



## EFFECTS OF SINTERING PARAMETERS ON THE MICROSTRUCTURAL CHARACTERISTICS OF CU/CNTS NANOCOMPOSITES

Ali Samer Muhsan<sup>1</sup>, Norani M. Mohamed<sup>2</sup>, Faiz Ahmad<sup>3</sup>, Thar M. Badri Albarody<sup>3</sup> and Muhammad U. Shahid<sup>2</sup>

<sup>1</sup>Petroleum Engineering Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia

<sup>2</sup>Fundamentals and Applied Sciences Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia

<sup>3</sup>Mechanical Engineering Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia

E-Mail: [ali.samer@petronas.com.my](mailto:ali.samer@petronas.com.my)

### ABSTRACT

Higher-powered electronics are being integrated into daily used devices rapidly. With these electronics, the need to remove the excessive heat generated from those devices efficiently and more economically became essential. In response to these critical needs, a unique nanocomposite material made of copper reinforced by carbon nanotubes was developed via powder injection molding technique (PIM). This work aims to study the effect of different PIM sintering parameters on the microstructural characteristics of carbon nanotubes reinforced copper nanocomposites (Cu/CNTs). The effect of these parameters has a significant effect on the mechanical and thermal properties of the produced composites. For instance, the influences of varying the sintering dwell time on the densification process showed that short sintering dwell times (90 and 120 min at 1050 °C) were insufficient for achieving complete sintered samples. Meanwhile, attempts were applied to increase the diffusion rate between the Cu particles and CNTs by increasing the sintering dwell time up to 180 min at 1050 °C. The results showed a clear enhancement on the densification process but led to a decomposition of the CNTs into amorphous carbon. The optimal sintering temperature for achieving fully dense nanocomposite was optimized to be 1050 °C. Fully dense nanocomposite can provide large phonon mean free path inside the microstructure resulting high thermally conductive material.

**Keywords:** metal composites, nanotubes, thermal conductivity, copper.

### INTRODUCTION

Miniaturization in the field of electronics packaging, along with faster circuits dissipating higher power has resulted in an increase in the heat flux for microelectronic devices. One of the major problems has always been to eliminate the heat generated by the device such that the thermal requirements for optimal performance are satisfied. Most semiconductor devices are fabricated on silicon wafers. Electrical performance is degraded when the junction temperature rises above 150 °C, lowering device gain, clock speeds and efficiency. Further, a 10 °C rise in the junction temperature will generally shorten operating life by a factor of 2:1 [1]. Therefore, the next generation of high performance electronic devices requires exceptional packaging materials with low cost, complex shape, with high mass production, and special thermal properties such as high thermal conductivity and low coefficient of thermal expansion.

The most attractive material for such applications is copper. Copper is a ductile metal having relatively low mechanical strength but good corrosion resistance, attractive colour, and high electrical and thermal conductivity. The thermal conductivity of pure copper is 395 W/m.K [2], which is approximately twice that of pure aluminium. The low hardness of copper can partly describe its high thermal conductivity. This is because the resistivity to electron transport in metal typically originates from scattering of electrons on thermal vibrations of the atomic lattice, which are relatively weak for soft metals such silver and copper. In the last decade, a passive heat sink made of Cu alloy with a cooling fan was sufficient to remove heat efficiently from many electronic

devices. However, these conventional Cu heat sinks couldn't meet the demands of the next generation of microelectronic chips. Therefore, the need of high performance heat sink composite material became an essential issue in thermal management design of electronic devices

However, due to their exceptional physical and mechanical properties, carbon nanotubes (CNT) caught the attention of enormous number of researchers and companies and led them to work on development of CNT based metal nanocomposites [2]. However, utilizing these unusual properties of CNT in metal matrix composite (MMC) for macroscopic applications is still a big challenge for science and technology. Only few successful attempts have been reported for commercial applications due to the difficulties incorporating CNTs in metals with up scalable processes [3-6]. By far the most important challenge is how to obtain a uniform dispersion of CNT in MMCs. CNT have a large specific surface area that can reach up to 200 m<sup>2</sup>/g, with the association of Van der Waals forces, CNT tend to agglomerate and form clusters [7]. CNT clusters have low strength, high porosity and so they behave as discontinuities. Thus, clusters increase the porosity of the fabricated composites and degrade the desired properties. In addition, clustering and non-uniform dispersion of CNT will lead to inhomogeneous property distribution in the structural component because the properties like coefficient of thermal expansion, thermal conductivity, strength and elastic modulus depend strongly on the volume fraction of CNT [8, 9]. The second important challenge is to ensure the structural and chemical stability of the CNT in the MMCs. Owing to the high temperatures and stresses involved in MMCs



processing, CNT may be damaged or lost due to reaction. In response to this challenge, our research group has managed to develop a composite material of CNT reinforced Cu matrix nanocomposites via modified powder injection molding technique (PIM). PIM is a near net-shape engineering technology that combines the shaping efficiency of plastic injection molding with the capability of powder metallurgy for processing metal powders resulting a complex shape with low cost and high volume production as well as homogeneous CNT dispersion in Cu matrix [10, 11]. The most attractive features of using PIM process is that this technique has the ability to fabricate metal matrix composites contain ingredient materials that are not compatible at molten state and difficult to be fabricated via conventional techniques, such as CNT-Cu nanocomposites. However, the main objective of this work is to study the effect of different PIM sintering parameters on the thermal properties and microstructural characteristics of carbon nanotubes reinforced copper nanocomposites (Cu/CNTs).

## EXPERIMENTAL METHODS

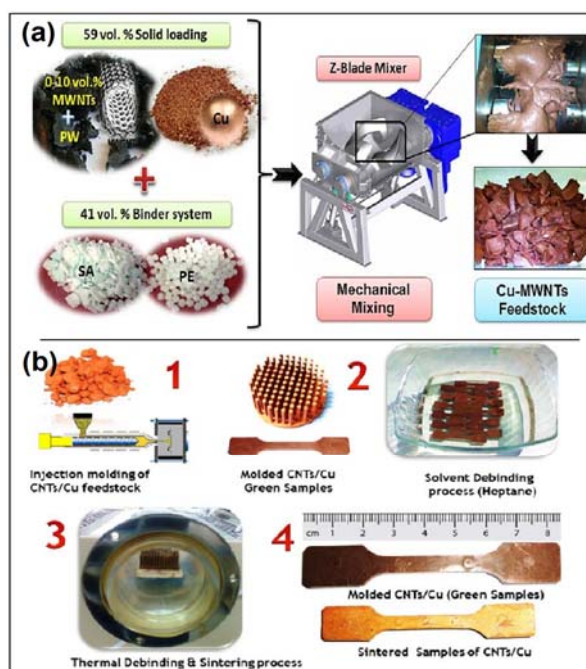
### Materials

Commercial Cu powder particles with diameter ranging of 15–20  $\mu\text{m}$  were purchased from Sandvik Osprey LTD., UK. Purified multiwalled carbon nanotubes with diameter of 60–80 nm and 5–15  $\mu\text{m}$  in length were purchased from Shenzhen Nano-Technologies Port Co., Ltd., China. The purity of CNTs was 95–98% with ash content of  $\leq 0.2$  wt. %.

### Powder injection molding process

In this stage samples were prepared using modified powder injection molding technique (PIM). This technique involves four main stages: feedstock preparation; injection molding of the prepared feedstock; binder removal or debinding process (solvent and thermal debinding) to get a shaped porous metallic part; and sintering process in which the debinded samples are heated below the melting point of the material to allow atoms of the powder particles to diffuse, thus shrinking the material in size as shown in Figure-1. To produce homogenous feedstock of Cu/CNTs nanocomposite, a combination of nanoscale dispersion of functionalized CNTs in Paraffin Wax (PM) solution diluted with Heptane followed by sonication and magnetic stirring agitation techniques was adopted. CNTs were functionalized using concentrated acids ( $\text{H}_2\text{SO}_4/\text{HNO}_3$ ) with the assist of heating and sonication process. Information about the degree functionalization processes, evidences on the existence of the functional groups ( $-\text{COOH}$ ), effects of sonication time on the treated CNTs, and microstructural analysis of the fabricated Cu/CNTs nanocomposites were determined using TEM, EDX, FESEM and Raman spectroscopy analysis. Each 1 gram of functionalized CNTs was mixed with 250 mL of PW/ Heptane solution (1:4) and agitated for 60 min using magnetic stirrer machine. After achieving homogenous mixture of CNTs/diluted PW, drying process at 80  $^\circ\text{C}$  for

12 h was performed. The dried CNTs/PW mixture was then mixed with the other components of the MIM binder system (Polyethylene and Stearic Acid) in twin screw mixer at 160 $^\circ\text{C}$ . This step provided a high viscous liquid media with high shear forces that allowed CNTs to be mixed properly by dispersing the CNTs clusters with uniform dispersion into the molten binder system. The copper powder was added gradually during mixing process to form Cu-CNTs-Binder feedstock prior to MIM process. The prepared feedstock was then plasticized in a heated barrel of injection molding machine, and a controlled volume of the molten feedstock was injected from the plasticator into a closed mould. The injection moulded samples were then solvent and thermally debinded to insure complete removal of the binder from the green samples. After the binder being totally removed, sintering process under argon atmosphere with different sintering temperature and dwell time of 950, 1000 and 1050 $^\circ\text{C}$  and 90, 120 and 150 min, respectively, was performed.



**Figure-1.** PIM Method of Cu/CNT Nanocomposites (a) Feedstock preparation; (b) Injection molding, debinding and sintering process

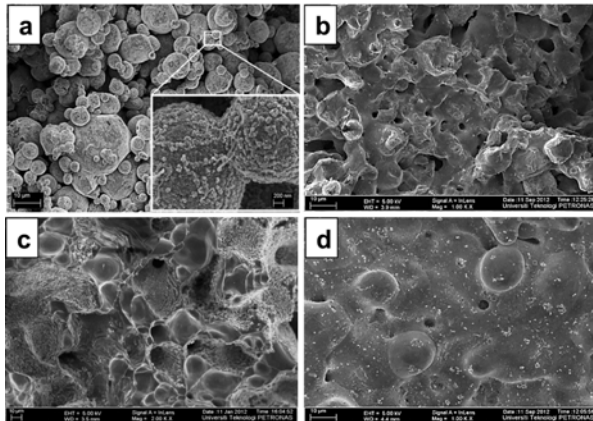
## RESULTS AND DISCUSSION

### Effects of Sintering Temperatures on Cu/CNTs Microstructure

The effects of sintering temperature variations on the densification process microstructure changes of the Cu/CNTs nanocomposites sintered at fixed sintering dwell time are shown in Figure-2. In this figure, FESEM micrographs of Cu/10 vol.% CNTs nanocomposites sintered at different sintering temperatures (900, 950, 1000 and 1050  $^\circ\text{C}$ ) for 2.5 hr. under argon atmosphere are



presented. It can be clearly seen that at low sintering temperature (900 and 950 °C), sintered composites exhibit the same feature of poor interfacial bonding with leaving the obvious pores in the microstructure as shown in Figure-2.a and b. This is probably due the fact that sintering densification usually occurs close to the melting temperature where the bonds between particles grow by the motion of individual atoms. Meanwhile, with increasing the sintering temperature to 1000 °C, the pores of the sintered nanocomposites showed significant decrease in amount and size as shown in Figure-2.c. This can be attributed to the fact that at high sintering temperature a greater diffusion of atoms and molecules between the contact points of particles will be occurred, which substantially reduces the amount of pores. As the sintering temperature (1050 °C) reached close to the melting point, the sintering process became faster because of the increased number of moving atoms resulted in the atoms settling at the bond between particles which helps annihilate surface area and surface energy. According to that, Figure-2.d showed near-fully dense microstructure with excellent distribution of CNTs inside the Cu matrix



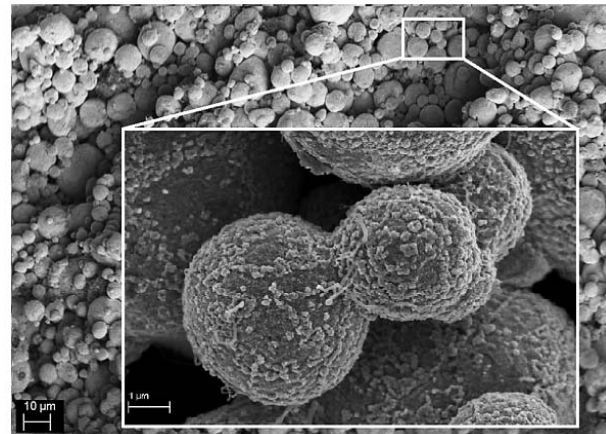
**Figure-2.** FESEM micrographs of Cu/10 vol.% CNTs fractured surface sintered for 2.5 hr. under Argon atmosphere at: (a) 900 °C; (b) 950 °C; (c) 1000 °C and (d) 1050 °C.

#### Effects of sintering dwell time on the Cu/CNTs microstructure

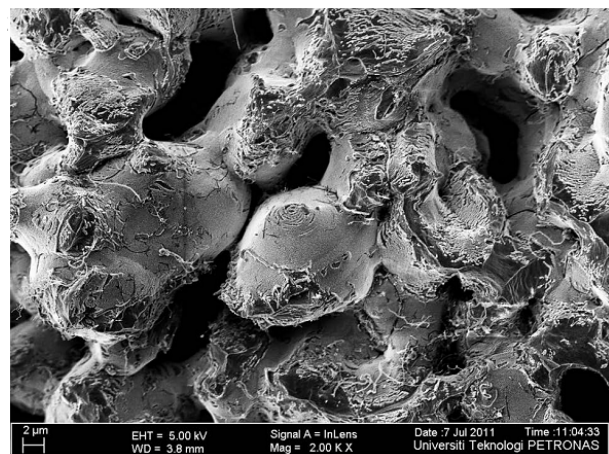
In this section, the test samples sintered at 1050 °C for various sintering dwell times and different CNT's contents of 1, 10 and 25 vol.% as critical volume fractions were studied and analyzed using FESEM observation. Figures-3, 4 and 5 present the FESEM micrographs of Cu/1 vol.% CNTs nanocomposite showing the influence of varying the sintering dwell time from 90, 120 to 150 minutes on the stability of CNTs in Cu matrix, densification and the composites microstructure. In Figure-3, CNTs showed high stability with no physical damages on their structure and CNTs were homogeneously distributed inside the Cu matrix. However, at this sintering dwell time, densification process stopped at the initial stage of sintering cycle. This

behaviour was most probably due to insufficient dwell time where Cu particles were partially diffused forming small necking spots between the adjacent particles. Figure-4 and 5 shows considerable changes on the microstructure with differences occurred in term of the porosity and densification when the sintering dwell time increased from 90 to 120 and 150 min, respectively. The pores were irregular in shape, opened, contacted to the neighbour pores and distributed across the grain boundaries as well as within the Cu matrix.

An attempt was made to enhance the diffusion process between composite phases by increasing the sintering dwell time up to 3 hr. at 1050 °C. Figures-6 and 7 show the FESEM microstructures of Cu/15 vol.% CNTs and Cu/25 vol.% CNTs, respectively, along with their EDX analysis. The results however showed that the Cu particles were diffused with each other with some pores located at the grain boundaries and sintered Cu particles.

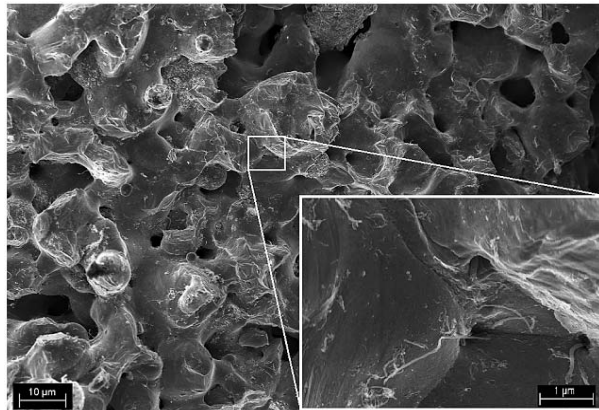


**Figure-3.** FESEM micrographs of Cu/1 vol. % CNTs sintered at 1050 °C for 90 min under Argon atmosphere.



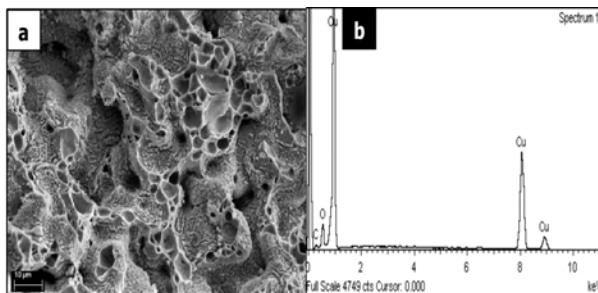
**Figure-4.** FESEM micrograph of Cu/1 vol. % CNTs sintered at 1050 °C for 120 min under Argon atmosphere.



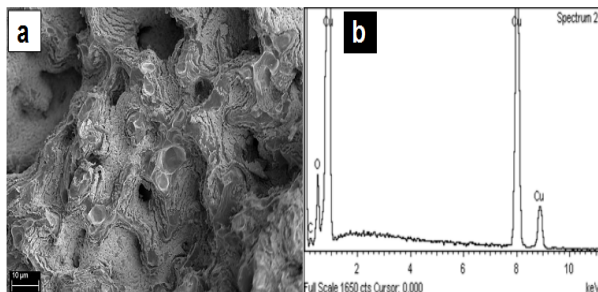


**Figure-5.** FESEM micrographs of Cu/1 vol. % CNTs sintered at 1050 °C for 150 min under Argon atmosphere.

These pores were mostly generated from the grain growth and incomplete diffusion process. Though EDX analysis has detected the carbon element, no visible CNTs were seen in the high magnification microstructures as shown in Figures-6 and 7. This indicates that CNTs have been degraded into amorphous carbon at that sintering dwell time.



**Figure-6.** Fracture surface of Cu/15 vol. % CNTs: (a) FESEM image showing some pores located at the grain boundaries and sintered Cu particles; (b) EDX analysis detecting some amorphous carbon.



**Figure-7.** Fracture surface of Cu/25 vol. % CNTs: (a) FESEM image showing some pores located at the grain boundaries and sintered Cu particles; (b) EDX analysis also detecting some amorphous carbon

## CONCLUSIONS

In summary, this work demonstrated the effects of using different sintering temperature and sintering

dwell time on the microstructures of the fabricated nanocomposites. It was found that sintering temperature has a significant effect on the nanocomposites microstructure where at low sintering temperature of 900 °C and 950 °C Cu particles were barely diffused in small contact spots due the insufficient kinetic energy required for densification process. In the case of 1050 °C, Cu/CNTs nanocomposites showed near-fully dense microstructures with obvious elimination of the formed pores. That was due to the increased number of moving atoms resulted in the atoms settling at the bond between particles which helps annihilate surface area and surface energy. Thus, 1050 °C was selected as the optimal sintering temperature for achieving full dense nanocomposite which provided large phonon mean free path inside the microstructure resulting high thermal conductivity material. Meanwhile, the influences of varying the sintering dwell time on the densification process showed that short sintering dwell times (90 and 120 min) were insufficient for achieving complete sintered samples. Therefore, in order to achieve stable reinforcement phase of CNTs, penetrated CNTs inside the Cu matrix with near-fully dense nanocomposite and low number of pores; dwell time of 150 min (2.5 hr.) was selected as the optimal sintering dwell time for attaining these desired properties. Furthermore, at high volume contents of CNTs (15 and 25 vol.%), increasing the sintering dwell up to 150 min showed no considerable effect on the densification process and by increasing the sintering dwell time up to 180 min at 1050 °C. The results however showed a clear enhancement on the densification process but led to a decomposition of the CNTs into amorphous carbon.

## ACKNOWLEDGEMENTS

The authors would like to thank “Universiti Teknologi Petronas” for providing funds and laboratory facilities to support this project.

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