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# Elaboration and Properties of Carbon Fibre Reinforced Copper Matrix Composites

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## 1. Introduction

Carbon fibres reinforced copper matrix composites (Cu/C composites) offer an excellent thermal conductivity and a low coefficient of thermal expansion. Then, these composites are compromising heat dissipation materials for electronic application.

The modern electronic devices consist of a variety of metallic, ceramic, plastic or composite components. The large difference of coefficient of thermal expansion (CTE) between ceramic substrates, such as  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$ , and heat dissipation materials, such as Cu and Al, and Si and GaAs semiconductors, induces thermal stresses resulting in failures at the interfaces between the different layers of the devices (fig. 1). In high power dissipation packages, thermal management is an important issue to prevent thermal damage of sensitive components on the silicon chip, especially for high density electronic packaging. Thermal management is thus one of the critical aspects in design of multichip modules to ensure reliability of electronic devices with high packing and power densities. In this context, there is an increasing demand of new heat dissipation materials having low CTE combined with high thermal conductivity, such as Cu/C composites.

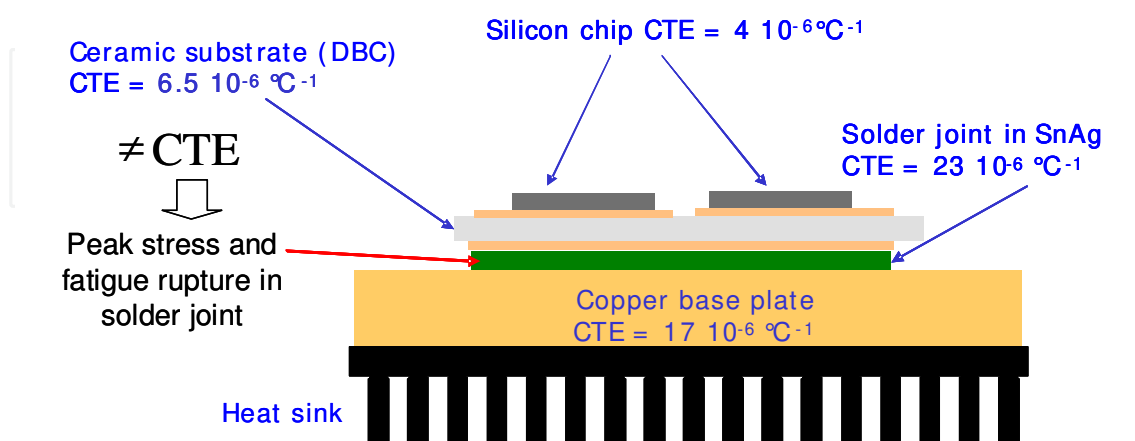


Fig. 1. Design of microelectronic devices with peak stress in solder joint.

Aluminium and copper are good candidate materials for the heat dissipation due to their thermal conductivity, but they have high values of CTE. Materials with low CTE and high

thermal conductivity, such as Al/SiC or Cu/W composites, have improved the reliability of electronic devices [Luedkte, 2004]. However, these composites are often too expensive for many applications. In addition, their machinability and the elaboration of thin sheets remain still very difficult and expensive.

Carbon fibres reinforced copper matrix composites corresponds to a good compromise between thermo mechanical properties and thermal conductivity [Korb et al., 1998]. Their main advantages are the following properties (Table 1):

- i. lower density than copper,
- ii. very good thermal conductivity,
- iii. low coefficient of thermal expansion,
- iv. good machinability.

Other advantages of copper/carbon fibre composites are adaptive thermal properties, which can be adjusted with the nature and the volume ratio of carbon fibres.

Function	Materials	CTE $10^{-6} \text{ }^{\circ}\text{C}^{-1}$ (RT- 250°C)	Thermal conductivity $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 25°C	Density
Chips	Si	4.2	150	2.3
	GaAs	5.9	45	5.32
Heat sinks	Copper	17	400	8.95
	Aluminum	23	230	2.7
	Aluminum /63 % SiC	8	165	3
	Copper /85 % W	6	180	17
	<b>Copper/40 % Carbon fibres (Pitch)</b>	<b>17 <math>\perp</math> 9-12 //</b>	<b>140-160 <math>\perp</math> &gt; 210 //</b>	<b>6.11</b>
Substrates	$\text{Al}_2\text{O}_3$	6.7	20-35	3.9
	AlN	4.5	170-250	3.26

Table 1. Properties of different electronic device materials (//: in plane properties;  $\perp$ : through-thickness properties).

The purpose of this chapter is to present the main research results during this last decade on the elaboration and properties of Cu/C composites. First, the different elaboration route of Cu/C composites is presented in this chapter. Then, the main physical properties of Cu/C composites are discussed, and a particular attention is given on the improvement of interface copper/carbon and thermal properties of Cu/C composites. Finally, the main potential applications of Cu/C composites are introduced, and their performances in focused applications are discussed at the end of the chapter.

## 2. Elaboration of Cu/ C composites

Several processes have been developed to elaborate copper carbon composites through hot pressing or squeeze casting [Praksan et al., 1997][Koráb et al., 2002]. However, all processes are difficultly perfecting and too expensive for elaboration of thin sheet materials. Besides, the poor wettability of carbon fibres with copper lead to low interfacial strength of composites obtained with casting or liquid process routes. This low wettability results often by large angle of the copper drop on graphite substrate (fig 2.). Then, one solution is the improvement of this wettability between copper and graphite with alloying element with

copper melt, such as Cr or Ti, in order to create a carbide layer to the copper/carbon interface [Goñi, 1998]. Then, the wetting angle decreases from  $137^\circ$  for the pure copper to  $46^\circ$  for the alloy Cu-1%wt Cr. This alloy has a good wettability with a final wetting angle lower than  $90^\circ$  because of the formation of chromium carbide ( $\text{Cr}_3\text{C}_2$ ) layer in the copper/carbon interface.

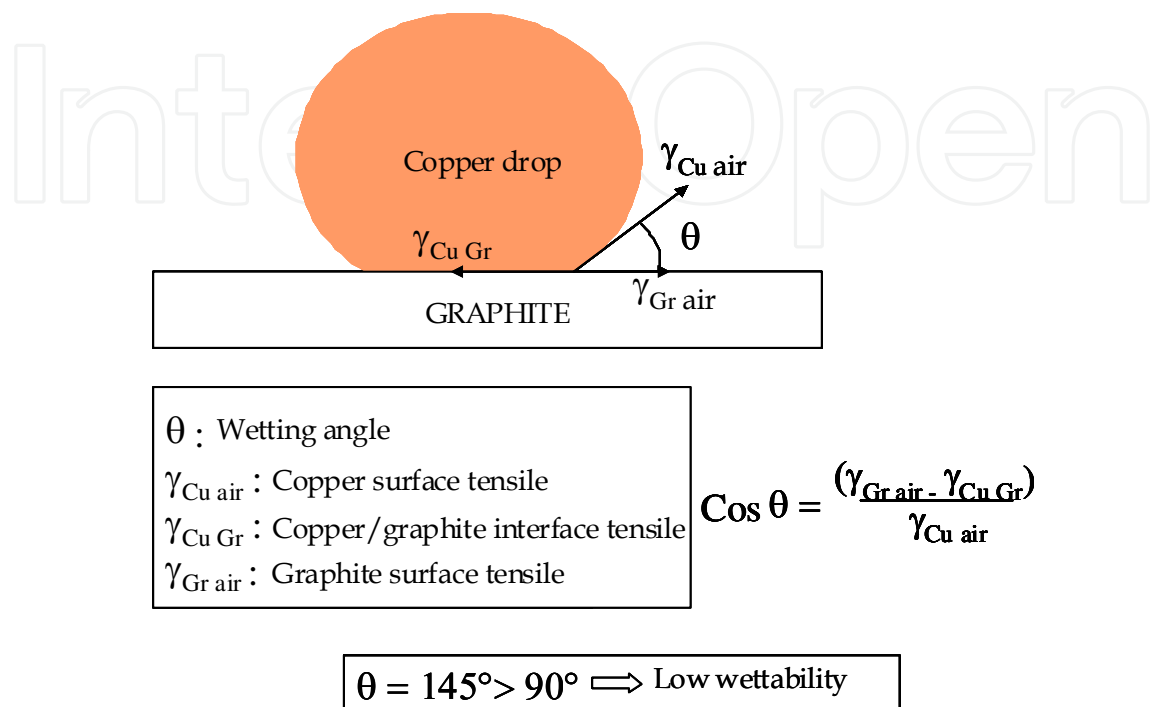


Fig. 2. Wetting angle of copper on graphite substrate.

Currently, the elaboration processes of Cu/C composites are based on powder metallurgy technology that offers many advantages such as the decrease of the machining cost (economical aspect), of power consumption (environmental aspect), and the better interfacial properties between copper matrix and carbon fibres. In opposite, the squeeze casting or liquid process route involves the low melting of matrix, low reactivity of metal liquid with carbon reinforced, and good wettability of metal liquid with carbon fibres.

Indeed, the no reactivity between carbon and copper leads to very low mechanical resistance of the interface and poor mechanical properties of composite. In order to improve the mechanical properties of interface, the carbon fibres require a previous surface treatment. These surface chemical treatments (in different acid solutions) of the carbon fibres, which may be used in order to create chemical bonding at the C-Cu interfaces, will be presented in more details in the following sections.

## 2.1 Starting copper powders and carbon fibres

The elaboration processes of Cu/C composites based on powder metallurgy technology require the starting copper powder, typically from 10 and 30  $\mu\text{m}$ , and short carbon fibres, typically from 1 to 10 mm of length. In opposite, the squeeze casting process does not require the short carbon fibres or copper powders, but continuous carbon fibres can be used in this route process.

The characteristics of copper powder and short carbon fibres have strong impact on the final structure and properties of composites. These characteristics can be listed as following points:

- Ratio size between copper particles and diameter of carbon fibres. High ratio is favourable to better distributions of carbon fibres in copper matrix, and a ratio higher than one is usually recommended.
- The electrolytic copper powders (dendritic shape) lead to better mixing with short carbon fibres that copper powders obtained by atomisation (spherical shape).
- The length of carbon fibres must be 100 times greater than their diameter in order to obtain the optimal thermo-mechanical properties.

The following figures (fig.3) show two main types of copper powder, the spherical copper particles obtained by atomisation and dendrite copper particles obtained by electrolytic route.

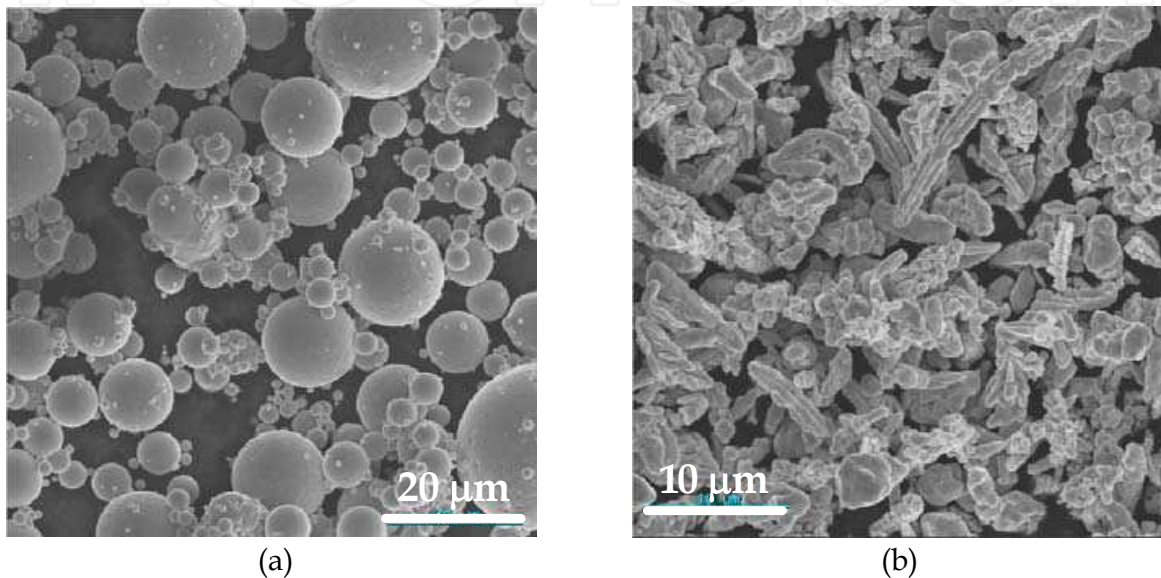


Fig. 3. (a) Copper powders obtained by atomisation from Nanoval, Germany (b) Copper powders obtained by electrolytic route (CH-UF 10) from Eckart Poudmet, Germany

Two main types of carbon fibres are usually used for industrial applications: polyacrylonitrile (PAN) and Pitch. Most of the carbon fibres currently produced in the world is based on PAN. Pitch fibres are produced using existing hydrocarbon resources (petroleum and/or coal) as the raw material to derive high performance carbon materials and product with a textile manufacturing approach.

In comparison to PAN, pitch carbon fibres have higher modulus capability, (equivalent) negative CTE, and higher thermal and electrical conductivity. These properties come from higher crystallisation of carbon fibre after graphitization step at high temperature. However, the Pitch carbon fibres are often more expensive than the PAN carbon fibres. Then, the Pitch carbon fibres are more appropriated for the thermal management applications.

Recently, Vapor Growth Carbon Nano Fibres (VGCNF) have been developed for potential thermal applications with theoretical thermal conductivity close to one of the diamond (1200 W/m.K). The VGCNF can be considered as an intermediate structure between carbon nanotubes and vapor growth carbon fibres. However, the properties of VGCNF have still been some controversy, since the strategy to measure their mechanical properties relies on non-conventional measurement techniques or inverse calculations from models.

The copper particles have dendrite shape with a range size from 25 to 30  $\mu\text{m}$  (Fig. 3b). Starting chopped carbon fibres have diameter ranging from 9 to 10  $\mu\text{m}$  and mean length of 6



mm. After milling, using planetary mill in alumina jar and alumina balls, the mean length of carbon fibres is decreasing down to 100 to 200  $\mu\text{m}$  (Fig. a, b and c). In fact, for carbon fibre length greater than 200 microns, the flowability of slurry decreases strongly leading to the impossibility of slurry casted thin film.

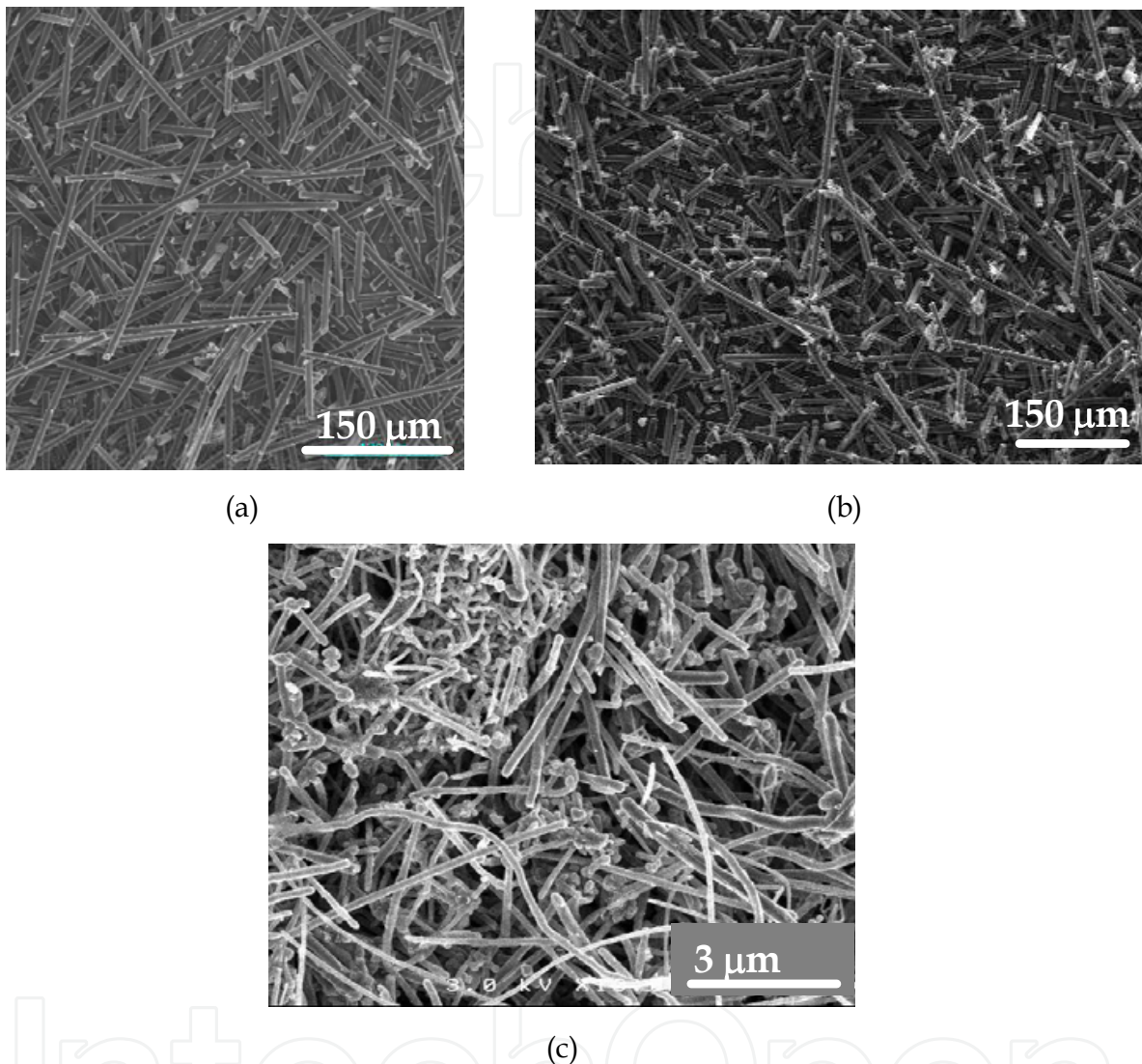


Fig. 4. Short carbon fibres, a) type PAN (T300), b) type Pitch (CN80C) and c) type VGCNF (Showa Denko)

The main physical characteristics of powders are given in Table 2.

## 2.2 Preparation of short carbon fibres or vapour growth carbon nanofibres (VGCNF)

After acid and ultrasonic treatments, the VGCNF are subjected to 3 consecutive steps (fig. 5). The sensitization (Sn absorption), activation (Pd absorption), and plating (Cu deposition) stages consist in the successive immersion of the VGCNF into the following baths:

- Sensitization bath: 10g/l  $\text{SnCl}_2$ , 40ml/l HCl 37%, distilled water;
- Activation bath: 0.25 g/l  $\text{PdCl}_2$ , 2.5 ml/l HCl 37%, distilled water;
- Plating bath: 10g/l  $\text{CuSO}_4$ , 50g/l  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , 10 g/l NaOH, 15 ml/l CHOHD distilled water

Materials	Specific surface area (m <sup>2</sup> .g <sup>-1</sup> )	Mean particle diameter (µm)	Apparent density (g.cm <sup>-3</sup> )	Density (g.cm <sup>-3</sup> )	CTE (10 <sup>-6</sup> /°C)	Thermal conductivity (W.m <sup>-1</sup> .K <sup>-1</sup> )	Young's modulus (GPa)
Spherical copper powder (Nanoval)	0.05-0.06	10-15	5.1	8.9	17	400	120
Electrolytic Copper powder (CH-UF 10)	0.3	5-10	1.8	8.9	17	400	120
Picht carbon fibres (KT120)	0.4	10 in diameter	(<1) Not applicable	2.12	-1,2 //	1-5 ⊥ 140 //	5-20 ⊥ 640 //
PAN carbon fibre (T300)	0.4	10 in diameter	(<1) Not applicable	2.10	-1,2 //	1-5 ⊥ 70 //	1-5 ⊥ 220 //
Vapour growth carbon nano fibres	13	0.06-0.15 in diameter	(<1) Not applicable	2.12	-1,2 //	1200 //	-

Table 2. Main characteristics of copper powders and carbon fibres.

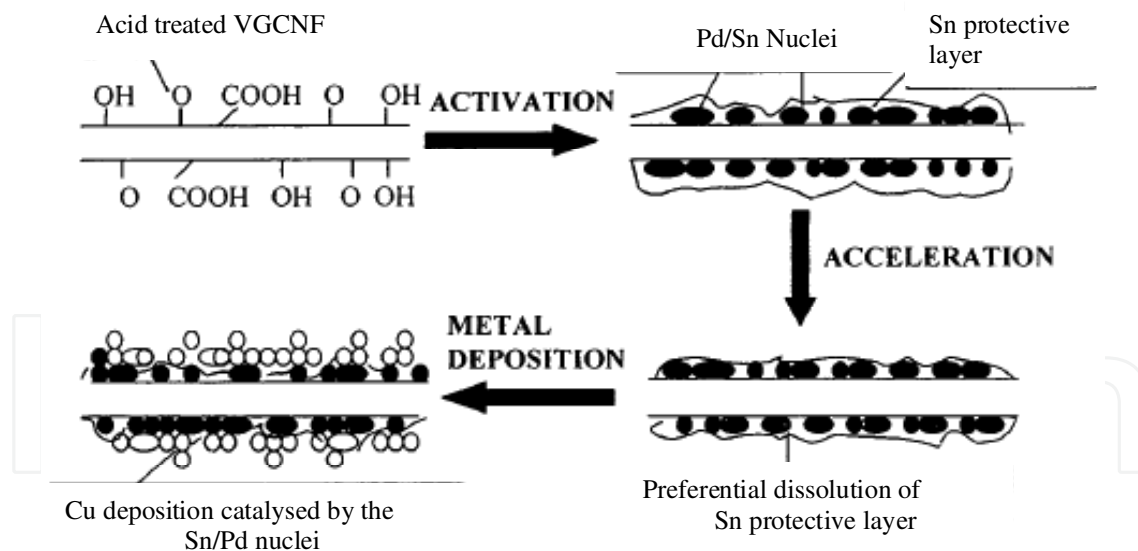
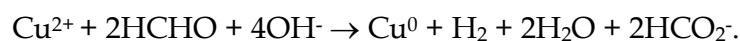


Fig. 5. General principles of electroless coating [Lang et al., 1999]

CHOH initiates the coating deposition by reducing the CuSO<sub>4</sub> according to the following reaction:



The main parameters, which have to be controlled, are: 1) the pH of the solution should be between 9 and 12 (the sodium hydroxide (NaOH) amount is adjusted in order to obtain the

desired pH), 2) the deposition time, 3) the temperature of the different baths and 4) the reaction rates.

After each immersion, the VGCNF are immediately rinsed with distilled water to stop the deposition process and, after the last step, the samples are carefully left dry.

Figures 6 and 7 show the evolution of the VGCNF Cu coating with different conditions. It has to be mentioned that the VGCNF have been treated with an acid solution (VGCNF + (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> 2/3 vol.) during 6 hours. before electroless coating.

Several points can be noticed from this study:

1. The pH of the solution is one of the key factors in order to obtain a homogeneous copper coating around each VGCNF. Homogeneous coating is obtained for pH greater or equal to 12 (fig. 6). For that pH value the VGCNF are mostly covered with homogeneous coating and the coating thickness can easily be controlled with parameters as Cu sulfate concentration, deposition time and VGCNF content.
2. Copper coating is more homogeneous when i) the reducer concentration (HCHO) is increased and ii) the water content of the solution is increased (fig. 7). Both conditions lead to a decrease of the coating speed (see for example fig. 7a and 7b for two water content 100 ml and 200 ml). The diagrams linked with these 2 water contents (fig. 7d and 7f) show the evolution of the bath temperature and Ph with the deposition time. For each diagram, the diagram background color (gray to white) shows the evolution of the color of the solution (non transparent from Ph going to 13 to 10 and transparent when all the Cu salt has reacted and therefore for a pH lower than 10) with reaction time. Whatever the starting point and solution the advancement of the reaction is linked with a decrease of the Ph and an increase of the solution temperature (the exothermicity of the reaction is linked with the VGCNF concentration within the bath)
3. Whatever the starting conditions, an increase of the bath temperature is always observed and linked with the decrease of the pH of the solution.

### 2.3 Squeeze casting

The squeeze casting is likely one of the most usual manufacturing processes for elaboration of metal matrix composites (MMC). This process consists in the production of rigid porous structures with reinforcement, in our cases carbon fibre structure, that are further infiltrated by metal molten under pressure (fig. 8). The molten copper is poured (1180°C) into the bottom half of the pre-heated die (close to 1000°C).

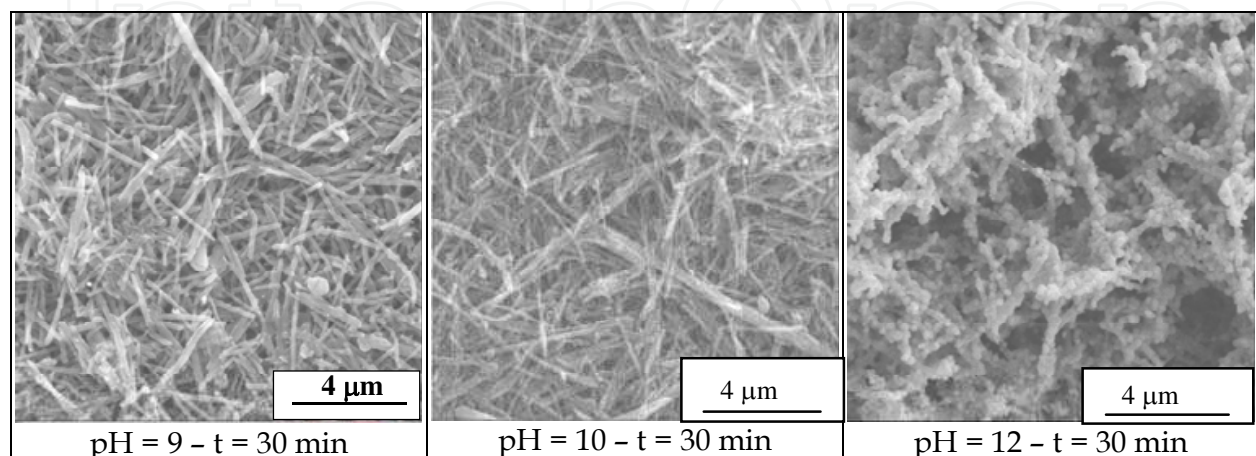


Fig. 6. Evolution of the coating behaviour with the pH of the solution



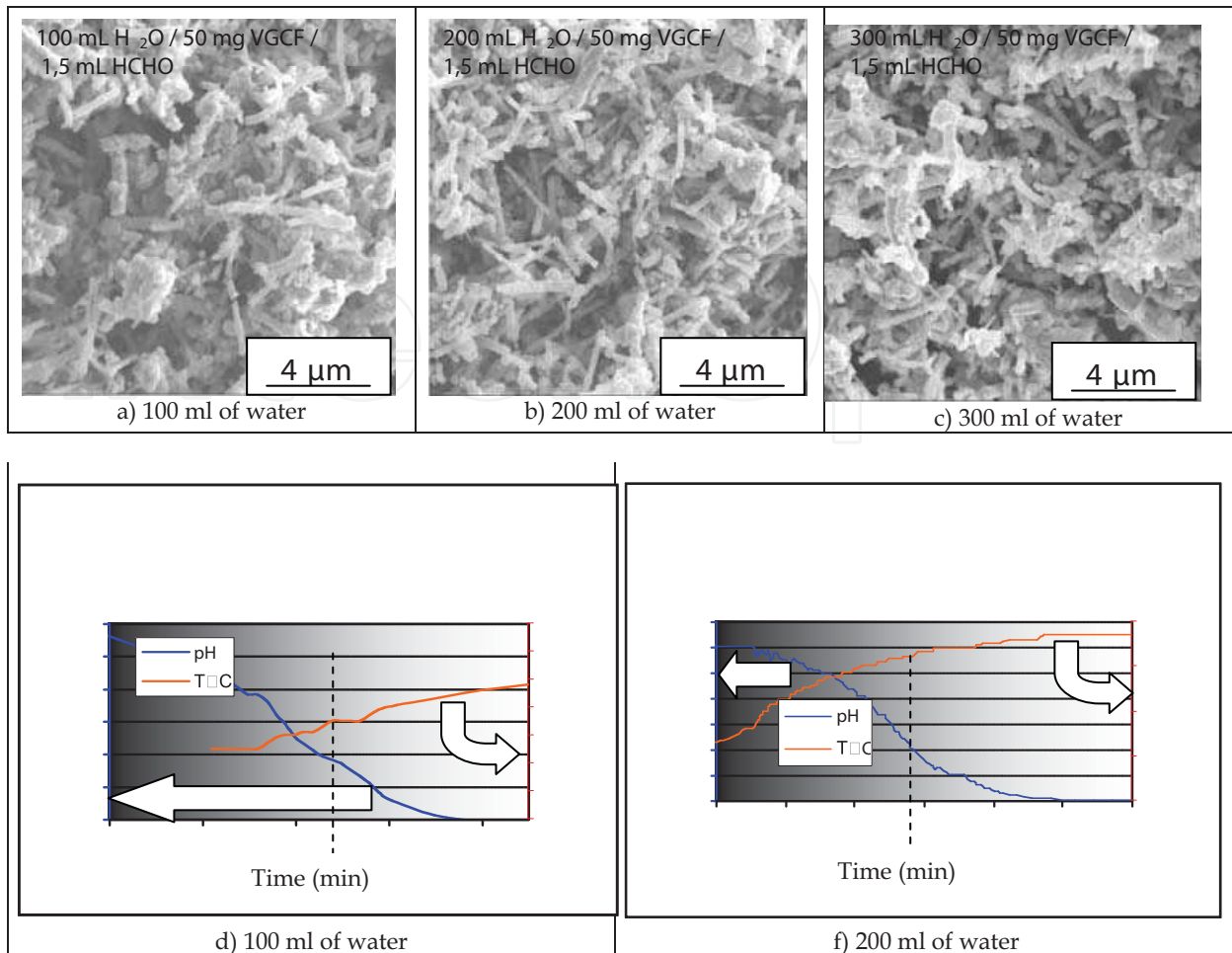


Fig. 7. Evolution of the coating behaviour with the water concentration

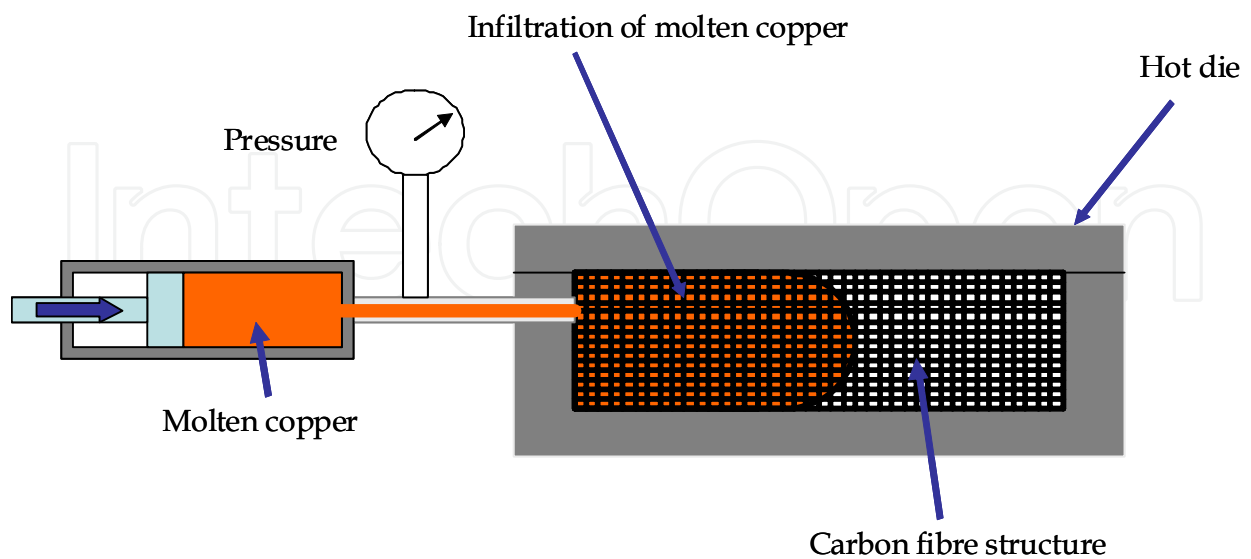


Fig. 8. Squeeze casting process

During the infiltration step, the carbon fibre structure is placed in the die. The main inconvenient of this technique is to keep steady the metal liquid during the infiltration step

because of the high melting point of copper (1083°C). Other inconvenient is linked to low wettability of copper with carbon, which involves the high infiltration pressure. This low wettability can lead to carbon fibre agglomerates and the presence of micro porosity in composites. Then, the squeeze casting is not the best process route for the elaboration of Cu/C composites.

#### 2.4 Tape casting process

The powder metallurgy process are mainly hot press for 3D design or thick substrate (3 mm of thickness) and tape casting process for thin film (from 100 to 500 microns of thickness). Tape casting process offers an original solution for the elaboration of thin sheets of metal matrix composites [Corbin et al., 1997] or, in our case, carbon fibre reinforced copper matrix composites. Tape casting process is currently used on the large scale to produce thin ceramic or multilayer structures of various materials for different applications, [Roosen, 1999] such as  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  substrates for electronic devices,  $\text{BaTiO}_3$  for multilayer capacitors, solid electrolytes for sensors or energy conversion, piezoelectric ceramics for actuators or transducers, etc.

The main characteristics of this process are low cost, accurate control of the thickness from 25 to 1000  $\mu\text{m}$ , good surface finish and high quality of laminated materials [Geffroy et al., 2007], (fig. 9).

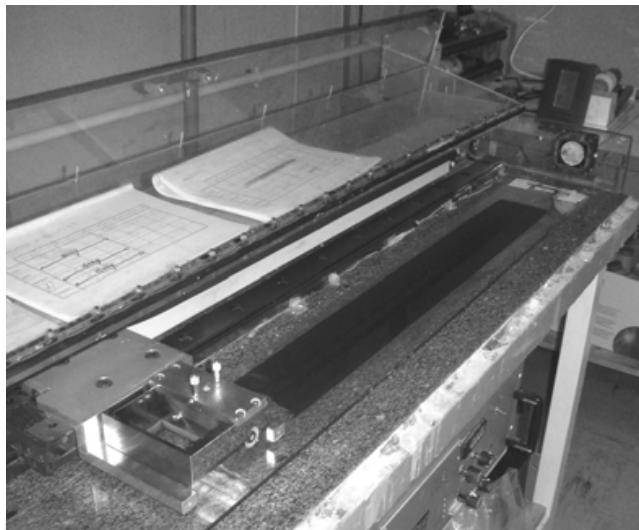


Fig. 9. Picture of discontinuous tape caster in SPCTS lab of Limoges, France.

One of the key points of tape casting process for the elaboration of the copper/carbon composite sheets is the elaboration of stable slurry with copper particles and short carbon fibres. Then, tape casting process (fig. 10) consists of the preparation of a suspension of the inorganic powder(s) in an aqueous or non-aqueous system. This slurry is a complex multicomponent system typically containing the following components: powder (ceramic and/or metallic), solvent, dispersant, binder, and plasticizer. The suspension must be stable, homogeneous and with a suitable rheological behaviour according to the tape casting process. The slurry is spread onto a support by means of a moving doctor blade. After evaporation of the solvent, the obtained dried tape, or green tape, was cut to the desired shape.

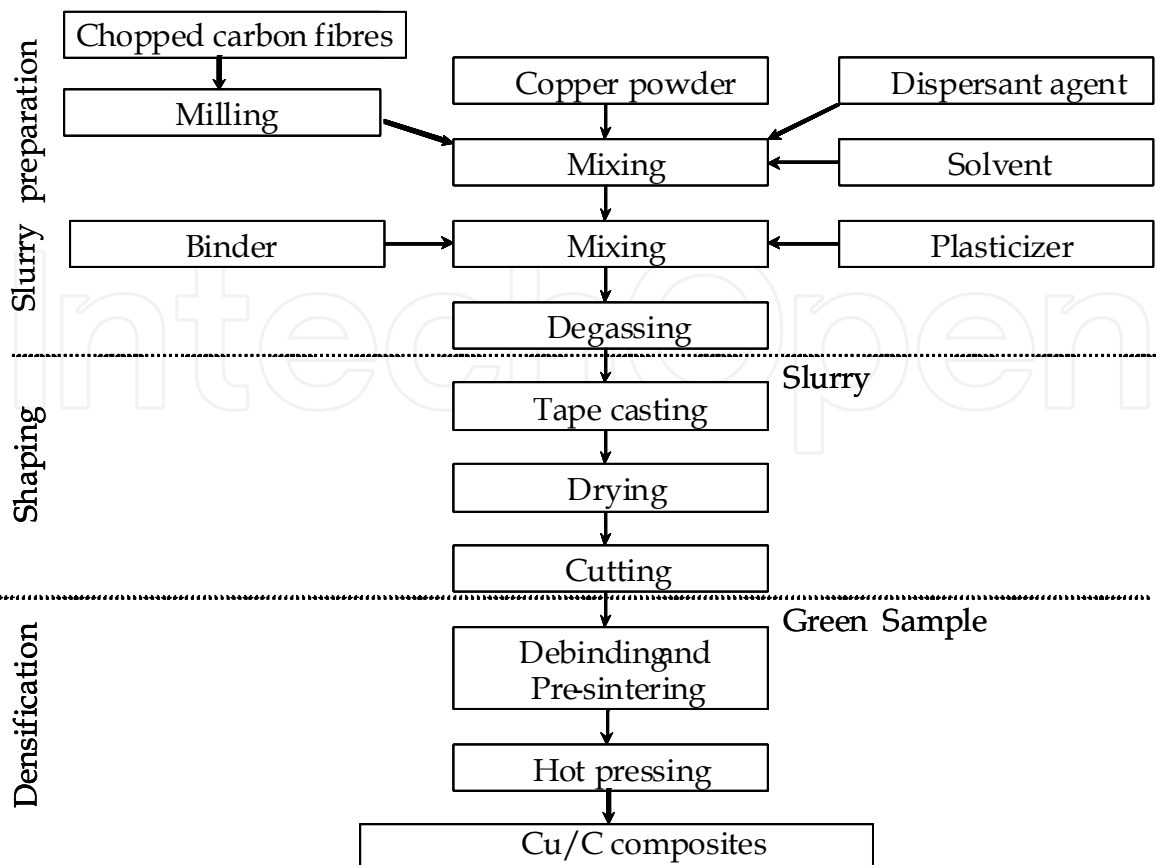


Fig. 10. Processing flow sheet of tape casting process

The main key points of tape casting process are discussed in the following sections.

#### a. Choice of organic components for tape casting

The solvent must wet the carbon fibres and the copper powder and should have a low temperature of vaporization. The solvent is the azeotropic mixture of ethanol and 2-butanone (40/60). Indeed, it offers a low boiling point (74.8°C) and a low dielectric constant that is favourable for a good wettability of carbon fibre [Johnson et al., 1987]. The nature of the solvent and of the powder determines the choice of organic additives, such as dispersant, binder and plasticizer [Moreno, 1992]. According to sedimentation tests in the azeotropic mixture of ethanol/2-butanone (40/60), one phosphate ester (CP213, Cerampilot, France) corresponds to the best desagglomeration and dispersion of copper and carbon particles. The optimum concentration of dispersing agent can be determined by rheological measurements or sedimentation tests. The minimum viscosity, then the best state of dispersion, is usually obtained for a dispersant concentration of 0.5 wt% on the dry powders basis.

The binder ensures the cohesion of the green sheet to avoid cracking during drying and for handling. After evaporation, the binder molecules form organic bridges between copper particles and carbon fibres, resulting in high mechanical properties of the green tape [Böhnlein-Mauß et al., 1992]. The binder must be easily removed at low temperature without residues. The binder is commonly a PolyMethyl MethAcrylate (PMMA) with a molecular weight ranging between 100 000 and 200 000 g.mol<sup>-1</sup>.

The plasticizer, which confers the flexibility to the green tape for easy handling, induces a decrease of the T<sub>g</sub> of the organic phase. An efficient plasticizer of the PMMA is usually the

dibutyl phtalate or polyethylene glycol with a low molecular weight close to  $300 \text{ g.mol}^{-1}$ . A good compromise between the flexibility and the mechanical strength of the green tape was obtained for a binder/plasticizer ratio close from 1 to 1.5.

#### b. Slurry preparation and tape casting

The tape casting suspension is prepared in two steps. The first one consists in dispersing, by planetary milling, the copper powder and carbon chopped fibres in 2-butanone/ethanol solvent with phosphate ester as dispersant. The binder and the plasticizer are added to the suspension in a second step and the complete slurry was homogenised, also by planetary milling, but at a lower rotating velocity. After homogenization, the slurry is degassed and directly casted onto a siliconed Mylar carrier film with a doctor blade. The doctor blade speed is fixed at  $0.5 \text{ m.min}^{-1}$  with a gap of 0.5 mm. The solvent evaporation is carried out at room temperature under air.

#### c. Green tape

The geometrical density of the green tapes varying from 2 to  $2.5 \text{ g.cm}^{-3}$  corresponds to a relative density ranging from 0.55 to 0.65 of TD (theoretical density), that suggests a rather good arrangement of particles, whereas the particle shapes, like short fibres or dendrite copper particles, are not favourable to a good compaction. However, the carbon fibres are oriented in the casting plan due to shear imposed during tape casting.

#### d. Thermal treatments

The organic components are removed during a thermal treatment at low temperature, i.e. debinding. The composites are then pre-sintering at higher temperature. The resulting composite structures have sufficient strength and flexibility for handling, but still present an important porosity. The thin sheets are then subsequently fully sintered by hot pressing (fig. 11?). In this densification step, 5 or 10 sheets (with thickness equal to  $200 \mu\text{m}$ ) can be pressed together for the elaboration of thick systems.

#### e. Debinding and pre-sintering

In the first step of firing, the organic additives, i.e. the binder, plasticizer and dispersant are burned out carefully. The removal of plasticizer and binder occurs, under air, between  $120^\circ\text{C}$  and  $350^\circ\text{C}$ , whereas the extraction, under nitrogen, is performed between 140 and  $400^\circ\text{C}$ .

Due to copper oxidation starting at  $150^\circ\text{C}$  under air, debinding of copper/carbon composite green sheets are performed at  $350^\circ\text{C}$  under nitrogen. In the second step of firing, the copper matrix is pre-sintered at  $750^\circ\text{C}$  during 30 mn in nitrogen. The resulting composite has a sufficient strength and flexibility for handling, but still presents an important porosity (20-30 % in volume), which results from the presence of carbon fibres. The densification of the copper/carbon composites starts at about  $650^\circ\text{C}$ .

#### f. Densification by hot pressing

The pre-sintered individual tapes or multilayers are introduced between the two pistons of the steel mould which were heated, under vacuum ( $0.66 \text{ Pa}$ ), by induction system and regulation monitor. The usual conditions of hot pressing correspond to  $650^\circ\text{C}$  with a heating rate of  $25^\circ\text{C.min}^{-1}$  under 50 MPa during 1 min. This last step of densification by hot pressing is presented in more details in the next section.

## 2.5 Hot pressing

Hot pressing process consists firstly in the preparation of powders mixing. This mixing, which contains ceramic, metallic powders and lubricant agents, must be stable and homogeneous.

The bad wettability of the carbon fibres by copper and the non reactivity between carbon and copper led to the formation of a stable porosity between the copper matrix and the carbon fibres during the densification stage. Thus, the full densification of copper/carbon composites is not possible by conventional sintering. Hot pressing technique, [Evans and McColvin, 1976][Jha and Kumar, 1997], under controlled atmosphere, is finally used in order to obtain fully dense materials.

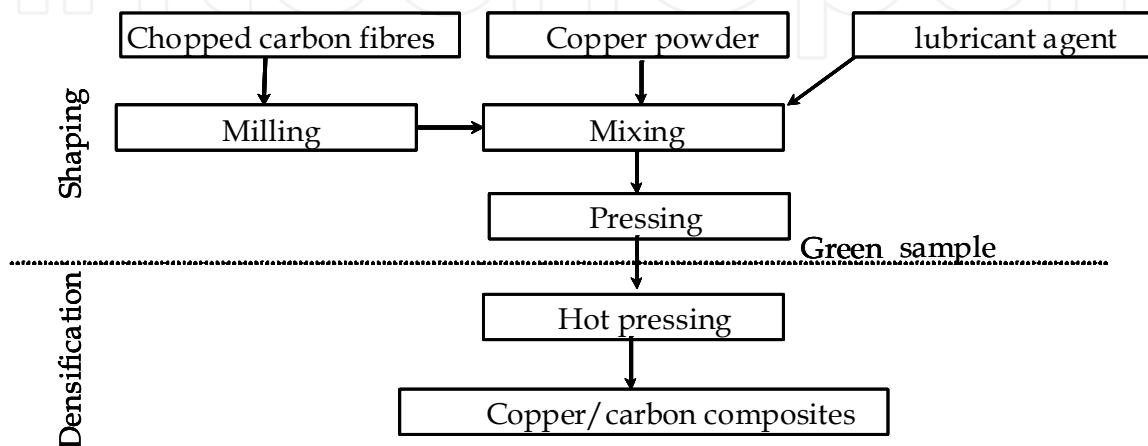


Fig. 11. Processing flow sheet of hot pressing

In a first step, powders are desagglomerated and mixed in ball milling with lubricant agent during 6 hours. Elaboration conditions, such as mixing conditions of the short carbon fibres and the copper powder, dimension and shape of the two powders must be optimized. The powders mixing is pressed to desired shape under 200 MPa, and the green sample obtained have finally sufficient strength and flexibility for handling but still shows important porosity close to 15-25%. Up to 200 MPa, the pressure can lead to the rupture of carbon fibres in green sample and the deterioration of final properties of composites.

In a second step, the green sample is heated and forged up to 600°C under 50 MPa. Figure 12 shows the hot press apparatus with the inducting heating system. The mould can be in steel or in tungsten carbide for higher temperature and pressure. To prevent copper oxidation or steel mould, the atmosphere of hot pressing chamber is usually inert atmosphere (nitrogen or argon) or primary vacuum. The temperature can be controlled with a thermocouple placed into the steel mould.

The temperature and pressure of hot pressing is adjusted in order to obtain full dense composite and to avoid the deterioration of carbon fibres. In the figure 13, the density of hot pressed sample increases with the pressure and the temperature of hot pressing. However, a high pressure can lead to breaks the carbon fibres if the copper is not enough soft. Then, the high temperature leads to a softening of copper matrix and to improving the copper flow around the carbon fibres during the hot pressing step. Finally, the optimal conditions correspond to a moderate temperature, 600-700°C, (which is a low sintering temperature of copper particles) with pressure between 50-100 MPa. The pressure must be higher than 20 MPa, which corresponds likely to the limit of elasticity deformation of copper particles before ductile deformation and copper flow step in composite materials.



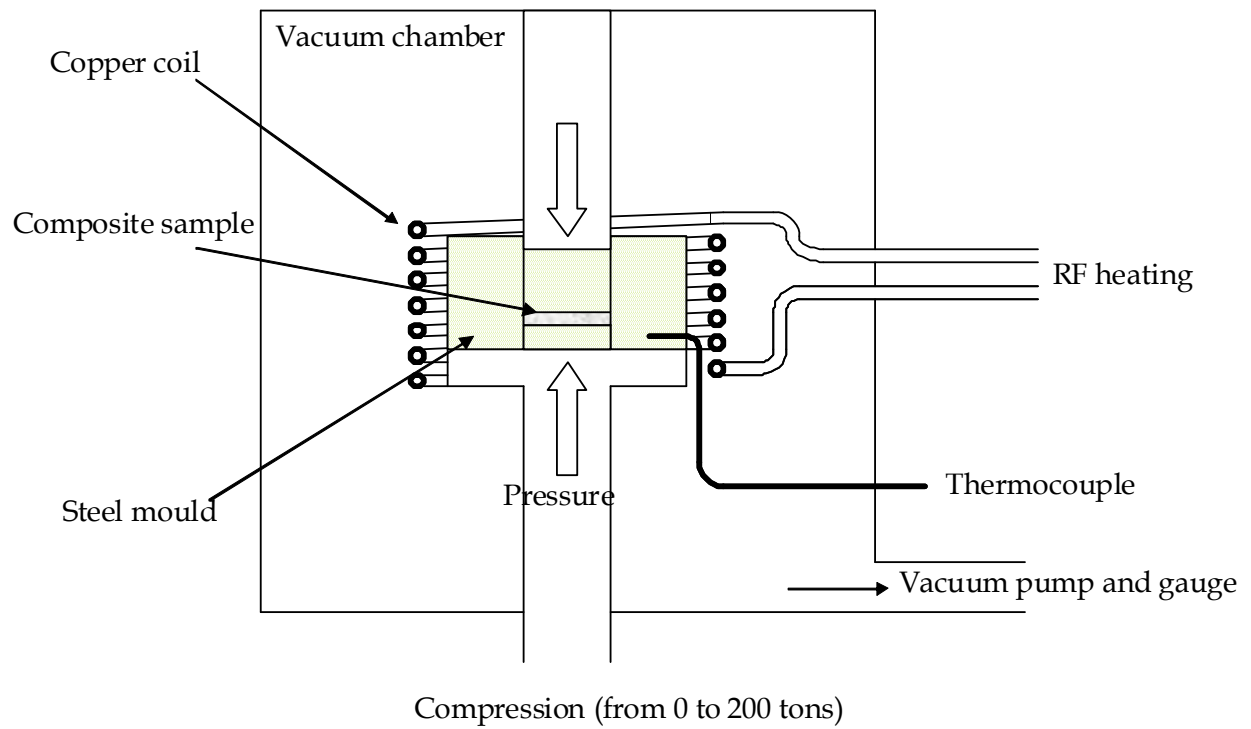


Fig. 12. Scheme of hot pressing facilities

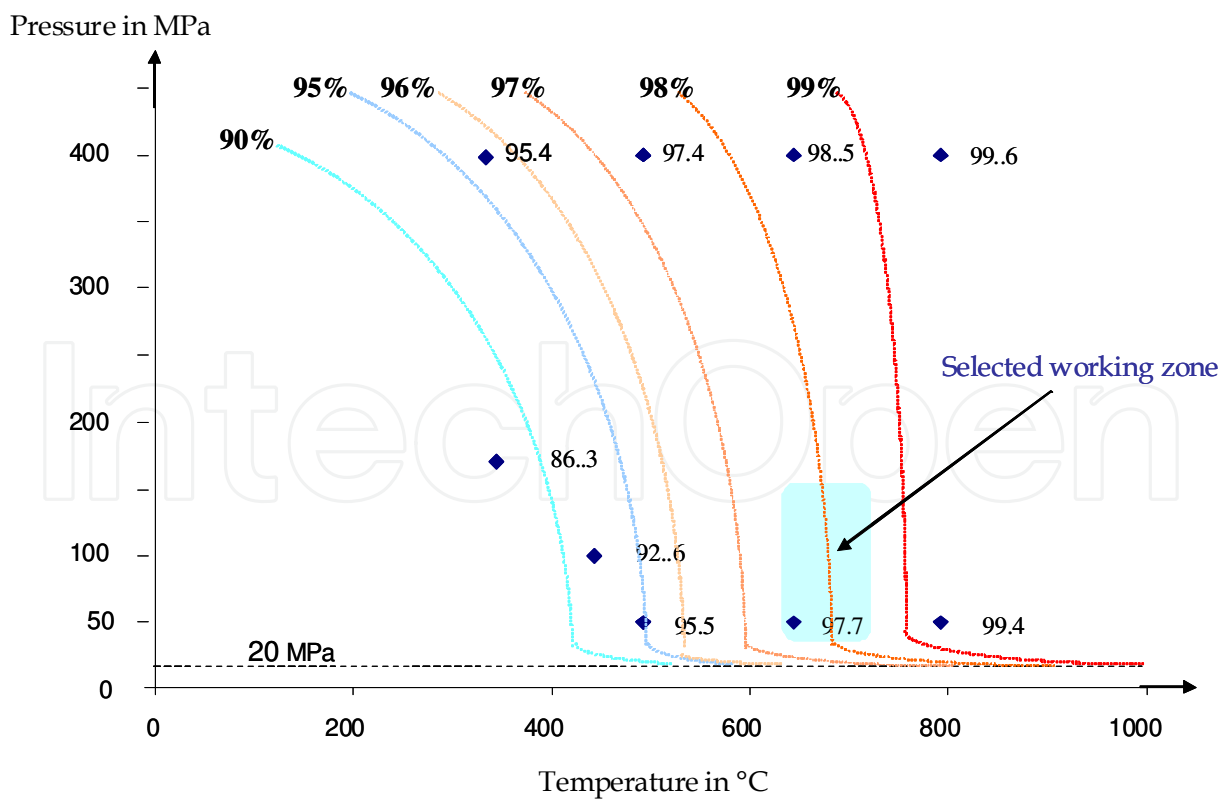


Fig. 13. Relative density of Cu/C composites in relation with temperature and pressure of hot pressing conditions

Besides, a high temperature of hot pressure involves the important technological cost, and it can lead the pre-sinterisation of copper particles, which is prejudicial to suitable softening of copper matrix during the hot pressing. Then, the optimal conditions of hot pressing correspond usually to the best compromise between optimal properties of Cu/C composites and process cost.

Finally, the main parameters of hot pressing, such as temperature, time and atmosphere in the thermal properties of the Cu/C composite materials must be adjusted in relation with the optimal mechanical and thermal properties of Cu/C composites.

## 2.6 Reporting of Cu/C composites

Composite heat-sink family shows the highest potential for application in heat sinks for electronic applications. The great advantage of this kind of materials is that they can combine metal, polymer and ceramics in a broad range of different products to tailor the final properties sought. Nevertheless, final properties of composites greatly depends on manufacturing processes.

Among the huge amount of different composites, the most efficient and so the most commonly developed for heat dissipation purposes, are metal matrix composites, and most specifically those based on copper and aluminum matrices with a broad range of different reinforcements.

Recently, some investigations in epoxy based composites reinforced with an extremely interesting new kind of carbon fibres (Vapour Grown Carbon Fibres, VGCFs) have shown outstanding thermal conductivities, near 650W/mK. These newly developed kinds of micro/nanofibres (commercially available since the nineties) exhibit the highest thermal conductivity of all materials known. Their special structure based on its manufacturing process (they are produced from gases) gives them a high potential to achieve a highly graphitic structure by a proper heat treatment, not achievable in other carbon fibres, thus leading to outstanding physical and mechanical properties. But the main problem encountered with epoxy based composites is their low highest temperature of use. Nevertheless, in any case, these composites could be applied up to a temperature near 120°C, where polymers can start degrading.

Undoubtedly, the most efficient composites for heat sinks are those based on Cu and Al with a number of different reinforcements. In general, metal matrix composites (MMCs) show several improvements in comparison with currently used materials in electronic packaging, among them the following can be underlined:

- Lower and tailorable CTE (the higher the volume fraction of reinforcement used, the lower the CTE is) to be as similar as possible to ceramic substrates. In the present development, in which a suitable electronic packaging component for GaN semiconductor device will be developed, the coefficient of thermal expansion must be as similar as possible to that of the electronic substrate. This reduction of the CTE mismatch supposes, therefore, a reduction of stresses between the components and their substrates during thermal cycling;
- High heat dissipation capability;
- Lightweight, suitable for space applications;
- High stiffness at high temperatures, being an useful characteristic in order to assure dimensional stability of electronic components working at high temperatures.

Due to their high conductivity, low CTE and lightweight, Al/SiC<sub>p</sub> (50-70%SiC<sub>p</sub>) composites represent one of the MMC kinds of materials that have found an easier way to be introduced

into real industrial applications [Luedkte, 2004]. Some manufacturing processes for this type of composites have been developed along the last years (infiltration and squeeze casting) for these materials, so they are already available (it depends very much on size, shape, etc...). Unfortunately, they are extremely difficult to machine, therefore, manufacturing processes must be net or near-net shape, in order to get a really profitable manufacturing process. Another interesting kind of MMCs for heat sinks is Cu/diamond composites. But their main problem, again, is that they are expensive because diamond is expensive and difficult to machine.

Looking, at the previous table 1, it can be said that copper based materials are the most promising among MMCs. Most of the composites based on this matrix are reinforced by ceramics (particles, short fibres, and long fibres) in order to reduce their extremely high CTE and match it with those of the semiconductor or other ceramic substrates. Nevertheless, carbon fibres also offer the big advantage of high heat and electrical conductivity. So, MMCs reinforced with long C fibres show excellent thermal conductivity along the fibre direction. Unfortunately, these types of composites are not usable in a broad range of heat sinks, as the excellent thermal conductivity is achieved in surface but not across the thickness. Of major interest are those composites reinforced with short fibres, as although in general terms thermal conductivity is more modest than those reinforced with continuous fibres, they have isotropic properties. In addition, their manufacturing processes are less sophisticated and expensive.

### 3. Properties of Cu/ C composites

The main properties of Cu/C composites depend strongly of process conditions. One of key points is the improvement of interfacial strength between copper and carbon during process. These main properties obtained by hot pressing and tape casting are discussed and presented in the following parts.

#### 3.1 Microstructure of Cu/C composites

The final density of materials is close to 94-98 %, and no specific degradation of carbon fibres is observed in the Cu/C composites materials microstructures.

Microstructure characterization (fig. 14) shows strong anisotropy structure between the perpendicular and parallel pressing directions. Carbon fibres are oriented in perpendicular plan of pressing direction due to the strains and stresses imposed by pressing conditions and geometry. It can be expected that carbon fibre orientation leads to anisotropic properties of the Cu/C composites.

#### 3.2 Coefficient of thermal expansion (CTE)

The CTE is measured using a differential dilatometer with a heating rate of  $10^{\circ}\text{C}\cdot\text{mn}^{-1}$  from room temperature to  $250^{\circ}\text{C}$  under nitrogen to prevent eventual oxidation of copper. Tested samples have typical size of  $5 \times 5 \times 20$  mm of length.

The CTE measured in parallel pressing direction of composite is close to  $17 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  (CTE of copper) for the different volume fractions of fibres. In opposite, CTE values in the perpendicular pressing direction decrease with carbon fibre volume fractions (fig. 15). These anisotropic properties are due to the strong anisotropy of carbon fibre properties (CTE =  $-1 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  in parallel axis and  $12 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  in perpendicular axis) and the orientation of the fibres in the perpendicular pressing direction. It has to be noticed that CTE values parallel and perpendicular to the fibre axis have same values whatever the carbon fibre type.

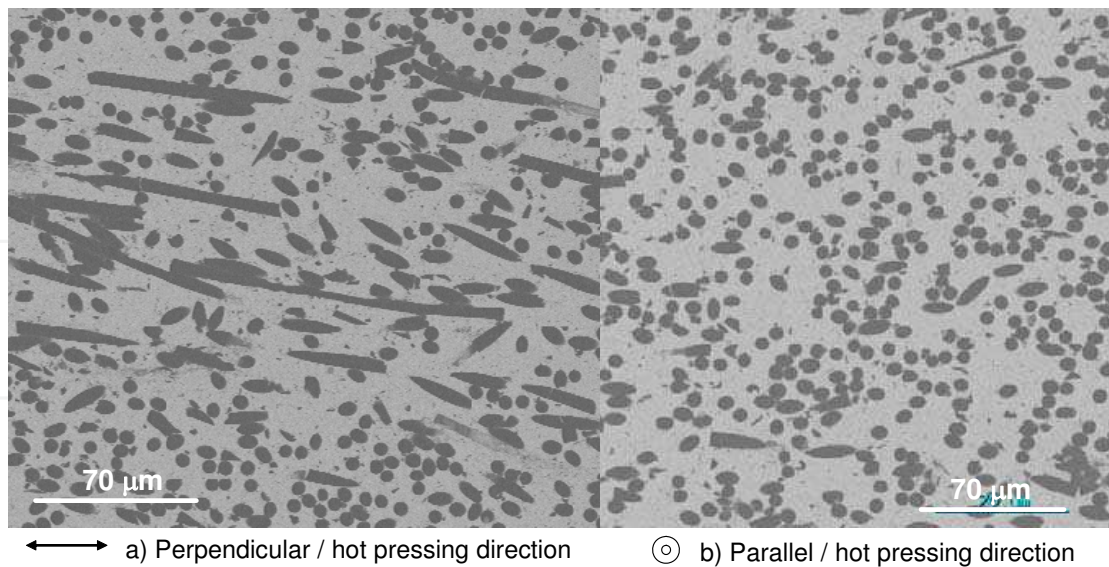


Fig. 14. SEM micrograph of hot pressed C/Cu composite material

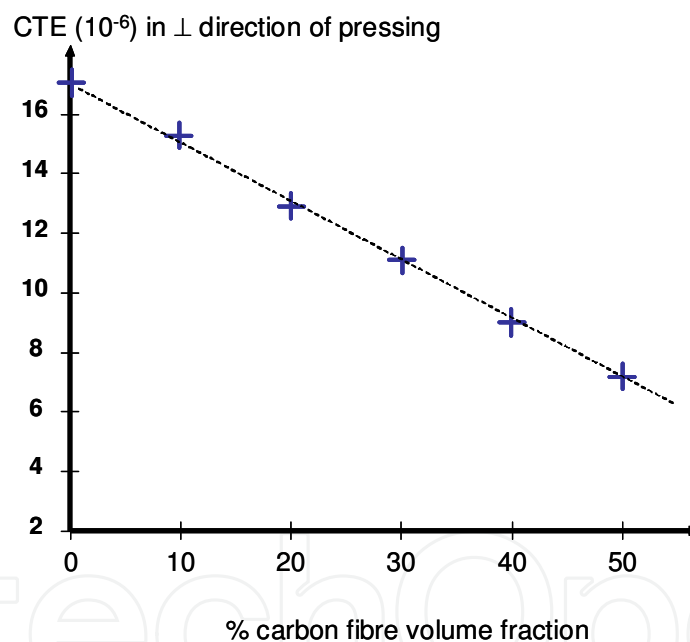


Fig. 15. CTE of Cu/C composites in perpendicular direction of pressing in relation with carbon fibre volume fraction.

### 3.3 Thermal conductivity (TC)

The thermal conductivity is commonly measured by flash laser method in axial direction of small cylinders, typically 6-15 mm diameter and 2-5 mm high. The small cylinders are machined in both parallel and perpendicular pressing directions in order to measure the thermal conductivity in parallel and perpendicular directions of pressing.

In opposite to CTE properties, TC of C/Cu composite materials is strongly linked with the thermal properties of the carbon fibres (CF) or vapor grown carbon nanofibres (VGCNF). Indeed, TC of CF along their main axis can go from 10 to 900 W/mK whereas TC are

constant perpendicular to CF main axis (close from 5 to 10 W/mK). Table 3 shows the evolution of CTE, TC and density of C/Cu composite materials for one type of CF (with TC = 140 W/mK in parallel to main axis). It can be seen that the thermal conductivity of composites materials decreases with volume fractions of fibres. However, the TC is strongly anisotropic, with 150 and 170 W.m<sup>-1</sup>.K<sup>-1</sup> in perpendicular direction, and 210 and 250 W.m<sup>-1</sup>.K<sup>-1</sup> in parallel and perpendicular direction of multilayer samples for 40 and 30 vol. % fibres, respectively (table 3). Also, the strong anisotropy of carbon fibre properties ( $\lambda_{//} = -1 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$  in axis and  $\lambda_{\perp} = 12 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$  in perpendicular axis of fibre) and orientation of fibres lead to strong anisotropic behaviour of thermal conductivity of Cu/C composite materials (table 3).

Material with %C	CTE 10 <sup>-6</sup> °C <sup>-1</sup>	Thermal Conductivity W.m <sup>-1</sup> .K <sup>-1</sup>	Density
Cu /10% C	15-16 ⊥	270 //	8.1
Cu /20% C	13 ⊥	230 //	7.5
Cu /30% C	11 ⊥	260 ⊥ 180 //	6.8
Cu /40% C	9 ⊥	220 ⊥ 160 //	6.1
Cu /50% C	7 ⊥	180 ⊥ 120 //	5.5
Cu/5% carbon nanofibre (VGCNF)	17 ⊥	450 //	8.5

Table 3. CTE and TC measures in parallel (//) and perpendicular (⊥) pressing direction on the copper carbon composites with pitch based carbon fibre (TC = 140 W/mK) [Geffroy et al., 2008] and with carbon nanofibre [Silvain et al., 2009].

The thermal conductivity obtained with Cu/C carbon composite is lower than one expected by inferior limit of Hashin and Shtrikman model [Hashin and Shtrikman, 1962]. This is likely due to the important thermal resistance of copper/carbon interface. Then, the thermal conductivity decreases strongly with an increase of carbon volume fraction. The thermal resistance of interface Cu/C decreases usually with an improvement of mechanical properties of interface copper/carbon by previous surface treatment of carbon fibre, as described in previous section. Indeed, the origin of thermal conduction in copper is electronic, while the one of carbon fibres is due to phonons. These different mechanisms of thermal conduction between copper matrix and carbon fibres explain likely that the interface carbon/copper has a large influence on thermal properties of composites, and is always one of the critical points of thermal properties of Cu/C composites.

Recent research results show that the TC of these composites materials can be improved with a higher thermal conductivity than copper (450 W.m<sup>-1</sup>.K<sup>-1</sup>) using a low amount (5% in volume) of carbon nanofibres [Silvain et al., 2009]. However, the elaboration of these composites requires, on the one hand, the previous surface treatment of short carbon fibres in order to improve the Cu/C interface properties, on the other hand, the excellent dispersion of carbon nanofibres in copper matrix.



### 3.4 Electrical properties

The electrical resistivity of composites is often measured by using conventional four points method. The electrical resistivity is increasing with carbon fibre content (fig. 16). The experimental values are close to those predicted by lower limit of Hashin and Shtrikman model, [Hashin and Shtrikman, 1962], taking  $\rho_{Cu} = 1.7 \mu\Omega.cm^{-1}$  and  $\rho_{fibre} = 1000 \mu\Omega.cm^{-1}$ .

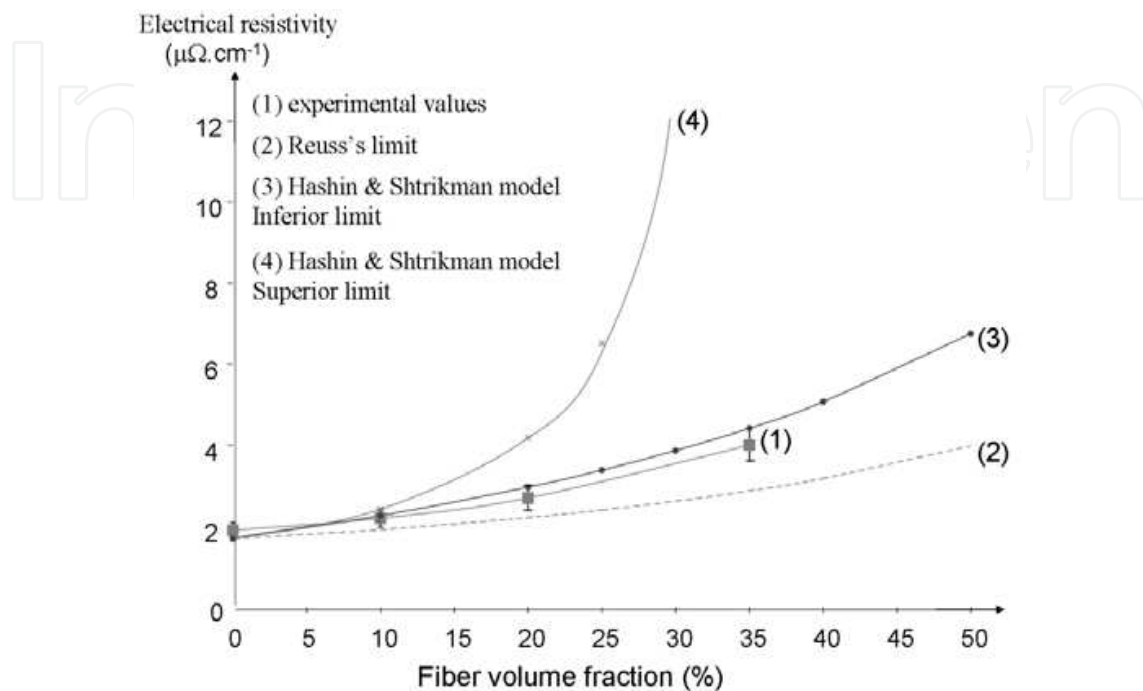


Fig. 16. Electrical resistivity of Cu/C composites in relation to fibre volume fraction [Geffroy and Silvain, 2007].

These models have been described as follow:

Reuss's model:

$$\rho_{composite} = \frac{1}{\frac{1-V_f}{\rho_m} + \frac{V_f}{\rho_f}}$$

upper limit of Hashin and Shtrikman model:

$$\rho_{composite}^+ = \rho_m + \frac{V_f}{\frac{1}{\rho_f - \rho_m} + \frac{V_m}{3\rho_m}}$$

and lower limit of Hashon and Shtrikman model:

$$\rho_{composite}^- = \rho_p + \frac{V_m}{\frac{1}{\rho_m - \rho_f} + \frac{V_f}{3\rho_f}}$$

$\rho_{composite}$  : Electrical resistivity of composite  $V_m$  : Volume fraction of matrix

$\rho_m$  : Electrical resistivity of matrix  $V_f$  : Volume fraction of fibres

$\rho_f$  : Electrical resistivity of fibres

This behaviour is linked to a good electrical contact between carbon fibres and copper matrix and to a low porosity at matrix/copper interfaces. Indeed, the both copper and fibres present a similar mechanism of electrical conduction with free electrons. This involves that the electrical resistance of interface copper / carbon has a low impact on electrical resistivity of composite.

#### 4. Potential applications of Cu/C composites

The electronic industry is involved in an endless search of new materials that enable electronic systems with increasing density of components, through higher heat dissipation capability, lower density, higher reliability while matching the CTE of materials currently used in electronic packaging components, ceramic substrates, Si, SiC and other semiconductors, etc. In fact, reliability appears nowadays as is one of the major problems that affect the electronics, microelectronics, telecom, automotive, and aeronautic industries.

Especially, thermal management is an increasingly critical part of achieving competitive functionality in these industries since it impacts speed, size, weight and reliability of components, mainly for future components which will need to dissipate heating from electric currents and packaging densities in order of magnitude higher than those in use today. Due to the high power dissipation capability of the current and future electronic semiconductors and high reliability demand, it is mandatory to develop a new electrical conductive layer based on Cu/C functionally graded materials with adapted CTE in order to adjust the thermal stresses between the FGM ceramic and the Si wafer.

Cu/C composites are so attractive materials for thermal conduction because of its high thermal conductivity and low CTE. Their potential primary applications are heat sinks, thermal planes, and substrates (fig. 17).

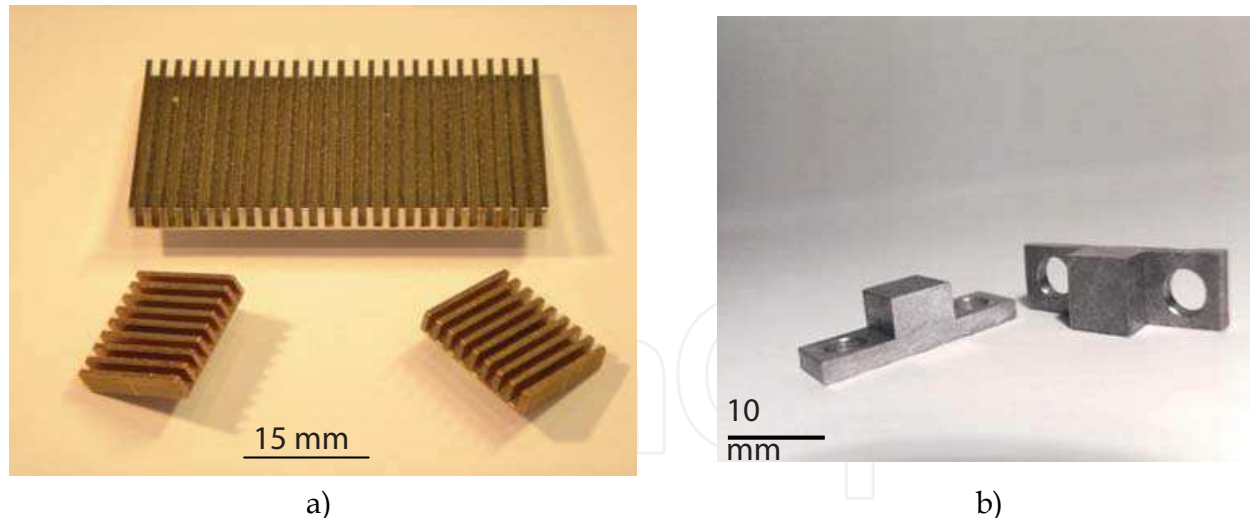


Fig. 17. Two examples of machined C/Cu composite materials for a) railroad application and b) aeronautic application

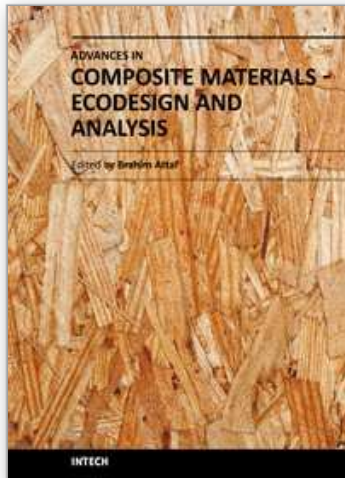
#### 5. Conclusion and outlooks

The properties of Cu/C composites depend mainly on conditions and routes process. Today, the powder metallurgy processes offer Cu/C composites with a low cost of elaboration, a low CTE and excellent thermal conductivity properties. However, physical properties obtained by power metallurgy process such as CTE and thermal conductivity are

strongly anisotropic. In addition, the lack of interfacial strength between copper and carbon requires a previous surface treatment of short carbon fibres in order to improve the interface properties between copper matrix and carbon fibres. Recent research developments suggest that the thermal conductivity of these composites materials should be largely improved by using nanofibres with a higher thermal conductivity than copper (up to  $400 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ).

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## **Advances in Composite Materials - Ecodesign and Analysis**

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By adopting the principles of sustainable design and cleaner production, this important book opens a new challenge in the world of composite materials and explores the achieved advancements of specialists in their respective areas of research and innovation. Contributions coming from both spaces of academia and industry were so diversified that the 28 chapters composing the book have been grouped into the following main parts: sustainable materials and ecodesign aspects, composite materials and curing processes, modelling and testing, strength of adhesive joints, characterization and thermal behaviour, all of which provides an invaluable overview of this fascinating subject area. Results achieved from theoretical, numerical and experimental investigations can help designers, manufacturers and suppliers involved with high-tech composite materials to boost competitiveness and innovation productivity.

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