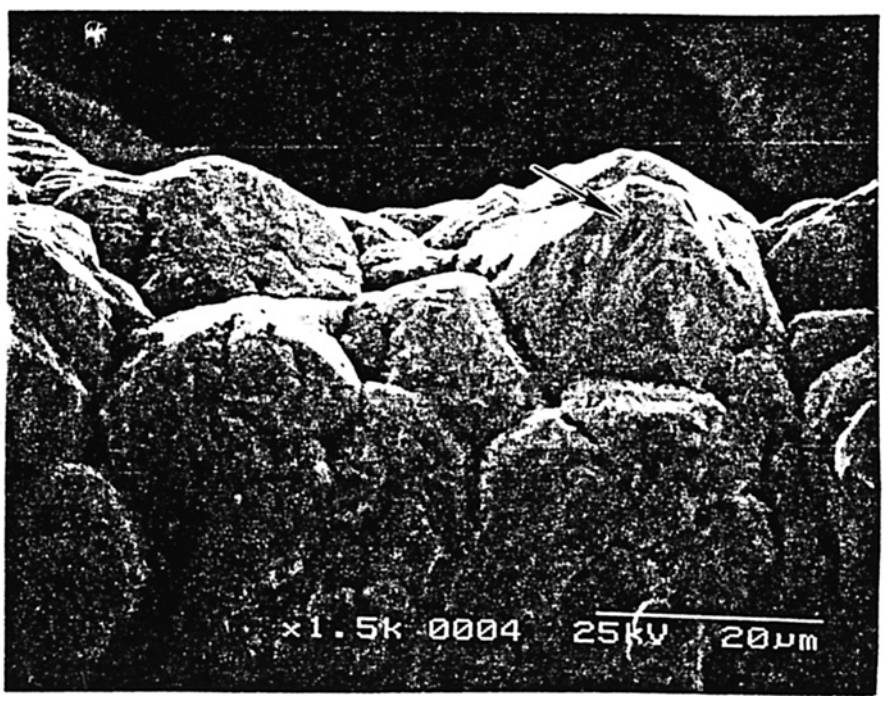

Fig. 4 - Secondary electron micrograph of the pyramid crystals visible on the growth front (300 milliampere-hours).

This type of morphology is maintained for some 300 milliampere-hour, at which stage the grains appear to become coarser and instead of the apex of the pyramid a truncated form of

grains growth occured on the fibers, see Figure 5b. A micrograph of the truncated growths, at higher magnification, is shown in Figures 5a, in some areas cracks could be observed between crystals, and no further change takes place increasing the bath life.

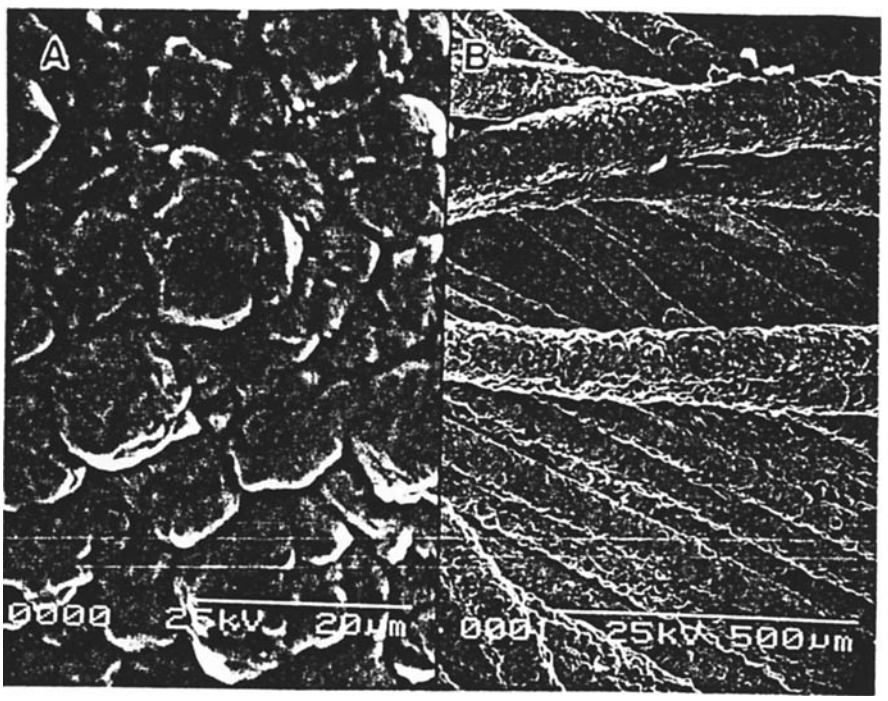

Fig. 5 - (A) SEM micrograph of the final structure of copper grains (600 milliampere-hour); (B) final aspect of coated carbon fibers.

4. DISCUSSION

In producing composites with a liquid infiltration method, the wetting kinetics is a fundamental question. One of the many factors which influence the wetting kinetics of a solid with a liquid is the surface roughness. Wetting of a rough surface is determined by the local angles of contact which can differ markedly from the apparent contact angle. When the surface roughness increases, the wetting, as a rule, decreases. Because many changes in growth morphology of the electrodeposited copper layer take place during the plating run the wettability of the modified carbon fiber can vary significantly with the deposition time. For an optimization of the coating process is therefore necessary to develop the less rough surface, and it is easily obtenable observing the development of the coating morphology with the increasement of the bath life.

It is clear from the scanning electron microscope observations that changes take place in the growth behaviour as the bath ages. Essentially three different growth morphologies have been recognized; those produced in approximately the first 50 milliampere-hour, those in the period 50-300 milliampere-hour, and finally those in the time between 300 milliampere-hour and bath exhaustion, for the particular bath made up for these experiments.

In the early stages of the bath life a fine dendritic structure results. The grains appeared spherical, coarse, and facetting are visible in some points. However, the number of grains do not increases within the first 50 milliampere-hour of plating. This because the nucleation process is an unfavourable process on the carbon fiber surface. Such a structure may result from bath contaminants which assist heterogeneous nucleation processes. An alternative suggestion is that contamination may have hindered the growth behaviour. Whichever process may occur, it becomes immaterial as the bath ages because a coarse pyramid growth structure results. This change can be interpreted in terms of the contaminating species having been plated out of the bath. When the fiber surface is full coated an high roughness of the surface resulted (Figure 3), and consequently the fiber wettability was low.

The 50 to 600 milliampere-hour period is the most important stage because the most useful and reproducible deposits are produced, and this represents a large portion of the bath life. A pyramid type of structure is mantained at the growth front during this stage; the size of the

pyramids changes, becoming coarser with bath ageing. Towards the middle of the period there is a tendency for the angle associated with the apex of the pyramids to become less acute and some of the pyramids are truncated. At this step of the growth the roughness of coating surface is very low because only smooth surface with low inclination are present, and consequently the wettability of the fibers results the maximum obtainable.
Beyond 600 milliampere-hour the growth surface at the top of the cathode takes on a much flatter topography, with evidence of cracks between grains. The cracks could have resulted from a relief of stress in the deposits. The surface roughness is again high and therefore inusuitable.
High-quality coating films were produced by this bath, and the porosity of the metal was extremely low up to 400 milliampere-hour of plating, i.e. when a pyramid type of structure is realized on the growth front.
The bonding between copper and carbon is, in the coated fibers, not very strong, but during the infiltration of the melt into the preform at high temperature and applied pressure the coating layer recrystallizes around the carbon producing increasement in the bonding.

5. CONCLUSIONS

Based on the data generated from the microscopical investigation, the following conclusions can be drawn: changes in growth morphology and consequently in the wettability of the electrodeposited copper take place when the bath is close to exhaustion. The growth morphology changes is from a spherycal grains structure to a coarse pyramid structure. In particular, a high roughness characterize the first copper layer produced on the carbon fibers (50 milliampere-hour); a smooth surface is obtainable with a pyramid structure, i.e. the morphology developed after 200÷300 milliampere-hour of plating; and new rough surface with some cracks among crystals could be observed after 300 milliampere-hours of plating.

REFERENCES

1. A. Okura, K. Motoki, "**Rate of Formation of Intermetallic Compounds in Aluminium Matrix-Carbon Fibre Composites**", *Comp. Sci. and Tech.*, **24** (1985) 243-252.

2. Y. Kimura, Y. Mishima, S. Umekawa, T. Suzuki, "**Compatibility Between Carbon Fibre and Binary Aluminium Alloys**", *J. Mater. Sci.*, **19** (1984), 3107-3114.

3. I.H. Khan, "**The Effect of Thermal Exposure on the Mechanical Properties of Aluminium-Graphite Composites**", *Metall. Trans.* A, **7** (1976) 1281-1289.

4. S.J. Baker, W. Bonfield, "**Stress Rupture of Aluminium-Coated Carbon Fibers**", *J. Mater. Sci.*, **13** (1978), 1822-1824.

5. M.F. Amateau, "**Progress in the Development of Graphite Aluminum Composites Using Liquid Infiltration Technology**", *J. Comp. Mater.*, **10** (1976) 279-296.

6. A. Kelly, S.T. Mileiko, "**Fabrication of Composites**", Vol.4, Chapter V, pag. 256.