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Anisotropic thermal conductivity and enhanced hardness of copper matrix composite reinforced with carbonized polydopamine.

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Abstract

For thermal management applications, copper (Cu) metal matrix reinforced by carbon are undoubtedly one of the most promising composites for heat spreaders. In the frame of this work, hard Cu matrix composites having anisotropic thermal conductivity were fabricated by using Cu flakes coated with carbonized polydopamine. The flakes were coated by simply immersing them into a dopamine aqueous solution, then they were submitted to a thermal treatment under dihydrogen. This easy synthesis method results in a ≈ 10 nm thick N-doped graphene-like film surrounding the Cu flakes. The subsequently densified composites that contains about 0.23 wt. % of C show an increase of hardness up 44% and 172% as compared to pure Cu in the parallel and perpendicular sintering direction, respectively. In addition an anisotropic thermal conductivity is obtained with an anisotropy ratio of 2.75.

Keywords: metal matrix composite, polydopamine, copper matrix, thermal conductivity, hardness

1. Introduction

Heat spreaders are a component or assembly in electronic packaging systems wherein the heat produced in electronic chips is dissipated externally to fluids or air both in the normal and tangential directions [1]. In general, metal matrix composites (MMCs) show several improvements in comparison with the currently used materials in electronic packaging, including: i) lower and tailorable coefficient of thermal extension (CTE), ii) high heat dissipation capability, iii) light weight, and iv) high stiffness at elevated temperatures.

The high thermal conductivity (TC) of copper (Cu) (385-410 W/mK) makes it a predominant material for electronic application [1]. However, for some specific applications, mechanical properties of Cu could be considered as too low. A common way to improve its mechanical properties is to fabricate metal matrix composites (MMCs). That is often made via a metallurgic powder route owing to its simplicity, cost-effectiveness, net shaping, and ability to manufacture anisotropic materials [2]. Carbon nano-reinforcements have been extensively used to increase the mechanical and thermal properties of MMCs. First, carbon nanotubes (CNT) have been considered, owing to their exceptional mechanical and good thermal properties [3-5]. Then, graphene (G) has also been studied due to its valuable thermal, electrical, and mechanical properties [6, 7]. Due to its lower price and more stable properties, research on graphene-type reinforcements has gained considerable attention and has led to significant advances in the creation of multifunctional composite materials with enhanced thermal and mechanical properties [8-10].

Nevertheless, one of the key challenges in MMC processing is to disperse homogeneously the reinforcement within the metal matrix. Naturally, aggregation of nano-reinforcements leads to severe degradation of the resulting nanocomposites mechanical and thermal properties [8-10]. Moreover, the size difference between the matrix powder (i.e., micrometer metallic particles) and the carbon reinforcement (i.e., nanometer size) cause several issues during the mixing step and heterogeneous mixture are often observed. Hence, the mixing stage appears to be a crucial step to fabricate functional metal-based nanocomposites [11, 12].

To reduce graphene aggregation and to improve metal-reinforcement chemical interfaces, different strategies have been considered such as metallic decoration of graphene [13, 14], flake powder metallurgy [15], electrochemical deposition [16, 17], molecular level mixing [18] and *in situ* chemical vapor deposition [12, 19-21]. In fact, direct growth of 2D G materials is rather difficult to realize on top of such substrates. On contrary, azote doped G obtained from calcinated polydopamine (c-PDA) [22, 23] can easily be grown on top of metallic powders.

Polydopamine (PDA) can be formed in aqueous solution by oxidation of dopamine [24, 25] and has high adhesive properties. As an example, Zou *et al.* fabricated graphene films, by vacuum filtration of a suspension containing graphene oxide and PDA nanoparticles, that presented high thermal conductivity (TC) [26].

Hsieh and Liu assembled a composite film by combination of N-doped graphene nanosheets (N-GNS) and copper foil. The N-GNS were obtained by thermal annealing of graphene in the presence of hexamethylenetetramine and were deposited on a Cu foil to obtain a composite that presented a significant enhancement of the TC compared to pure Cu [27]. Zheng *et al.* have also shown that the deposition of silk fibroin (a protein) followed by a microwave plasma treatment can improve the mechanical properties of Cu without changing too much its thermal properties [28].

In this work, we have developed a simple strategy to directly synthesize a graphene-like reinforcement on the surface of Cu flakes to avoid any dispersion/aggregation problem and favor an optimal Cu-reinforcement chemical interface. Cu flakes were coated with a very thin film of polydopamine (few nm) obtained by simply immersing them in a dopamine aqueous solution. After thermal treatment, the resulting Cu particles are coated with a N-doped graphene-like film. The densification of such composite powders resulted in a dense material that presented good mechanical performances. Moreover, as several authors have been able to show, enhanced anisotropic thermal conduction can be obtained, considering the two-dimensional 2D structure of graphene during the processing [29-31]. The hot-pressing technique used allows us to obtain in a simple way such a good anisotropic thermal conduction.

2. Material and methods

2.1 Materials. Dopamine hydrochloride (98% purity), tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl) and H₃PO₄ solution were obtained from Sigma-Aldrich. Cu flakes were purchased from Ecka Granules Poudmet™.

2.2 Cu PDA coating (Cu/PDA). For the polydopamine coating formation, the Cu powder, previously annealed under H₂ to reduce Cu oxides, was immersed into dopamine solution prepared by dissolving 0.5 mg·mL⁻¹ dopamine hydrochloride in 10 mM Tris-HCl at pH 8.5, under stirring for 3 hours leading to a PDA thickness about 10 nm [24, 32, 33]. This PDA thickness was notably determined by ellipsometry [33]. It is in good agreement with our XPS

analyses (see below). After this treatment the Cu powder was obtained by centrifugation of the suspension, then it was rinsed twice with pure water and finally it was dried at 70 °C for 240 min.

2.3 Cu/c-PDA preparation: Cu flakes coated with the PDA film were treated under 5% H₂-Ar atmosphere at 500 °C for 1 hour.

2.4 Fabrication of the MMC materials using powder metallurgy process

Composite materials have been fabricated using conventional powder metallurgy process. Sintering of the Cu/c-PDA powder was carried out using a Termolab press. A reference Cu sample, without c-PDA reinforcement, was produced in the same conditions. The powders were cold pressed in a carbon mold of 10 mm in diameter and then pressed/heated using an induction system. Powders were hot pressed at 650 °C under 70 MPa for 30 min. A thermocouple inserted into the graphite mold close to the powder was used to control the temperature. Primary vacuum (10⁻¹ mbar range) was used to prevent Cu oxidation during both heating and cooling steps of the composite materials.

2.5 Investigation methods

The morphological aspect of the Cu powders and of the composites was examined under a field emission gun scanning electron microscope (FEG-SEM) (Ultra55, Zeiss) operating at 15 kV. For the SEM analysis of the C reinforcements (c-PDA), dissolution of Cu present at the composite surface was done. For that, using a classical three-electrode setup with the Cu composite as working electrode, a Pt grid as counter electrode and a saturated calomel electrode (SCE) as the reference electrode, electrochemical dissolution of Cu at the sample surface was performed in 85% H₃PO₄ solution under anodic polarization at 1.6 V vs. SCE for 5 min.

Carbon content in the composites (Cu/PDA and Cu/c-PDA) was determined by high temperature combustion, typically induction. The CO, CO₂ gases resulting from the combustion were analyzed by infrared absorption in an Eltra CS800 apparatus.

FTIR spectra were recorded using a Bruker Equinox 55 in the range of 500–4000 cm⁻¹ to study the surface functional groups of Cu/PDA and Cu/c-PDA powders, that were mixed with dried KBr. Cu coated powders were characterized by Raman spectroscopy using a high-resolution Horiba spectrometer equipped with a 532 nm laser in a backscattering micro-configuration (accuracy equal to 0.1 cm⁻¹). Laser power was kept in the range between 5 and 10 mW. All the

tests were carried out at room temperature with a 50× objective having a laser spot size of about 400 nm. X-ray photoelectron spectroscopy (XPS) analyses were performed using an Omicron Argus X-ray photoelectron spectrometer with monochromatized Al K α excitation (1486.6 eV) with a pass energy of 100 eV and 20 eV for acquisition of the survey and high-resolution spectra, respectively. The XPS peak areas were determined after subtraction of a background using the Shirley's method. Element peak intensities were corrected by Scofield factors. All spectrum processing were carried out using CasaXPS software (Casa Software Ltd., UK).

Thermal diffusivity (TD) was measured at 70 °C by laser flash technique using a NETZSCH LFA 45 instrument. Relative density was calculated through dividing the experimental one measured via Archimedes principle by the Cu theoretical one (8.96 g/cm³). Specific heat capacity (HC) of the composite materials was calculated using the linear rule of mixture. TC of as-sintered samples was calculated by multiplying TD, density and HC. Sample (cylinder shape with Φ 6 mm \times 4 mm) used for TD measurement was machined along x-y plane. To check the anisotropic thermal properties of the Cu/c-PDA materials, both the directions, namely parallel to the pressing direction TC_{//} and perpendicular to the pressing direction TC_⊥, were analyzed. Hardness measurements of the Cu materials and Cu/c-PDA composites, both sintered in the same conditions, were analyzed with Wilson hardness Vickers 452 SVD indenter with a force of 20 N.

3. Results and discussions

3.1 Coating of the Cu flakes by c-PDA

Figure 1 shows SEM micrographs of typical Cu flakes at different stages of the processing. The flake dimensions range from 20 to 40 μ m in diameter and 80 to 200 nm in thickness. Annealed Cu flakes under Ar/H₂ (5%) atmosphere are presented in Figure 1-a). One can notice the presence of submicronic open pores that were not present on the initial Cu flakes (not shown). It could correspond to the decomposition of the stearic acid, added to the flakes to limit their agglomeration, and to the reduction of small copper oxide spots, leading to holes where the thickness of the flake was low. After PDA coating (Figure 1-b) and annealing under a reducing atmosphere (Figure 1-c), the surface morphology of the Cu flakes does not really seem different. At most, one could notice in Figure 1-c a weakening of the steps observed in Figure 1-a. However, since the PDA and c-PDA thicknesses were of about 10 nm, no major change, nor increase of the Cu flakes thickness could be observed.

The carbon analysis of the coating before (PDA) and after annealing (c-PDA) shows a 20% decrease of the carbon content after annealing process (0.30 wt.% to 0.23 wt.%). This decrease could be related to C-O desorption.

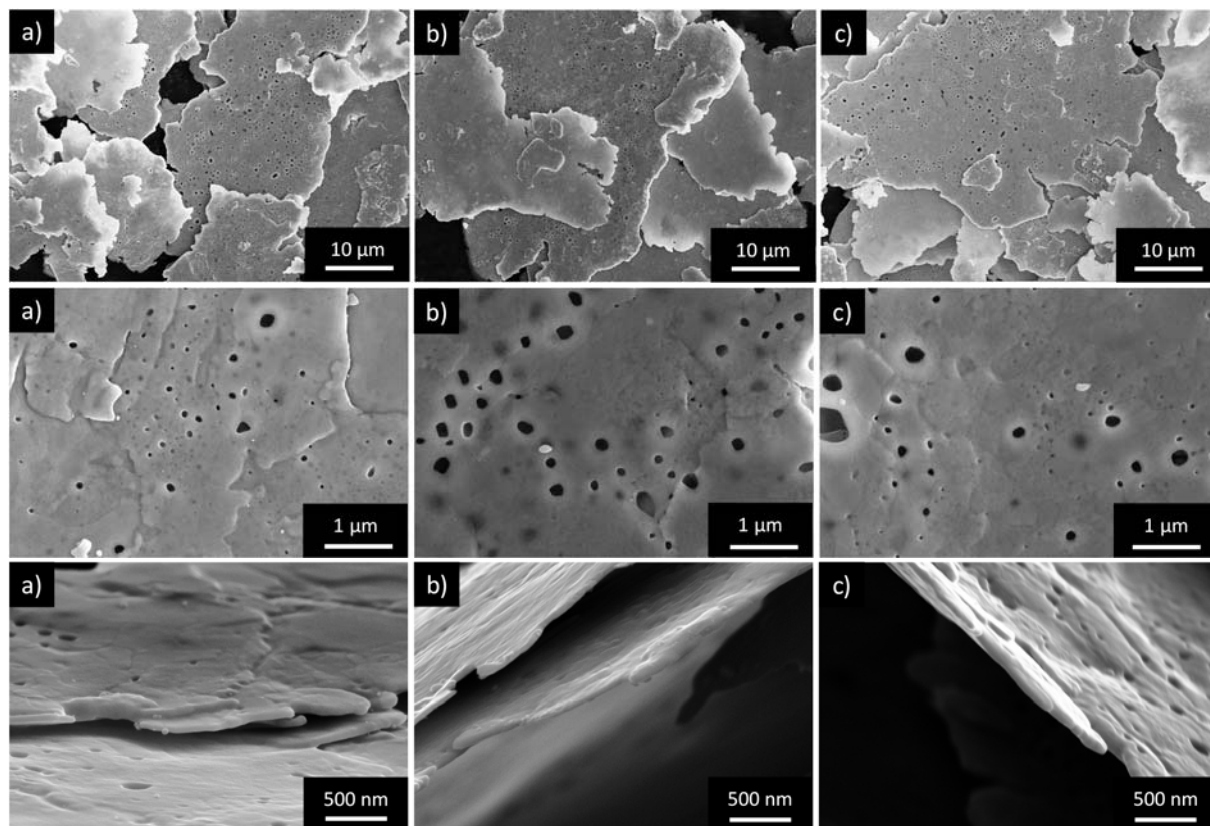


Figure 1: SEM micrographs of a) Cu flakes (after H₂ treatment), b) Cu/PDA flakes and c) Cu/c-PDA flakes.

Infrared spectra obtained for Cu/PDA and Cu/c-PDA powders are presented in Figure 2A. The spectra show the presence of characteristic bonds of polydopamine with a strong band between 3000 and 3500 cm⁻¹ attributed to aromatic rings, C-N, C-O and N-H bonds. The O-H, C-O and N-H bonds were not observed after heat treatment of the material, confirming the efficiency of the graphitization. It is necessary to note that the characteristic band of the C-N bond is always present in the spectrum of the calcined PDA, indicating that nitrogen remains in the film.

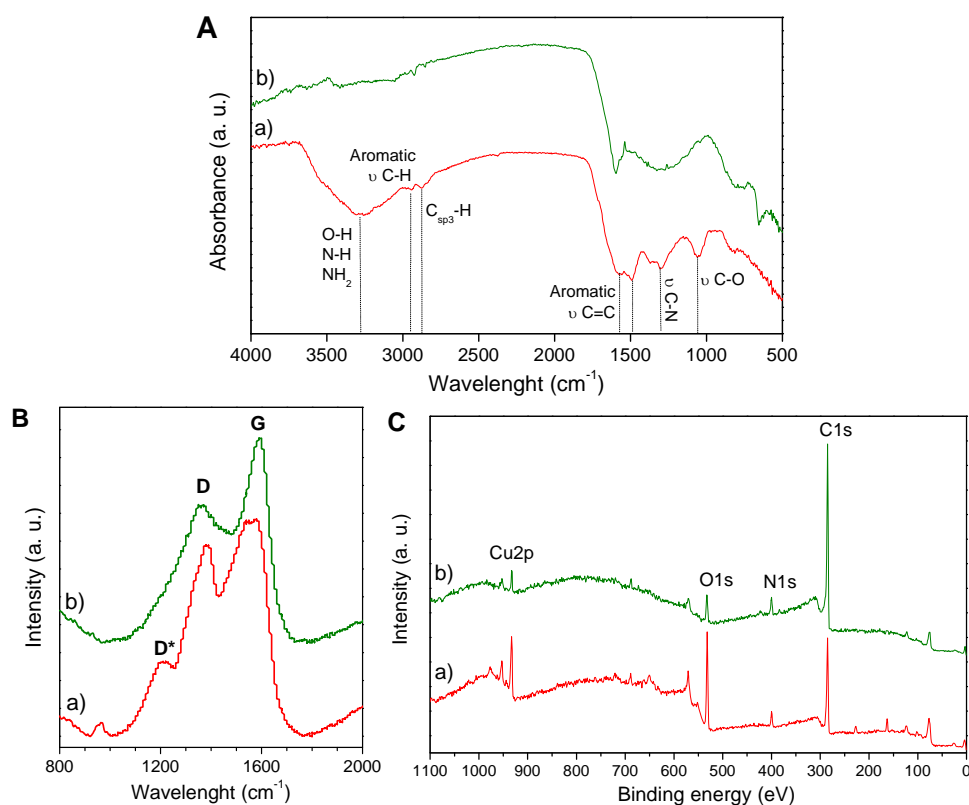


Figure 2: (A) Infrared spectra, (B) Raman spectra and (C) XPS survey spectra of a) Cu/PDA powder and b) Cu/c-PDA powder.

Raman spectroscopy is widely used to characterize graphene and graphene-based compound, focusing on the 800-2000 cm⁻¹ range where 2 main bands can be observed. The G peak at about 1590 cm⁻¹ (associated to the first order allowed Raman mode E_{2g}) is relative to pure crystalline graphene, while the D one at about 1350 cm⁻¹ (A_{1g} mode), appears when a high number of defects is present, i.e., when the periodic lattice of graphene is broken by defects. D and G bands are the predominant features in the Raman spectra of Cu/PDA and Cu/c-PDA materials, confirming their graphene like structure (cf. Fig. 2B). A D* peak is also present in the Cu/PDA spectrum, but it is no more observed after heat treatment. This D* peak, at about 1200 cm⁻¹, is sometime present for graphene oxide and was reported and attributed to disordered graphitic lattices [34].

Fig. 2B shows that the FWHM of the G peak decreases after annealing going from around 90 cm⁻¹ for the PDA material to 55 cm⁻¹ for the c-PDA one. It has been shown that PDA gives broad Raman peaks at 1580 cm⁻¹ and 1350 cm⁻¹ resulting from deformation and stretching vibration of aromatic rings together with a contribution around 815-800 cm⁻¹ that is attributed to aliphatic C-C and C-O bonds [35-37].

The evolution of the peak positions and of the I_D/I_G ratio are reported in Table 1. For the Cu/c-PDA composite powder the decrease of the I_D/I_G ratio can be attributed to the following factors: (i) amorphization of graphite or (ii) conversion of amorphous carbon to nanocrystalline graphite [27]. It is also known that the I_D/I_G ratio can be related to the sp^2 crystallite size in these compounds, by being inversely proportional to it.

Table 1: Band parameters of Raman spectra (Figure 2B) and surface concentration of elements, in at.%, determined by XPS (Figure 2C).

Materials	Name, wavelength of the main Raman bands (cm^{-1}) and I_D/I_G ratio				Surface concentration of elements (at.%)		
	D*	D	G	I_D/I_G	C	O	N
Cu/PDA	1215	1380	1570	0.89	69.37	25.45	5.18
Cu/c-PDA	-	1359	1588	0.67	88.02	6.54	5.44

To verify that nitrogen atoms are still present in the PDA film after the thermal annealing, XPS analyses were performed on the Cu/PDA and Cu/c-PDA powders. The XPS survey spectra are shown in Figure 2C and the atomic concentrations of C, O and N (in at%) are reported in Table 1. From these spectra it is clear that, after the thermal treatment, N is always present into the Cu coating and there is less oxygen. The O/C ratio decreases from 0.37 to 0.07 after the calcination step, and the O/N ratio from 4.9 to 1.2. Conversely, the N/C ratio remains almost stable, between 0.075 to 0.063 which confirms that the annealing treatment does not affect the C-N bonding. Finally, one can notice in Figure 2C that, for both samples, Cu is detected. It confirms that the thickness of the PDA coating is less than 10 nm (*i.e.* XPS depth detection).

3.2 Thermal and mechanical properties of Cu/c-PDA materials

Figure 3 shows the microstructures of Cu/c-PDA sintered composites after dissolution of the Cu surface. A lamellar structure can be observed in Figure 3-b1 and b2 perpendicular to the hot-pressing direction. This is due to the stacking of the c-PDA coated Cu flakes. The

anisotropic microstructure observed after sintering is induced by the platelet geometry (large length to thickness ratio) of the Cu flakes. No grain growth nor grain morphology evolution were observed after the hot-pressing process. The porosity level of the Cu/c-PDA materials, measured by Archimedes method, was lower than 4% confirming a full densification. In Figure 3-a2, the graphene-like carbon membrane is observable, confirming that the Cu/c-PDA composite has anisotropic physical properties.

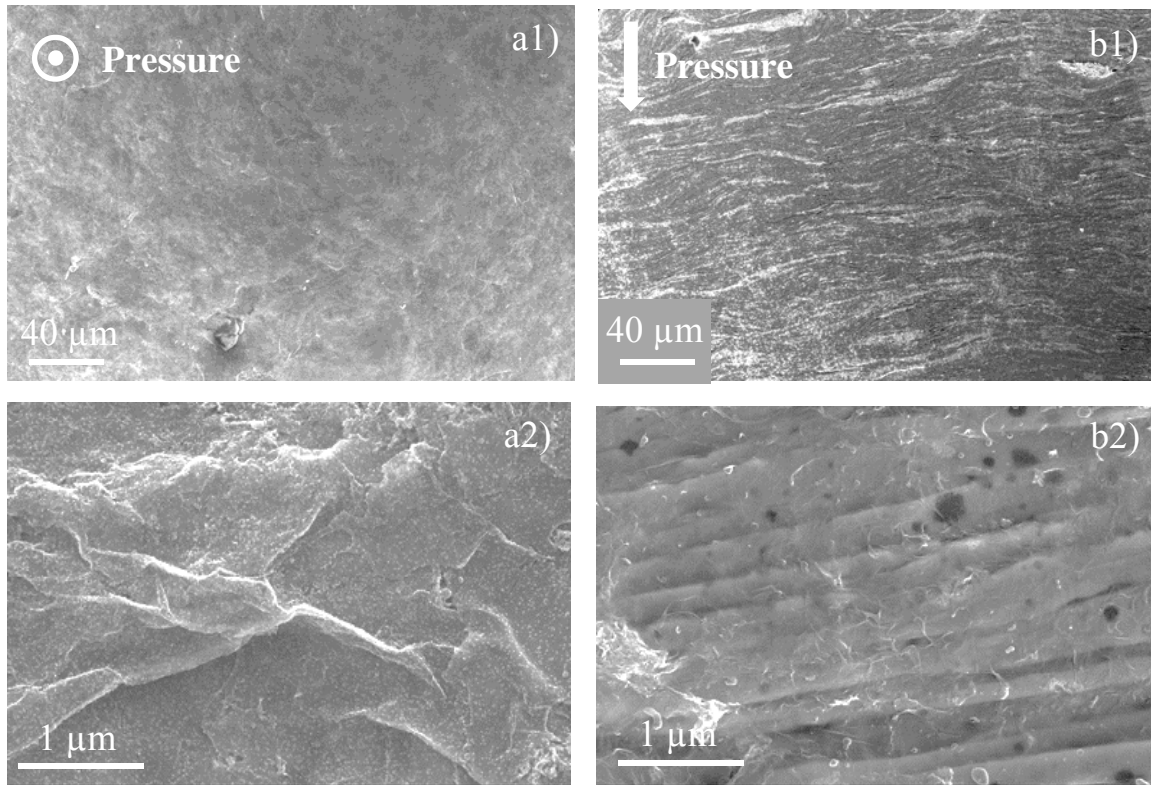


Figure 3: SEM micrographs in the directions perpendicular (a1-a2) and parallel (b1-b2) to the hot-pressure direction of the Cu/c-PDA sintered composites after electrochemical dissolution of the Cu surface allowing evidence of the carbon structures.

The calculated TC and measured Hv hardness of both Cu and Cu/c-PDA materials, in the directions parallel (Fig. 4-a) and perpendicular to the hot-pressing direction (Fig. 4-b) are given in Figure 4. Each measurement is an average of at least 2 different samples.

Whatever the measured direction (Figure 4a), TC of Cu-PDA composite materials is almost identical and close to pure Cu materials fabricated with Cu flake powders (close to 370 W/mK) which should mean that an isotropic material was formed. Conversely, the Vickers hardness behavior is quite different from the TC. Indeed, hardness is anisotropic with a perpendicular hardness lower than the parallel one. Identical behavior has already been observed for Al

materials, fabricated by powder metallurgy with Al flake powders [38]. It has to be mentioned that after electrochemical etching no flake structure has been observed by SEM on the pure densified Cu_{Flake} materials. On the contrary, for Al_{Flake} materials, after chemical etching, flake structure has been observed due to the presence of Al oxide at the surface of the Al flakes. [38]. If we assume that Cu_{Flake} materials as similar microstructure that Al_{Flake} materials, the anisotropic hardness properties of Cu_{Flake} materials can be correlated with its flake like geometry and a “higher quantity of Cu-Cu grain boundaries” parallel to the pressure direction with respect to the perpendicular one.

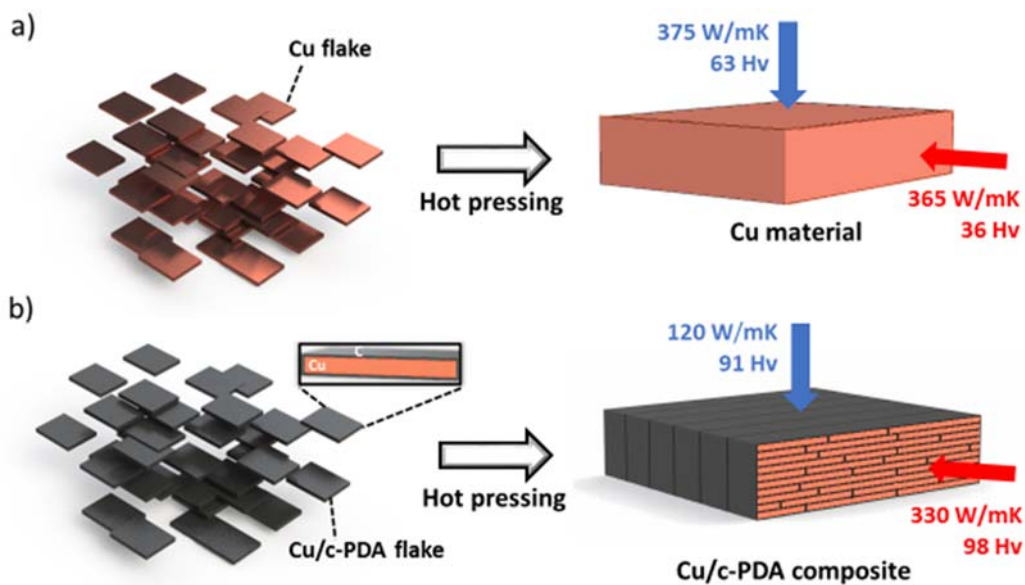


Figure 4: Hardness values (in Hv) and thermal conductivity (in W/mK) measured in both directions (parallel in blue, perpendicular in red to the hot-pressing direction of the composite fabrication) for a) pure Cu and b) Cu/c-PDA composite material.

Interestingly, for the Cu/c-PDA composites, a quite lower TC value is measured for the parallel direction (120 W/mK). This value is divided by 3 in comparison to TC of pure Cu material (375 W/mK). In the perpendicular direction TC is slightly lower (330 W/mK) than pure Cu (365 W/mK). This difference of TC with pure Cu can be correlated to the intrinsic thermal property of the c-PDA film. Indeed, as for typical graphene materials, TC of 2D graphene is low in the perpendicular direction to the carbon plane but elevated in the other direction and reaching up to 5000 W/mK [39]. Therefore, the intrinsic properties of the c-PDA film are in good agreement with graphene sheet, perpendicularly to the basic plane, leading to a decrease of the TC from 375 W/mK to 120 W/mK. In the other direction, perpendicularly to the pressure axis,

improvement of the TC is not measured (330 W/mK for the composite material and 365 W/mK for pure Cu). Obviously, the intrinsic TC properties of the c-PDA film is equivalent or slightly lower than the Cu material leading to a slight decrease of the composite TC.

In opposite to these TC values, a huge increase of the Vickers hardness is measured in both directions for the Cu/c-PDA composite material, even if the parallel hardness is slightly lower than the perpendicular one. This behavior is typical of metal matrix composite reinforced with nanoscale material which lowers the displacement of dislocations induced during the test and so increases the macroscopic hardness of the composite materials. Finally, the anisotropy of hardness property has to be correlated with composite effect and with a uniformly distribution of c-PDA inside the Cu matrix.

4. Conclusions

Cu/c-PDA composite materials have been fabricated using a simple strategy to directly synthesize the graphene-like reinforcements onto the surface of Cu flakes. To consider this material for heat sink application mechanical and/or thermal properties should be improved. The main advantage of this process is that it avoids all the dispersion/aggregation problems usually faced during the solid or liquid phase fabrication of composite materials with nano-reinforcements. In this process, Cu flakes were coated with a very thin film of polydopamine obtained by a simple immersion of the Cu powder in a dopamine aqueous solution. The thermal treatment of the Cu/PDA composite powders leads to the formation of Cu particles coated with an N-doped graphene-like film. The presence of this coating on the Cu flakes allows to obtain a composite having higher hardness than the pure Cu material. Moreover, considering the anisotropy of the Cu flakes, coated by the c-PDA film, the final composite presents an anisotropic thermal conductivity, with an anisotropy ratio of 2.75.

Declarations of interest

None

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