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Research paper

Fabrication and Characterization of Copper Matrix Composites Reinforced Silver-Coated Carbon Fibres

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Abstract

Silver interface was developed to improve the thermal properties of copper matrix reinforced carbon fibre. The composites were made by coating the carbon fibres with silver and copper layers via the electroless coating process. The thermal conductivity and the thermal expansion of the composites were profiled by means of JMP Pro software. The experimental results showed that the weight-percent of silver and the volume-percent of the carbon fibre have significant effect on the thermal properties of the composites. The thermal conductivity and thermal expansion of the composites were also profoundly influenced by the anisotropic structure of the composites.

Keywords: *copper-carbon fibre composite, electroless copper, electroless silver, thermal expansion, thermal conductivity.*

1. Introduction

Advance metal matrix composites were developed to meet the intricate thermal design requirements of the semiconductor packaging. These composites were engineered to optimize their thermal conductivity (TC), coefficient of thermal expansion (CTE) and density as required by the International Technology Roadmap for Semiconductors (ITRS) [1,2]. Among these advance composites, copper matrix reinforced carbon fibres (Cu-CF) composites are the most promising candidates as the thermal packaging materials especially in many applications where finding the balance between thermal performances and material cost is very critical. However, the full potential of these composites was not attained due to the weak bonding between the constituents [3]. To overcome this challenge, carbide compounds were introduced as bonding interfaces. Molybdenum carbide, titanium carbide and boron carbide bond well to the carbon fibres thus improve the overall CTE of the composites [4-9]. But these carbides also have some disadvantages due to their low thermal conductivity and high density [10]. Acknowledging the drawbacks of these carbides, a new alternative material for the interface was studied. Silver was proposed as the new bonding interface mainly because it has good TC value. Even though the CTE and density of silver are inferior to copper and carbon fibre, these disadvantages are compensated by its noble property. It does not react with copper. Hence, it can prevent the formation of unwanted secondary phase during sintering process which can degrade the thermal performance of the composites. Copper atoms are also able to diffuse into the silver interface thus suppress the volume expansion of silver at high temperature. So, by coating a thin layer of silver around the carbon fibres, via an electroless coating process, light weight copper matrix reinforced silver coated carbon fibre (Cu-Ag/CF) composites with high TC and low CTE properties can be fabricated.

2. Methods

2.1. Composite fabrication

XN-100 milled carbon fibre from Nippon Graphite Fibre Corporation was selected as the reinforcement materials because of its outstanding thermal properties. The axial TC and CTE of this carbon fibre are 900 W/m.K and -1.0×10^{-6} K^{-1} respectively. On average, the carbon fibres have diameter of 10mm and length of 300mm. The FESEM image of this mesophase-pitch-based carbon fibre is shown in Figure 1. The oriented-sheath region of the fibre consists of radial arrangement of ribbons and the core region was engineered to be more random to optimize the mechanical and thermal properties of the carbon fibres [11,12].

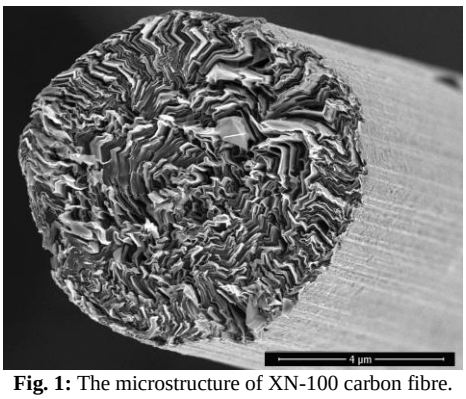


Fig. 1: The microstructure of XN-100 carbon fibre.

Prior to the electroless coating process, the carbon fibres were pretreated as in Figure 1. First, the carbon fibres were ultrasonically cleaned with acetone solution and etched with nitric acid. Then, the carbon fibres were sensitized under continuous stirring at 40 ^{o}C for 2 hours and finally activated at 40 ^{o}C for 1 hour.

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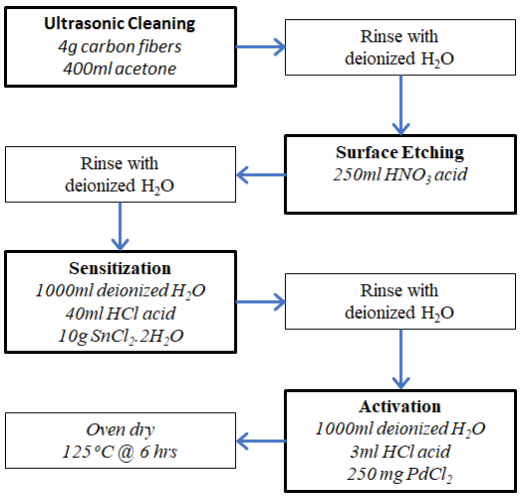


Fig 2: The surface treatments of carbon fibres.

The electroless coating processes shown in Figure 3 are modifications of those developed by Chang et al. (1999), Yuen et al. (2013) and Tao et al. (2016) [13-15]. In the silver electroless coating process, the reducing solution A was boiled for 5 minutes and then cooled down to room temperature. Once cooled, 20ml of ethanol (C_2H_5OH) was added into the solution under continuous stirring. Then ammonium hydroxide (NH_4OH) solution was added into solution-B until the solution turned transparent. The pH of solution-B was adjusted to pH 12 by adding sodium hydroxide (NaOH) solution. Then, carbon fibres were added into solution-B. Finally, solution-A was transferred into a funnel and slowly added into solution-B drop by drop.

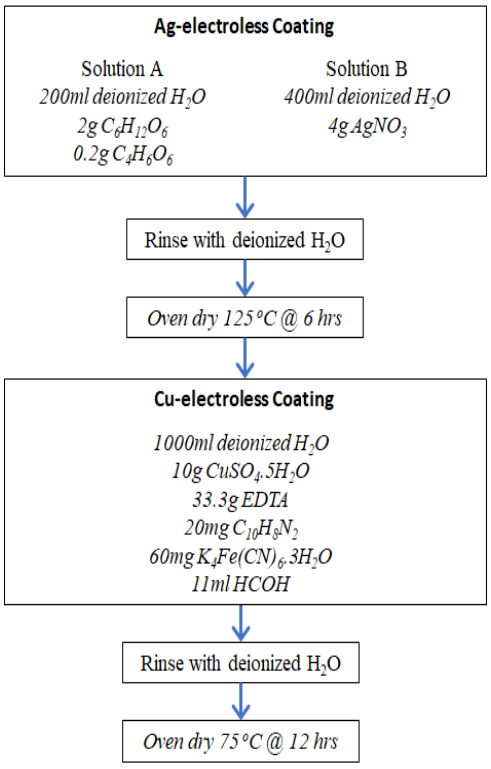


Fig 3: The electroless coating of carbon fibres.

The pH of the mixed solution was closely monitored by using pH paper and maintained at pH 12. After 30 minutes, the pH of the solution would be stabilized and the coating process was ended. The silver-coated carbon fibres were then rinsed thoroughly with deionized water before dried in the electric oven at 125 °C for 6 hours. The copper chemical bath was prepared in a beaker under continuous stirring and heating. NaOH solution was added until the solution reached pH 12. Then, air was bubbled into the solution by using a small pump. At 75 °C, the silver-coated carbon fibres were introduced into the solution. The solution was maintained at 75 °C and pH 12 throughout the coating process. After an hour, when there was no change in the pH and the solution turned transparent, the electroless coating process was ended. Then, the solution was thoroughly rinsed until it reached pH 7. Finally, the coated carbon fibres were dried in the oven at 75 °C for 12 hours. After the drying process, the carbon fibres were compacted under 6 metric tons of hydraulic press into small green pellets. The weight, diameter and thickness of the green pellets were measured by using analytical balance, vernier calliper and micrometre respectively. Then the pellets were sintered in a tube furnace under a controlled atmosphere of 98% argon and 2% hydrogen, at 925 °C for 1 hour.

2.2. Characterization

After the sintering process, the weight, diameter and thickness of the sample were measured again to calculate the sintered density of the pellets (ρ_{sin}). The absolute density (ρ_{abs}) of the sintered samples were measured using Micromeritics AccuPyc II 1340 gas pycnometer. The porosity of the sample was calculated by using equation 1:

$$\text{Porosity} = (\rho_{abs} - \rho_{sin}) / \rho_{abs} \times 100\% \quad (1)$$

The heat capacity (C_p) of the sample was measured by using a differential scanning calorimetry (TA Instrument Q10). Sapphire was used as the calibration standard. The measurement followed the 3-run method set by ASTM E1269 standard. The value of C_p for each sample is given by equation 2:

$$C_p = (HF_s - HF_b) / (w_s \,.\, dT/dt) \times 60 \times K \quad (\text{J/m.°C}) \quad (2)$$

Where HF_s is the heat flow of the sample and HF_b is the heat flow of the baseline. The weight of the sample, w_s is in the unit of mg, and the heating rate, dT/dt is in the unit of °C/min. The calibration constant, K is the ratio of the literature value of the heat capacity of sapphire ($C_{p\text{-}lit}$) to its actual measured value ($C_{p\text{-}mea}$) as shown in equation 3:

$$K = (C_{p\text{-}lit} \text{ of sapphire}) / (C_{p\text{-}mea} \text{ of sapphire}) \quad (3)$$

The thermal diffusivity (TD) of the composites was measured by using a laser flash apparatus (Netzsch LFA 457). Based on the measured values of the heat capacity and thermal diffusivity, the thermal conductivity, TC of the sample was calculated by using equation 4:

$$TC = TD \times C_p \times \rho_{sin} \quad (\text{W/m.K}) \quad (4)$$

Linseis L75PT dilatometer was used to measure CTEs of the samples. The measurements were performed up to 450°C and the heating rate was set at 2.5°C/min. Argon gas was used to protect the sample from oxidation. JMP Pro statistical software was used to analyze the thermal properties of the composites. Only two factors were considered in the 2 by 2 full factorial design, the weight-percentage of silver in the metal matrix (wt.% Ag) and the volume percentage of carbon fibre in the composite (vol.% CF). The low level of wt.% Ag was set to 4wt.% because anything lower than that would not produce homogeneous silver coating on the carbon fibres. The high level was only set at 12vol.% because the silver-coated carbon fibres were inclined to agglomerate at higher wt.% Ag. The maximum vol.% CF was only set to 55% due to the limitation of the conventional sintering process in removing pores. Based on the results of the statistical analysis, the predicted CTE and TC profilers of the composites were developed. However, the details of the statistical analysis will not be touched in this report because it was published elsewhere [16].

3. Results and Discussion

3.1. Ag-Cu coatings on carbon fibres

Figure 3 shows the XRD patterns of the Cu-Ag/CF composites. Only XRD patterns of copper, silver and graphite elements were detected. Four main sharp peaks at 2θ = 38.2°, 44.4°, 64.6° and 77.8° correspond to diffraction from the 111, 002, 022 and 113 crystal planes of silver phase (cubic F m -3 m space group). The copper phase is represented by diffraction peaks at 2θ = 43.1°, 50.7° and 73.7°. The peak at 2θ = 26.3°, 50.7° and 54.7° represent the 002, 102 and 004 crystal planes of graphite phase. The presence of secondary phase was not observed even on the sample with high wt.% Ag. These findings prove that copper and silver do not react with each other to form new phase during sintering process. It also implies that the interior structure of the carbon fibre still remains unchanged after the sintering process.

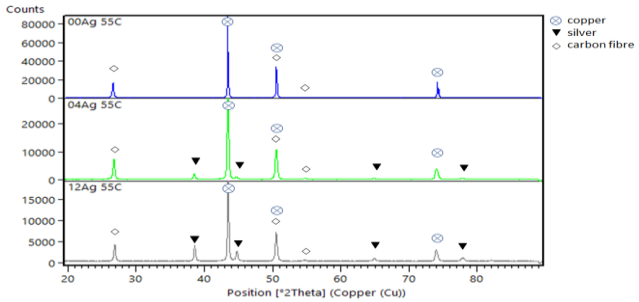
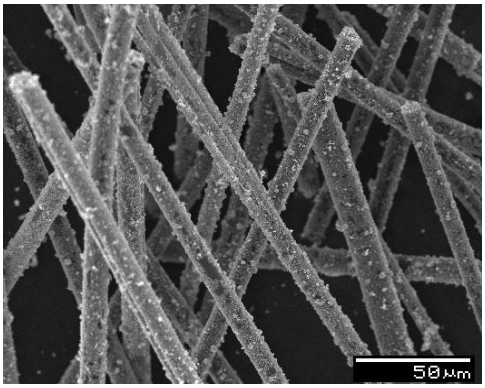


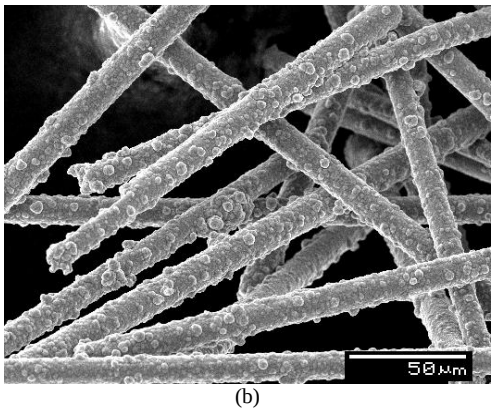
Fig. 3: The XRD pattern of the Cu-Ag/CF composites at 55 vol.% carbon fibres.

Figure 4 reveals the homogeneous coating of the carbon fibres after the electroless coating processes. Initially, the silver microlite were formed on the surface of the carbon fibres. Over time, the silver deposition continued and turned into a complete silver layer as shown in Figure 4(a). In the copper electroless coating process, copper microlites were deposited onto the silver layer. Once the nucleation of copper was initiated, the copper atoms themselves act as a catalyst for further copper deposition. This continuous copper deposition turned into a homogeneous copper layer as shown in Figure 4(b).

The Ag-Cu coating on the carbon fibres was very homogeneous as shown by the cross-sectioned image of carbon fibres in Figure 5(a). The thickness of the coating was uniform as shown in Figure 5(b). The silver coating layer was not clearly observed which suggests that copper diffused into the Ag layer to some extent during the sintering process. Since the coating thickness is very consistent, non-uniform diffusion of copper into the silver layer can be avoided. This is very critical because heterogeneity in the copper diffusion can cause undesirable thermal stress at high temperature [17,18].

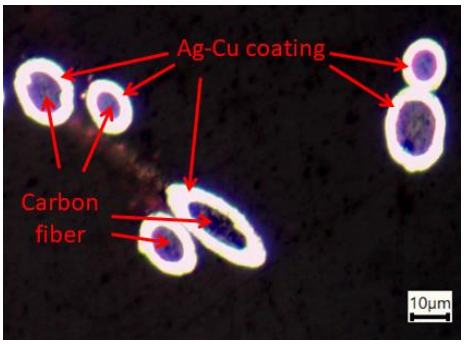


(a)

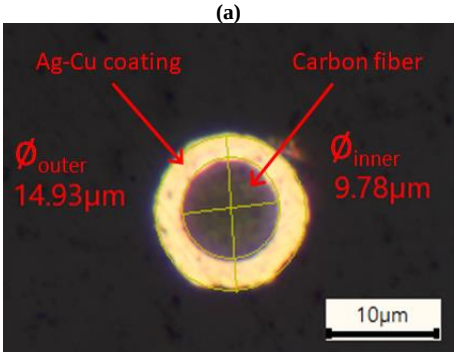


(b)

Fig 4: Images of carbon fibres after (a) silver electroless coating and (b) copper electroless coating.



(a)

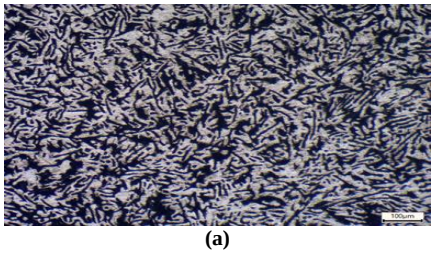


(b)

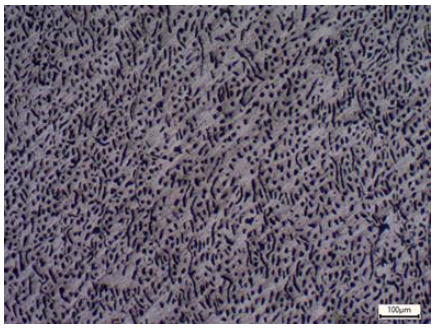
Fig 5: The cross-section images of Ag-Cu coated carbon fibres show evidences of (a) homogeneous coating and (b) consistent coating thickness.

3.2. Microstructure of Cu-Ag/CF composites

Figure 6 shows the micrographs of the composites at 4wt.% Ag and 55vol.% CF. Figure 6(a) shows the micrograph of the composites in the direction perpendicular to the pressing direction, while Figure 6(b) is in the parallel direction. The compaction process induced a preferential orientation of the carbon fibres perpendicular to the direction of the applied pressure as large numbers of CF "sticks" can be observed in Figure 6(a) and large numbers of CF "spots" can be observed in Figure 6(b). The dispersion of the fibres in the matrix is homogeneous in both figures. Nevertheless, porosities are inevitable. This is due to the limitation of the conventional sintering process, where no post densification process such as hot press is performed.



(a)



(b)

Fig. 6: The distribution of the carbon fibres in the direction (a) perpendicular to the pressing direction and (b) parallel to the pressing direction.

3.3. Thermal properties

The prediction profiler in Figure 7, indicates that the CTEs of the Cu-Ag/CF composites are significantly correlated to the content of silver and carbon fibres. The lowest CTE value was achieved when the highest content of silver and carbon fibre was incorporated into the composite. However, the thermal conductivity profile shows the opposite trend. The lowest content of silver and carbon fibre gave the highest thermal conductivity. Furthermore, the anisotropic structure of the composites, which was due to the preferred orientation of the carbon fibres, had profound effect on the thermal properties. The measured TC and CTE values were actually corresponded to the transverse thermal properties of the carbon fibres. Since the thermal properties of the carbon fibres are very poor in the transverse direction (TC = 5 W/m.K and CTE $=12x10^{-6}$ K^{-1}), it should be noted that the measured results were actually corresponded to the lowest thermal properties of these Cu-Ag/CF composites. Any measurement performed parallel to the axis of the carbon fibres should give better values of TCs and CTEs, as reported by Veillere et al. (2012) and Liu et al. (2013) [17,19].

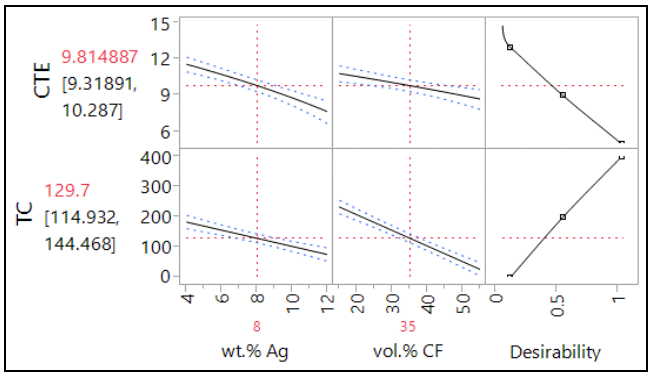


Fig. 7: Predicted profiler for CTE and TC of Cu-Ag/CF composites.

The interaction profile in Figure 8 demonstrates that at low level of vol.% CF, the silver content had relatively large effect on the thermal conductivity of the composites. When both wt.% Ag and vol.% CF were at their low levels, the thermal conductivity value was at its maximum level. Moreover, the thermal conductivity of the composites with low carbon fibre content (vol.% = 15) showed a steep decreasing trend when the silver content was increased from 4 wt.% to 12 wt.%. However, the composites with high content of carbon fibre (vol.% = 55) did not show the same trend. The thermal conductivity of these composites shows an increasing trend as the wt.% Ag was increased. This is very positive finding because the composites with high volume of carbon fibres are the most interesting due to their light weight property.

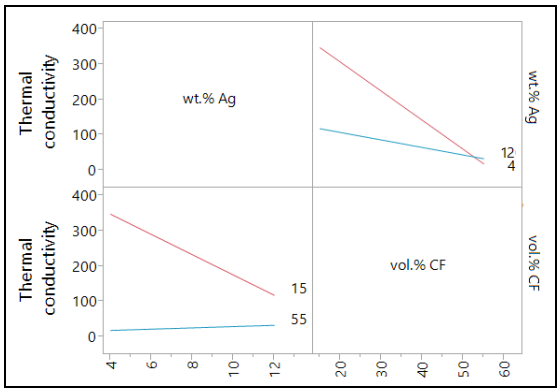


Fig. 8: Interaction profiles of the thermal conductivity of Cu-Ag/CF composites.

To measure the effect of the silver interface on the overall thermal performance of the Cu-Ag/CF composites, the CTEs and TCs values were relatively compared to the non-silver coated Cu-CF composites. As shown in Figure 9, the presence of silver interface had significantly improved the CTE and TCs of the Cu-Ag/CF composites with a small increase in the density value. The composites with 12 wt.% Ag and 55 vol.% CF had their TC values increased up to 170% and CTE values improved to 50%. Because of the difference in atomic size, the copper atoms could diffuse into the silver interface. Hence the thermal expansion of the silver interface could be suppressed by the presence of copper atoms. The thicker the Ag interface, the deeper the copper atoms could diffuse into. As a result, the interface became stronger and the CTE of the composites were improved. Furthermore, no secondary phase was formed in the interface because copper and silver did not react with each other. For this reason, as the percent-weight of silver increased, the overall TC of the composites also increased, as long as the fibres distribution could be maintained homogeneously.

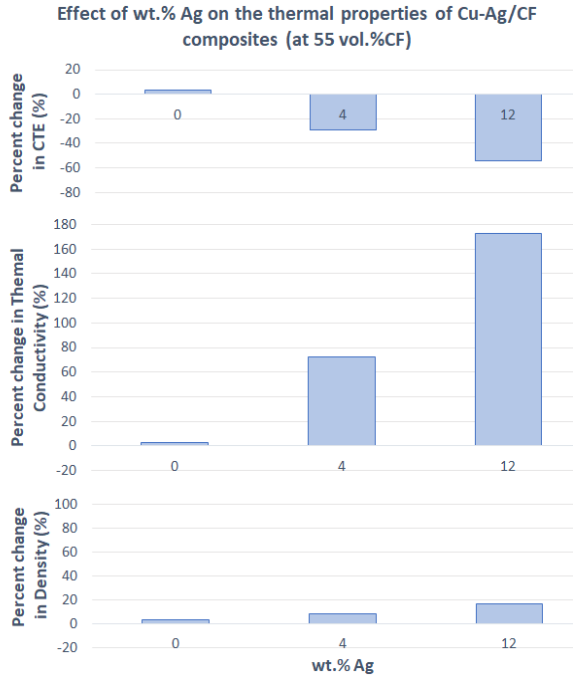


Fig. 9: Thermal performance of Cu-Ag/CF composites relative to the normal Cu-CF composites.

4. Conclusion

Based on the experimental results, the presence of high volume of carbon fibres was crucial to lower the density of the Cu-Ag/CF composites. The thermal properties of the composites were opti-

mized by the silver interface as clearly corroborated by the experimental results. Nevertheless, the presence of silver interface would slightly increase the density of the composites. But this drawback was compensated by the improved overall thermal properties of the Cu-Ag/CF composites.

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