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Formation of Cu Nanodots on Diamond Surface to Improve Heat Transfer in Cu/D Composites

Thomas Guillemet^{a,b,*}, Jean-Marc Heintz^a, Mélanie Majimel^a, Bruno Mortaigne^c, Yongfeng Lu^b, Jean-François Silvain^{a, b}

^aInstitut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS, 87 avenue du Docteur Albert Schweitzer, F-33608 Pessac Cedex, France

^bDepartment of Electrical and Computer Engineering, University of Nebraska – Lincoln, Lincoln, NE, 68588-0511, USA

^cDGA/DS/Mission pour la Recherche et l'Innovation Scientifique, 60 Boulevard du Général Martin Valin, 75509 Paris cedex 15, France

*Corresponding author: *Email address:* thomas.guillemet@gmail.com

Postal address: ICMCB-CNRS, 87 Avenue du Dr. Albert Schweitzer, 33608 Pessac, France,

Phone: +33540008810, *Fax:* +33540008321.

Abstract

Diamond-dispersed copper matrix (Cu/D) composite materials with different interfacial configurations were fabricated through powder metallurgy and their thermal performances were evaluated. An innovative solution to chemically bond copper (Cu) to diamond (D) has been investigated and compared to the traditional Cu/D bonding process involving carbide-forming additives such as boron (B) or chromium (Cr). The proposed solution consists of coating diamond reinforcements with Cu particles through a gas-solid nucleation and growth process. The Cu particle-coating acts as a chemical bonding agent at the Cu-D interface during hot pressing, leading to cohesive and thermally conductive Cu/D composites with no carbide-forming additives. Investigation of the microstructure of the Cu/D materials through scanning electron microscopy, transmission electron microscopy, and atomic force microscopy analyses was coupled with thermal performance evaluations through thermal diffusivity, dilatometry, and thermal cycling. Cu/D composites fabricated with 40 vol.% of Cu-coated diamonds exhibit a thermal conductivity of 475 W.m⁻¹.K⁻¹ and a thermal expansion coefficient of 12×10⁻⁶ °C⁻¹. These promising thermal performances are superior to that of B-carbide-bonded Cu/D composites and similar to that of Cr-carbide-bonded Cu/D composites fabricated in this study. Moreover, the Cu/D composites fabricated with Cu-coated diamonds exhibit higher thermal cycling resistance than carbide-bonded Cu/D composites, which are affected by the brittleness of the carbide interphase upon repeated heating and cooling cycles. The as-developed materials could be applicable as heat spreaders for thermal management of power electronic packages. The copper-carbon chemical bonding solution proposed in this article might also be found interesting to other areas of electronic packaging, such as brazing solders, direct bonded copper substrates, and polymer coatings.

Key words: Interface, Metal matrix composites (MMCs), nucleation and growth, thermal conductivity, thermal cycling.

Introduction

Current technological trends place the electronics industry in front of a challenging future. The constant increase of performance and reliability requirements of electronic packages along with their continuous miniaturization raise concerns about technological barriers that have to be overcome in order to maintain these inclinations steady. Moore's law, which states that the packing density (cm^{-2}) of integrated circuits (ICs) doubles every eighteen months, has been the basis to guide long-term planning and set research and development goals in the semiconductor industry since the 1960's [1]. Therefore, it has been the driving-force for the miniaturization effort, integration level increase, and performance improvement of semiconductor-based devices [2,3,4,5].

The impact of Moore's law has been especially spectacular on low-power electronic components such as computing processing units (CPUs) and memories, of which progress in terms of clock speed (Hz) are tremendously enlightened by the constant ramp-up in processing capacity of widespread laptops and smartphones. Power electronic components, such as Schottky diodes, MOSFETs, IGBTs, as any other semiconductor-based devices, follow that lead. Although such an exponential trend cannot continue indefinitely due to the fundamental limits imposed by the laws of physics, such barriers have to date been overcome through technological innovation. The continuous decrease of the size of a unit IC has allowed a dramatic improvement of the overall circuit performance and an equally significant reduction of cost per manufactured component. In addition, the development of multichip modules (MCMs) and three-dimensional high-density packaging technologies, allowing mounting a large number of chips extremely close together, induce significant reductions in signal path length and contribute reaching higher operating frequencies. These combined trends lead to a constant increase in electrical power density ($\text{W}\cdot\text{cm}^{-2}$), junction temperature ($^{\circ}\text{C}$), and heat flux density ($\text{W}\cdot\text{cm}^{-2}$) in electronic packages [1].

Current heat flux levels in power electronic packages can typically reach $100 \text{ W}/\text{cm}^2$, leading to junction temperatures located between 125°C and 175°C [1,6,7]. Heat flux levels are expected to increase in the near-future with the spreading of high-power chips made of wide band-gap compound semiconductor materials such as silicon carbide (SiC) and gallium nitride (GaN). With such materials, power densities and junction temperatures as high as $[150-200] \text{ W}\cdot\text{cm}^{-2}$ and $[300-350] ^{\circ}\text{C}$, respectively, have to be considered [1,7]. Consequently, the constant increase in heat flux that has to be dealt with for safe

operation has made thermal management of electronic packages a key aspect of the development of smaller and more efficient power devices.

Al and Cu are two widely used heat dissipation materials because they exhibit high thermal conductivities ($237 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $404 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ respectively [1,7]). However, they present a large CTE mismatch with Si ($20.4\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between Al and Si, and $14.4\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between Cu and Si, respectively). Materials with high thermal conductivity and low CTE, such as aluminum/silicon carbide (Al/SiC) composites, copper/molybdenum (Cu/Mo) and copper/tungsten (Cu/W) alloys, offer CTEs compatible with chip materials but insufficient thermal conductivity to provide efficient cooling to high power modules [7,8]. Diamond (D) has exceptional thermal properties with the highest thermal conductivity at room temperature of all known materials ($\lambda = [800 - 2000] \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for 1b diamond) [1]. However, its very low CTE ($\alpha = 1.0\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) remains a drawback [9,10]. Thus, it is interesting to explore the use of diamond as reinforcements embedded in a thermal package substrate, such as a Cu matrix. Thermal and mechanical properties of D and Cu can thus be combined to obtain Cu/D heat-dissipative composite materials with thermal conductivity and a CTE that can be tailored with respect to the volume fraction of the diamond reinforcements. From this perspective, Cu/D composites have attracted significant interest in recent years [11-15] and are considered as promising thermal management materials with the following advantages over pure Cu: (i) lower density, (ii) higher thermal conductivity, (iii) lower CTE. The costly aspect of Cu/D composites, of which scope of application has long been restricted to small volume markets such as the military and the aerospace industries, has long been a major limit to their development. Current heat flux levels combined with the inception of cheaper ways of processing Cu/D composites [11] now allow to consider the use of such materials in a manner that is economically rational.

Interfacial bonding in composites is critical since it governs the transfer of properties between the matrix and the reinforcements. Thus, the efficiency of a composite not only relies on the intrinsic properties of both forming materials, but also on their ability to combine their strengths through bonding at their interface. For thermally conductive composite materials, the heat transfer process at the matrix/reinforcement interface has to be optimal in order to reach the highest conductivity. Cu/D composites fabricated through powder metallurgy typically suffer from weak interfacial bonding because of the chemical stability of the two components. Therefore, the non-reactive Cu/D interface is critically detrimental to the thermal properties of Cu/D composites.

Carbide-forming materials, namely chromium (Cr) or boron (B), have been long employed to bond diamond reinforcements to the Cu matrix, either by being alloyed to the matrix or by being directly coated onto diamonds [12-15]. In a previous study [11], we developed a process to fabricate Cu/D composites for thermal management applications without carbide forming additives to bond the Cu matrix to the diamond reinforcements. This process consists of coating the diamond powder with Cu submicronic and nanometric particles before sintering. The Cu-coating of the diamond reinforcements acts as a chemical bonding agent between the Cu powder matrix and the diamond reinforcements during sintering, thus carbide-forming additives are not needed at the interface to ensure the Cu/D adhesion. The process developed has led to Cu/D composites presenting high density, high thermal conductivity, and low thermal expansion. The Cu coating is efficient as interfacial bonding agent, heat transfer agent, and thermo-mechanical load transfer agent. The Cu coating process also shows high repeatability, tunability, and scalability [11].

This study aims to hot-press Cu/D composites with different chemical bonding solutions at the Cu/D interface and to compare their thermal performances. Thermal conductivity and CTEs of Cu/D composites processed without any bonding solution (pure Cu/D composites) have been compared to those of similar materials fabricated using carbide-forming additives at the interface (either chromium (Cu-Cr/D composites) or boron (Cu-B/D composites)) and, finally, to those of Cu/D composites processed using the Cu-coating solution we developed (labeled as Cu/D(Cu) composites) [11]. Thermal cycling has finally been carried out to investigate the resistance of the different Cu/D composite materials to thermal fatigue. Our goal is to evaluate the impact of the interfacial bonding on the thermal performance of the Cu/D composite and to determine the most efficient solution for use as a heat dissipative material in power electronic packages.

2. Materials and methods

Diamond dispersed copper matrix composite materials with four different interfacial configurations were fabricated: Cu/D composites, Cu-B/D composites, Cu-Cr/D composites, and Cu/D(Cu) composites. The diamond volume fraction was set to 40% for all samples (thus the composites will be labeled as Cu₆₀D₄₀, 60 and 40 being the respective volume fraction of copper and diamond). This volume fraction was chosen based on our previous studies which showed that it led to the highest thermal conductivity [11].

2.1 Starting powders

MBD6 quality grade diamonds from Henan Zhongxin Corporation, China, were used as reinforcements. Dendritic copper powder from Eckart Granules Poudmet, Germany was used as pure matrix material and spherical copper powders, from Nanoval GmbH, Germany, were used as doped matrix materials. The boron-allied and chromium-allied copper powders contained respectively 0.05 at.% of boron and 0.6 at.% of chromium. SEM analysis (Fig. 1) has shown that diamond powders were faceted with hexagonal or octahedral shapes and diameters ranged between 40 and 50 μm (Fig. 1(a)). Dendritic copper powders had dendrite lengths between 20 and 50 μm (Fig. 1(b)). Spherical Cr and B-allied copper powders had diameters between 2 and 20 μm (Fig. 1(c) and 1(d)). Table 1 shows the main characteristics of the diamond powders and of the densified copper matrices. Pure Cu/D composites were fabricated using only a mixture of dendritic copper powders and diamond powders. Cu-B/D and Cu-Cr/D composites were fabricated through mixture of spherical Cr-allied and B-allied copper powders, respectively, and diamond powders. The fabrication of Cu/D(Cu) composites required chemical and heat treatments of dendritic copper and diamond powders before sintering, which are detailed in section 2.2.

Table 1: Main physical characteristics of the studied materials

Material	Copper	Diamond
Particle shape (μm)	Dendritic/Spherical	Hexagonal / Cubo-octahedral
Mean particle dimension (μm)	30 /10	50
Density (g/cm^3)	8.95	3.51
Thermal conductivity (W/mK)	360	1000
CTE ($\times 10^{-6}/^\circ\text{C}$)	18.9	1
Specific heat at 70°C (J/kgK)	391.9	681.1

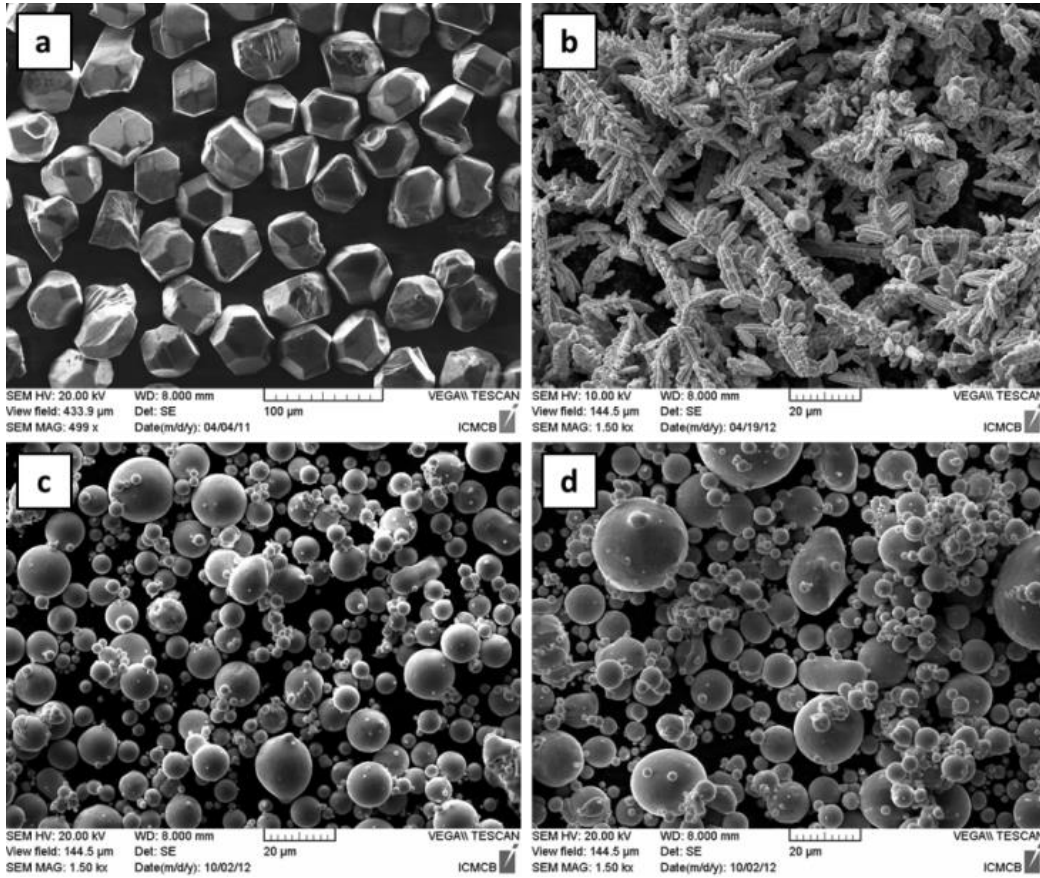


Figure 1: SEM micrographs of initial powders. a) Diamond particles; b) Dendritic Cu; c) Cr-allied spherical Cu; d) B-allied spherical Cu.

2.2 Deposition of Cu nanodots onto diamond powders

To process Cu/D(Cu) composites, we first had to coat the surface of the diamond reinforcements with Cu particles. To do so, we followed the same experimental path as that described in our previous studies [11,16,17] which consisted in chemically and thermally treat diamond and copper powders prior to sintering. This original Cu coating process allows the fabrication of dense and thermally performant Cu/D composite materials without any resort to carbide-forming additives such as chromium or boron, thus providing an innovative alternative to traditional carbide-interphase bonding for heat-transfer at the copper/diamond interface.

2.2.1 Chemical treatment

Dendritic copper powders and diamond powders were first mixed with respect to the fixed diamond volume fraction of 40%. A solvent was then added to allow fluidity of the powder mixture. The solvent must

have a low temperature of vaporization and wet both copper and diamond powders. Moreover, the powders must not react with the solvent. Based upon these requirements, an azeotropic mixture of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and 2-butanone ($\text{CH}_3\text{COCH}_2\text{CH}_3$) (40/60 vol.%) was chosen. It indeed offers a low boiling point ($T_b = 74.8\text{ }^\circ\text{C}$) and a low dielectric constant that is beneficial to the wettability of the powders by the solvent [8,11]. A dispersant agent was added to the mixture in order to uniformly disperse the powders by developing repulsive forces between particles using electrosteric mechanisms. The dispersant agent used is a phosphate ester (CP213, Cerampilot, France). It was demonstrated in previous work that it led to the best desagglomeration and dispersion of copper and diamond powders [8]. It was also shown that the optimum viscosity was obtained with a dispersant concentration of 0.5 wt.% on the dry powder basis. The whole mixture was then mixed 15 hours at 20 rpm through planetary milling.

2.2.2 Thermal treatment

2.2.2.1 Debinding

Following the 15-hours mixing step, the slurry was submitted to a 2-hours debinding heat treatment at 400°C under air in order to eliminate the organics, thus having only the powders left. Thermo-gravimetric analysis (TGA) has shown that this debinding treatment was efficient in exhaustively removing the organic solvents from the slurry. However, such heat treatment under air necessarily leads to Cu powders oxidation.

2.2.2.2 Reduction

The presence of copper oxide in the powder mixture being critically detrimental to the forthcoming sintering process, a second reductive heat treatment is required prior to densification. After debinding, the copper oxide/diamond composite powder mixture was heat treated at 400°C under argon/hydrogen (Ar/H_2) flux with a 60 minutes hold at 400°C . X-ray diffraction analysis demonstrated that this second heat treatment was efficient in completely reducing the copper oxides into metallic copper. Hot pressing was finally employed to obtain dense copper/diamond composite materials.

2.3 Hot pressing

The uniaxial hot press employed in this study was the same as the one described in our previous study [11]. Pure Cu/D composite powder mixture and Cu/D(Cu) composite powder mixture were introduced between two steel pistons into a steel mold which was induction-heated to 650°C under vacuum. Cu-B/D and Cu-Cr/D composite powders mixtures were introduced between two graphite pistons into a graphite mold which was induction-heated to 850°C under vacuum. Steel molds offers a higher mechanical resistance to hot pressing than graphite. However, it cannot be heated up above 650°C without triggering microstructural changes of the mold material and therefore degrading its mechanical properties. Thus, graphite was employed to hot press Cu-Cr/D and Cu-B/D composites made from spherical copper powders, which require higher sintering temperatures relative to dendritic copper powders due to their lower aspect ratio. Vacuum was set to 10^{-1} Pa and the effective applied pressure on the pistons was 50 MPa. The materials were maintained under hot pressing during 30 minutes. The heating was controlled through a regulation monitor. The temperature was controlled through a thermocouple placed into the mold. 6 mm diameter cylindrical composite materials samples with height of 4 mm (+/- 0.4 mm) were fabricated in order to fit the dimensional requirements of further thermal characterizations.

2.4 Characterization

2.4.1 Density and Microstructure

The densities of the composites were measured using Archimedes method and compared to the theoretical densities, calculated using the rule of mixture (ROM):

$$\rho_c = \rho_m V_m + \rho_d V_d \quad (1)$$

Where ρ_m and ρ_d are the densities of the copper matrix and diamond reinforcements, respectively ($\text{g}\cdot\text{cm}^{-3}$) (see Table); V_m and V_d are the volume fractions of the copper matrix and diamond reinforcements, respectively. Starting materials and resulting composite materials microstructure were observed through scanning electron microscopy (SEM) (Vega Tescan, USA). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations as well as Energy Dispersive Spectroscopy (EDX) analyses were performed using a Jeol 2200FS equipped with a field emission gun operating at 200 kV and with a point resolution of 0.23 nm. High-resolution TEM micrographs were acquired with a Gatan Ultrascan CCD 2k x 2k and digital diffractograms were calculated using the Gatan Digital Micrograph program. In order to

be representative and statistically meaningful, several images from several regions of a sample were recorded and the most characteristic results are presented here. The samples for TEM observations were prepared through focused ion beam (FIB) cutting. Atomic Force Microscopy (AFM, Veeco, USA) was employed to obtain topographic images of the Cu-coated diamond powders.

2.4.2 Thermal conductivity

Thermal diffusivity of the composites was measured through flash laser method in axial direction of the cylindrical samples using a Netzsch LFA 457 device. Thermal diffusivity was measured at 70°C for reasons of measurement stability. Thermal conductivity was calculated from thermal diffusivity measurement using the following formula:

$$\lambda_c = D_c \rho_c C_{p,c} \quad (2)$$

Where λ_c is the thermal conductivity of the composite ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), D_c the thermal diffusivity of the composite ($\text{m}^2\cdot\text{s}^{-1}$), ρ_c the density of the composite ($\text{kg}\cdot\text{m}^{-3}$), and $C_{p,c}$ the specific heat of the composite ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$) calculated using the ROM:

$$C_{p,c} = C_{p,m}V_m + C_{p,d}V_d \quad (3)$$

Where $C_{p,m}$ and $C_{p,d}$ are the specific heats of the copper matrix and diamond reinforcements, respectively. Specific heats of the copper and diamond powders were measured through differential scanning calorimetry (see Table). The thermal conductivity of the composites was assumed to be isotropic.

2.4.3 Thermal expansion coefficient (CTEs)

CTEs of the composites were measured on the cylindrical samples, using a horizontal Netzsch dilatometer DIL402C. The device was calibrated using an alumina sample. Since the CTE of the composites was assumed to be isotropic, the thermal expansion could be accurately measured in only one direction.

2.4.4 Thermal cycling

After the thermal conductivity of the Cu/D(Cu), Cu-Cr/D, and Cu-B/D composites has been measured, the composites were submitted to thermal cycling. The composite materials were cycled using a Clima. Temperature System device (CTS, Germany). The thermal cycle applied was based on reliability

standards used in semiconductor and aeronautics industries. The cycle started at $-45\text{ }^{\circ}\text{C}$, the temperature then increased up to $+150\text{ }^{\circ}\text{C}$ following a ramp up of $+6\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature was held at $+150\text{ }^{\circ}\text{C}$ during 40 minutes. The temperature then decreased to $-45\text{ }^{\circ}\text{C}$ following a ramp down of $-9\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and the temperature was held at $-45\text{ }^{\circ}\text{C}$ during 30 minutes. A series of 100 cycles followed by a series of 400 additional cycles were applied to all samples. Therefore, Cu/D composites were submitted to a total number of 500 thermal cycles. The thermal conductivity of the materials was measured after 0, 100, and 500 cycles in order to investigate their resistance to thermal cycling.

3. Results and discussion

3.1 *Cu nanodots deposition on diamond surface*

The debinding treatment in air triggers the oxidation of the Cu powder into cupric (CuO) and cuprous (Cu₂O) oxides, which leads to the formation of nano-sized, wire-shaped copper oxide structures on the dendrites, as shown on Fig. 2(a) to 2(c). This phenomenon was already observed and discussed in previous publications [17,18].

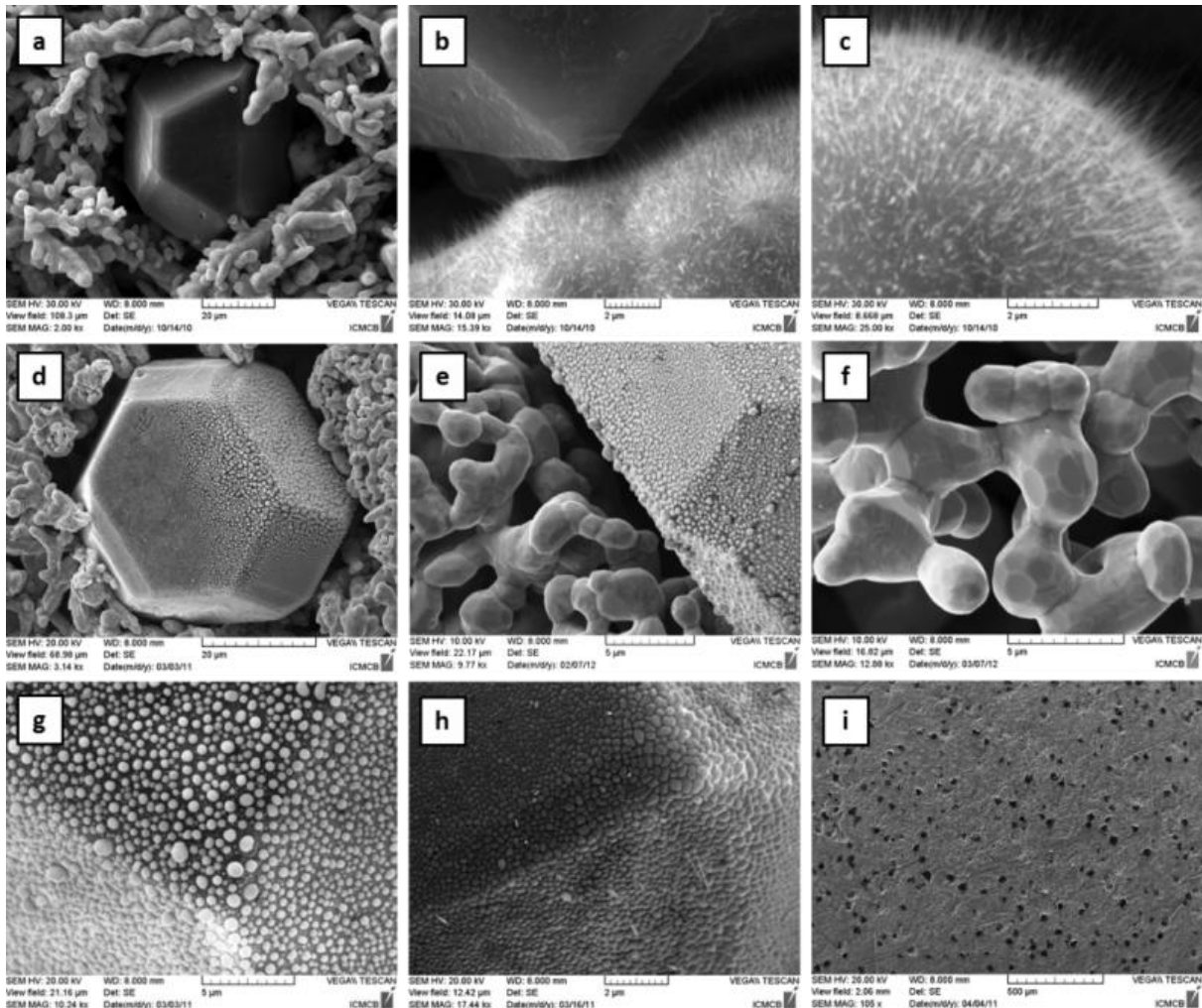


Figure 2: SEM micrographs of a Cu/D(Cu) composite powder mixture. a) b) c) After debinding in air at 400°C and oxidation of copper; d) e) f) After reduction under Ar/H₂ at 400°C.

Sizes and coverage effect of Cu particles deposited on diamond after reduction g) 60 min under Ar/H₂ at 400°C; h) 1 min under Ar/H₂ at 350°C; i) Cross-section of a Cu/D(Cu) composite after hot pressing.

SEM micrographs of a reduced Cu/D(Cu) composite mixture where diamond reinforcements are Cu-coated after chemical and thermal treatments are shown in Fig. 2(d) to 2(h). These figures show that the wire-shaped copper oxide nanostructures observed on the oxidized Cu dendrites after debinding (Fig. 2(a) to 2(c)) are no longer present after dendrite reduction. The reduced Cu dendrites are faceted (Fig. 2(e) and 2(f)). In addition, it is remarkable in the reduced composite mixture that the diamond reinforcements are now coated with spherical particles (Fig. 2(d)). The coverage of the diamond surfaces by the particles is remarkably uniform on each crystallographic facet of the reinforcements. Various sizes of particles are

observed to coexist on the diamond reinforcements (Fig. 2(g)). The size of these particles typically range from 100 nm to 1 μ m. Moreover, the size and coverage effect of the Cu particles deposited were observed to be tailorable by tuning the time and temperature of the reduction process, as shown in Fig. 2(g) and 2(h), where Cu coatings obtained after 60 min at 400°C under Ar/H₂ and after 1 min at 350°C under Ar/H₂, respectively, are shown [11]. The Cu particles size range from 400 nm to 1 μ m after 60 min at 400°C while they range from 100 nm to 400 nm after 1 min at 350°C under Ar/H₂. Fig. 2(i) shows the cross-section of a Cu/D(Cu) composite after sintering. The homogeneous repartition of the diamond reinforcements in the Cu matrix can be noted.

Figure 3(a) corresponds to an SEM micrograph of a Cu-coated diamond surface while Fig. 3(b) shows a two-dimensional (2D) phase image of the Cu-coated diamond surface obtained through atomic force microscopy (AFM).

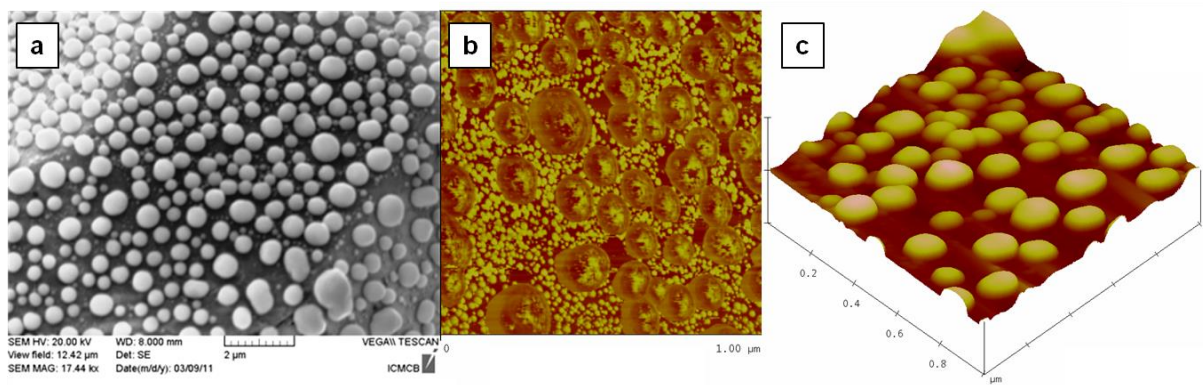


Figure 3: (a) SEM micrograph of a Cu-coated diamond surface; (b) Two-dimensional (2D) phase image of a Cu-coated diamond surface obtained through AFM; (c) AFM three-dimensional topographical image.

Figure 3(b) shows that nanosized copper particles, which are hardly detectable through a topographical analysis of the surface through SEM, exist among the submicronic particles coating the diamond surface. This smaller particle population, coexisting on the surface with larger particles, is believed to contribute to the chemical bonding of the Cu matrix to the diamond reinforcements during sintering. Figure 3c shows the same image as figure 3b in three dimensions (3D), revealing the spherical shape of the Cu nanodots. Figure 4 shows transmission electron microscopy (TEM) micrographs of the Cu-coated diamond surface while Fig. 5 corresponds to high-resolution TEM micrographs of the interface between the diamond surface and the deposited Cu particles.

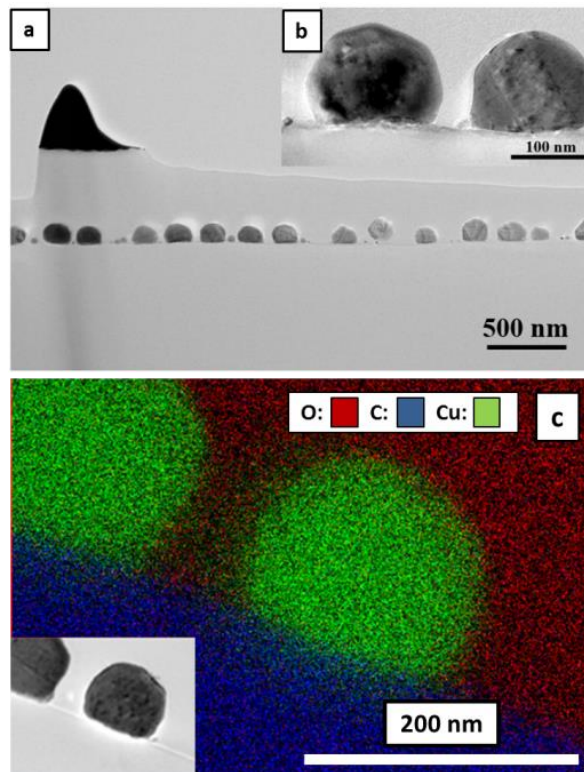


Figure 4: (a) (b) TEM micrographs of a Cu-coated diamond surface; (c) EDS image of the Cu particles deposited on a diamond surface.

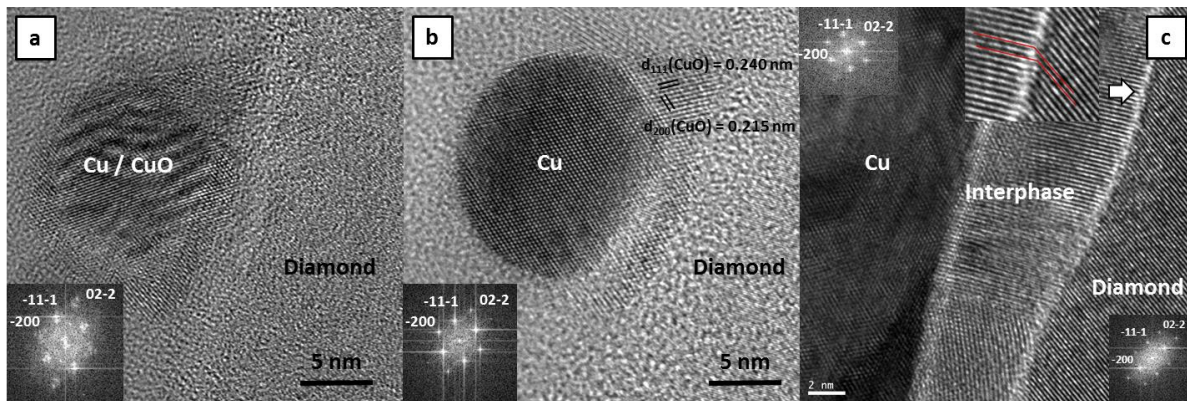


Figure 5: High-resolution TEM micrographs of Cu particles deposited on diamond after nucleation and growth. (a) At the early stage of the exposure to the electron beam; (b) After having been exposed to the electron beam for several minutes; (c) Interface between the diamond surface and a deposited Cu particle.

Given the morphology of the Cu particles grown onto diamond, it is obvious that they originate from a process involving 3D growth. It is also possible that a first step of 2D growth precedes the growth of the 3D Cu structures. In such case, the primary 2D atomic layer would only be a few nanometers thick and could not be detected through the characterization techniques we used (Franck Van-der-Merwe growth mode [19]). However, the strong lack of chemical affinity between the surface atoms (carbon) and arriving atoms (copper) suggests that the growth follows an island growth mode (Volmer-Weber mode) [20].

It was demonstrated using Energy Dispersive X-ray spectroscopy (EDXS, Fig. 4(c)) that the particles deposited on the surface of the diamond reinforcements were metallic Cu particles. Our understanding of the Cu deposition process relies on the fact that the reductive heat treatment leads to the sublimation of the CuO nanowires existing on the surface of the dendritic Cu powders after oxidation (Fig. 2(a) to 2(c)) through a solid-vapor process [17, 18]. Indeed, due to their high aspect ratio, the copper oxide nanowires sublime at a lower temperature relative to bulk Cu. As shown in Fig. 6, X-ray photoelectron spectroscopy (XPS) analysis demonstrated that the mixing of a dispersant agent (phosphate ester) with the diamond powder led to the creation of phosphorus functionalized nucleation sites on the surface of the diamond reinforcements. Typical survey taken on the surface of the diamond powders after oxidation step is shown on Fig. 6(a). In Figure 6(b), the two lowest P2p_{3/2} binding energy peaks, at 134.5 eV and 135.2 eV, can be assigned to phosphorus-oxygen (P-O) and/or phosphorus-oxygen-carbon (P-O-C) bonds, while the highest binding energy peak at 136 eV can be assigned to P-C bonds. Therefore, Cu sublimated from CuO nanowires during the reduction treatment settles again onto the chemically active sites of the surface of the diamond particles through C-O-P-O-Cu and/or C-P-O-Cu chemical bridges (see Fig. 6(c)). During the hot pressing step, Cu-Cu metallic bonds are formed between the Cu particles coating the diamond reinforcements and the copper powder which will form the Cu matrix after densification. The Cu particles deposited thus enable the formation of an adhesive interface between the copper matrix and the diamond reinforcements through strong chemical bonding without requiring any carbide-forming materials.

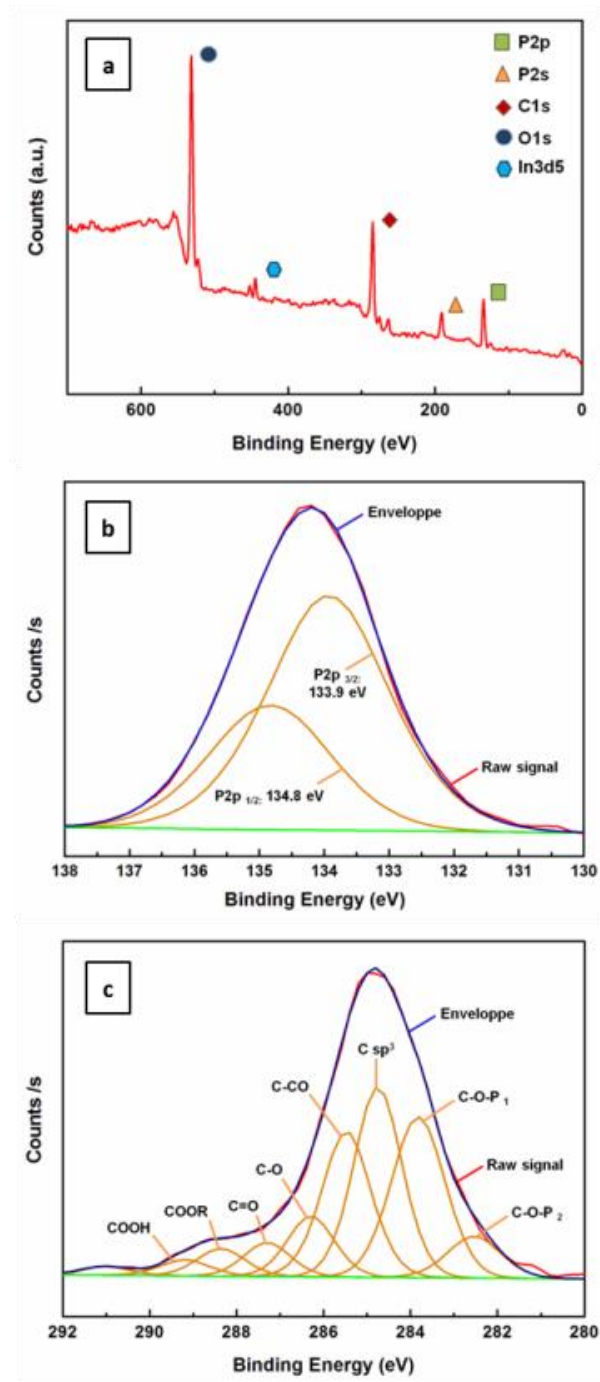


Figure 6: XPS spectra of a Cu-coated diamond surface. (a) Survey photoemission spectrum; (b) P 2p photoemission spectrum; (c) C 1s photoemission spectrum.

TEM micrographs of a Cu-coated diamond reinforcement presented in Fig. 4 and 5 show that the largest Cu particles deposited were mainly polycrystalline, although some single crystal particles were detected. Twin boundaries are visible in the structure of some of the Cu particles grown on the diamond surface

(Fig. 5(a)). In Figure 5(a), the Cu dots seem to be faceted. This observation corroborates the faceted aspect of the Cu dendrites due to the reductive heat treatment upon Ar/H₂ (Fig. 2(f)). The facets follow the Wulff growth process [21,22]. Smaller single crystal particles around 10 nm in diameter are also observed, as shown in Fig. 5. Therefore, the TEM observations confirm the phase image obtained from AFM which highlights the presence of several populations of particles. Figures 5(a) and (b) show high-resolution TEM micrographs of a small Cu particle at the early stage of the exposure to the electron beam (Fig. 5(a)) and after having been exposed to the electron beam for several minutes (Fig. 5(b)). In Fig. 5(a), Moiré fringes are clearly detected from the Cu particle, meaning that two crystalline networks interact. The Fourier transform of the image of the particle shows that only one orientation is highlighted where each of the displayed spots are doubled. This demonstrates that two networks with the same symmetry interact together. These networks are assumed to be those of Cu and CuO which are both Fm-3m and present a [110] zone axis. Therefore, the Cu particle was found to be initially coated with an oxide layer due to the air exposure between the sample preparation and its observation through TEM. Upon exposure to the reductive electron beam, the CuO layer reduced to metallic Cu, as shown by the resulting Fourier transform where double spots are now clearly defined single spots. Despite the oxide layer reduction upon electron beam exposure, the interphase observed between the Cu particle and the diamond surface was not affected. Figure 5(c) shows a high-resolution TEM micrograph of the interface between a large Cu particle and a diamond reinforcement. This micrograph demonstrates that an interphase exists between copper and diamond. This interphase is polycrystalline and about 7 nm large (+/- 2 nm). The measurement of interplanar distances on the interphase confirm that the material involved in the Cu/D bonding is copper oxide (CuO). Some dislocations are observed in the copper oxide interphases to accommodate the lattice mismatch between the CuO and diamond networks.

3.2 Density after hot pressing

As expected, pure Cu/D composites fabricated without any interfacial bonding solution (Cu/D) exhibit the lowest relative density with an average of 93.4%. Cu-B/D and Cu-Cr/D composite materials respectively involving B and Cr carbide forming additives exhibit relative densities of 98.3% and 95.8%. Cu/D(Cu) composites fabricated through the Cu coating process of diamonds exhibit an average relative density close to 100%, which means that the fully-dense state was reached for all of the composite samples of

this type. This demonstrates that Cu particles deposited onto diamond facilitate densification and effectively act as an interfacial chemical bonding agent.

3.3 Thermal conductivity

Consistently with their low compaction level, pure Cu/D composites exhibited low thermal conductivity (Fig. 7(a): $\lambda_{\text{Pure Cu/D}} = 260 \text{ W.m}^{-1}.\text{K}^{-1}$). The relatively high porosity level of these composites (6.6%) led to heat transfer loss and critically degraded their thermal conduction performance. Cu-B/D composites (Fig. 7(a): $\lambda_{\text{Cu-B/D}} = 440 \text{ W.m}^{-1}.\text{K}^{-1}$) and Cu-Cr/D composites (Fig. 7(a): $\lambda_{\text{Cu-Cr/D}} = 500 \text{ W.m}^{-1}.\text{K}^{-1}$) exhibit strongly enhanced thermal conductivities relative to pure Cu/D composites processed without any bonding solution. In the same manner, average thermal conductivity results obtained from Cu/D(Cu) composites fabricated through the innovative Cu coating process (Fig. 7(a): $\lambda_{\text{Cu/D(Cu)}} = 475 \text{ W.m}^{-1}.\text{K}^{-1}$) demonstrated that Cu particles deposited onto diamond reinforcements prior to sintering effectively act as chemical bonding agents between diamonds and the copper matrix and enable efficient interfacial heat transfer between electronic and phononic heat conductions. Cu/D(Cu) composites exhibit thermal conductivity that is superior to that of Cu-B/D composites and comparable to that of Cu-Cr/D composites. These results demonstrate the primary role played by interfacial chemical bonding, either through carbide interphases or Cu coating of diamonds, on the heat transfer process at the Cu/D interface in Cu/D composite materials. Indeed, the use of boron carbide, Cu coating, and chromium carbide bonding solutions at the Cu/D interface lead to an increase in thermal conductivity of 70%, 82%, and 92%, respectively, relative to the thermal conductivity of pure Cu/D composites.

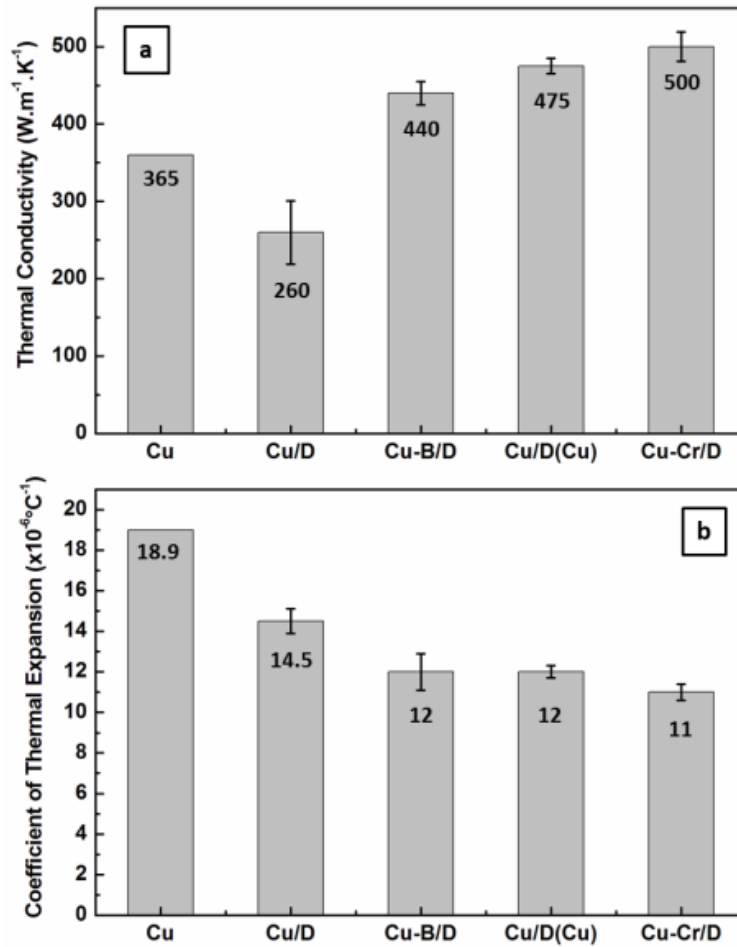


Figure 7: Thermal properties of the different hot pressed materials. (a) Thermal conductivity; (b) Coefficient of thermal expansion.

3.4 Coefficient of thermal expansion

The results obtained from the CTE evaluation demonstrate that the innovative diamond Cu coating process we developed allows to reach similar thermo-mechanical performances relative to traditional carbide-bonded Cu/D materials (Fig 7(b)). Indeed, Cu/D(Cu) composites exhibit a CTE of $12 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ while Cu-B/D and Cu-Cr/D composites respectively exhibit CTEs of $12 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ and $11 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. Therefore, it shows that the deposition process of copper submicronic particles leads to a strong interfacial bonding, thus enabling efficient thermal expansion load transfer at the matrix/reinforcement interface. The relatively high CTE exhibited by pure Cu/D composites is due to the absence of adhesion at the Cu/D interface. Cu-Cr/D composite materials exhibit the lowest CTE of all samples, which is due to the strong

carbide interphase they embed. Figure 8 shows a cross-sectional chemical mapping of a Cu-Cr/D composite material through Electron Probe Micro Analysis (EPMA). It is clearly demonstrated that the chromium additives (red-colored on the chemical map) initially contained in the Cr-allied copper matrix have diffused during sintering and are located at the interfaces between the copper matrix and the diamond reinforcements. It is also visible on Fig. 8 that, at that scale of analysis, all the interfaces do not contain chromium. This is due to the low Cr content of the initial chromium-allied copper powder (0.6 at.%). The chromium-rich areas lead to a chemical interfacial bonding through the creation of a chromium carbide at the Cu/D interface (C_2Cr_3 or C_3Cr_7 according to the C-Cr phase diagram), thus enhancing the heat-transfer process in the composite. EPMA could not be efficiently carried out on Cu-B/D composites since the boron content in the boron-allied copper powder was too low (0.05 at.%). However, the carbide interphase of Cu-B/D and Cu-Cr/D composites being brittle beyond a certain thickness of the carbide layer, it might be affected through thermal cycling, thus leading to degraded thermal performances along lifetime.

Although CTE mainly relies on mechanical bonding between the matrix and the reinforcements, the comparative CTE evaluation enlightens the influence of interfacial chemical bonding on the thermo-mechanical load transfer process: the use of boron carbide, copper coating, and chromium carbide bonding solutions respectively lead to a decrease of CTE of 17%, 17%, and 24% relative to the level reached by pure Cu/D composites ($\alpha_{\text{Pure Cu/D}} = 14.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). The CTE of Cu-B/D, Cu/D(Cu), and Cu-Cr/D composites decrease by 36.5%, 36.5%, and 41% relative to the CTE of pure copper ($\alpha_{\text{Cu}} = 18.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), respectively.

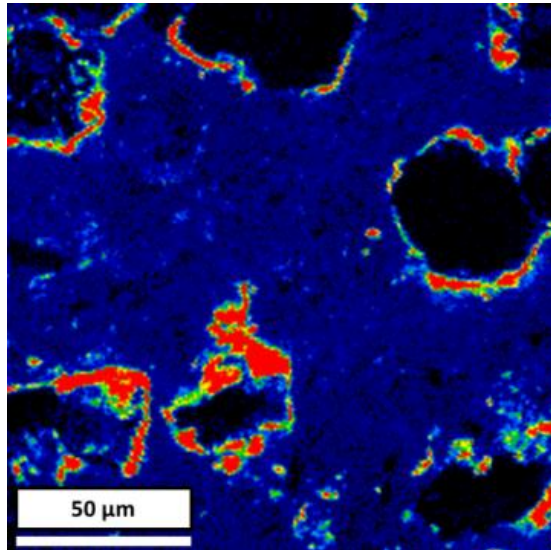


Figure 8: Chromium chemical mapping of a Cu-Cr/D composite material through EPMA.

3.5 Thermal cycling

Thermal cycling evaluation provides crucial information on the resistance of the materials to thermo-mechanical fatigue in their future operating environment. Complementary to the initial thermal conductivity of the material, its ability to stand thermal cycling is a key point in the material selection process. Figure 9 shows the thermal conductivities exhibited by Cu/D composites after 0, 100, and 500 thermal cycles. It demonstrates that Cu/D composites fabricated through the Cu coating process exhibit higher resistance to thermo-mechanical fatigue than carbide-bonded Cu/D composites. Indeed, Cu-Cr/D composites experience drops of 7% and 10% after 100 and 500 cycles, respectively, while Cu-B/D composites experience drops of 20% and 34% in their thermal conductivity after 100 and 500 cycles, respectively.

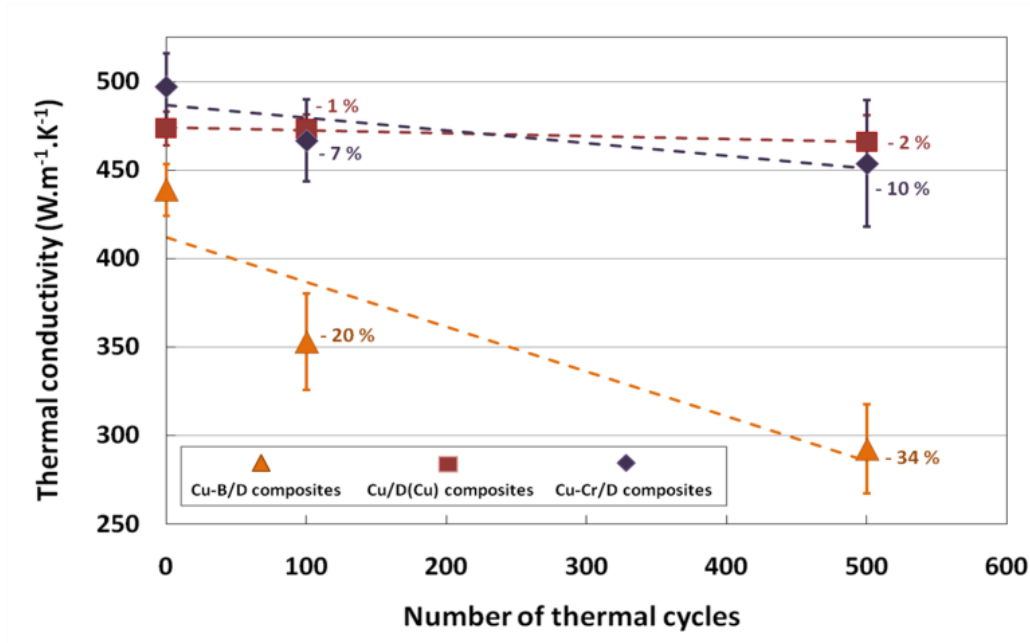


Figure 9: Evolution of the thermal conductivity of Cu-B/D, Cu-Cr/D and Cu/D(Cu) composite materials with respect to thermal cycling (- 45°C/+ 150°C).

On the other hand, Cu/D(Cu) composites only experience drops of 1% and 2% in their thermal conductivity after 100 and 500 thermal cycles, respectively, demonstrating that Cu/D(Cu) composite materials fabricated through the innovative Cu coating process developed are remarkably stable upon thermal fatigue. The larger thermal conductivity drops experienced by carbide-bonded Cu/D composites (either B or Cr) are understood to be due to the brittleness of the grown carbide interphase at the Cu/D interface. During thermal cycling, the composite repeatedly expands and retracts. Therefore, the CTE mismatch between the copper matrix, the diamond reinforcements, and the carbide interphase (either B carbide or Cr carbide) leads to thermo-mechanical stresses that affect the mechanical integrity of the brittle carbide interphase. This critically degrades the heat conduction performances of the cycled composite. Cu/D(Cu) composites, on the other hand, do not suffer from mechanical degradation of the Cu/D interface because no carbide bonding additives were used to process them. The Cu coating bonding provides high resistance to thermal cycling since the bonding material is, from a crystalline point of view, close to the matrix material, thus limiting the thermo-mechanical stresses at the interface. By allowing to maintain steady the thermal performance of the Cu/D composite for a longer time relative to traditional

materials, the developed Cu/D bonding solution may lead to more durable heat dissipative components, thus improving the lifetime of the overall electronic package.

Conclusions

Diamond dispersed copper matrix composite materials with four different chemical bonding configurations at the matrix/reinforcements interface were fabricated. Pure Cu/D composites were processed from pure dendritic copper and diamond powders mixture, thus without any interfacial bonding solution to overcome the low chemical reactivity of the Cu-C binary system. Cu-B/D and Cu-Cr/D composites were processed from the mixture of diamond powder with boron-allied and chromium-allied spherical copper powders, respectively, thus involving carbide forming additives to bond copper and diamond. Finally, Cu/D(Cu) composites were fabricated through an innovative process consisting in Cu coating the diamond powders prior to sintering in order to create a covalent chemical bond between the diamond reinforcements and the copper matrix upon densification. TEM and AFM analyses demonstrated that two populations of Cu particles were deposited onto the diamond surface, the largest one being mainly polycrystalline and the smallest one being single crystals. The interphase between Cu particles and diamond was found to be a CuO layer with a thickness of a few nanometers, thus allowing efficient heat transfer between electronic conduction in metallic copper and phononic conduction in diamond. It was shown that Cu/D(Cu) composites exhibited thermal conductivity and CTE that were comparable when not superior to those of Cu-B/D and Cu-Cr/D composites, and a resistance to thermal fatigue that is by far superior to that of carbide-bonded materials, thus enlightening the high bonding potential of this novel Cu coating process. This combination of properties makes these Cu/D(Cu) composites very promising candidate materials for heat dissipation purposes in power electronic packages. The Cu-D bonding solution proposed in this article might also be found interesting to other electronic materials, such as brazing solders, direct bonded copper (DBC) substrates, and polymer coatings.

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