EFFECT OF ULTRASONIC-ASSISTED COMPACTION ON DENSITY AND HARDNESS OF Cu-CNT NANOCOMPOSITES SINTERED BY CAPSULE-FREE HOT ISOSTATIC PRESSING

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Abstract

Cu-CNTs composites were prepared with and without ultrasonic-assisted compaction in this work. The samples were sintered by capsule-free hot isostatic pressing at 920°C and 50 MPa Ar gases. The results showed that the higher relative density and Brinell hardness were obtained for ultrasonic assisted compaction samples (at the same CNT content). For both cases, the highest hardness values was achieved at 0.5 wt.% CNT (49.2 HB and 45.8 HB for specimens with and without the ultrasonic-assisted compaction, respectively). The hardness was then decreased as the CNT content increased. The higher hardness values were resulted from higher densification of the sintered samples with ultrasonic-assisted compaction compared to the others.

Keywords: Cu-CNT composites, carbon nanotubes, ultrasonic, compaction, hot isostatic pressing

1 Introduction

Due to the unique properties of carbon nanotubes (CNT) such as high strength, good thermal conductivity and electrical properties, it's considered to be an ideal reinforcement for metal matrix composites [1-3]. An increasing of researches concerning with CNTs reinforced metal matrix composites (CNT-MMC) has been carried out in recent years. There are several techniques to fabricate CNT-MMC including powder metallurgy, electrodeposition, electroplating, melting and spray coating methods [3-9]. In which, powder route is the most popular method being used. The basic steps of the method include mixing CNT with metal powder (Al, Cu, Ni, etc.) via a mechanical alloying, and following by compaction and sintering. Up to date, the challenge is how to induce a uniform dispersion of CNT in metal matrix, especially, for high CNT amount. The strong van der Waal's force of attraction among CNT, the density discrepancy between CNT and metal matrix, the tendency to agglomeration and tangle together of CNT are attributed to the poor dispersion of CNT in the metal matrix. Besides that the weak interface bonding between CNT and metal matrices due to the poor wettability characteristic of CNT with metal matrices also restrict the incorporation of CNT with metal matrix. And so, these cause the reduction in their expected properties of the composites. Several methods have been proposed to improve the homogeneity

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of CNTs such as chemical vapor deposition [7], molecular level mixing [10], electroplating [5] and high energy ball-milling, etc. [2,11]. However, the agglomeration of CNT clusters is still a challenge for uniform distribution of CNT and metal matrix. These CNT clusters will bring to an enhancement of porosity and a reduction of properties of composites. Several methods have been proposed to restrict the effect of these CNT clusters such as hot extrusion [7], hot isostatic pressing [9], spark plasma sintering [10,12] or severe plastic deformation [13,14] and the results have shown the improvement of density and properties of composites.

Recently, ultrasonic have been used to obtain better dispersion of a range of nanomaterials including CNTs [15-17]. Besides that, ultrasonic also emerged as the potential technique in material research and processing [18-20]. Khasanov and Dvilis [20] have showed that the better density and green strength of ZrO_2-Y_2O_3 nanoparticles were obtained by the application of ultrasonic on the compaction step. Considering the promising of ultrasonic, in this research, Cu-CNTs composites were produced by powder metallurgy, in which the technical ultrasonic had been used to assist in the compaction step. The sintering was done by hot isostatic pressing. The density, microstructure and mechanical properties of sintered composite will be discussed.

2 Experimental materials and procedures

Commercial Cu powders (> 99.5 % purity) having average particle size of less than 20 μm was used as matrix material. Commercial carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs –COOH) (95 % purity), supplied by Chengdu Organic Chemicals Co. Ltd., with 1.24 wt.% -COOH content, were used as reinforcement material. According to previous study, the density of multi-walled carbon nanotubes was calculated to be about 1.85 g/cm^3 [9]. The used CNTs were firstly ultrasonic dispersed in absolute ethanol for 3h to obtain an ethanol-CNTs suspension. The ratio of CNTs to absolute ethanol is 0.5g per 50 ml ethanol. Subsequently, the Cu powders were added into the ethanol-CNTs suspension and then stirred and simultaneously heat treated at a temperature of 80^{o}C to evaporate a part of ethanol until obtaining a slurry state of Cu-CNTs-ethanol. The slurries were then ball-milled in a planetary ball milling for 3h at a speed of 300 rpm using stainless steel balls and jar. The ball-to-powder ratio was 10:1 with stainless steel balls of 10 mm in diameter. After drying at 50^{o}C in a vacuum oven, the composite powders were ultrasonic compacted into pellets by pressing in a cylindrical of 7 mm diameter. The scheme of compaction is shown in Fig. 1a. The upper punch of the mold was fixed and connected to an ultrasonic generator (UZG1, Institute of Technical Acoustics, Belarus). When the applied load was reached at the pressure of 500 MPa, the 22 KHz frequency ultrasonic was applied to the upper punch. The applied pressure and ultrasonic were kept for 1 min. The ultrasonically compacted samples were named as UT.Cu (pure Cu), UT.Cu-0.5CNTs, UT.Cu-1.0CNTs and UT.Cu-1.5CNTs respected to 0, 0.5, 1.0 and 1.5 wt.% of CNTs added to Cu matrix. The compacted samples without applied ultrasonic were also prepared for comparison, namely as NU.Cu (pure Cu), NU.Cu-0.5CNTs, NU.Cu-1.0CNTs and NU.Cu-1.5CNTs. Finaly, the pellets were consolidated at 920^{o}C by capsule-free hot isostatic pressing (AIP6-30H, the American Isostatic Press Inc's). The sintering cycle is described in Fig. 1b. The samples were heated to 920^{o}C at heating rate of 10^o/min and consolidated for 120 min in vacuum. The Ar gas was then pumped to the pressure of 50 MPa. The samples were then socked at this temperature and pressure for 30 min and subsequently cooled with the furnace.

The microstructure of powders and sintered samples was observed using a field emission scanning electron microscope (FESEM, Hitachi S-4800). Phase identification of sintered samples was investigated using a X-ray diffractmeter (Advanced Brucker D8) with CuKα radiation. The sintered density of samples was measured based on the Archimedes principles (AND GR 202).

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Brinell hardness (HB) test was carried out on the polished surface under a applied load of 1kg for 10s (AVK-CO, Mitutoyo).

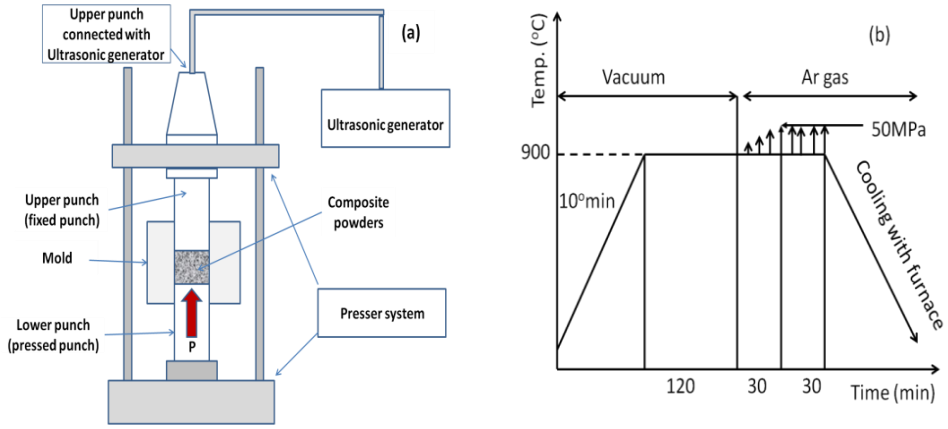

Fig. 1 a) Scheme of pressing with ultrasonic assisted compaction and b) sinter cycle for sample hot isostatic pressing

3 Results and discussion

The FESEM images of raw materials, carbon nanotube (CNT) and Cu powders, have seen in **Fig. 2a** and **b**. The CNT have a tendency to agglomerate and tangle. The outer diameters of MWCNTs were estimated less than 20 nm from the FESEM. Meanwhile, the raw Cu powders have round edges and globular protrusions on the particles' surfaces. **Fig. 2c** and **d** show the fracture surfaces of compacted UT.Cu-0.5CNTs samples indicating the distribution of invidual CNTs and CNTs clusters in the Cu matrix. The trend to agglomerate of CNTs clusters is difficult to avoid during powder process as mentioned before in literature.

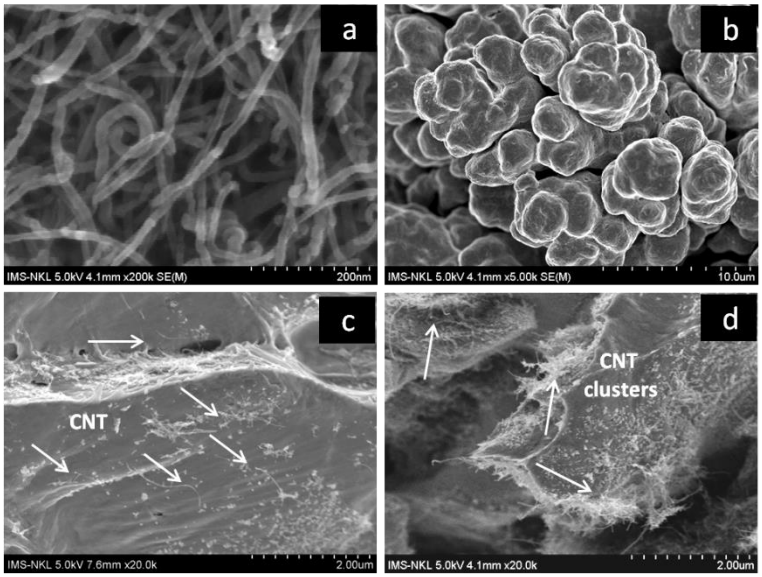

Fig. 2 FESEM images of a) CNTs, b) Cu powders and c), d) fracture surface of UT.Cu-0.5CNTs after compaction

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The effect of sintering and ultrasonic assisted compaction on the phase components of sintered samples has shown in the XRD patterns, **Fig. 3**. The results have indicated that only diffraction peaks of cubic Cu were observed in all the sintered samples with and without ultrasonic-assisted compaction. The main peaks of Cu have been observed correspondingly to (111), (200) and (220) planes. The diffraction peaks of CNTs were not clearly observed in all the sintered samples. This may be due to the low contents of added CNTs. Significant peaks of Cu oxide were not detected indicating that the sintering did not cause the oxidation to the Cu metal matrix.

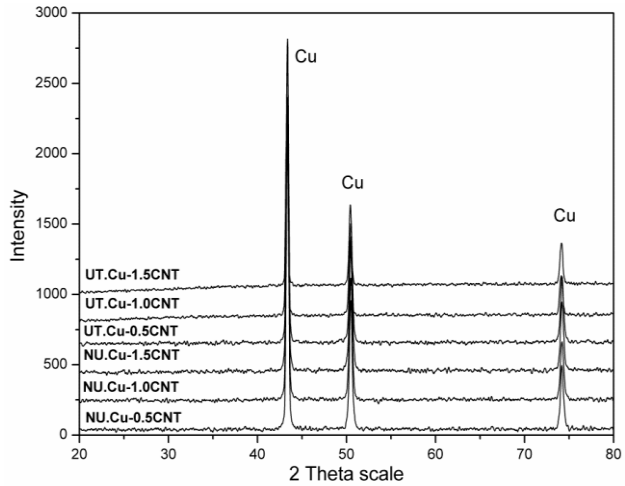

Fig. 3 XRD patterns of HIPed samples with and without ultrasonic-assisted compaction

Fig. 4 shows the FESEM images of sintered samples focused on the CNTs clusters. It is clearly to observe the effect of ultrasonic treatment on the CNTs clusters of sintered composites. The high pore amount can be seen in CNTs clusters of all samples without the ultrasonic-assisted compaction. In the contrast, the CNTs clusters obtained higher densification and better incoherent with Cu matrix. The ultrasonic treatment may bring to a rearrangement of CNTs in their clusters that led to a higher consolidation of the CNTs clusters and consequently, resulted in a better consolidation of sintered Cu-CNTs composites.

The relative density of as-sintered samples is shown in **Fig. 5**. The relative density indicated the consolidated performance of sintering process. The relative density of Cu samples without reinforced CNT obtained higher than 99,5% after sintered by capsule-free hot isostatic pressing at 920^{o}C. This shows that the hot isostatic pressing can be used to generated nearly full density of sintered Cu samples without CNT reinforcement. The relative density was then decreased as the CNT content increased. The more CNT clusters at higher CNT contents led to the more difficult for consolidation of the composites. Previous study has indicated that the existence of CNT clusters acts as barriers to restrict the particle boundary diffusion during sintering and hence limits the densification of the composites [9]. The results had also shown a higher relative density of ultrasonic-assisted compaction samples compared to the sample without ultrasonic-assisted compaction at the same CNT content. This shows a good effect of ultrasonic to the compaction step evidenced in the reduction of pores in the sintered samples as shown in FESEM images, **Fig. 4**.

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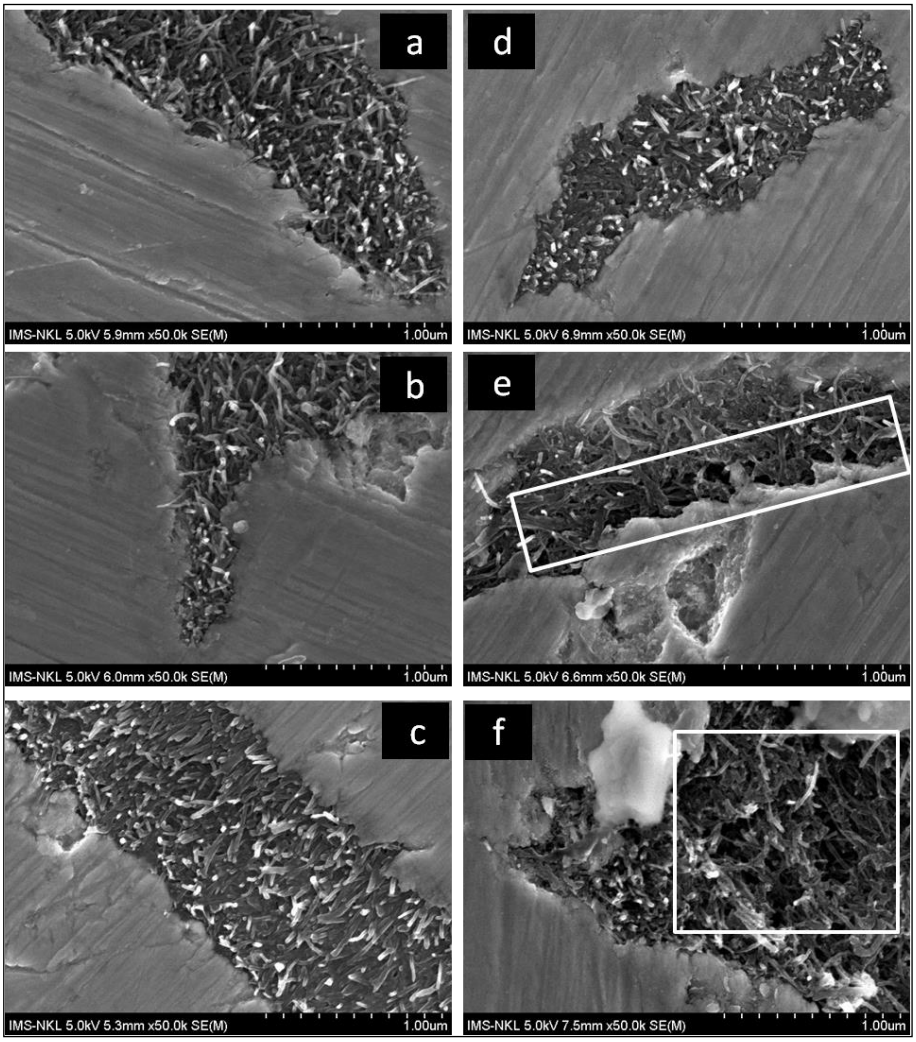

Fig. 4 FESEM images of sintered samples focused on CNTs clusters: a) UT.Cu-0.5CNT, b) UT.Cu-1.0CNT, c) UT.Cu-1.5CNT, d) NU.Cu-0.5CNT, e) NU.Cu-0.5 and f) NU.Cu-1.5CNT

Fig. 6 presents the effect of CNT contents and the ultrasonic assisted compaction on the Brinell hardness sintered samples. The hardness of samples was obtained the highest values at 0.5 wt.% content of CNT in both sample series. However, the hardness had a trend to decrease as the CNTs contents increased from 1 to 1.5 wt.%. This is resulted from the agglomeration of CNTs clusters in the Cu matrix. The weak bonding at the interface of Cu and CNTs clusters due to the poor wettability of CNTs with Cu will restrict the load transfer to CNT and therefore, it leads to a reduction of the reinforced effect of CNTs [2, 3, 9]. The more CNTs clusters were presented, the lower strength of the composite was achieved. The results have also shown a higher hardness of ultrasonic-assisted compaction samples at the same CNTs content. This was attributed to the higher consolidation and the better bonding of CNTs clusters with Cu matrix.

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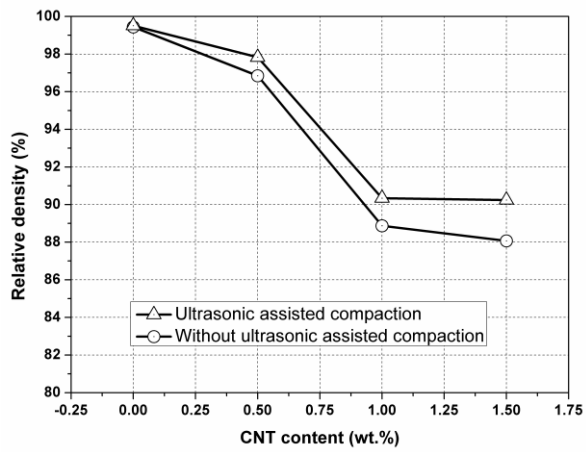

Fig. 5 Measured density of sintered samples

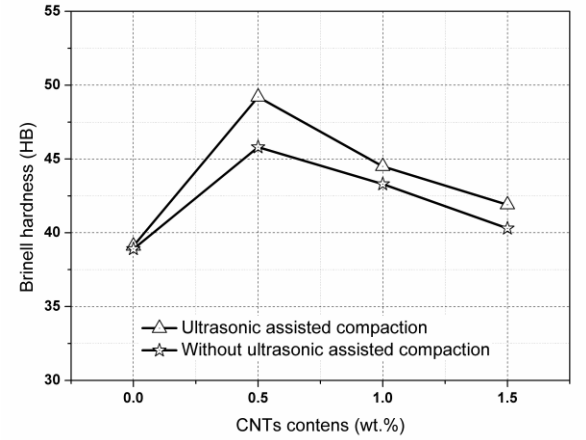

Fig. 6 Brinell hardness of sintered samples

4 Conclusion

The Cu-CNT composites were fabricated with and without using the ultrasonic-assisted compaction in this work. It shows a high potential of ultrasonic application to reduce the effect of CNT clusters on the density and hardness of sintered Cu-CNT composites by the assistance of ultrasonic in compaction step. The higher densification and hardness of sintered composites were obtained in the ultrasonic-assisted compacted samples at the same CNT content. This was indicated by the higher relative density and the reduction of pore amount in the microstructure of the composites evidenced by FESEM images. The highest hardness values were obtained at 0.5 wt.% CNT and then decreased as the CNT increased in all the samples with and without the ultrasonic assisted compaction.

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