Cu/CNT composite materials with enhance mechanical and thermal properties

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Abstract

In this present work, two methods for dispersing carbon nanotubes into the copper matrix were tested: a Solid Route process where CNTs are simply mixed with the copper powder and a Liquid Route process where CNTs are dispersed in a copper salt solution and then mixed with the metallic copper powder. Powders are sintered by uni-axial hot pressing process under vacuum atmosphere at 650°C and thermal conductivities of composite materials were measured using the laser flash method. Results are compared with a theoretical model of Nan et al. which enables to predict the thermal conductivity of materials containing CNTs. Comparison of experimental and theoretical results tends to prove that CNTs are 2D-randomly dispersed in a plane perpendicular to the pressing direction during uni-axial hot pressing process. Moreover, an increase of +7% of the thermal conductivity is shown for the composite material containing 1 vol.% of CNTs into the copper matrix.

Introduction

Since their discovery in 1991 by Iijima[1], carbon nanotubes are intensively studied. Theory predicts huge mechanical (E_{Young}=1 TPa), thermal (3000 to 6000 $W.m^{-1}.K^{-1}$) and electrical (10^7 to 10^9 $A.cm^{-2}$) properties to carbon nanotubes that makes them interesting as reinforcements in material composites. Several publications already exist on the addition of carbon nanotubes into a polymer matrix showing an enhancement of physical properties. The resulting composite material possesses better mechanical[2][3], thermal[4] and electrical[5][6][7] properties than the pure matrix. However just a few limited studies exist in the literature [8][9][10] concerning the use of metal-matrix due to the extreme conditions of processing for the composite. Furthermore, some difficulties are still a critical issue like the dispersion of the CNTs inside the matrix and the interface resistance, *i.e.* thermal, mechanical, between the CNT and the metal-matrix. Despite that, the perspective of obtaining better properties than pure metallic matrix encourages scientists to persevere in this way.

As shown in the literature, the thermal properties of Cu-CNTs composite material depend i) on the quality of the dispersion of carbon nanotubes into the matrix and ii) on the interface thermal resistance between the reinforcement and the matrix. Cho et al.[11] prepared materials containing Multi Wall Carbon Nanotubes (MWCNT) by spark plasma sintering and shows that the thermal conductivity of the composite materials increase of 3% compared with pure copper for a volume fraction of 1% nanotubes. Chu et al [12] [13] fabricated Cu-CNTs materials with a novel technique for dispersing carbon nanotubes into the matrix. Despite a relative good dispersion of the reinforcement, the thermal conductivity of the composite materials was lower than the copper reference.

Quantify the dispersion of nanotubes into a matrix is mandatory for the understanding of final results. SEM and TEM observations may give some local information. Nevertheless, microscopic observations are not sufficient to quantify the dispersion at macroscopic scale. The use of a theoretical model, using an effective medium approach like the model of Maxwell-Garnett modified by Nan et al.[14] for composite materials containing CNTs, could be a solution. This model enables to predict the thermal conductivity of materials if and only if carbon nanotubes are well-dispersed inside the matrix and with CNT concentration smaller than the percolation threshold. This model takes into account the conductivity and the aspect ratio of the tube, the conductivity of the matrix and the interfacial thermal resistance between CNTs and the matrix. Nowadays, it is well known that the interface between the components remains one of the major problem areas in which copper properties can be improved. In 2003, Huxtable et al.[15] determined the value of the thermal resistance of a carbon nanotube suspended in surfactant micelles in water with a value of 8.3 10^{-8} $m^2.K.W^{-1}$.

Using powder metallurgy process, MWCNT have been dispersed inside a dendritic copper powder using two different methods that we have called “Solid Route” and “Liquid Route”. After densification using uni-axial hot pressing, the dispersion of CNTs inside the matrix is quantified through the use of the Maxwell-Garnett model modified by Nan et al. Thermal conductivities parallel and perpendicular to the pressing direction are measured using conventional laser flash method.

Experimental procedure

Multi-walled carbon nanotubes (NC7000), with a diameter of 9.5 nm and a length of 1.5 µm have been purchased from Nanocyl™ Company to conduct the following experiments. Dendritic shape copper powder (20-30 µm mean grain size) from Ecka Granules Company were used without any additional purification.

Two routes of dispersion for carbon nanotubes have been conducted. A “Solid Route” (SR) where carbon nanotubes were simply mixed 2 hours in a planetary mixer with the metallic copper powder and a “Liquid Route” (LR) where the use of chemical species and physical methods allows a good dispersion of nanotubes into the matrix [16][17][18][19][20][21]. Then the Cu@CNTs powders are uni-axial hot pressed at a temperature of 650°C during 20 minutes in a vacuum atmosphere. For each route, several composite materials (pellet) were fabricated with a diameter of 6 mm diameter and a thickness of 3.2 mm. Thermal diffusivity measurements are then conducted on the fabricated materials.

Thermal diffusivities are measured at 70°C with laser flash method on LFA 457 device from Netzsch Company. Thermal diffusivities were converted into thermal conductivities with the following formula: $\lambda=\alpha\rho C_p$ where λ is the thermal conductivity ($W.m^{-1}.K^{-1}$), α is the thermal diffusivity ($m^2.s$), C_p is the heat capacity of the composite material at constant pressure ($J.kg^{-1}.K^{-1}$) at 70°C and ρ is the density ($kg.m^{-3}$) of the composite material. ρ was measured by the geometrical method. C_p of copper and C_p of carbon nanotubes have been measured by Differential Scanning Calorimetry (DSC) on a 8000/8500 Perkin-Elmer apparatus. C_p of composite material was calculated with a simple rule of mixture from raw materials.

Scanning Electron Microscopy analysis was performed in two modes (Secondary Electron (SE) and Back-Scattered Electron (BSE)) with a Tescan Vega II from Eloise France Company. Pellets micrographs of the Cu-CNTs composite material were obtained on a Leica microscope with VZ80 RC lens and a DVM 2500 digital camera from Leica Microsystems Company.

Results and discussion

Cu and Cu-CNTs pellets composite materials produced by the use of the Solid and Liquid Routes processes have been analyzed by thermal diffusivity measurements and then converted into thermal conductivities as shown in Table 1. For each carbon nanotube content the thermal conductivity is an average of three different pellets and measurements are done in the direction parallel to the axis of compression.

Table 1: Thermal conductivities of Cu-CNTs composite materials obtained by Solid Route and Liquid Route.

Volume fraction of CNTs (%)	Solid Route		Liquid Route	
	Thermal conductivity ($W.m^{-1}.K^{-1}$)	Relative density (%)	Thermal conductivity ($W.m^{-1}.K^{-1}$)	Relative density (%)
0	375	98	375	98
0.5	372	97	373	98
1.0	339	95	364	98
1.5	336	97	362	98
3.0	272	96	337	99

Copper materials fabricated with a powder metallurgy process

Table 1 shows pure copper pellets fabricated using powder metallurgy method with an average thermal conductivity of 375 $W.m^{-1}.K^{-1}$. This thermal conductivity value is slightly lower than the thermal conductivity of bulk copper reference material known as 400 $W.m^{-1}.K^{-1}$. This lower thermal conductivity value can be attributed to the microstructure (smaller grain size) of the powder metallurgy materials and of the 2% remaining porosity measured. Moreover, Cernushi et al.[22] have shown that, the graphite layer, which is sputtered on both sample faces before laser flash measurement and which prevent the laser reflection, has a negative effect on the thermal conductivity value measured. Using the Voigt-Reuss model for in series material, the total thermal conductivity can be calculated for the three-layers material. Thickness of the graphite spray onto the surface was measured by optical profilometry. Results show that the graphite layer is non-homogeneously sputtered onto the surface with a thickness varying from 2 µm to 12 µm. Moreover, the thermal conductivity of the graphite spray is assumed to be close to 24 $W.m^{-1}.K^{-1}$ as mentioned by Cernushi et al. Considering the thermal conductivity of pure copper equal to 400 $W.m^{-1}.K^{-1}$. If we consider that the graphite layer on the top and on the bottom face of the pure copper pellet ranges from 0 µm to 12 µm, so the average calculated –using Vogt-Reuss model- thermal conductivity of the pellet is equal to 378 $W.m^{-1}.K^{-1}$. This calculated thermal conductivity value is equal to the thermal conductivity measured on pure copper pellet (375 $W.m^{-1}.K^{-1}$) obtained by powder metallurgy process and measured by the laser flash method. Consequently, if we consider that the technique for sputtering graphite onto the surface of the composite materials is repeatable, in this case we can consider that the measured thermal conductivities of the material are lowered of 6%.

Cu-CNTs composite materials fabricated with a powder metallurgy process

According to Table 1, with a carbon nanotubes content of 0.5 vol.%, no difference is observed between the Solid and the Liquid Routes whereas a different thermal conductivity is measured for a volume fraction of carbon nanotubes higher than 0.5 vol.% of CNTs. Materials produced by Solid Route present a decrease of the thermal conductivity higher than the materials produced by the use of the Liquid Route. This thermal conductivity difference between the two fabrication processes may be attributed to the formation of carbon nanotubes clusters inside the metal matrix material.

For materials fabricated with the LR process, **Erreur ! Source du renvoi introuvable.** shows the experimental values of thermal conductivity in the parallel (Liquid Route //) and in the perpendicular (Liquid Route ⊥) directions compared to the axis of compression. The predictions of MG model are also presented for a value of $\left\langle \cos^2\theta \right\rangle$ equal to 1 which corresponds to a perfect alignment of carbon nanotubes along one direction in the copper matrix. As it can be shown, Cu-CNTs materials present anisotropic thermal conductivities since the values in the parallel direction are different of the thermal conductivity values in the perpendicular direction. These calculated values confirm that carbon nanotubes are not 3D-randomly dispersed in the material. Moreover, thermal conductivity values in the perpendicular direction are higher (+7%) than the copper reference showing a composite effect between the matrix and the reinforcements. This observation confirms that carbon nanotubes are able to enhance the thermal properties compared to a pure copper matrix.

Summary and conclusion

The concept of Cu-CNTs composite materials with enhanced thermal properties compared with the pure matrix has been demonstrated. Indeed, an increase of the thermal properties of +7% for a carbon nanotube content of 1% has been measured. Moreover, we demonstrate that the use of a theoretical model like Maxwell-Garnett modified by Nan et al. is an indirect method to quantify the dispersion of reinforcements into the matrix and for concentrations under the percolation threshold. The comparison of experimental thermal conductivity values with the predicted ones is an alternatively way to the microscope observations. MG model show that better enhancements of the thermal properties can be expected by aligning the tube in the matrix and a new process, different than uni-axial hot pressing, has to be developed.

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