第15卷 第2,3期 广东有色金属学报 Vol. 15, No. 2,3
2005年9月 JOURNAL OF GUANGDONG NON-FERROUS METALS Sep 2005

Article ID: 1003-7837(2005)02,03-0496-05

Studies on copper coating on carbon fibers

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Abstract: The weak interface bonding of metal matrix reinforced by carbon fibers is the central problem of fabricating such composites. Depositing copper coating on carbon fibers is regarded as a feasible method to solve the problem. In this paper, copper coating has been deposited on the fibers through both electroless deposition and electroplating methods. Two kinds of complexing agents and two stabilizing agents are taken during the electroless plating process. The solution is stable, and little extraneous component is absorbed on the surface. After adding additive agents and increasing the concentration of H_2SO_4 to the acid cupric sulfate electrolyte, the "black core" during usual electroplating process is avoided. The quality of copper coating is analyzed using SEM and XRD, etc.

Key words: carbon fiber; copper coating; electroless plating; electric plating

CLC number: TQ153.1 **Document code**: A

1 Introduction

Metal matrix composites reinforced by carbon fibers are promising composites for various applications due to their high specific properties such as high specific strength and modulus ratio. However, applications of such composites are limited because of its interfacial problem: the lack of wetting of carbon fibers with molten metals and a deterioration of the fiber properties during composite processing. To overcome these problems, coatings can be deposited on fibers by various methods, such as electroless plating, electroplating, vapour deposition and plasma spraying. In particular, it is shown that copper coatings help improve wetting of carbon fibers and metal matrix[1]. Besides, Carbon is insoluble in copper up to very high temperature[2].

Various of methods were used to gain copper plating on carbon fibers, including electroless plating[3], electroplating[4], electroless-electroplating[5], and double-step electroplating[6]. Because of the large superficial area of carbon fibers, the solution is usually unstable during electroless plating. And Cu_2O is easily adsorbed on the surface of fibers. In this study, double complexing agents and two stabilizing agents are used to gain stable solution. The "black core" is the central problem during electroplating, and methods applied at present are generally complex and hard to control. In this paper, an acid cupric sulfate electrolyte, the most wildly used method in copper plating industry, is studied to gain copper plating on carbon fibers.

Received date: 2005-05-27

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2 Experimental

2.1 Materials

The carbon fibers used are 12K per bundle, and its diameter is 7-8 μm. The fibers' SEM micrograph is shown in Fig. 1. The additive agents consist of M, N, SP etc. Other chemicals are all of analytically pure reagent

2.2 Pretreatment of carbon fibers

Carbon fibers were heated to 400℃ for 40min at air, then put into 40% HNO_3 solution, and boiled for 30 min, finally dried after washing.

2.3 Electroless copper plating process

Carbon fibers after pretreated are sensitized by $SnCl_2$, then activated by $AgNO_3$ instead of $PbCl_2$, which is more expensive and poisonous. Copper coating was deposited on carbon fibers in the bath, and the solution composition is shown in Table 1.

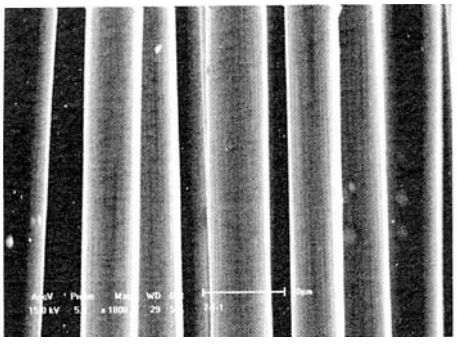

Fig. 1 SEM micrograph of carbon fiber

Table 1 Solution composition of electroless deposition

$CuSO_4 \cdot 5H_2O$	16 g/L
$C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$	25 g/L
$C_4H_4KNa_6 \cdot 4H_2O$	15 g/L
NaOH	16g/L
2-2'-Dipyridyl	40 mg/L
$K_4Fe(CN)_6 \cdot 3H_2O$	80 mg/L
HCHO	15 mL/L

Table 2 Composition of electroplating solution

$CuSO_4 \cdot 5H_2O$	80—120 g/L
H_2SO_4	60—90 mL/L
Additive agent	5 mL/L

2.4 Electroplating process

A MPS702 direct current power supply was used. Positive electrodes are two phosphorous copper plates which surface area is 2 mm×100 mm×300 mm. As long as 40 cm carbon fibers were coated each time and the solution composition is shown in Table 2.

2.5 Coating evaluation methods

The surface morphology and characteristics of the Cu coating were observed by scanning electron microscopy (SSX-550) and X-Ray Diffraction (XRD).

3 Results and discussion

3.1 Effects of pretreatment on carbon fibers

A study[7] has shown that oxidation in air at high temperature and oxygenation in HNO_3 can enlarge the amount of hydrophilic grouping, which greatly improves hydrophilicity of

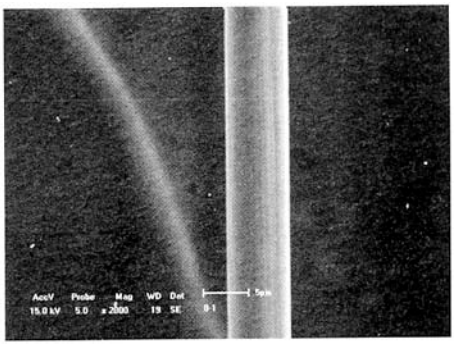

Fig. 2 SEM micrograph of carbon fiber after pretreated

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the fibers. The SEM micrograph of carbon fibers after pretreatment is shown in Fig. 2. After pretreated, the surface of carbon fibers is much more rough, which can strengthen the cohesion between fiber and plating. Besides, there is no apparent damage on the surface of the fibers.

3.2 Quality of electroless copper plating

Ethylenediamine telraacetic acid sodium salt and potassium sodium tartrate are taken as double complexing agents, 2,2'-dipyridyl and potassium ferrocyanide as stabilizing agents. The stability of the solution is improved, but the reaction speed is somewhat slower. Fig. 3 shows SEM micrographs of the fibers covered with electroless coating. Thickness of the copper coating is 0.2-0.6μm. There is little extraneous component absorbed on the surface and the coating is uniform, compact and smooth. However, because of its low reaction speed, it's hard to gain much thicker coatings.

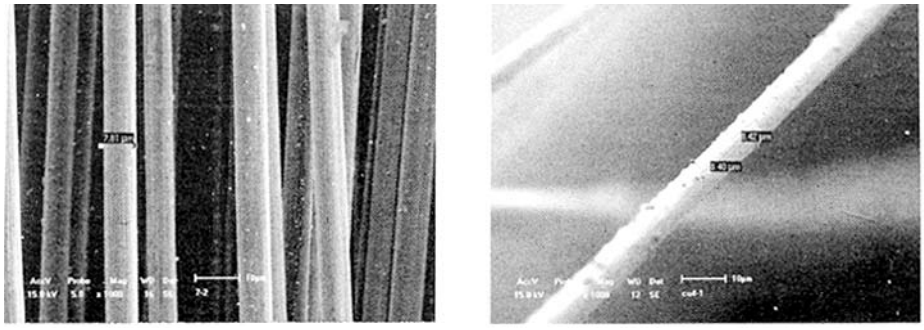

Fig. 3 SEM micrograph of copper coating deposited by electroless plating

3.3 Mechanism of crystallization of copper coating in electroplating bath

Constant-potential electroplating is adopted. The relationship between current flow and time during electroplating is plotted in Fig. 4. The current value is quite small at the very beginning, and then grows very fast in the following several minutes. At the last period, it grows more and more slowly to steadily.

The electrical conductivity of carbon fibers is not good. Its line specific conductance is $10^{-2}\Omega$/cm. When electroplating process begins, copper is deposited on the fibers near the connecting terminal, and the current flow is very small. Because of the electro-adsorption of the additive agents and the effects of large quantity of free acid, excess voltage of Cu^{2+}/Cu and cathode polarization greatly increase, which make it hard for copper coating to grow diametrically, but easy to grow longitudinally. As copper coating grows, cathode of good conductance area grows fast, which lead to fast growing of the current flow. The growing speed of current flow decreases when some fibers are fully covered by copper. After all the fibers are covered by copper coating, the growing of current flow results from the growing of fibers diameter, and it is slow and steady.

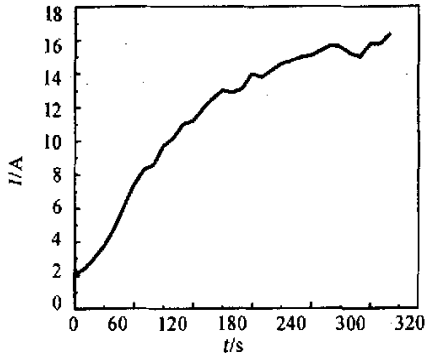

Fig. 4 Relationship between current flow and time

Surface active agent consists in the additive agents can improve hydrophilicity of the fibers, result in high degree of scatter of the fibers in the bath. Besides, the effects of additive agents and large quatity of free acid[9] guarantee the uniform of the thickness of copper coating on fibers both inside and outside the

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bundle. During the electroplating process, copper coating covers 35 cm at longitude direction, but only 1. 5-4 μm at the diameter direction, which lead to the unity of the thickness of copper coating on fibers.

3.4 Quality of electroplating copper coating

Fig. 5 shows the XRD diagram of copper coating. It is quite anastomotic to the standard diagram. And it indicates that there is no preferred orientation of crystal plane. Hence the coating is bright because the grains are fine[9]. SEM micrographs of the fibers covered with copper is shown in Fig. 6, and it's smooth and uniform. From the sectional micrograph, it can be seen that the copper coating is compactly adhered to the fibers.

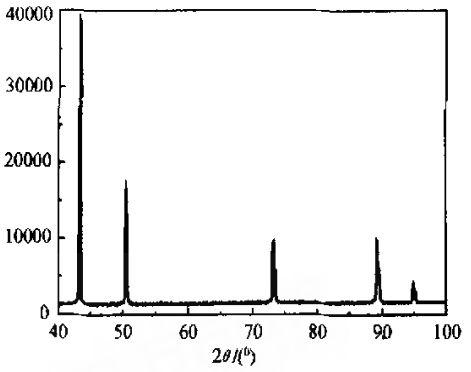

Fig. 5 XRD diagram of copper coating by electroplating method

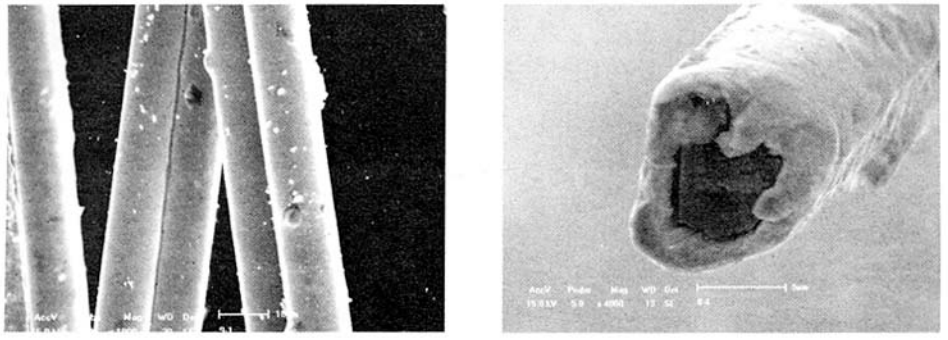

Fig. 6 SEM micrographs of copper coating deposited by electroplating

4 Conclusions

(1) Oxidation in air at 400℃ and oxygenation in HNO_3 can improve hydrophilicity and roughness of the surface of carbon fibers, which can make it easy to gain good adhesion copper coating on fibers.

(2) The solution of electroless copper deposition taken double complex agents and stabilizing agents is stable, and copper deposited on the fibers absorbs little extraneous component absorbed on the surface, and the coating is uniform, compact and smooth. Its thickness is 0. 2-0. 6 μm.

(3) It is feasible to gain smooth and uniform copper coating through electroplating progress in an acid cupric sulfate electrolyte. The effects of additive agents and high concentration of H_2SO_4 o can guarantee the uniform of copper coating. The coating is 1. 5-4 μm thick, and of good adhesion to the fibers.

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