

# CARBON NANOFIBERS REINFORCED Cu MATRIX NANOCOMPOSITES BY THERMAL DESCOMPOSITION

M.I. Barrena, J.M. Gómez de Salazar, G. Morales, R. Pinillos and N. Merino

Dpto. Ciencia de los Materiales e Ingeniería Metalúrgica, Facultad de Ciencias Química  
Universidad Complutense de Madrid  
Avda. Complutense s/n 28040 Madrid, España.  
ibarrena@quim.ucm.es

## ABSTRACT

In the present work, Cu/CNFs nanocomposite materials have been obtained by calcinations and reduction process, which have been named as molecular level process by other authors. In order to obtain this material, two mineral salts have been used as source of copper ions,  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . On the one hand, both of them, the transformation temperature has been found and on the other hand the influence of concentrations values of impregnation solutions on thin copper coatings has been studied. In all cases, reduction step was carried out into furnace tube at 550-600°C for 2h with 10% $\text{H}_2$ /90%Ar flow.

## 1. INTRODUCTION

Carbon nanotubes are known for their unique structure, high surface, low resistance, high stability and other properties such as their high length to diameter ratio, strength, flexibility, and electrical conductivity [1]. Due to these characteristics, CNT-based materials constitute a new generation of composites [2]. These materials operate as reinforcing fibers for composites and they are optimal raw materials for different applications [3].

CNF/metal nanocomposites attract less attention than CNF/polymer due to good interfaces are difficult to be obtained. However, many studies have been focused on depositing metal or oxide metal nanoparticles on the nanotubes surface by various chemical and physical methods, due to the great interest in metallization process for creating new-matrix-based carbon nanotubes composites. Therefore, the electrical and mechanical properties of carbon nanotubes may be changed or justified by coating [4].

Previous studies have demonstrated that a pre-treatment on surface substrate is needed to form functional groups on the CNF surface providing for the nucleation of metal or their compounds [5]. In these studies, CNF reinforced Cu matrix nanocomposites have been obtained by calcinations and reduction steps, which have been named as molecular level process by other authors [6]. Copper as coating metal is of particular interest, since it shows high electrical conductivity and is suitable for potential applications. Normally, Cu nanoparticles are prepared by electrochemical and wet chemistry methods, for example Electroless, which can provide Cu particles as small as several nanometers [7]. Often, the nanoparticles are required to be non-aggregated and smaller than 50nm in diameter so that thin dense metal layers can be synthesized. Hence, these are a significant interest in obtaining copper nanoparticles of small size dispersity and to arrange them in periodically ordered particulate material.

In this work, carbon nanofibers reinforced Cu matrix (CNF/Cu) nanocomposites are fabricated by calcinations and reduction process, using different mineral solutions in impregnating step. This way, Cu particles size and thin coating obtained over CNF have been evaluated.

## 2. EXPERIMENTS

CNF used in the present work were manufactured by Grupo Antolin Ingeniería S.A. [8]. Pre-treatment of the as-received CNFs were purified and functionalized by  $\text{HNO}_3$  acid solution [5], filtrated, washed and dried at  $110^\circ\text{C}$ .

The preparation procedure for CNF/Cu involved fully dispersing a certain amount of carbon nanofibers in impregnation solutions to room temperature for about 2h in magnetic stirring. These solutions were prepared with mineral salts ( $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) using ethanol and  $\text{H}_2\text{O}$  desionized, respectively, as solvent. These inorganic salts are precursor of copper and provide as source of ions to obtain the coatings, and the concentrations used, in both cases, have been 0.01g and 0.25g in 55ml of their solvent. After, the suspensions or the mixture of reaction solutions were heated at  $80^\circ\text{C}$  until the solvent was vaporized completely and calcined into furnace. When the samples have been prepared with  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ , calcinations step carried out at  $400^\circ\text{C}$  for 1-2h, however, in the case of they were prepared with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , this step was at  $300^\circ\text{C}$  for 1h. Both of them, the atmosphere furnace has been ambient atmosphere.

This way, CuO/CNF formed was placed into furnace tube at  $550\text{-}600^\circ\text{C}$  for 2h with  $10\%\text{H}_2/90\%\text{Ar}$  flow to obtain Cu/CNF nanocomposites

In order to know the transformed temperature of inorganic salts, DSC (Model DSC 25 Mettler Toledo) technique was used.

Microstructural characterization of Cu coated carbon nanofibers was carried out by scanning electron microscopy (SEM), using a JEOL 6400 microscope and by a field emission scanning electron microscope (JEOL 6330F). The composition of the copper coatings was determined by X-Ray diffraction using a Philips X'Pert PD P3040.

## 3. EXPERIMENTAL RESULTS

The thermal decomposition process can be described in four steps: Funcionalizing CNF, mixing CNF/Cu salts, dried the mixture in order to remove solvent and finally, calcinations and reduction CNF/CuO obtained.

In order to determinate the temperature from which Cu salts were oxidized to its oxides, DSC studies were realized. As illustrated in Figure 1, samples burned when furnace temperature was to  $300^\circ\text{C}$ . On the other hand, using  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  as source ions  $\text{Cu}^{2+}$ , CuO formation was faster than in the case  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was used. For this reason, calcinations step were carried out to  $300^\circ\text{C}$  for about 2h, by two mixtures of reaction solutions.

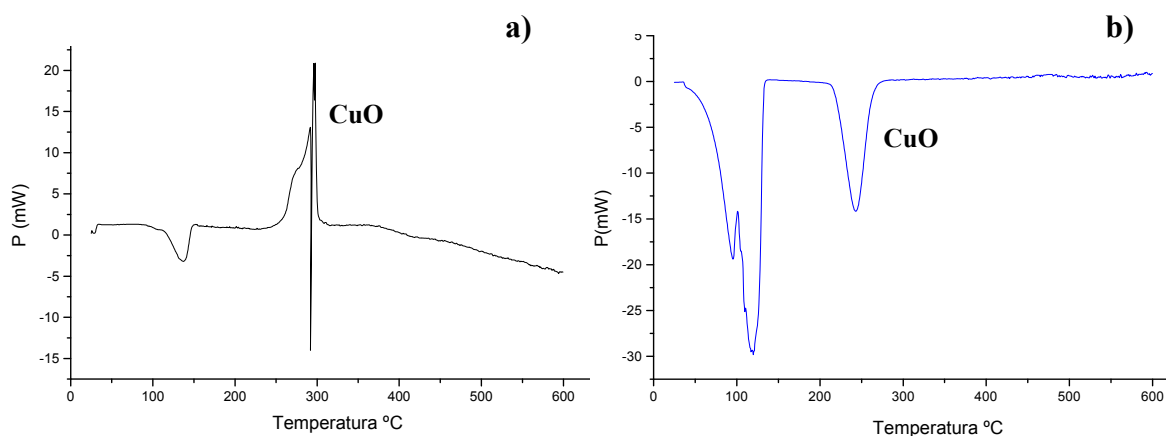


Figure 1: DSC studies: a)  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  and b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

Figure 2 compares the XRD pattern of the CNFs material, after calcinations step. The samples obtained used  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ , they exhibited CuO (Tenorite) more crystalline by showing clear diffraction pick than  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Furthermore, in the first case, NiO diffraction pick were shown, which come from Ni used as metal catalysts in the floating catalyst technique [8].

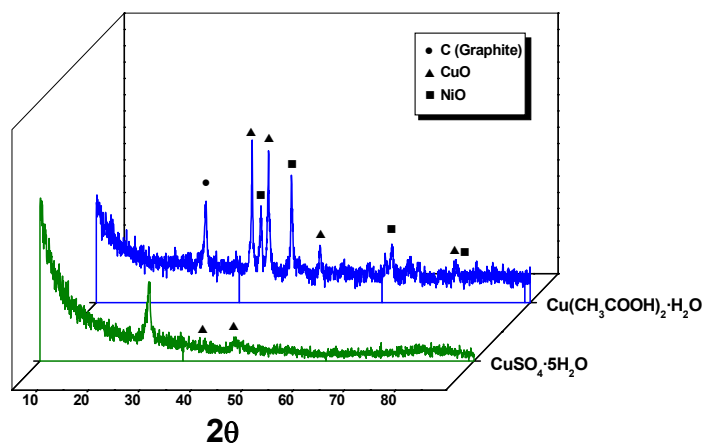
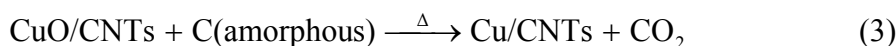
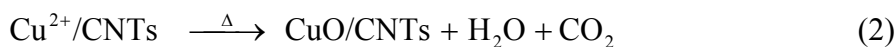


Figure 2: XRD patterns of CNF/CuO composite material using two Cu salts, a)  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  and b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

Other investigations have proposed a formation mechanism of CNF/Cu using this method [9]:



In this work, the reduction step were carried out into furnace tube at 550-600°C for 2h with 10% $\text{H}_2$ /90%Ar flow, without C (amorphous).

In all studied concentrations values, using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as source of ions, the coatings obtained were heterogeneous over CNFs. This reactive do not generate enough link points with substrate; do not show a increasing of the thin Cu on CNFs (Figure 3). Aggregates of Cu nanoparticles have been obtained, however, these Cu-clusters were between CNFs and they will not act as “binder” joining CNFs coarsed.

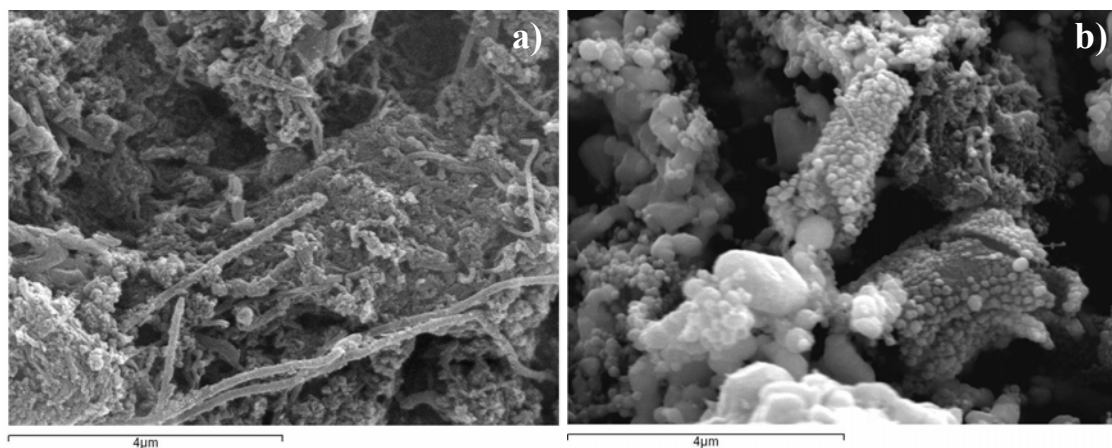


Figure 3: SEM images of Cu coating over CNFs obtained using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  a) 0.01g and b) 0.25g.

Cu/CNFs nanocomposites materials obtained using  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ , the influence of the concentrations values have been studied. On the one hand, the minor concentration value studied generates Cu coatings over CNFs. However, using the highest concentrations value, Cu coatings over CNFs surface and aggregate of copper nanoparticles have been obtained. This salt generate additional possible copper nucleation points as  $-\text{OH}$  and  $=\text{C}=\text{O}$  over CNFs surface.

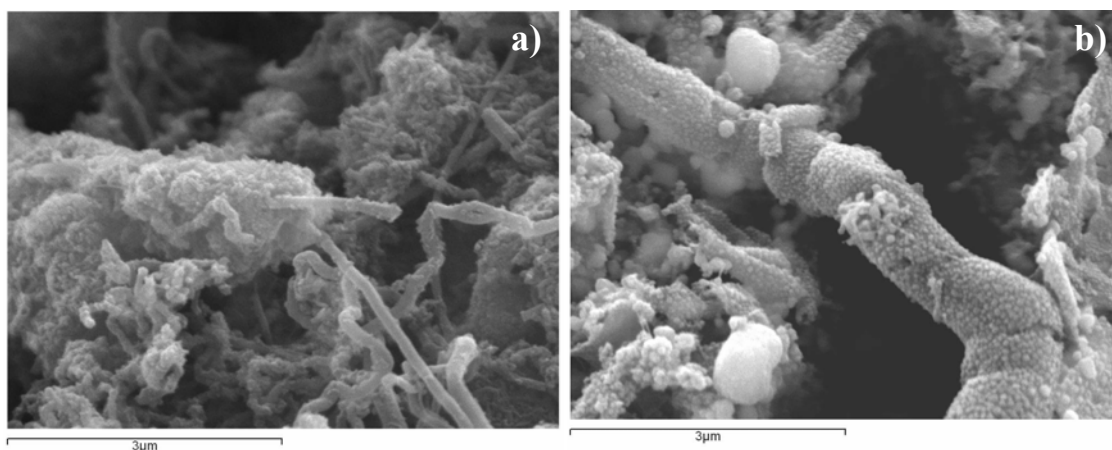


Figure 4: SEM images of Cu coating over CNFs obtained using  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  a) 0.01g and b) 0.25g.

## 6. CONCLUSIONS

The aim of the study was to obtain composite material in situ, which involves two facts. On the one hand, the copper coating obtained must be homogeneous over CNFs surface and on the other hand, nanoparticles copper aggregates must be form. These nanoparticles will act as “binder” joining CNFs coarsed. Therefore, the process used must be economically viable.

Among the two source ions  $\text{Cu}^{2+}$  under study,  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  is considered the optimal one because it resulted in both CNFs coating and copper aggregates.

## REFERENCES

- 1- Ebbesen, T.W., “Wetting, filling and decorating carbon nanotubes”, *Journal of Physics and Chemistry of Solids*, 1996;57 (6–8): 951-955.
- 2- Zhan, G-D., Kuntz, J. and Mukherjee, A.K., “Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites”, *Nature Materials*, 2003; 2: 38-42.
- 3- F. Wang, S. Arai, M. Endo, “Metallization of multi-walled carbon nanotubes with copper by an electroless deposition process”, *Electrochemistry Communications*, 2004; 6: 1042-1044.
- 4- Xu, C., Wu, G., Liu, Z., Wu, D., Meek, T.T. and Q. Han, “Preparation of copper nanoparticles on carbon nanotubes by electroless plating method”, *Materials Research Bulletin*, 2004; 39: 1499-1505.
- 5- Gómez de Salazar, J.M., Barrera, M.I, Merino, C. and Merino, N. “Preparation of CNFs surface to coat with copper by electroless process”. *Materials Letters*, 2008; 62: 494-497.
- 6- Kim. K.T., Cha, S.I. and Hong,, S.H., “Hardness and wear resistance of carbon nanotube reinforced Cu matrix nanocomposites”, *Material Science and Engineering. A.*, 2007; 449-451; 46-50.

- 7- Ferrer-Anglada, N., Gomis, V. El-Hachemi, Z. Weglikouska, U., Kaempgen, M. and Roth, S., "Carbon nanotube based composites for electronic applications: CNT-conducting polymers, CNT-Cu", *Physica Status Solidi, A Appl. Res.*, 2006; 203: 1082-1087.
- 8- Arenillas, A., Cuervo, S., Domínguez, A., Menéndez, J.A., Rubiera, F., Parra, J.B., Merino, C. and Pis, J.J., "Effects of oxidative treatments with air and CO<sub>2</sub> on vapour grown carbon nanofibres (VGCNFs) produced at industrial scale", *Thermochimica Acta*, 2004; 423: 99-106.
- 9- Wang, P., Huang, B., Wei, J., Qin, X., Yao, S. and Zhang, Q., "Preparation of Cu nanoparticles on carbon nanotubes by solution infusion method and calcining in ambient atmosphere", *Materials Letters*, 2007; 61: 5255-5257.