

Electroless Coating Process of Carbon Nano Fibers by Copper Metal

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Keywords: Carbon nano fibre, Copper, Electroless process, Surface

Abstract. A study of the different stages of the electroless deposition of copper on carbon nano fibers activated firstly by a chemical treatment of the carbon nano fiber and secondly by a two-step method has been performed from both a chemical and a morphological point of view. The combination of XPS measurements and scanning electron microscopy imaging has allowed optimizing the 2 different stage conditions. On a first hand, the different oxide concentration and treatment time of the carbon nano fibers and on a second hand the different conditions of the sensibilisation (Sn bath), activation (Pd bath) and coating (Cu bath) have ben studied. The control of the homogeneity and thickness of copper thin films on carbon nano fiber can be obtained and further more sintered in order to obtain fully dense materials.

Introduction

Thermal management is one of the key critical aspects in the design of multichip modules to ensure reliability of electronic devices. There is thus a strong need for the developments of novel heat dissipation materials having a low coefficient of thermal expansion combined with high thermal conductivity. Carbon nano fibers (CNF) reinforced copper matrix composites offer a good compromise between thermo mechanical properties and high conductivity [1]. Their advantages are lower density than copper, very good thermal conductivity, low coefficient of thermal expansion and good machinability. Homogeneous dispersion of the reinforcement inside the metal matrix is one of the key point in order to obtain reproducible, homogeneous and optimum thermal properties. Powder metallurgy process has been chosen in order to elabore these CNF/Cu composite materials due to the non-weeting behaviour of carbon with liquid copper. Therefore, due to the large size difference between commercial copper powder (diameter ranging from 5 to 30 2 m) and CNF (diameter around 100 nm) CNF were directly coated with copper using conventional electroless process. In order to be able to grow electroless copper on CNF substrate, localised catalytic centres have to be created on the carbon surface; they will help to initiate electroless metal deposition. Palladium clusters chemisorbed on the substrate surface constitute these sites. In our method, CNF surface were firstly chemically treated using different acid baths (in order to create oxygenated sites on the CNF surface and to have a good dispersion of the CNF in water) followed by conventional two-step electroless process (dilute solutions of SnCl₂ (sensitisation bath) and then PdCl₂ (activation bath) [2]). In that sense, we have investigated in details the mechanism of electroless Sn and Pd coating of CNF with the help of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) for the three steps method (acid solution + SnCl₂ + PdCl₂ solution).

Experimental

The CNF were subjected to the following steps before deposition: i) acid treatment (cf. table 1) and ii) rinsing with distilled water. The sensitisation (Sn absorption), activation (Pd absorption) and

plating (Cu deposition) stages consisted in the successive immersion of the substrate into the following baths [3,4]:

- Sensitisation bath: 10g/l SnCl₂, 40ml/l HCl 37%, distilled water;
 - Activation bath: 0.25 g/l PdCl₂, 2.5 ml/l HCl 37%, distilled water;
- Plating bath: 10g/l CuSO₄, 50g/l KNaC₄H₄O₆·4H₂O, 10 g/l NaOH, 15 ml/l CHOH distilled water

CHOH initiates the coating deposition by reducing the CuSO₄ according to the following reaction $Cu^{2+} + 2HCHO + 4OH^{-} \rightarrow Cu^{0} + H_2 + 2H_2O + 2HCO_2^{-}$.

Main parameters which have to be control are: 1) pH of the solution between 9 and 12 (the sodium hydroxide (NaOH) amount is adjusted in order to change the pH of the solution between 9 and 12), 2) the deposition time, 3) the temperature of the different baths and 4) the reaction rates.

After each immersion, the substrates were immediately rinsed with distilled water to stop the deposition process and control the deposition time and, after the last step, the samples were carefully left dry.

XPS was used to investigate chemical surface evolution of the CNF after each step of the electroless process. Depth profiling by XPS was conducted using a VG ESCALAB 220 i-XL instrument, with a monochromated Al K α radiation source (150 µm spot diameter). In all cases, the spectra charged referenced to hydrocarbon contamination C 1s peak at a binding energy (BE) of 284.5 eV. After copper coating, composite materials were polished for microstructural analysis using a Jeol 840 SEM.

Results

CNF oxide treatment

Table 1 shows the evolution of the surface oxygen content of the CNF with different acid treatments. In that way, the evolution of the oxygen and carbon species have been analysed by XPS. It has to be noticed the carbon peaks, located around 286 eV and 288 eV, which are assigned to C-O and C=O + COOH, respectively, disappear after the first run of sputtering in all studied samples leading to a treatment thickness of around 1monolayer.

Fiber	Dispersion in water	Oxyen surface content (XPS)
CNF	No	0.8%
$CNF + HNO_3 (12h)$	No	2.2%
$CNF + (HNO_3 + H_2SO_4 2/3 \text{ vol.}) (2h)$	Yes	11%
$CNF + (HNO_3 + H_2SO_4 2/3 \text{ vol.}) (6h)$	Yes	15%

Table 1: Evolution of the surface oxygen content of the CNF after acid treatment

Two different acid treatments have been used; the main analysed parameters are the oxygen surface content and the dispersion behaviour of the treated CNF inside water. Table 1 clearly shows that mixed ($HNO_3 + H_2SO_4$) acids have to be used in order to achieve good results. For this acid solution, the oxygen content increases slightly with the treatment time.

Cu coating of CNF using electroless process

Fig. 1 shows the evolution of the CNF with different coating conditions. It has to be mentioned that the CNF have been treated with an acid solution (CNF + (HNO₃ (1/3 vol)+ H₂SO₄ (2/3 vol.)) (6h)) before electroless coating.

Several point s can be noticed from this study:

- 1. Thickness of non-coatred CNF is around 150 nm (cf. Fig. 1 a).
- 2. The pH of the solution is one of the key factor in order to obtain an homogeneous copper coating around each CNF. Homogeneous coating is obtained for pH greater or equal to 12 (cf. Fig. 1 b and c).

3. Copper coating is more homogeneous when 1) the reducer concentration (HCHO) is increased and 2) the water content of the solution is increased. Both condition leads to a decrease of the coating rate (cf. Fig. 1 d, e and f).

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- 4. Whatever the conditions an increase of the bath temperature is always observed and a decrease of the pH of the solution during the deposition bath (see for example Fig. 2)
- 5. The exothermicity of the reaction is linked with the CNF concentration within the bath.

Figure 1: Scanning electron micrographs of a) non-treated CNF and b) to f) coated CNF for different bath conditions. (b) and c) increasing pH with identical other parameters) (d), e) and f) increasing HCHO vol with identical other parameters). Black lines show typical diameter and length of the CNF before coating.



Densification of the copper coated CNF

and 40% volume fraction of CNF (cf. Fig. 3 b and c).

Copper thicknesses ranging from 10 to 100 nm have been acheived depending on coating conditions. After Cu deposition, the coated CNF are dried in an oven at temperature close to 70°C. After drying the coated CNF are partly or totally oxidised (colour goes from red (after Cu bath) to black (after drying). Therefore, the dried Cu(O)/CNF nano composite are reduced under argon/hydrogen (5%) gas at 350°C during 1 hour and then kept in an inert atmosphere. After this treatment Cu(O) is completely reduced leading to pure Cu/CNF nanocomposite (cf. Fig. 3 a). After this reduction step, Cu/CNF nano composite are hot pressed at 650°C and 50 MPa during 1 minute. The relative density of obtained densified samples is 0.98 and 0.94 with respectively 30%

Figure 2: Evolution of the pH and the temperature (T(°C)) of the bath with the deposition time



Figure 3: Scanning electron micrographs of a) Cu coated CNF after hydrogen reduction; b) partly densified CNF/Cu composite material. Black line show typical diameter and length of the CNF before coating.



Conclusion

The influence of main parameters, like 1) the dipping time and the temperature of the different baths (sensibilisation, activation and coating), 2) the pH of the coating bath and 3) the HCHO content, on the copper homogeneity and thickness have been shown. Conditions of electroless coating process have been optimized in order to obtain Cu/CNF nano composite with controled CNF volume fraction. After reduction inside controled argon/hydrogen atmosphere Cu/CNF nano composite have been densified. Optimum porosity levels have been measured on densified Cu/CNF composite materials.

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