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The Effect of Sintering Temperature on Cu-Cnts Nano Composites Properties Produced by Pm Method

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Abstract: In this research work, copper and CNTs have been processed using high energy milling in different milling times (5, 10 and 15 hours). FESEM and XRD have been used to characterize the milled powders. The FESEM micrographs of the milled powders indicated that the morphology of powders changed from spherical shape to flake as milling time increased. The effect of sintering temperature as well as CNTs content on the properties of Cu-CNTs nanocomposite has been investigated. The optimum sintering temperature to produce Cu-CNTs nanocomposites is determined to be 900 °C. The microstructure and phase analysis of Cu-CNTs nanocomposites were studied by field emission scanning electron microscopy and X-ray diffraction. Mechanical properties of nanocomposite samples at various sintering temperatures were investigated. Cu-CNTs nanocomposite with 4 vol.% CNTs fabricated by powder metallurgy method indicated the highest value of the micro-hardness and bending strength as compared to pure copper.

Keywords: Milling time; Sintering temperature; CNTs Vol. %; Cu-CNTs nanocomposites.

1. Introduction

Carbon nanotubes (CNTs) have been suggested as a new type of reinforcement to enhance the poor mechanical performance of some metals and produce advanced engineering composites [1-5]. They have received noticeable interest in the research study due to their extraordinary properties such as high elastic modulus of 0.5-2 Tpa [4, 6-9], the tensile strength of 20-150 GPa [8, 10-11] and great flexibility [12-13]. In addition, high aspect ratio, extreme chemical stability and excellent thermal and electrical properties of CNTs change them to an outstanding choice for distinct applications [4].

A broad range of studies have reported that CNTs improve the performance of ceramic and polymer matrix in the last decades [14-15], and researches on metal matrices reinforced with CNTs are to some extent restricted [16]. The main issue in the synthesis of metal-CNTs nanocomposites is to achieve a homogeneous dispersion of CNT powders in the metallic matrices [1-2, 16-17]. However, many research groups have employed efficient methods to enhance dispersion. Cha et al [18] used molecular level mixing method between metal ions and functionalized CNTs. Kima et al [19] reported a method to produce Cu-CNTs composites as called mechanical mixing process. In addition, ball milling has been a promising technique includes impact, fracture and welding of powders continuously during ball-powder-ball and ball-powder-container collisions to obtain optimum dispersion of powders [20-22] that has been used by a number of research groups [16, 22-30].

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Copper has always been an ideal candidate for applications of important requirements such as rocket engines [31-32] and magnetic confinement fusion reactors [1], and used in aerospace, automotive, military and electrical industry [33] due to high electrical and thermal conductivity. A large number of the high-temperature applications require excellent mechanical properties. Therefore, copper is reinforced with materials which are able to improve its mechanical properties and overcome the problem of low strength of it [32, 34]. In order to produce Cu-CNTs nanocomposites, various synthesis methods which improve the mechanical properties have been used such as electroless deposition [2, 25], hot pressing [26-27], spark plasma sintering [1-2, 28, 35] and powder metallurgy [28, 36] which includes mixing, cold compaction and sintering the starting powders. The sintering temperature of the cold compacts depends on the volume fraction and melting temperature of the constituent with lower melting point [29].

In this research study, Cu-CNTs nanocomposites were produced after high energy milling of Cu and CNTs powders by powder metallurgy method. The effects of milling time on agglomeration and shapes of powders as well as sintering temperature and CNTs Vol.% on the mechanical properties were investigated.

2. Experimental Procedures
2.1. Materials

Copper powder (purity 99.9 % and particle size $\leq 25$ µm supplied by powder metallurgy complex of Iran) and multi-wall carbon nanotube (MWCNT) (5-10 nm in diameter and density of 2.1 g/cm$^3$ provided by US Nano of America) were used in this study.

2.2. Production of Cu-CNTs nanocomposites

Cu powders and the CNTs with 2, 4 and 6 vol.% were mixed using a planetary ball mill at 120 rpm in a stainless steel jar including stainless steel milling balls of 4, 7.5 and 10 mm diameter with ratio ball to a powder of (BPR) 10:1 under argon atmosphere. Small diameter balls (4 mm) were also used to increase the contact area between powders and balls. In order to determine the optimum of milling time, various milling durations (5, 10 and 15 hours) were employed to mill Cu powder containing 4 vol.% CNTs and finally the optimum duration was chosen to produce nanocomposites samples with different volume percentages of CNTs. The samples have been fabricated by conventional powder metallurgy method. The milled powders were put into a uniaxial die of stainless steel at 450 MPa. The compact powders were sintered in a tube furnace in the range of 850-950 °C under argon atmosphere for 2 h.

2.3. Characterization

Microstructural examination of mixed powders and nanocomposites samples were carried out using field emission scanning electron microscope (FESEM) fitted with energy-dispersive X-ray spectroscopy (EDX). XRD analysis of Cu-CNTs nanocomposites powders was conducted by Xpert (Philips PW 3710) diffractometer ($\lambda_0$ K$_\alpha$ radiation with $\lambda_0$ = 1.54 Å) with voltage and current setting of 40 kV and 30 mA. The Archimedes technique was used to measure the density of samples according to ASTM B311. Vickers micro-hardness of the Cu-CNTs nanocomposites samples were measured using a HVS-1000A model micro-hardness tester, with a loading 50 g and dwell time of 10 s according to ASTM E92. The bending strength tests were carried out using a Zwick Roell-Z100 universal testing machine with an initial strain of 0.5 mm/min at room temperature according to ASTM D790.
3. Results and Discussion

3.1. Preparation of homogeneous powders mixture

SEM and TEM images of MWCNTs are indicated in Fig. 1. According to this Fig, MWCNTs are curled and in some area, twisted CNTs are shown, because of the van der walls attraction.

![Fig. 1. Micrographs of the MWCNTs (a) SEM, and (b) TEM.](image)

Fig. 2 indicates the FESEM micrographs of the as-received copper powder and mixed powders of Cu-CNTs nanocomposites containing 4 vol.% of CNTs which has been chosen according to previous researches [2, 28, 32] using high energy ball milling at various times. The shape of Cu powder is approximately mixture of spherical, smooth and granulated as it is observed in Fig. 2(a). It is obvious that the morphology of powders is altering. The behavior of milled powders has been considerably affected by the existence of CNTs due to lack of interaction of Cu and CNT powders that led to poor bonding [32]. As the Fig. 2(b, c) shows no particular change in milled powders during the initial hours (1 and 2 h) can be seen. However some changes in the shape of powders with increasing of milling time up to 5 h (Fig. 2(d)) are obvious, but whole grains have not been changed to flake shape entirely.

In milling durations up to 10-15 h (Fig. 3(a, b)) morphology of the powders has been changed to flake shapes and flat surfaces that led to lamellar microstructures. These layered microstructures are obviously illustrated in Fig. 3(c, d) with higher magnification. In the Fig. 3(e) the presence of CNTs in composite powders milled at 15 h has been detected by EDX analysis. According to this Fig, the weight percent of carbon for this sample of powders has the highest peak. In other words, when the milling duration increases up to 15 h, agglomerated CNTs also increases in the microstructure as it prevents homogenous dispersion of CNTs between copper powders, as it has been shown by FESEM micrograph of agglomerated CNTs region and its EDX analysis (point A) during 15 h milling (Fig. 3(e)).

There are two main occurrences in milling processes such as cold welding and fracturing [32]. As the process continues, on the one hand agglomeration of the powders and increase in particle size occur by cold welding. On the other hand, the fracturing phenomenon leads to reduce particle size by breaking the powders. Milling parameters have significant effects on these occurrences. As a consequence, uniform dispersion of CNTs into copper powders can be achieved by a cycle of flattening of copper powders, cold welding and fracturing. However, the milling duration is a major factor in the dispersion.
Fig. 2. FESEM micrographs of a) the as-received copper powder and Cu-4 vol.% CNTs powders b) 1 h, c) 2 h, and d) 5 h after milling.

Fig. 3. FESEM micrographs of Cu-4 vol.% CNTs powders a, c) 10 h, and b, d) 15 after milling, and e) agglomerated CNTs region during 15 h of milling and its EDX analysis.
The XRD patterns of copper composite powders reinforced with 4 vol.% CNTs milled at different milling durations and as-received copper powder as a reference pattern to compare peaks are indicated in Fig. 4. Cubic structural of copper is shown with three peaks by the planes (111), (200) and (220) at 2θ of about 43°, 50° and 74° respectively, and the XRD patterns of pure MWCNTs should have had three peaks with lattices of (002), (101) and (004) [16, 37], but in these patterns due to less amount of MWCNTs in powders [38], low diffraction efficiency of carbon [39-40], and mechanical alloying of powders [41] there is no conspicuous peaks of MWCNTs.

![XRD patterns of copper composite powders](image)

**Fig. 4.** XRD patterns of A: Cu powder (as-received) and Cu-4 vol.% CNTs nanocomposite powders after B: 1 h, C: 2 h, D: 5 h, E: 10 h, F: 15h of milling.

In addition, as it has been shown in other studies [41], ball milled (BM) powders have broad peaks and they are moved into values lower than 2θ degree in comparison with copper powders which have not been milled (Fig. 4(b)). According to the patterns and using Xpert software, values lower than 2θ degrees have been achieved. These slight differences between 2θ values of peaks in BM powders could be due to the particle deformation and fine grains. As it was proved that the homogeneous dispersion of CNTs in the copper powders could not be obtained through high energy ball milling at higher duration up to 15 h, and it has detrimental effects on nanocomposite samples and prevents improving the properties. Therefore, according to the results the optimum duration to mill the powders is about 10 h.

### 3.2. Sintering temperature and CNTs effect

In this part of research study, the effect of sintering temperature on properties of Cu-CNTs nanocomposites was investigated in three different temperatures of 850, 900 and 950 °C for 2h.

Fig. 5 shows the microstructure of Cu-4 vol.% CNTs nanocomposites produced by powder metallurgy technique at three different sintering temperatures as observed by FESEM micrographs. These micrographs clearly indicate that sintering process probably has not been conducted at the temperature of 850 °C entirely due to the presence of void and porosity in the microstructure, but at the temperature of 900 °C and 950 °C the porosity decreases as it could be because of the performance of sintering process completely.

As it is observed in this micrograph grain growth during sintering at the temperature of 950 °C has been occurred which could be an inherent problem in the sintering and densification of nanocomposites. Coarse grain size is not desirable to achieve higher hardness and strength.
Fig. 5. FESEM micrographs of Cu-4 vol.% CNTs nanocomposites sintered at temperatures of a) 850 °C, b) 900 °C and c) 950 °C.

Relative density values of Cu-CNTs nanocomposite samples as a function of CNTs volume fraction are indicated in Fig. 6. As this Fig shows measured relative density decreases with increasing vol.% CNTs. The sintering mechanism of the composites includes the diffusion of Cu atoms during the sintering. When the volume percent of CNTs increases, agglomeration of nanotubes and clustering of them inhibit the diffusion of Cu into the minor spaces between the CNTs, as resulted in the heterogeneous distribution of CNTs and creation of large pores during the sintering process. Moreover, the agglomeration in a high percent of CNTs prevents interfacial bonding between Cu and CNTs effectively [42].

Fig. 6. The effects of sintering temperature as well as CNTs Vol.% on the relative density of Cu-CNTs nanocomposites.

In addition, the density of nanocomposites at the temperature of 900 °C achieves the highest value, while the presence of porosity leads to the lowest density at the temperature of 850 °C. Sintering mechanism of the composites involves the diffusion of Cu atoms at the sintering temperature. Therefore, the sintering temperature is the main factor in the synthesis process.
Sintering ability could be improved at higher temperatures; however it has been limited to the optimum temperature and by further increase of the sintering temperature, it has had an adverse impact on microstructure. Grain growth during sintering process is the phenomenon which could be obtained due to increasing of sintering temperature, and led to low mechanical properties.

Variation of the micro-hardness and bending strength as a function of CNTs content is indicated in Fig. 7. According to this Fig, a major enhancement of the hardness and bending strength is observed by addition of CNTs to copper. The movement of dislocations in the matrix is effectively blocked by CNTs. Moreover, the difference in thermal expansion coefficient of Cu and CNT cause thermal mismatch stresses resulting higher dislocation density as a consequence of dislocation generation which led to higher micro-hardness and bending strength. However, by addition of CNTs more than 4 vol.% the hardness and bending strength decrease, because of agglomeration of CNTs and presence of pores at higher volume% of CNTs. Furthermore, the agglomeration leads to extremely weak interface between CNT clusters, hence the composite would fail because of this poor bonding.

Fig.7. The effect of sintering temperature on a) micro-hardness and b) bending strength of Cu-CNTs nanocomposites.

The lowest and the highest values of micro-hardness and bending strength of Cu-CNTs nanocomposites have been obtained at the temperature of 850 °C and 900 °C, respectively. As it was mentioned, more porosity in the microstructure of Cu-CNTs nanocomposites sintered at the temperature of 850 °C which was evident in FESEM micrograph led to a marked drop in mechanical properties. In other words, the presence of pores and voids prevents fully sintering and reaching optimum properties at the temperature of 850 °C. With increasing of sintering temperature up to 950 °C micro-hardness and bending strength decreased. This considerable reduction could be explained by the phenomenon of grain growth, which led to lower hardness and strength based on Hall-Petch theory [43].

4. Conclusion

In summary, the effect of milling durations on Cu-CNTs composite powders has been studied, and the results indicated that the optimum duration to mill the powders using high energy milling is about 10 h which led to the homogeneous distribution of CNTs in a copper matrix in comparison of other durations. Among the different sintering temperatures to produce Cu-CNTs nanocomposites, the optimum temperature based on obtained results was determined to be 900 °C which included the highest values of hardness and bending strength. Furthermore, the nanocomposite with 4 vol.% CNTs fabricated by powder metallurgy method indicated the highest value of relative density, micro-hardness and bending strength compared
to pure copper.

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5. References
