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**Effect of the incorporation of interfacial elements on the thermophysical properties of Cu/VGCNFs composites**

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**Abstract**

Vapour grown carbon nanofibres exhibit high mechanical properties and thermal conductivities. Therefore they are potential reinforcements in composites materials for high strength and high thermal conductivity applications. A problem not yet solved is the promotion of an improved copper/carbon interface. Several strategies have been envisaged for the incorporation of alloying elements (Ni, Co, B and Ti) at the interface. These techniques are based on duplex electroless plating coatings (combination of Cu and Ni or Cu and Co), electroless plating of alloys (Cu-B) and addition of metal nanoparticles (Ti) to Cu matrix deposited by electroless plating. The effect of the incorporation of these metallic elements on the microstructure and thermophysical properties is discussed. B and Ti lead to higher interaction at the Cu/C interface over Ni and Co. This allows the reduction of the coefficient of thermal expansion but regarding the thermal conductivity it was not possible to obtain a value higher than that of copper.

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## **1. Introduction**

Vapour Grown Carbon Nanofibres (VGCNFs) exhibit excellent mechanical and thermophysical properties. Therefore they are very promising reinforcing materials for metal matrix composites (MMCs) in multiple applications [1,2]. The large volume production of VGCNFs enables an immediate availability and excellent performance-to-cost ratio for the mass production of industrial components [2], better than other candidates such as carbon fibers or nanotubes (CNTs). However, the manufacturing of components containing such kind of material is not trivial, especially at high volume fraction of VGCNFs. Three key issues must be fulfilled in order to obtain high quality MMCs: dispersion of the reinforcement, high degree of densification and promotion of a suitable matrix/reinforcement interface. Regarding interface there is a lack of interaction between copper and carbon [3]. This is a problem that is urgent to solve in order to get advantage of the performance of VGCNFs in MMCs, especially for thermal management applications, where low coefficient of thermal expansion (CTE) and high thermal conductivity are required [6].

## **2. Experimental Work**

### *2.1. Manufacture of composites*

The carbon nanofibres used in the present study were purchased from Showa Denko KK (VGCF grade, 150 nm diameter, 100-200  $\mu\text{m}$  length). One of the main problems of the incorporation of CNTs and VGCNFs is the lack of wetting, diffusion and interaction between

carbon and inert metals such as silver and copper [3-5] (i.e the wetting angle between carbon and copper is  $120^\circ$  and no physical bond is formed at the interface [3]). The fibre reinforcements must maintain their graphitic structure and be strongly bonded to the matrix, in order to achieve improved thermophysical properties. Therefore it is necessary to study in detail this interface in order to achieve composites with the required properties. One interesting solution is the addition of elements able to interact at interfacial level. The electroless plating technique has been earlier discussed for the manufacture of plain Cu/VGCNFs composites by the present authors in a previous work [7]. This process allows obtaining composite powders with the desired amount of reinforcement by controlling the deposited copper. Controlling these conditions, samples containing 20 vol. % of nanofibres were manufactured. Different methods, derived from this copper electroless plating technique, have been envisaged for the incorporation of the interfacial elements (Ni, Co, B and Ti) at the copper/carbon interface. The first method consists of duplex coatings through the electroless plating methods. In this method a thin layer of nickel [8] or cobalt [9] has been placed on the surface of the nanofibres, followed by a second layer of copper [7], which will be the matrix after the consolidation. By this duplex method an interfacial element below 10 wt. % is typically added. The second method consisted of the coating of the nanofibres by an electroless copper alloy, in this case copper plus few ppm of boron [10]. The last method is based on the mixture of copper coated nanofibres with metallic nanopowders, in this case, Ti nanoparticles (Argonide Corp, USA). The Ti nanoparticles were sonicated under ethanol for 30 min. and then mixed with the coated nanofibres in an ethanol solution with Argon bubbling to prevent oxidation. Two different amounts of Ti (0.3 and 5 wt %) were studied. Once the composite powders were vacuum dried they were consolidated by hot-pressing at  $900^\circ\text{C}$  and 35 MPa for 2 h.

## 2.2. Characterization (Materials and methods)

Chemical, microstructural and thermophysical characterisation has been carried-out on composite powders and consolidated composites. The chemical characterisation was performed

by the EDS (Energy Dispersive Spectrometry) microprobe attached to the Scanning Electron Microscope (SEM) in order to assess the presence of possible contamination during the coating process, the oxygen amount and interfacial elements. Furthermore a more accurate value for these elements was given by the ICP-OES (Inductively coupled plasma - Optical Emission Spectrometer) technique. The extent of densification was calculated by comparing the real density with the theoretical one, taking into account a density of 2.0 g/cm<sup>3</sup> for the pristine nanofibres. The microstructure of the consolidated composites was inspected by optical, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The samples were cut and embedded into epoxy resin holders. Once cured, the samples were progressively polished using a silicon carbide grid, and finally polished with diamond paste to a mirror finish. These samples were etched with a FeCl<sub>3</sub>:HCl:H<sub>2</sub>O (1:1:1) solution for 7 seconds. The presence of an interfacial layer and the distribution of the alloying element was observed by TEM (Transmission electron microscopy) where a focused ion beam (FIB) mills away material to obtain a proper surface to be further observed. The coefficient of thermal expansion (CTE) and the thermal conductivity were measured in the x-y direction (assuming that the z axis is the pressing direction). The CTE was measured by dilatometry in the RT-100 °C range (two cycles). The room temperature CTE was calculated from the second cycle to prevent the effect of residual stressed during the consolidation of the material.

The room temperature thermal conductivity was calculated by the indirect method (measurement of the thermal diffusivity). The thermal conductivity can be derived through the expression (1).

$$\lambda(T) = a(T) \cdot c_p(T) \cdot \rho(T) \quad (1)$$

In which  $\lambda$  is the thermal conductivity (W/mK),  $a$  is the thermal diffusivity ( $\text{m}^2/\text{s}$ ),  $C_p$  is the specific heat (J/kgK) and  $\rho$  is the density ( $\text{kg}/\text{m}^3$ ). The thermal diffusivity was measured through the laser flash technique, while the specific heat was measured through Differential Scanning Calorimetry (DSC). The density was measured by the Archimedes method under absolute ethanol.

### 3. Results and discussion

#### 3.1. Microstructure

The inspection and the microstructure of the pristine nanofibres was analyzed in a previous work [7]. It was concluded there that this type of nanofibres present a more graphitic structure than the ones from other manufacturers. Moreover the nanofibres were clean of the metallic seeds employed for their synthesis. The copper coating description and characterization was also reported there, as well as the microstructural characterisation after hot-pressing. A rearrangement of the nanofibres to form a random planar configuration was observed.

Figure 1 shows the microstructure of the composites modified with Ni. The nickel coating is successfully deposited on the surface of the nanofibres forming a continuous coverage (see Figure 1a). The copper coating on the nickel coated VGCNFs is shown on Figure 1b. The copper coating on the nanofibres was seen to be granular and homogeneous. As shown in Figure 1c the consolidated composite shows a fine distribution of the nanofibres in the matrix with a low presence of nanofibre agglomerates. The distribution of the composite elements was checked by EDS mapping (see Figure 1d for Ni). This confirmed a uniform distribution of the nickel along the microstructure composite. The amount of nickel was 7 wt % (ICP-OES). In addition, the oxygen content was shown to be very low (< 0.1 wt %). It would be probably

completely removed if the consolidation were carried out under reductive gases (such as  $H_2$ ) instead of vacuum. The TEM inspection revealed that a low amount of nickel was present in the proximity of the interface, but the amount of nickel in the copper matrix was high. This measurement suggested that the amount of nickel, formerly present on the interface, diffused into the copper rather than reacting with the nanofibres, while the consolidation was carried out. This could be explained by the low solubility between nickel and carbon, like in the case of copper.

Figure 2 shows the microstructure of the Cu/VGCNFs modified with Cobalt, following a similar procedure as for the Cu/Ni/VGCNFs composites. The microstructure of the cobalt coated nanofibres is shown in Figure 2a. Cobalt deposits were found not only on the nanofibres, but also as tiny particle precipitates between the nanofibres. The microstructure of the consolidated composite is shown Figure 2b. After the consolidation the nanofibres were well distributed in the matrix, although some small agglomerates ( $< 5 \mu m$ ) are present. The final amount of cobalt was around 9 wt %. The distribution of the different constituents of the composite was inspected by SEM inspection and EDS mapping, showing that interfacial element (cobalt) was present in terms of isolated deposits. This suggested that the interfacial element was not located on the copper/carbon interface. A similar explanation of this phenomenon than the above explained for Ni can be given. The presence of oxygen in the composite was quite low.

The microstructure of the composites containing Boron is shown in Figure 3. The Boron was incorporated during the deposition of copper, coming as impurity from the reducing agent employed in the electroless plating process (from the Sodium Borohydride). The Boron content in the samples was very low (0.001 wt % by ICP-OES). The microstructure was inspected by SEM and TEM. Firstly the coating resulted to be smooth and homogeneous with small amounts of VGCNFs bundles. From the inspection by SEM an excellent distribution of the nanofibres and a homogeneous microstructure were observed. Moreover, the detailed observation by TEM



(Figure 3b), shows that the carbon-copper interface is continuous, leading to a good physical contact between these two phases.

Figure 4 shows the composites samples after the Ti nanoparticles addition. The mixture with copper coated nanofibres was intensively inspected by SEM. As shown in Figure 4a no evidence of the presence of Ti particle agglomeration was seen during the SEM inspection even at 5 w % of Ti. This suggested that the nanoparticles were finely distributed through the coated nanoparticles. The consolidated samples are shown in Figure 4b and c for the 0.3 and 5 w % of Ti (optical images, in order to give a representative macroscopic view). The microstructure of the sample with 0.3 wt % of Ti resulted to be more homogeneous as compared with the one containing 5 wt %. In this case the lower amount of Ti prevented the formation of carbon nanofibre agglomerates. The mechanism of the formation of these carbon nanofibre agglomerates is still unknown and more work is required to elucidate this effect. The presence of TiC was detected by XRD and EFTEM mapping. As shown in Figure 4d, in the case of the composite with 5 wt % of Ti an interfacial layer of TiC of about 100nm is formed after the diffusion of Ti through the copper. The TEM inspection has not shown evidences of the presence of TiC at the interface of the 0.3 wt % Ti composite. Furthermore, the random planar configuration was observed in both the samples with 0.3 and 5 wt. % of Ti, showing that the nanofibres are rearranged on planes perpendicular to the pressing direction. This configuration has been observed on the samples containing Ni and B as interfacial material as well as on the plain composite [7].

### 3.2. Thermophysical properties

The thermophysical properties are shown in Table 1. The properties of pure copper and a Cu/VGCNFs plain material with no additives [11] are shown as a comparison of properties. These properties have been measured “in plane”, i.e. the most favourable direction due to the

random planar configuration. The composite with Co additions was discarded due to the inhomogeneous microstructure. The values of the densification are also shown. In all the cases was above 95 %, although the composite with 5 wt. % of Ti has the lowest value. This should be connected with the high presence of carbon nanofibre agglomerates (see Figure 4) in the composites with higher amount of Ti. Extra Ti would also alloy with the Cu and reduce the thermal conductivity of the matrix.

Regarding the CTE, only slight reduction as compared with copper was achieved (see the last column of Table 1). The composite with nickel expanded even more than the copper. Moreover the composites containing Boron and the Ti were more effective over those including Nickel. The composite with the lowest amount of Ti showed the lowest value of CTE. This can be attributed to a better distribution of the nanofibres (less agglomerates) that allows the transmission of stressed more homogeneously.

Concerning the thermal conductivity a similar trend as for the CTE was observed. On the one hand the composite containing Nickel showed the lowest value of thermal diffusivity and conductivity. This can be explained through the observed microstructure. The Nickel, instead of being placed at the interface, was solubilised through the copper matrix. This was detrimental for the thermal conductivity of the matrix. On the other hand the composites containing B and Ti showed better results. This would be attributed to the formation of carbides, which are beneficial for the thermal transport at the metal/carbon interface [12].

In any case the values of the thermal conductivity were lower than the pure copper. Several possibilities are arisen that would explain these low values of thermal conductivity:

- 1) The presence of small defects in the composite, such as low amount of impurities (oxides, carbides and other elements), porosity, poor quality of the interface and so on.

- 2) The thermal conductivity of the carbon nanofibres was claimed to be 1200 W/mK [13]. This should be considered as an ideal upper value, since it does not take into account defects, structure disorders and fully straightness. On the other hand, Yu et al. reported an experimental value close to 10 W/mK [14], but they also concluded that the defect density and thermal resistance at the contact of the VGCNFs with the transmission line device would have a significant effect on the measured values.
- 3) Poor metal/carbon. The thermal transport in metals (like copper) is based on electrons, while the thermal transport of nanofibres is based on phonon [14]. Therefore scattering at the interface will take place [12].

As shown in Table 1 the thermal diffusivity is the factor than in accordance with the expression (1) mainly dominates the final value of the thermal conductivity therefore the efforts should be addressed to the increase of the thermal diffusivity especially through the interface. The results of the thermal diffusivity on Table 1 showed an improvement of the composites containing B and Ti (0.3 w %) over the plain composite (no interface), but this enhancement was not enough. Further efforts must be addressed to the optimization of the Ti and B amount of the composites or the inclusion of alternative elements at the interface able to react with carbon to promote the formation of carbides such as Mo, Ta, Cr or W.

#### 4. Conclusions

The present study contains a preliminary work for the modification of the interface of copper/carbon nanofibre composites with alloying elements such as nickel, cobalt, boron and titanium. A comparison of the effect of these elements on the microstructure and thermophysical properties (coefficient of thermal expansion and thermal diffusivity) is given. The incorporation of nickel and cobalt is less effective than boron and titanium. On the one hand nickel and cobalt led to heterogeneous distribution of these elements in the final composites, which prevent to obtain the required properties. On the other hand, the incorporation of boron and titanium have given better results in terms of microstructure and therefore in thermophysical properties, presumably due to the formation of interfacial carbides. There was a significant reduction in the CTE in the end but regarding the thermal conductivity it has not been possible to obtain a value higher than the value of copper. Two likely explanations are arisen. The first one assumes to take into account a low thermal conductivity of the carbon nanofibres. The second one concerns a loss in thermal conduction at the metal/carbon interface.

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**Figure Captions**

**Fig. 1.** Microstructures of the Cu/Ni/VGCNFs composites: a) Nickel plating, b) Duplex coating after copper deposition, c) Consolidated composite and d) EDS Ni mapping.

**Fig. 2.** Microstructures of the Cu/Co/VGCNFs composites: a) Cobalt plating and b) Consolidated composite.

**Fig. 3.** Microstructures of the Cu/B/VGCNFs composites: a) Cu-B electroless plating and b) TEM images of the Cu/C interface.

**Fig. 4.** Microstructures of the Cu/Ti/VGCNFs composites: a) Coated VGCNFs + Ti nanopowders (5 wt %), b) Consolidated sample (0.3 w % Ti), c) Consolidated sample (5 w % Ti) d) EFTEM Ti mapping.

Figures

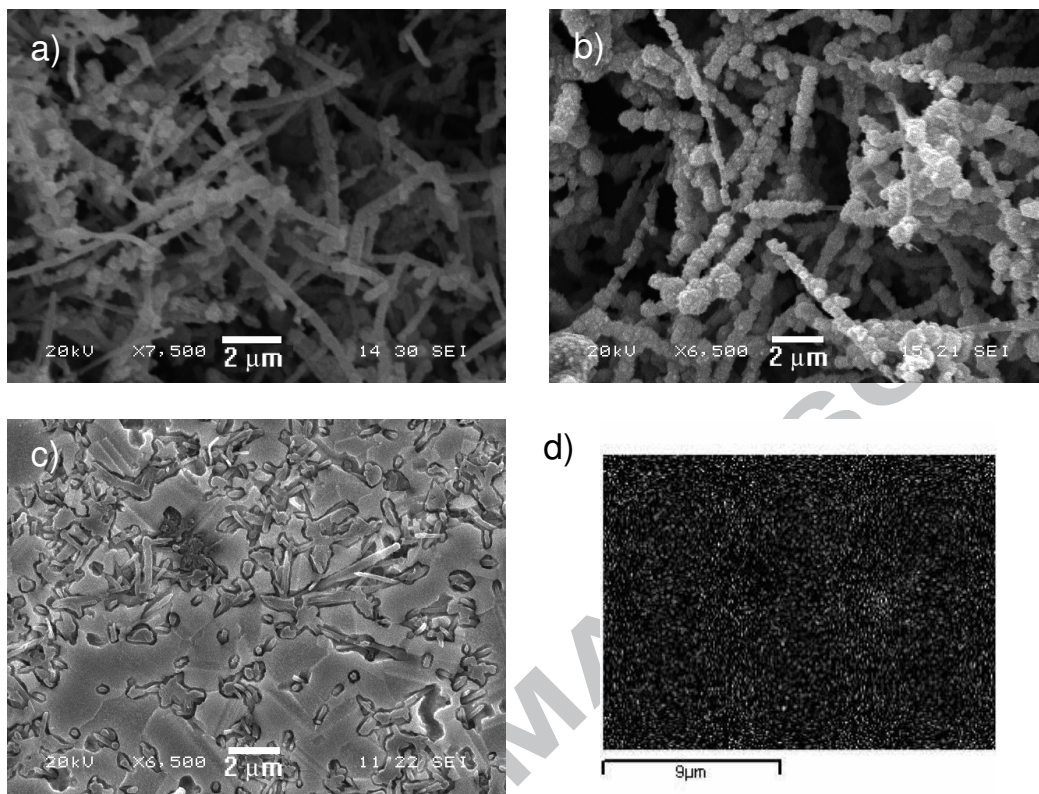


Figure 1

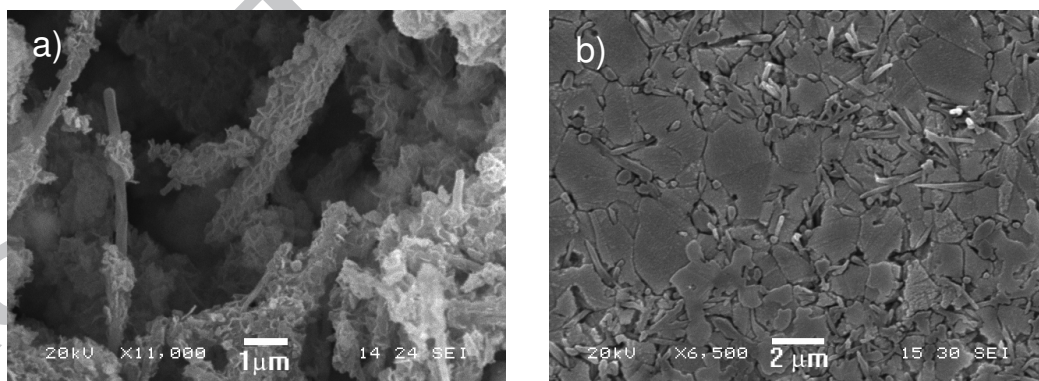


Figure 2



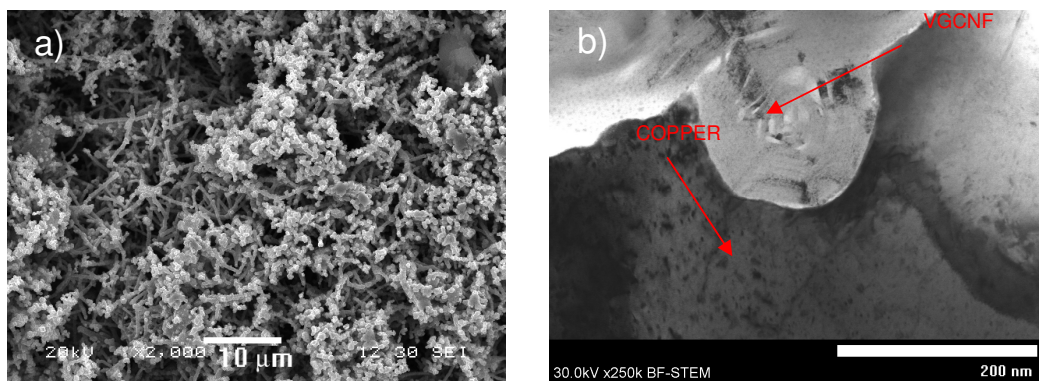


Figure 3

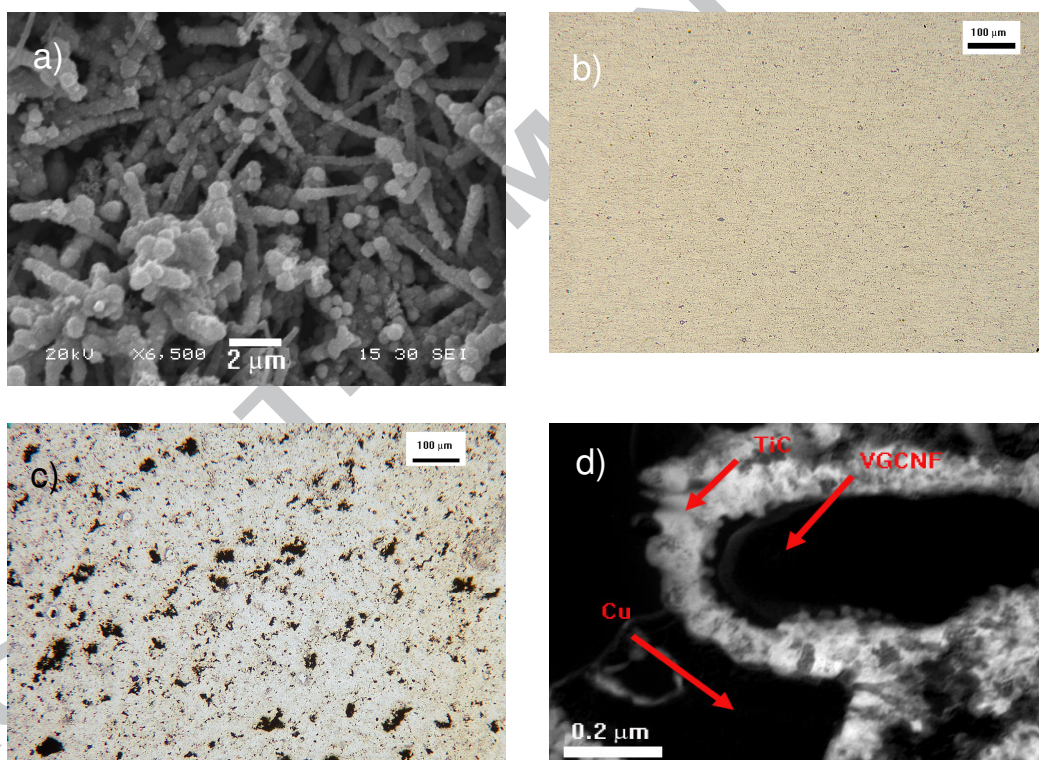


Figure 4

## Tables

Table 1  
Thermophysical properties of Cu/VGCNFs composites

Sample Ref.	Thermal Diffusivity* (cm <sup>2</sup> /s)	Specific Heat (J/KgK)	Density (g/cm <sup>3</sup> )	Degree of densification (%)	Thermal conductivity* (W/mK)	CTE* (room T)
Pure Copper	1.12	384	8.93	100	395	16.5
Cu/CNFs	0.74	503	7.51	99.67	280	16.4
Cu/Ni/CNFs	0.17	505	7.47	98.30	64	17.0
Cu/B/CNFs	0.78	514	7.56	98.51	306	15.6
Cu/0.3Ti/CNFs	0.80	517	7.52	99.16	311	13.6
Cu/5Ti/CNFs	0.56	493	7.27	97.47	200	15.7

\*Measured in the x-y direction