Novel Copper/Carbon Nanofibres Composites for High Thermal Conductivity Electronic Packaging

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ABSTRACT

Due to its outstanding thermal conductivity and coefficient of thermal expansion (CTE) vapour grown carbon nanofibres fibres (VGCNFs) are one of the most promising reinforcing materials of metal matrix composites (MMCs) for the thermal dissipation of future power electronics. VGCNFs provide currently an immediate availability at industrial scale and excellent performance-cost ratio for industrial production of electronic packaging components, specifically for space applications where higher power densities and weight save are crucial. This allows the jump from laboratory scale to massive manufacturing in a near future. MMCs reinforced with nanofibres lead to tailorable CTE, low density and high thermal conductivity. This makes these kinds of nanocomposites an optimal material for heat sinks in high power electronic devices working at high temperatures and high power densities, such as those based on new GaN semiconductors. The present work shows a manufacturing procedure of Cu/VGCNFs composites, based on electroless plating and further hot-pressing. Preliminary thermo-physical characterisation shows encouraging results for its use as heat sinks of power electronic devices.

INTRODUCTION

Currently, improvement of heat management in electronic devices is the most relevant problem to be urgently solved for current and future electronic industry, specifically for space applications where microdevices sizes are being decreased and thus powder densities increases. An efficient heat removal is the only way to improve power, reliability and efficiency of existing semiconductors such as Si, SiC and GaAs [1] and new semiconductors such as GaN [2] able to work at much higher operational temperatures. For instance, the new GaN technology for RF [3] amplification has a power density significantly higher than other technologies. Therefore, enhancing housings of new electronic components is essential for a very broad range of future telecom, space, defence and other applications. In this sense, a novel copper based composite material is presented as a suitable candidate for electronic packaging due to its outstanding high thermal conductivity and a Coefficient of thermal expansion (CTE) matching that of most ceramic semiconductors.

Devices for high power electronic applications increase cyclically their inner temperature as a consequence of their own operation. Traditionally, the way to dissipate heat from electronic devices (chips, boards, etc…) is carried out by passive strategies, which mean by the use of high thermal conductivity metals, such as copper or silver, as heat sinks. Nevertheless, large mismatches in coefficient of thermal expansion in between the heat sink (17 and 19 ppm/ºC for Cu and Ag respectively) and the electronic substrate leads to thermo-mechanical fatigue in the junction, thus finally leading to premature failure of devices. In conclusion, CTE and thermal conductivity of heat sinks have to be engineered for every specific application; otherwise lifetime of electronic devices can be limited dramatically. Several works review some advances and progresses for electronic packaging [4, 5]. Some advanced materials have been developed that combine low CTE and high thermal conductivity, from alloys like CuW, CuMo… , that possess medium thermal conductivity and tailored CTE; or alloys like Invar®, Kovar®… which although possesses good tailored CTE, have high densities and very limited thermal conductivities. In the last years some fibre reinforced MMCs have been also

developed, allowing CTE reduction at considerably high thermal conductivity. In this group there are numerous studies of MMCs with micrometric carbon fibres [6-8] in which the CTE mismatch with electronic substrates is notably improved, while the thermal conductivity can achieve values of around 400W/mK in the best case. Such conductivity can be achieved with copper reinforced with long carbon fibres, in the longitudinal direction. This is because conductivity of conventional reinforcement is frequently lower than those of metals, except for some highly graphitic carbon fibres or diamond particles, but at an extremely high cost.

Table 1: Summary of physical properties of the most promising MMCs for electronic applications.

Matrix		**Reinforcement Type**	**Vol %**	**Density g/cm^3**	**CTE 10^{-6}/K**	**Thermal conductivity W/mK**
METALS						
W/Cu	**75/25**		0	15.7	8.5	236
Mo/Cu	**75/25**		0	9.8	9.0	180
Al/Si	**50/50**		0	2.5	11.0	140
W/Ni/Cu	**95/3.5/1.5**		0	18.0	4.5	173
Cu/Invar/Cu			0	8.3	6.5	138(XY); 40(Z)
Cu/Mo/Cu			0	9.8	6.0	210(XY); 170(Z)
COMPOSITES						
C fibre		-	0	1.8	L=4-5, T=-1	100-500
Carbon Nanotubes (SWCNTs)		-	0	2	-1.0	6600
Vapour Grown C Fibres		-	0	1.8-2	-1.0	1950
Carbon		VGCF	70	1.8-2		910
Epoxy		C fibre	60	1.85	-1.1	310 (XY)
Epoxy		VGCF	73	1.87		661
SiC		VGCF	20	2.9		310
Copper		Diamond	50	5.35	5.5	420
Copper		C fibre	28	7.2	6.5	290 (XY)
Copper		CNTs	50	5.45	-	1024
Copper		**VGCNF**	**50**	**5.45**	**5.5**	**840**
Copper		C particles	50	5.9	8-9	150-300
Beryllium		BeO	-	-	6.1	320
Aluminium		VGCF	37	2.44	5	642
Aluminium		C fibre short	40	2.40	4.0	230
Aluminium		SiCp	60	2.9	9-10	180
Aluminium		Graphite p.	50-70	2.2-2.0	6.5-9.5	190-270

The above Table 1 gives an overview of thermal properties of a variety of advanced metal and metal matrix composites for electronic packaging applications. While no experimental data are available on the literature, values reported for VGCNFs and carbon nanotubes (CNTs) composites based on them are obtained from theoretical calculations.

During the 70s the larger study of new carbon fibres grown from vapour phase hydrocarbons took place [9]. From here, further studies were carried-out showing outstanding mechanical and thermophysical properties, being thermal conductivity as high as 1950 W/mK [10]. Traditionally, there are two methods for the production of these vapour grown carbon fibers (VGCFs) named as “Fix bed” and “Flying seed”. The former is based on the growth from catalytic particles and is used to obtain high quality of VGCFs. The main disadvantage is that leads to low production yield. The latter is based on the continuous feed of catalytic seeds in a furnace and subsequently collection of the fibres at the bottom furnace exit. It is being used for mass production of novel carbon nanofibres (VGCNFs), typically some ten microns in length and diameter in the 30-150 nm range.

A plethora of papers can be found on the literature regarding properties, manufacturing routes and characterisation of CNTs and their composites (the most part of them with polymer matrix). However VGCNFs had been much less studied. Although CNTs shows considerably higher conductivity (higher than 6000W/mK at room temperature is reported based on theoretical calculations [11], VGCNFs provide much better availability and performance-cost ratio (see Table 2) for industrial production of electronic packaging components. Due to their tailorable CTE, low density and high thermal conductivity, VGCNFs reinforced MMCs constitute an ideal material for heat sinks in high power and high frequency electronic devices working at much higher temperatures, such as those based on new GaN semiconductors. Table 2 contrasts carbon nanofibres with other reinforcement based in carbon: conventional high

thermal conductivity carbon fibres and single walled carbon nanotubes. As it can be seen mechanical and thermophysical properties are in the middle. From this point of view VGCNFs can be considered as an intermediate material between carbon fibres and carbon nanotubes.

Table 2: Summary of physical properties of the most promising MMCs for electronic applications.

Reinforcement	Diameter	Length	Young Modulus	CTE (10^{-6}/K)	Thermal Conductivity (W/mK)	Price ($/kg)
Conventional carbon fibre (High modudulus and conductivity)	7-10 μm	200-500 μm	1 GPa	-0,5/-1,6	400-1000	1000
Nanofibre (VGCNF)	30-200 nm	30-200 μm	7 GPa	-1,0	1200-1900	200
Nanotube (SWCNT)	3-30 nm	1-10 μm	1 TPa	-0,6	6000	1000-60000

Several attempts have been carried out during the last years to use VGCNFs as reinforcement in polymers for several purposes [12, 13]. Nevertheless, few studies have been successfully carried out using VGCFs as reinforcement in a metallic matrix [14] and much less with VGCNFs The most part of the developments of carbon nanofibres/metal composites have been carried-out only in the powder state [15, 16], being those consolidate into bulk material very scarce [17]. Many problems not yet fully overcome, such as dispersion of nanofibres, blending nanofibres and metallic powders, absence of wettability between carbon and copper, compaction, sintering, etc.., make the production of this material a really challenging task but, at the same time, a really interesting development with huge potential use in industrial components.

PROCESSING ROUTES

One of the main drawbacks in VGCNFs handling and mixing with a matrix is dispersion. By its nature, with high aspect ratio (L/d) and Van der Waals attracting forces, VGCNFs tend to keep entangled in big clusters difficult to disperse in any media. However, some other difficulties, such as absence of wettability, solubility and reactivity between carbon and copper or other metals [18, 19], or density mismatches with most of metallic matrices, makes it very difficult to apply production routes of metal matrix composites in liquid state (stir-casting, rheocasting or liquid infiltration of porous performs). Therefore, the most interesting manufacturing routes are those based on powder metallurgy and its many variants, in which the matrix is handled in powder state and composites are consolidated in solid state. However, dispersion of nanoreinforcements inside the matrix, and more in particular VGCNFs, is a problem that has to be addressed and solved before arriving to encouraging results, that means the lowest porosity values in the composites consolidated.

It is important to underline that the present investigation is focused towards the manufacturing optimisation of Cu/VGCNFs for electronic packaging applications, so a reasonable target for volume fraction of reinforcement inside copper will be always over 20%vol. in order to minimise CTE on composite samples and match it with electronic substrates as much as possible. The work carried out in the present investigation is based on the use of VGCNFs from different suppliers: APSCI from United States (Pyrograf Products, 60-150 nm in diameter and 30-100 μm in length), and Showa Denko from Japan (150 nm mean diameter and 100-200 μm in length).

First steps of the present investigation were focused towards the application of conventional powder metallurgy procedures [20]. In these experiments VGCNFs were blended with micrometric copper powder (Ecka granules, mean size 45 μm) in "Turbula Mixer", aided with and without the use of small Zirconia balls (2mm in diameter). This results in an inhomogeneous mixture, poor disentanglement and to excessive damage of the nanofibers as well. Preliminary dispersion test were also carried-out by VGCNFs predispersion in N-Methyl Pirrolidone (NMP) and then subsequently mixed with conventional copper powders. These results were very similar to the previous ones, having also in mind that VGCFs and Cu powders are quite different in size, being this mismatch several orders of magnitude higher than diameter of nanofibres. This wet route was then improved by the use of copper nanopowders as matrix. While the homogeneity of the composite in powder state was considerable better, once consolidated into a bulk , the material shows excessive oxidation and porosity as well as worse distribution of the embedded nanofibres into the matrix.

With the aim of improve these poor preliminary results, other manufacturing techniques were assessed. In particular, as the reactivity between filler and matrix does not exist during the consolidation process, this can lead to materials with

inappropriate interface. Thus, it is necessary to address those manufacturing techniques that improve this aspect, which means those processes that promote a good contact between matrix and reinforcement. In this way VGCNFs were coated by copper by the so-called electroless plating technique [21], which is also reported for coating other nanometric reinforcements [22-24].

Table 3: Catalysing and Plating baths characteristics.

Step	Composition	Concentration	Time
Sensitization	HCl	40 ml/l	30 Min
	$SnCl_2$	10 g/l	
Activation	HCl	0,5 ml/l	30 Min
	$PdCl_2$	0,25 g/l	
Plating	$CuSO_4$	10 g/l	Up to end of reaction
	$NaK(COO)_2(CHOH)_24H_2O$	50 g/l	
	NaOH	10 g/l	
	HCHO	15 ml/l	

There are some other techniques for coating nanofibres; nevertheless this was selected due to its simplicity and because it does not need expensive facilities. This plating technique is based on a chemical reaction leading to the deposition of metallic elements on top of the substrate. Prior to the coating process it is necessary to catalyse the VGCNFs surface. Thus, the fibre is immersed in two catalysing baths composed by hydrochloric acid and Tin (sensitizing bath), followed by a bath containing hydrochloric acid and Palladium (activation bath). After catalysing, nanofibers are soaked into the coating solution, in which the red-ox reaction is carried-out. VGCNFs are maintained into the solution until the bath turns into transparent. At this point all copper from the metallic salt is converted into metallic copper on the nanofibre surface. By this route several samples were performed. Processing conditions are described in Table 3. The whole catalysing process was aided by the application of ultrasounds and mechanical stirring into the baths. VGCNFs were rinsed and filtered at the end of each step and finally dried under vacuum at 100 ºC. Arai et al. have studied [15] how polyacrylic acid (PAA) increases VGCNFs dispersion, in the co-deposition with copper by electrodeposition. In this way this agent, PAA (Aldrich), was added to the plating bath in 140 µm/l concentration.

The cover thickness, and as a result the vol. % of the copper matrix in the final composite, were controlled by means of VGCNFs concentration into the plating bath. In this way different samples containing 20 vol. % and 40 vol. % of reinforcement have been assessed. Finally, copper coated VGCNFs are consolidated into dense samples by hot pressing. The consolidation was performed in the semisolid state (The melting temperature of copper is 1083 ºC). Thus, composite powders were inserted in a high strength graphite die (25 mm innner diameter) and hot-pressed under high vacuum with different pressure and temperature parameters: 25 and 35 MPa, and 700, 900 and 1000 ºC for 2 hours (See table 4).

RESULTS

A complete material assessment for thermal management has been done, including preliminary copper/VGCNFs thermophysical properties. Microstructural study has been performed in both loose composite powders and consolidated bulk material by Scanning Electron Microscopy (SEM - JEOL JSM 5910 LV) and in more detail by Transmission Electron Microscopy (TEM - JEOL-JEM 3000 F, at CME–UCM facilities, Spain). Total porosity was obtained by direct calculation, while open porosity was measured by Helium Pycnometry (Accupyc 1330). Material identification and contamination was done by Energy dispersive scanning – EDS while oxygen content evaluation (by LECO TC-436 analyzer). This last, along with porosity, is of great importance for achieving good thermophysical behaviour. Table 4 shows some physical characteristics of various composite samples.

Table 4: Processing conditions and physical characteristics of consolidated samples

Sample Ref.	**Supplier**	**Vol. % of reinforcement (Aprox.)**	**Temperature (ºC)**	**Pressure (MPa)**	**Density (g/cm^3)**	**Porosity %**	**Open Porosity %**
1	APSCI	20	1000	25	7.22	3.23	1.74
2	APSCI	40	1000	25	5.54	7.12	6.40
3	Showa Denko	20	700	35	7.15	2.27	1.68
4	Showa Denko	20	900	35	7.31	1.14	0.00

The morphology of the cooper coating and the distribution of the coated fibres was observed by SEM while TEM was employed to study some characteristics in detail, like copper/carbon interfaces. Fig 1 shows some images of composite powders before sintering. Nanofibres are homogeneously and continuously coated along the whole fibre surface (Fig 1a). Small areas of irregular copper coating are also observed, suggesting dendritic copper growth perpendicularly to the fibre axis. This kind of growth was also observed by TEM (Fig. 1b). Some hollow nanofibres (APSCI) are also coated on their inner walls (Fig. 1c). Fig 1d illustrates copper-VGCNF interface of Ref. 3 composite powders. Although the wettabiliy of copper with VGCNFs is very low, a continuous interface is formed along the surface of the fibres. In the copper region (dark zone) it can be observed a crystalline structure, composed by some nanosized grains. In the carbon region (light zone) it can be distinguished some atomic planes, that point-out the highly graphitisation degree that is characteristic of Showa Denko carbon nanofibres.

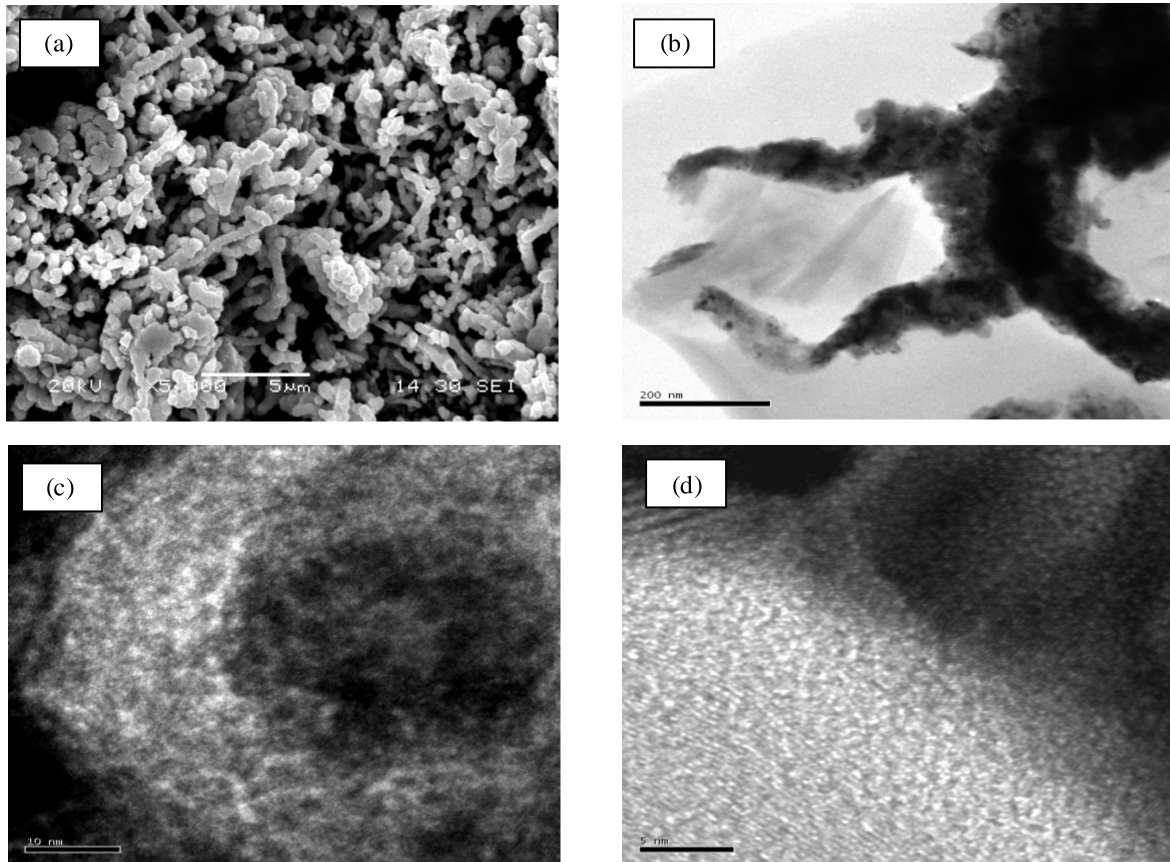

Fig. 1: Microstructure of samples before hot-pressing: (a) SEM image of coated nanofibres (Ref.1 - 20 vol. %), (b) TEM image isolated coated fibre (Ref 2 - 40 vol. %), (c) TEM image of coated outer and inner walls (Ref 2 - 40 vol. %) and (d) Cu/VGCNFs interface (Ref 3 and 4 - 40 vol. %).

In the same way, the microstruture of the bulk composites (after sintering) are shown in Fig. 2, where the showed composite sections are those perpendiculars to the pressing direction. Fig. 2a shows ref. 4 (20 Vol. %), where nanofibres are quite well dispersed and embedded in the copper matrix. Fig. 2b illustrated ref. 2 (40 vol. %). In this case nanofibres are closer, decreased the distance between them and standing some of them in contact. The homogeneity is quite good. By TEM microscopy (Fig 2c- Ref. 2) it can be seen that VGCNFs are correctly embedded in the copper matrix and the interface is highly continuous after hot-pressing at temperature as high as 1000 ºC. Fig 2d shows the analysis spectrum by EDS of ref. 1. There is no contamination of plating baths. The Au content is attributed to sample preparation for SEM.

The porosity degree increases proportionally to vol. % of reinforcement, since the higher content of nanofibre the more entanglement is presented; consequently the quantity of gaps to fill by copper is higher. With respect to open porosity, it increases with vol. %, being for Ref. 4 null. This makes of this composite a good material for electronic housing in

space, reaching suitable hermeticity. Nevertheless it is necessary to make specific hermeticity testing. It is clear that a temperature decrease and pressure rise lead to obtain composites with improved density. Although the compaction was done below the melting temperature of copper, there is some oxygen content that forms some cuprous oxide (Cu_2O) amount. This creates a eutectic point that reduces cooper melting temperature. This temperature could also be reduced by the high specific surface, as a consequence of the formation of nanosized copper grains during the coating of the VGCNFs [22]. Therefore at 1000 ºC some amount of copper can migrate from the coating of VGCNFs and coalesce into big clusters, avoiding the consolidation of coated VGCNFs and making in this way quite difficult to achieve complete densification. At 700 ºC copper have high plastic behaviour, but not enough to diffuse appropriately and avoid the formation open porosity during sintering. Consequently, there is a compromise between temperature and pressure. As a result 900 ºC and 35 MPa are suitable parameters to achieve good properties in terms of densification and reinforcement distribution.

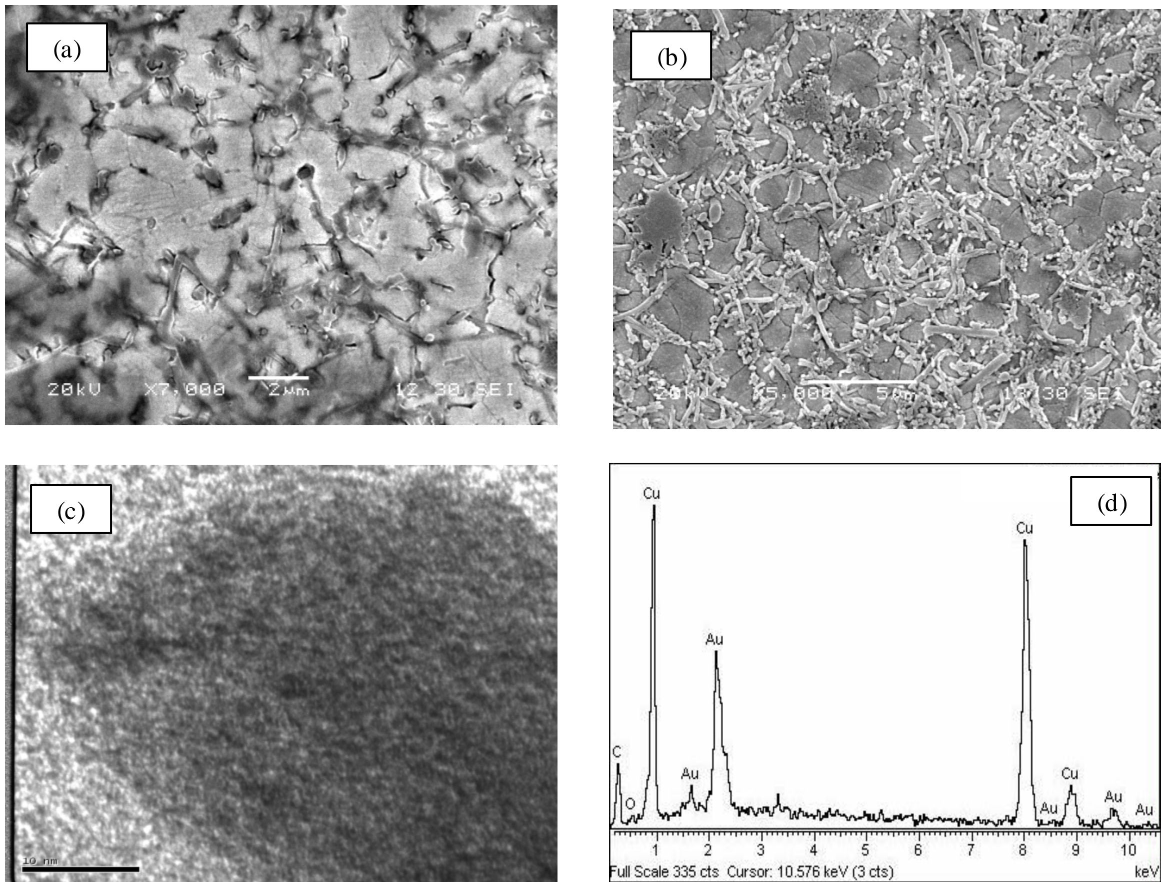

Fig. 2: Microstructure of samples after hot-pressing: (a) TEM image of sample consolidated at 900 ºC (Ref.4 - 20 vol. %), (b) TEM image of sample consolidate at 1000 ºC (Ref 2 - 40 vol. %), (c) TEM of Cu/VGCNFs interface (Ref 2 - 40 vol. %) and (d) Cu/VGCNFs interface (Ref 3 and 4 - 40 vol. %).

Another remarkable point is that nanofibres act as grain refiner. It is seen by TEM microscopy (Fig 3a - Ref 1) that copper matrix is composed by nanograins with sizes less than five nanometres, even the consolidation was completed at 1000 ºC. This low grain size causes some oxidation of copper that is likely formed during copper plating and may also during drying. Therefore Ref. 3 was plated under argon bubbling to obtain oxygen free copper coatings. The oxygen content (wt. %) of Ref. 1 and 3 were measured by LECO. The result for Ref. 1 was 1.3 wt. %, while for Ref. 4 was 0.35 wt. %. fig. 5(a).

Finally, some preliminary thermo physical characterisation has been carried-out. Here are reported for the first time thermal conductivity and coefficient of thermal expansion (CTE) for consolidated Metal/VGCNFs composite. The thermal conductivity measured on Ref. 1 was 220 W/mK, while CTE measurement is shown on fig. 4. At room temperature CTE is 7x10-6 /K, and increases quickly, reaching the copper value at 80 ºC. This thermal behaviour

points-out that there are not strong bonding at the copper/VGCNFs interface. In fact, as shown in Fig 2c the electroplating process only leads to a physical attachment of VGCNFs with the matrix. At temperatures over 80 ºC this physical bonding is not enough to support the stresses due to shrinkage of nanofibres. At this point the expansion behaviour is similar to copper. The target properties of this composite material are shown in table 1. The typical temperature use for space application is in the 25 – 400 ºC range. Therefore, in view of the obtained results it is necessary to focus towards the development of stronger and more conductive interfaces, such by chemical bonding or functionalisation with compatible groups.

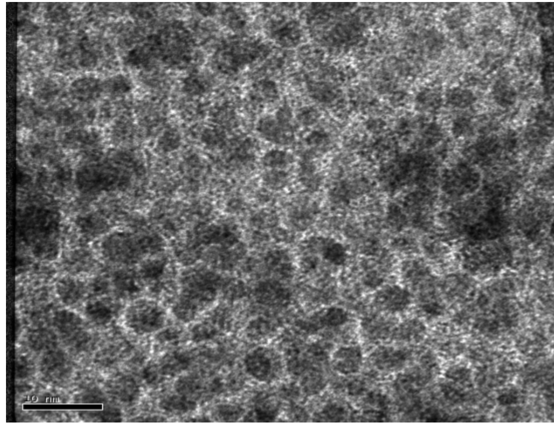

Fig. 3 – TEM image showing grains of copper matrix after hot-pressing.

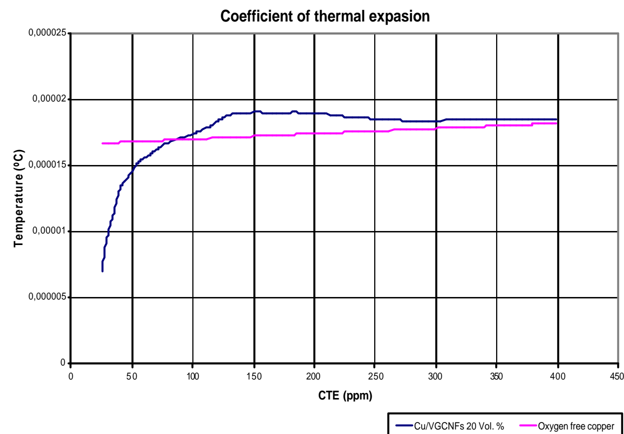

Fig. 4 Coefficient of thermal expansion of ref.1

CONCLUSIONS AND FURTHER WORK

A processing route based on electroless plating and further hot-pressing for VGCNFs reinforced copper matrix composites have been studied and assessed. Consolidation at 900 ºC and higher pressures is beneficial for porosity and VGCNFs dispersion in the matrix. Minimum oxide amount is formed at the end of the process, which will be beneficial for the final thermophysical properties (CTE and thermal conductivity). Microstructure observed and physical properties measured suggest that the manufacturing processes here addressed are both suitable for the production of copper matrix composites reinforced by VGCFs and other type of nanoreinforcements (CNTs, nanoparticles, etc…) although a further reduction of remaining porosity at high vol. % and avoid oxide formation would lead to better thermophysical properties. Further work will also address some other critical characteristics of composites, such as interface modification by coating and/or functionalisation of fibres without degrading their physical properties in order to promote a better coupling of matrix and reinforcement, thus leading to improved physical and mechanical characteristics. Nowadays an extensive interface study is being carried out for the development of electronic packaging for high power of wide band-gap semiconductors (GaN).

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REFERENCES

[1] T. Sheppard, W.L. Pribble, D.T. Emerson, Z. Ring, R.P. Smith, S.T. Allen andJ.W. Palmour, "High power demonstration at 10 Ghz with FaN/A1GaN HEMT hybrid amplifier", *Device Research Conference, Conference Digest. 58th DRC*, pp. 37-38, June 2000.

[2] M. Micovic, A. Kurdoghlian, P. Janke, P. Hashimoto, D.W.S. Wong, J.S. Moon, L. McCray and C. Nguyen, "AlGaN/GaN heterojuntion field effect transistors grown by nitrogen plasma assisted molecular beam epitaxy", *IEEE Trans. Electron Devices*, vol. 48, pp. 591-596. March 2001.

[3] J.W. Palmour, S.T. Sheppard, R.P. Smith, S.T. Allen, W.L. Pribble, T.J. Smith, Z. Ring, J.J. Sumarekis, A.W. Saxler and J.W. Milligan, " Wide bandgap semiconductor devices and MMIC's for RF power applications", *Electron Devices Meeting Tech. Dig.*, pp.17.4.1-17.4.4, Chicago 2001.

[4] C. Zweben, "Advances in composite materials for thermal management in electronic packaging". *JOM*, vol. 50, issue 6, pp. 47-51, June 1998.

[5] P.K. Schelling, L. Shi, K.E. Goodson, "Managing heat for electronics", *Materials Today*, vol. 8, issue 6, pp. 30-35, June 2005.

[6] W. Buchgraber, G. Korb, T. Schubert, B. Kempf, "Carbon fibre reinforced copper matrix composites: Production routes and functional properties", *Proceedings of the Euromat Conference,* vol. 5, pp. 150-155, München September 1999.

[7] J. Coleto, C. Foruria, A. Madroñero, J. Cruz., "Liquid state processing of metal matrix composites reinforced by electroless plating copper coated carbon fibres". *Proceedings of the Conference Depots Metalliques Avec Particules*. pp. 199-205, France 1996.

[8] D.L. Ellis, D.L. McDaniels, "Thermal Conductivity and thermal expansion of graphite fiber-reinforced copper matrix composites", *Metall. Trans. A,* 24, 1993, pp. 43-52.

[9] T. Koyama, "Formation of Carbon Fibers from Benzene ", *Carbon*, vol. 10, issue 6, pp. 757-758 December 1972.

[10] J. Heremans and C.P. Beetz, "Thermal conductivity and thermopower of vapor-grown graphite fibers", Phys. Rev. B, vol. 32, issue 4, pp. 1981-1986, August 1985.

[11] S. Berver, Y.K. Kwon, D. Tománek, "Unusual high thermal conductivity of carbon nanotubes", Phys. Rev. Let., vol. 84, issue 20, pp.4613-4616. May 2000.

[12] K. Lozano, "Vapor-grown carbon-fiber composites: Processing and electrostatic dissipative applications*", JOM,* Vol. 52, issue 11, pp. 34-36, November 2000.

[13] G.G. Tibbetts, J.J. McHugh, "Mechanical properties of vapor-grown carbon fiber composites with thermoplastic matrices", *Journal of Materials Research,* Vol. 14, issue 7, pp. 2871-2880, July 1999.

[14] J.M. Ting, M-L. Lake and D.R. Duffy "Composites based on thermally hyper-conductive vapour grown carbon fiber", *Journal of Materials Research,* Vol. 10, issue 2, pp. 247-249, June 1995.

[15] S. Arai and M. Endo, "Carbon nanofiber-copper composites fabricated by electroplating", *Electrochemical and solid-sate letters*, vol. 7, issue 3, pp. C25-C26, 2004.

[16] I.S. Kim and S.K. Lee, "Fabrication of carbon nanofiber/Cu composite powder by electroless plating and microstructural evolution during thermal exposure", Scripta Materialia, vol. 52, pp. 1045-1049, February 2005.

[17] Y. Jang, S. Kim, S. Lee, D. Kim and M. Um, "Fabrication of carbon nano-sized fiber reinforced copper using liguid infiltration process", Composites Science and Technology, vol. 65, issue 5, pp. 781-784, April 2005.

[18] D.A. Mortimer and M. Nicholas, "The wetting of carbon by copper and copper alloys", *J. Mater. Sci.,* vol. 5, issue 2, pp. 149-155, 1970.

[19] G.A. López, E.J. Mittenmeijer, " The solubility of Cin solid Cu", Spripta Materialia, vol. 51, pp. 1-5, April 2004.

[20] J. Barcena, J. Maudes and J. coleto. "Manufacturing of new copper/vapour grown carbon nanofibres (VGCNFs) composites for heat management of power electronics", *Proceedings of ICCM15 conference*, Durban South Africa, July 2005.

[21] M. Paunovic, "Electroless deposition of Copper", *Modern Electroplating*, Ed. Schlesinger, M y Paunovic, M., John Willey and Sons, New York, pp. 645-665, 2000.

[22] R. Zhang, G. Lian, J. Guo, "Effect of Cu_2O on the fabrication of SiC_p/Cu nanocomposites using coated particles and conventional sintering", *Composites: Part A*, vol. 35, issue 11, pp. 1301-1305, 2004.

[23] Y. Feng, H. Yuan, "Electroless plating of carbon nanotubes with silver", *Journal of materials science*, vol. 39, pp. 3241-3243, May 2004.

[24] Wang, F., Arai, S., Endo, M., "Metallization of multiwalled carbon nanotubes with copper by an electroless deposition process", *Electrochemistry communications*, vol. 6, pp. 1042-1044, October 2000.