Thermal Conductivity of Copper Matrix Composites Reinforced with Multi-wall Carbon Nanotubes

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Abstract. Carbon nanotubes (CNTs) reinforced with metal matrix composites (MMCs) have attracted an increasing interest due to their promising properties. One of the challenges in metal matrix-CNTs composites research is producing a uniform dispersion of CNTs. A poor dispersion of CNTs within the matrix, attributed to strong CNT entanglement caused by Van der Waals forces. In this study, Cu/CNTs composites have been successfully fabricated by the powder metallurgy (PM) route. The thermal conductivity of Cu/CNTs composites showed that the thermal conductivity decreased after the incorporation of CNTs. The analysis revealed that the interfacial thermal resistance between the Cu matrix and CNTs plays a significant role in determining the thermal conductivity performances. Besides, the influences of porosity and distribution of CNTs also affected the thermal conductivity results.

1. Introduction
A major consideration in the bearing materials and electrical applications for production of metal matrix composites (MMCs) based on copper (Cu) is extensively used due to their excellent electrical conductivity and thermal properties [1]. It is usually mixed with graphite, then compacted to form an electrical brush which can carry current in the electric motors [2]. Multi-wall Carbon nanotubes (MWCNTs) is one of the possible reinforcements in MMCs is owing to its excellent mechanical strength and outstanding in electrical and thermal conductivities. Thus, it has been led to highly interest of carbon nanotubes in metal matrix composites which will be the outstanding reinforcing fillers for functional devices and structural engineering in self-lubricating composites. The MWCNT reinforced copper composite is a novel material which having higher potential for electrical sliding contact applications such as electrical brushes for electric motors [3-4]. The use of MWCNTs in copper could improve the properties of the current material. It is known that copper is a good electrical and thermal conductivity and the nanosized carbon tubes (CNTs) exhibit superior mechanical properties and excellent thermal and electrical conductivity. However, the major problem using CNTs in metal matrix composites is poor dispersion of CNTs within the matrix, caused by Van der Waals forces attributed to strong CNT entanglement [5-9].

It is predicted that the thermal conductivity value can be enhance by the addition of CNTs in the metal like copper or aluminum due to the high thermal conductivity being as high as 3000 W/m.K
A few papers have aimed in improving the thermal conductivity value of metal-CNTs composites [5][9][11-12]. For example, Cho et. al. reported on increasing value of the thermal conductivity of CNT/Cu compared to the sintered Cu [5]. However, some studies also show a decrement after adding carbon nanotubes. Chu and co-workers have fabricated Cu/CNTs using a particle composites system (PCS) followed by spark plasma sintering (SPS) which reported that no enhancement of thermal conductivity after the addition of CNTs into the copper matrix. The drop in thermal conductivity value of CNT/Cu composites was due to the existence of CNT clusters, which give serious weakness, such as large porosity and lower effective conductivity of CNT clusters themselves [11]. Koppad et al., also shows decreased in thermal conductivity of the composites after CNTs compared to pure Cu. This is due to the dispersion of MWCNTs in copper matrix [12]. When the CNTs were agglomerated, the phonon in such nanotubes with kinks get blocked at these sites leading to the decrease in conductivity of nanocomposites. Thus, this study aims to prepare CNTs/Cu composite by improvement of the interfacial bonding between CNTs and Cu matrix and to investigate the effects of thermal properties of the composites.

2. Materials and Method
2.1. Materials Preparation
Copper powder which had dendritic shape with particle size in average of <45 μm from Acros Organics is used as a matrix material. While, Flotube 9000 MWCNTs having 11 nm average in diameter and 10 μm average in length were used as reinforcement material was supplied by CNano Tech, China.

2.2 Experimental Procedures
In this study, the pristine CNTs are labelled as PCNTs while acid treated CNTs as ACNTs. The composite samples were fabricated by mixing copper with pristine CNTs (Cu/PCNTs) and copper with acid treated CNTs (Cu/ACNTs) which mixed using planetary ball mill at 250 rpm for 5 hours. For acid treated CNTs, the carbon nanotubes were functionalized in the mixture of acid (H2SO4:HNO3, 3:1) was refluxed at 80 °C for 4 h to attach carboxylic (-COOH) or hydroxyl (-OH) functional group and mixed with ethanol. By evaporating the ethanol, the CNTs were wrapped onto the surface of each Cu particles [13]. To fabricate the series of Cu/CNTs composites, the as-mixed powder was compacted into a rectangular shape. The mixtures of copper and CNTs powder were pressed into a steel dies under a compression force and the green part was produced. Sintering was done at a temperature of 900°C for 2 hours using quartz tube furnace under an argon atmosphere.

The microstructure of sintered samples of Cu/PCNTs and Cu/ACNTs was observed using Scanning electron microscope (SEM). The thermal conductivity, k of the composite was calculated using the following expression [14]: k (W/m.K) =α x Cp x ρ where α is the thermal diffusivity, ρ is the sample density and Cp is the specific heat. The thermal diffusivity of the sintered composites was measured at room temperature by a laser flash apparatus (LFA 447), Netzsch, Germany in accordance with ASTM E1461-13 standard test method. The samples were machined using EDM wire cut to a square shape with a thickness of 2-3 mm. To ensure a more accurate measurement of thermal conductivity, samples with flat and parallel faces have been used. Then, samples were coated on the top and bottom surface using a thin film of carbon spray to avoid the laser light and plasma generation at the surface [5].

3. Results and Discussion
3.1 Microstructural of Sintered Cu/CNTs
Figure 1 (a) and (b) show the microstructures of sintered samples for Cu/PCNTs and Cu/ACNTs, respectively. The goal of microstructural analysis is to ascertain that the particles were diffused with each other to form as-sintered part. From the SEM micrograph, both samples show the existence of pores in the sintered parts and the diffusion of powder particles can be noted. Figure 1 (a) shows the micrograph image of Cu/PCNTs which depicts a diffusion between the particles. However, wide
pores size distribution is visible at a few locations. This might be because of the cluster and agglomeration of carbon nanotubes at certain areas thus lead to a big pores formation as reported by author in the previous work [13]. While for Cu/ACNTs Figure 1 (b) shows the grain growth occurred between the particles. The porosity was observed which leads to the scattering pores pinching off into closed and isolated voids over the surfaces. This is probably due to the carbon nanotubes were separately embedded in the copper grain boundary without obvious gaps because of the functional groups that form on the surface of the carbon nanotubes cause homogeneous dispersion of CNTs [5][13].

Figure 1. Micrograph images of sintered samples; (a) Cu/PCNTs and (b) Cu/ACNTs

3.2 Thermal Conductivity
Tabel 1 shows the values of thermal diffusivity, specific heat and thermal conductivity of the samples. The relative densities of the sintered compact samples for all specimens were measured and reported previously by the author as in the range of 88.72% to 97.17% [15]. Figure 2 (a) and Figure 2(b) show the calculated thermal conductivities of Cu/PCNTs and Cu/ACNTs respectively. Table 1 shows that the pure copper sample in the present work shows thermal conductivity of 374.08 W/m.K which is slightly lower compared to the thermal conductivity of bulk copper which is 404 W/m.K. The lower thermal conductivity value can be related to the microstructure of the powder metallurgy materials and the porosity in the sample [16]. It should be known that the powder sintered materials pertaining to polycrystals show lower thermal conductivity compared to the bulk single-crystals with the existence of grain boundaries and defects in polycrystals [11]. Previous researchers have also reported a lower thermal conductivity value of pure copper compared to copper bulk references [5][9][11-12][16-17].

|                    | Pure Cu | Pristine CNTs (vol%) | Acid treated CNTs (vol%) |
|--------------------|---------|----------------------|--------------------------|
|                    | 0       | 1                    | 2                        |
| Thermal diffusivity (mm²/s) | 113.0   | 77.8                 | 79.8                     |
| Specific heat (J/g.K)    | 0.384   | 0.387                | 0.390                    |
| Thermal conductivity (W/m.K) | 374.1   | 252.5                | 258.6                    |
|                    | 3       | 4                    | 1                        |
|                    | 88.5    | 68.5                 | 90.1                     |
|                    | 0.393   | 0.396                | 0.387                    |
|                    | 288.6   | 215.6                | 252.2                    |
|                    | 3       | 4                    | 2                        |
|                    | 98.5    | 97.4                 | 269.6                    |
|                    | 0.393   | 0.396                | 267.4                    |
|                    | 4       | 4                    | 3                        |
|                    | 97.4    | 256.7                | 256.7                    |

Table 1. Thermal diffusivity, specific heat, and thermal conductivity of Cu/CNTs composites
Figure 2. (a) Relative density and thermal conductivity of copper/pristine CNTs composites and (b) relative density and thermal conductivity of copper/acid treated CNTs composites

The Cu/CNTs composites samples were measured, and it shows that the value of thermal conductivity of Cu/PCNTs composites significantly decreased in comparison with pure Cu. Similar observation was discovered on the Cu/ACNTs composites, where the addition of CNTs reduces the properties of thermal conductivity. From the results obtained, the thermal diffusivity of Cu/ACNTs composites show better performances compared to Cu/PCNTs but is still lower compared to pure Cu. This result shows that Cu/ACNTs led to a better thermal diffusion or how quickly the Cu/ACNTs samples react to a temperature applied. This is because of the functionalization treatment process that provides the functional groups which are attached on the surfaces of CNTs that help in obtaining a better dispersion of carbon nanotubes into the copper matrix as compared to Cu/PCNTs. However, the underperformances of Cu/CNTs composites in thermal conductivity properties may be related to three factors. The factors are (i) interfacial thermal resistance between the metal matrix and CNTs reinforcement, (ii) porosity and (iii) inhomogeneous distributions or clustering of CNTs [5][11][18]. The addition of carbon nanotubes is predicted to enhance the thermal conductivity of metal because the thermal conductivity value of CNTs was reported as much as 3000 W/m.K along the tube axis at a room temperature [10].
Figure 3 (a) shows the schematic diagram of the expected formation of copper particles with the carbon nanotubes. The flash energy flows through the Cu particles and across the CNTs particles which help to transport the heat along the nanotubes in the matrix thus, the thermal conductivity could be significantly enhanced \([11]\). However, from the results obtained, the presence of an interfacial thermal resistance between the carbon nanotubes and the copper matrix is believed to be the one of the reasons in causing the value of the thermal conductivity to be much lower than expected. A study done by Chu et al. and Nan et al., recorded the findings that, this interfacial thermal resistance or also known as interface barrier layer (RK) acts as a barrier layer to the heat flow and thus decreases the performance of Cu/CNTs matrix \([11][18]\). The interfacial thermal resistance value across the interface of Cu/CNTs has been done by Chu et al. using an analytical model \([11]\). This interfacial thermal resistance value was initially recommended by Nan et al. in which this model predicts that a significant degradation in the thermal conductivity enhancement is due to a large interface thermal resistance across the nanotube-matrix interface \([18]\). They found that by assuming RK = 0, the absence of interfacial thermal resistance in Cu/CNTs composites lead to a large enhancement in thermal conductivity. Therefore, it is deduced that even a small interface thermal resistance could greatly limit the heat transport in Cu/CNTs composites and resulted in a low value of overall conductivity. Figure 3 (b) illustrates the formation of interfacial thermal resistance between the CNTs and Cu matrix. In addition, the degradation in thermal conductivity is related to the low density of Cu/PCNTs composites and Cu/ACNTs composites, corresponding to the high porosity of the samples. Cu/ACNTs composites have a higher porosity attributed to the reduce in the density of CNTs after the treatment process. The effect of porosity on the thermal conductivity of copper processed by powder metallurgy has been studied by Vincent et al. which stated that porosities are inherently introduced and affect the thermal conductivity of the composite’s material, among other factors including interfaces and reinforcement distribution \([19]\). Another study by Noorsyakirah et al., stated that the existence of open pore in sintered sample would increase the heat dissipation because of the open network of the interconnected open pores \([20]\). However, the existence of closed pore decreases the thermal conductivity of the sample. It is attributed to the heat trap inside the pores \([20]\). Figure 3 (c) depicts the schematic diagram of the proposed mechanism for pore formation and inhomogeneous of CNTs which affect the flash energy flow in Cu/CNTs composites. When powders are sintered, it would be expected that the particles are not completely perfect for diffusing. It would ideally affect the heat flow through the specimen. Pores among the copper particles and bundles of CNTs can affects the thermal conductivity. When the phonon travels along the nanotubes and if the phonon encounters the twists or kinked nanotubes, it would be blocked at these sites. The heat or the flash energy then will flow to the nearest particles to avoid the pores. Thus, the heat loss will reduce the thermal conductivity \([10]\). It is known that most of the CNTs are naturally twisted and kinked.
4. Conclusions
Referring to the theoretical study, the addition of CNTs in composites should increase the value of thermal conductivity. However, the value of thermal conductivity of Cu/PCNTs composites significantly decreased from the pure Cu (374.1 W/m.K). Cu/ACNTs composites showed a similar observation, where the addition of CNTs reduced the properties of thermal conductivity. The decrease in thermal conductivity with the addition of CNTs may be related to the following factors: the interface of thermal resistance between the metal matrix/CNTs reinforcement, porosity and clustering or inhomogeneous distribution of CNTs.

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