Journal of Engineering Science and Technology
Vol. 5, No. 3 (2010) 272 - 283

MICROSTRUCTURAL STUDIES OF SINTERED CARBON NANOTUBES REINFORCED COPPER MATRIX COMPOSITE

GEHAD GOUDAH*, FAIZ AHMAD, O. MAMAT

Mechanical Engineering Department, Universiti Teknologi PETRONAS, Malaysia
*Corresponding Author: jehad_jouda@hotmail.com

Abstract

This research is about developing carbon nanotubes reinforced copper matrix composite by using the powder metallurgy process. The test samples were mixed with different 1-2% volume of carbon nanotube and compacted at 80 kN. The green and sintered density of the samples was recorded. The samples sintered at 900°C in Argon gas for different times. Sintered samples were examined for micro structure in optical microscope and scanning electron microscope. The results of the sintered and theoretical densities showed 98% of the theoretical density.

Keywords: Powder metallurgy, Microstructure, Carbon nanotubes, Copper, Density, SEM, Compaction, Sintering.

1. Introduction

Composite materials are combination of different constituent materials which can lead to the desired combination of low weight, stiffness and strength. At present, knowledge has advanced to a level that materials can be modified to exhibit certain required properties [1]. At the same time, the fact that these materials are composed of different constituents makes their mechanical behavior complex. Moreover, density and homogeneity of composites are very important factors in engineering applications because in homogeneity and residual pores are harmful to mechanical and physical properties [2, 3].

Great interest has recently been developed in the area of nanostructures carbon materials and it is becoming of considerable commercial importance. Besides, with much interest growing rapidly over the decade, the discovery of carbon nanotubes (CNTs) [4, 5] at the beginning of the last decade has been the focus of

Abbreviations

CNT	Carbon nanotube
PM	Powder metallurgy
SEM	Scanning electron microscope
XRD	X-Ray diffraction

the growing attention of scientific communities, due to their vast interesting properties as well as their large potential for practical applications.

Consequently, based on their unique size and structural diversities, CNTs have attractive properties with their tensile strength to be at least 10 times higher, and their weight is less than half that of conventional carbon fibers. The Young's modulus of a single-wall nanotube was theoretically estimated between 1.8 and 5 TPa [6, 7]. However, because of their exceptional conductive properties of carbon nanotubes, reinforced copper composites have attracted electronic industry for their heat sink requirement [8]. In addition, in developing a suitable formulation of carbon nanotubes, reinforced copper may provide a solution for thermal management of electronic industry. So, reinforcing carbon nanotubes in copper is a challenging task [9, 10].

Powder metallurgy (PM) is an established technique for developing state of component [11]. The process of PM starts with homogenous mixing of reinforcement with powder matrix. The mixing is followed by compaction and compacted samples which are sintered in selected environments for densification of components. However, when using the conventional PM route, the interfacial bonding of matrix alloy and reinforcements proves to be weak due to their mutual insolubility and/or non-wetability [12], which results in low density, high porosity content, and segregation of reinforcements. Several alternative processing techniques have been researched to develop composites through hot isostatic pressing and liquid phase sintering. Despite these techniques could overcome the problem of low density, they failed to solve the problem of inhomogeneity [9, 10, 13].

This research focused on developing the carbon nanotubes with reinforced copper composite via powder metallurgy technique. Besides, included in this study are characterization and compaction, microstructures and dispersion of CNTs and then loading between CNT/Cu.

2. Experiment Materials and Procedures

2.1. Powder and carbon nanotubes

A 99% pure spherical shape copper powder produced by gas atomization and carbon nanotubes with length and diameter of 5~20 μm and 1~1.2 nm grown by vapor deposition were used in this study. The properties of the copper powder and carbon nanotubes are given in Table 1.

2.2. Pre-Blending

The test samples from copper powder (as a matrix) and carbon nanotubes (as a reinforcement) are prepared accordingly by weighting them accurately and

blended in a shear type mixer for 60 minutes to ensure a uniform dispersion of carbon nanotubes in copper powder. Volume fractions of 1% to 2% of carbon nanotubes were used. Table 2 shows the sample formulation used in this study with note that all the values in volume fraction percentage.

Table 1. Physical and Thermal Properties of the Research Materials.

Property	Materials	
	Copper	Carbon nanotubes (CNTs)
Thermal Conductivity	401 W/m°K	1100~ 3000 W/m/°K
Coefficient of thermal expansion	17×10^{-6} /°C (20-100°C)	Negligible (theoretically)
Density	8.96 g/cm^3	SWNT = 1.33-1.40 g/cm^3[7]

Table 2. Sample Formulation in Vol. %.

Sample	1	2	3
Cu	100	99	98
CNT	0	1	2

2.3. Compaction of mixture

The mixture of copper powder and carbon nanotubes was compacted in a circular-die to produce a disc shape of solid green sample at room temperature. The dimension of the test sample was 13 mm in diameter and 3 mm in thickness as shown in Fig. 1. Auto pellet press machine made by VARVER, USA, with a compaction force of 80 kN was used to compact the test samples. Figure 2 shows the auto pallet machine which is used for compaction process. A series of test samples were compacted. The dimensions of the samples were recorded for the purpose to measure shrinkage in the sintered samples.

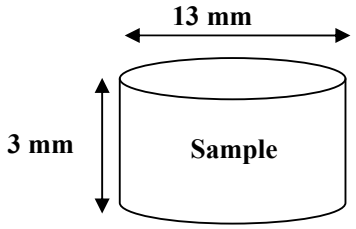


Fig. 1. Test Sample Dimensions.

2.4. Sintering

Sintering is a process in which compacted samples or known as 'green samples' are fired and consolidated into strong solid. The sintering process was done in a tube furnace for densification of powder particle and held at 80 to 85% of the melting temperature of the matrix material (900°C). This process takes 90

minutes to heat up from room temperature to 900°C with heating rate of 5°C/min and hold at constant 900°C temperature for sintering time varied between 45-90 minutes. All the samples were sintered in the argon gas to avoid the surface contamination and controlled by flow rate of 1100cm^3.

Fig. 2. Compaction Press Used in the Research.

3. Characterization Techniques

The definition selected for the ASM-International Materials Characterization Handbook is as follows: "Characterization describes those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material." This definition limits the characterization methods included in the handbook to those that provide information about composition, structure, and defects and excludes those methods that yield information primarily related to materials properties, such as thermal, electrical, and mechanical properties [14].

3.1. Particle size distribution

Particle size distribution of copper powder was measured using a particle size analyzer model Mastersizer-2000 from UK. The mean particle size was found to be 100 μm. Particle shape was determined using scanning electron microscope model 1430 from Germany.

3.2. X-Ray diffraction

X-Ray diffraction (XRD) analysis was done to verify the purity of the copper powder. In this process, powder was placed into XRD chamber and the chamber was evacuated. The spectrum produced by the copper powder was matched with standard copper sample.

3.3. Density measurement

Green density of composite compacts were measured and compared with sintered density of the compacts. A water immersion technique was used for this purpose.

3.4. Scanning electron microscopy

Sintered test samples were imbedded in the resin and polished for microscopic studies. The samples were ground using a grinding paper grit 1200 that was followed by polishing using 1μm alumina paste. The polished sample was etched using an etchant to reveal the microstructure and examine under scanning electron microscope (SEM).

4. Results and Discussion

4.1. Particle shape and particle size distribution

A scanning electron micrograph of copper powder is shown in Fig. 3. Micrograph shows shape of powder particles that ranges from 40 μm to 150 μm. Particle size distribution of copper powder is shown in Fig. 4.

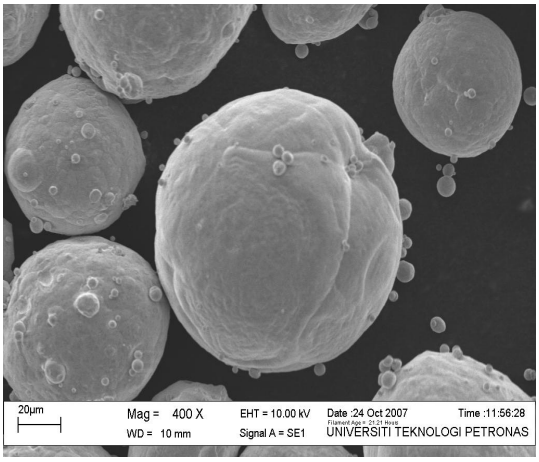


Fig. 3. Particle Shape of Copper Powder.

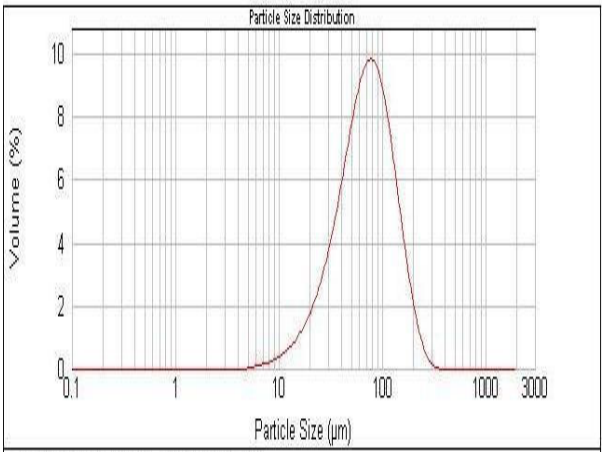


Fig. 4. Particle Size Distribution of Copper Powder.

X-Ray Diffraction

The XRD result showed that no existence of the oxidation layer on the surface of the powder particles. As shown in Fig. 5, the red wave line is the spectrum of copper powder sample while the black wave line is pure copper which is in the database. The sample indicates that there is no oxide layer since the match is perfect.

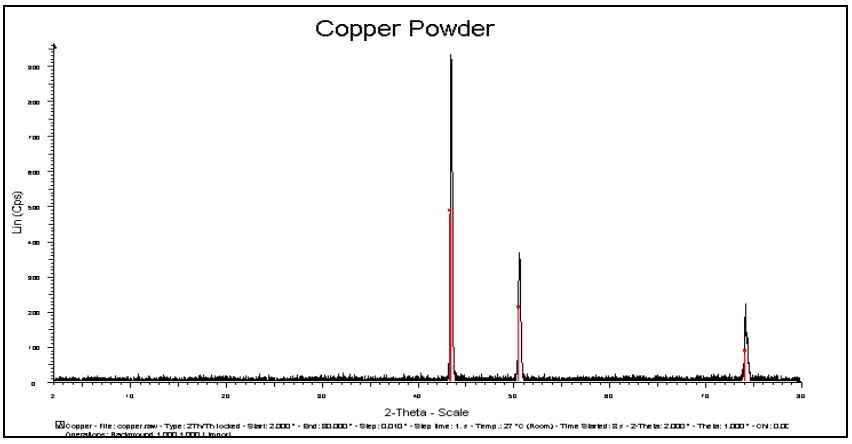


Fig. 5. XRD of Copper Powder Shows no Oxides on Copper Surface.

4.2. Physical characterization

Density

The green density and sintered density of the sample with CNTs and without CNTs was measured and compared. The green density of copper compact and composite compacts was 8.71 and 8.63 g/cm^3 for 1% and 2% carbon nanotubes respectively. This indicated the presence of porosity in the green compact. The sintered density of the copper and composites was also measured and found to be 8.76 and 8.67 g/cm^3 for 1% and 2% carbon nanotubes respectively. Pictures of green and sintered test samples are shown in Figs. 6(a) and (b) respectively and Table 3 shows the density variations of the samples.

(a) Green Copper Compact. **(b) Sintered copper Compact**

Fig. 6. Green and Sintered Test Samples at 900°C.

Table 3. Density Variation of the Samples.

Vol.% of CNT	Theoretical Density (g/cm^3)	Green Density (g/cm^3)	Sintered Density (g/cm^3)		
			45 min	60 min	90 min
Pure Cu	8.940	8.906	8.899	8.911	8.911
1	8.863	8.714	8.746	8.706	8.763
2	8.785	8.629	8.658	8.610	8.640

The comparison between the green and sintered densities is represented in Fig. 7. Results showed that there are slight different of the density between the theoretical and the sintered products because of some reasons:

- Theoretical density is base on the exact density of copper and CNT.
- The actual density of copper might be difference due to the production route of the copper. Manufacturers usually come with their own material data sheet. Same goes the properties of copper powder.

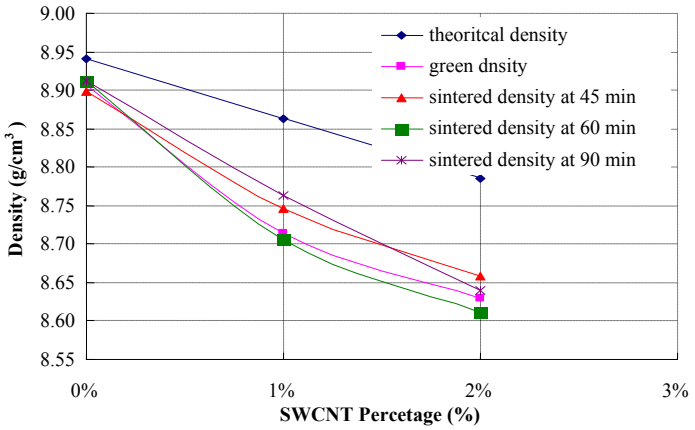


Fig. 7. Comparison between the Green and Sintered Densities.

4.3. Dimensional changes

The dimensions of the green and sintered samples were measured, recorded and compared to analyze the sample size and volume before and after sintering process. Percentage changes in diameter of the sintered samples were noted. Percentage expansion in diameter was approximately 1.5%. This indicated that sintering process caused densification and resulted in reduction in porosity of the green compacts However, grain growth resulted in increased dimensions, in accordance [8, 9]. The results of percentage changes in dimensions are illustrated in Fig. 8.

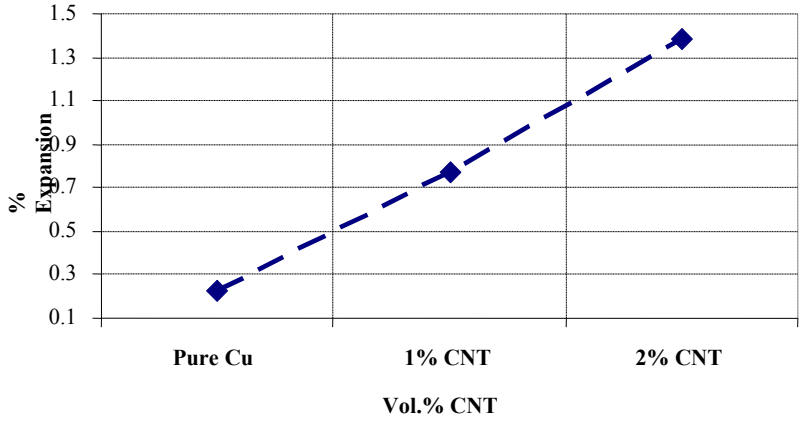
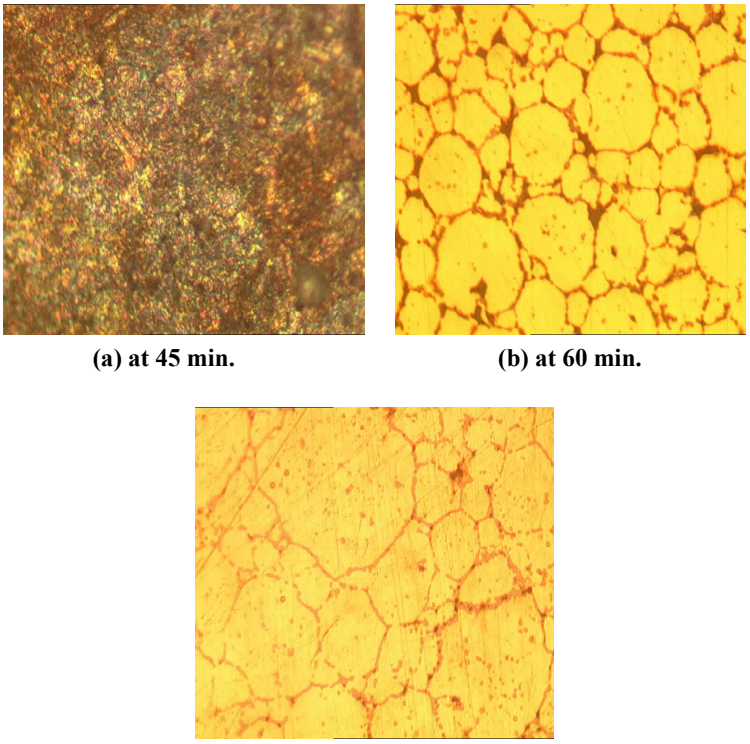


Fig. 8. Variation in Dimensions after Sintering the Green Parts.

4.4. Micro structural characterization

Scanning Electron Microscopy

The green compacts were sintered for 45, 60 and 90 minute at 900°C in argon. The micrographs showed good grains of copper. However porosity is still visible at few locations. An optical micrograph of sintered copper powder is shown in Fig. 9 which shows the diffusion of copper particles as a result of sintering at different times.



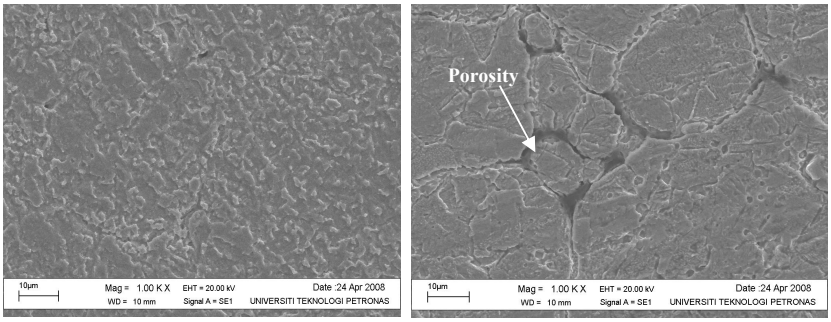
(a) at 45 min. **(b) at 60 min.**

(c) at 90 min.

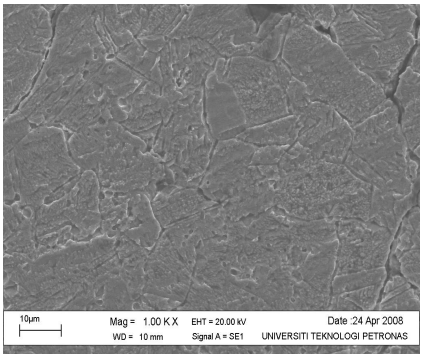
Fig. 9. Optical Micrograph for Sintered Samples.

The SEM micrograph of sintered copper powder is shown in Fig. 10, which shows clearly the particle diffusion bonding between copper-copper particles as result of sintering with controlled atmosphere. Controlled atmosphere refer to the sintering environment which was done in the argon gas continuous flow. Sintered copper and sintered copper composites imbedded in a resin during cold mounting processes and polished with 1μm of diamond paste. The scanning electron micrograph (SEM) images below show the surface of the sample and inner surface of polished and etched samples. There is a defect that occurs on the surface which contributes to void contents. The hole represents the void that

happened during compaction process, where the copper powders are not perfectly compact.



(a) at 45 min. **(b) at 60 min.**



(c) at 90 min.

Fig. 10. SEM of Sintered Samples.

Examination of dispersion of Carbon Nanotubes in Composites

Micrograph taken from FESEM shows that CNTs were uniformly dispersed in the copper matrix and no agglomeration of CNTs was noted during this observation, Fig. 11(a). The micrograph in Fig. 11(b) shows that CNTs are bonded with the copper matrix.

5. Conclusion

Carbon nanotubes reinforced copper matrix composites had been successfully developed through powder metallurgy and characterized their microstructure properties. With about 17 ton load, sufficient enough to produce near full density copper-fiber composite. Sintering temperature at 900^{o}C in the argon gas atmosphere is sufficient to produce good sintered product at the 90 minutes sintered time. The powder particle diffusion bonding can be seen clearly in SEM

images and also the carbon nanotubes imbedded in the powder particle bonding. There is a slight change of density between theoretical and sintered density, about 1% decrement due to some reason mentioned before. Furthermore, the reinforcement of the carbon nanotubes proves to enhance the properties of the copper composite such as density and thermal conductivity.

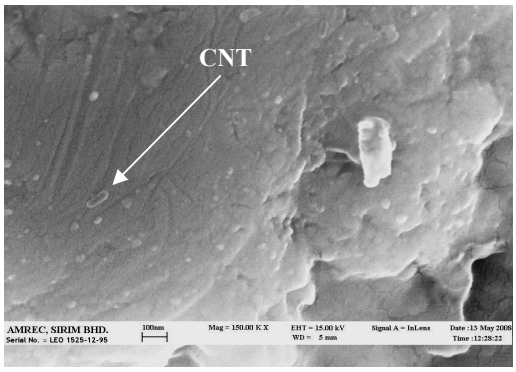


Fig. 11(a). Dispersion of CNTs in Copper Matrix.

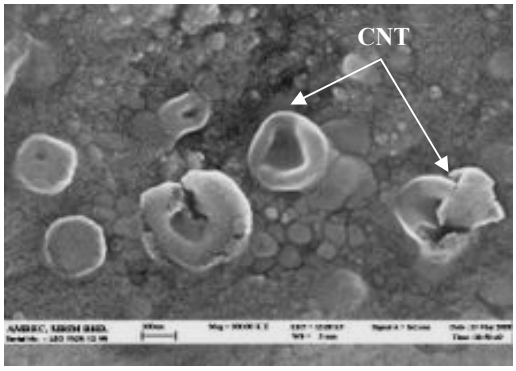


Fig. 11(b). Bonding of CNTs and Copper Matrix.

Acknowledgement

Authors are thankful to University Technology PETRONAS for providing fund for this research.

References

1. Borst, R.D.; and Sadowski, T. (2008). *Lecture notes on composite materials*: *Current topics and achievements*. Springer Science + Business Media B.V.
2. Mazumdar, S.K. (2002). *Composites manufacturing*: *Materials, product, and process Engineering*. CRC Press LLC.

3. Chawla, N.; and Chawla, K.K. (2006). *Metal matrix composites*. Springer Science+Business Media, Inc.
4. Dresselhaus, M.S.; Dresselhaus, G.; and Avouris, Ph. (2001). *Carbon nanotubes: synthesis, structure, properties, and applications.* Springer-Verlag Berlin HeidleberG.
5. Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354, 56-58.
6. Daoush, W.M. (2007). Processing and characterizations of CNT/Cu sintered materials. *The International Conference in Advanced Materials Science and Nanotechnology*, December 3-5, NRC, Cairo, Egypt.
7. Coleman, J.N.; Khan, U.; Blau, W.J.; and Gun'ko, Y.K. (2006). Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon*, 44(9), 1624-1652.
8. Neubauer, E.; Angerer, P.; and Korb, G. (2005). Heat sink materials with tailored properties for thermal management. Electronics technology. In Meeting *the challenges of Electronics Technology Progress*, 272-277.
9. Daoush, W.M. (2008). Processing and characterization of CNT/Cu nanocomposites by powder technology. *Powder Metallurgy and Metal Ceramics*, 47(9-10), 531-537.
10. Kim, K.T.; Cha, S.I.; Hong, S.H.; and Hong, S.H. (2006). Microstructures and tensile behavior of carbon nanotubes reinforced Cu matrix nanocomposites. *Materials Science and Engineering A*, 430, 27–33.
11. ASM Handbook, Volume 7 (1998). *Powder metal technologies and applications.* 7, Ohio: ASM International Handbook Committee.
12. Daoush, W.M.; Lim, B.K.; Mo, C.B.; Nam, D.H.; and Hong, S.H. (2009). Electrical and mechanical properties of carbon nanotube reinforced copper nanocomposites fabricated by electroless deposition process. *Materials Science and Engineering A,* 213–214, 247–253.
13. Li, H.; Misra, A.; Zhu, Y.; Horita, Z.; Koch, C.C.; and Holesinger, T.G. (2009). Processing and characterization of nanostructured Cu-Carbon nanotube composites. *Materials Science and Engineering A,* 523(1-2), 60-64.
14. Metals Handbook, Volume 10 (1986). *Materials Characterization*. ASM Handbook Committee.