Evaluation of Cu- CNT nanocomposite fabricated by powder metallurgy

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Abstract

Multi- walled carbon nano tubes (MWNT) were introduced into copper matrix to obtain Cu- CNT composites containing 0.5 and 1 wt. % CNT. The composites were fabricated by means of powder metallurgy process, consisting mechanical milling of pure commercial copper powder with MWNT followed by hot pressing of the resultant powder. The structural characteristics of powder particles and consolidated samples were studied by scanning electron microscopy (SEM). Mechanical properties of MWNT reinforced copper matrix composite were investigated. The mechanical properties of the MWNT reinforced copper matrix composite enhanced compared to those of pure copper specimen. However Cu matrix composite containing incorporated CNT showed a brittle behaviour in comparison with pure copper.

Keywords: Cu-CNT nanocomposite, mechanical alloying, hot press sintering, mechanical properties

Introduction

Copper matrix composites have a wide range of applications among which, those with a relation to outstanding electric and thermal properties as highly conductive materials in various switches, thermal and electric conductors, microwave tubes, etc [1]. Utilizing a proper reinforcement in a metal matrix can result in a combination of high strength and stiffness. Carbon nanotubes (CNTs) are currently being considered as a potential reinforcement for various matrix materials including copper and its alloys. CNTs cover a high Young's modules of 0.5-2 TPa, large ultimate tensile strength of 20-150 GPa and high flexibility [2]. CNTs also have very superior thermal and electrical conductivity, mostly because of their nearly perfect atomic structures on the surface [3], which have developed a great interest and attracted the attention of scientific as well as commercial communities [4]. However, obtaining a good distribution of well bonded CNTs in the composite materials, especially in metal matrix materials is still a challenging objective [5]. By application of an adequate fabrication method this target can be achieved [2, 6]. There are some main routes to synthesis CNT reinforced MMCs such as powder metallurgy, Electro-deposition and electroless deposition [7, 8]. Among all of the mentioned processes, powder metallurgy is the most popular and widely used technique which can provide a homogenous dispersion of CNTs in the metal matrix as well as adequate bonding of CNTs [5]. Fabrication of metal matrix composites by hot press sintering (HPS) has also been reported in the literature. Composites synthesized via HPS have shown improved mechanical properties (hardness, compressive strength and bend strength) due to uniform distribution of CNTs [9]. Moreover, in hot pressing, CNTs would not be damaged or reacted with metal matrix [2]. It is reported previously that Cu-CNT composites fabricated by mechanical alloying and hot pressing present improved hardness with no significant reduction in electrical conductivity [8]. In this study the CNTs were introduced to copper matrix through mechanical milling using a planetary ball mill followed by HPS to investigate the influence of CNTs on tensile properties of the material.

Experimental Procedure

Commercial pure Cu (99.5 % purity, Khorasan powder metallurgy company, Iran) was reinforced with CNT (99.5% purity, Oil industry research center, Iran) by using mechanical milling. The average diameter multi-walled CNTs was about 20 nm with a length of 10 to 17 μm and Cu powder had a particle size of <63 μm. The morphologies of starting materials are shown in Figure 1.

Powder mixtures of 0.5 and 1 wt. % CNT with Cu were milled by a high energy planetary ball mill having a rotating speed of 600 rpm. The balls to powder weight ratio was chosen to be 10 and the diameter of the chromium steel balls was 15 mm. Hard chromium steel vial was evacuated and filled with argon to prevent oxidation during the mechanical alloying process. 1 wt. % zinc stearate was added to the mixture as the controlling agent.

The resultant milled powder was sintered by hot pressing under 100 MPa at 790˚C for 1 hr to fabricate tablets of 40 mm diameter and 14 mm thickness. The powder was placed inside a graphite die, and argon (99.99 % purity) was used as the protecting atmosphere during hot pressing. Densities of the compacted samples were determined using ASTM B962 standard method based on Archimedes' principle.

Morphologies and cross-sectional microstructure of the powders as well as cross-sectional microstructure of hot pressed samples were investigated by field emission scanning electron microscopy (HITACHI S4160 FESEM). Microhardness examination of the powders was conducted by KH- Prüftechnikmicrohardness testing machine using ASTM E384 Standard test method for microhardness of materials. Powder particles were embedded in a mounting resin and prepared by metallography techniques to provide cross sections of the particles. The hardness of consolidated samples was measured by a Zwick macrohardness machine using ASTM E92 standard method. Tensile behavior at ambient temperatures was studied by a Hounsfield H50KSS machine at a strain rate of 0.02 mms^{-1} using ASTM E8M standard test method for tension testing of metallic materials. Tensile samples were cut from the center of compacted tablets with a gage length of 20 mm and a diameter of 4 mm. Powders and sintered samples were subjected to XRD analysis by employing monochromatic CuKα1 radiation (Kα= 0.15406 nm) with a step size of 0.5°in the diffraction range of 20-90°.

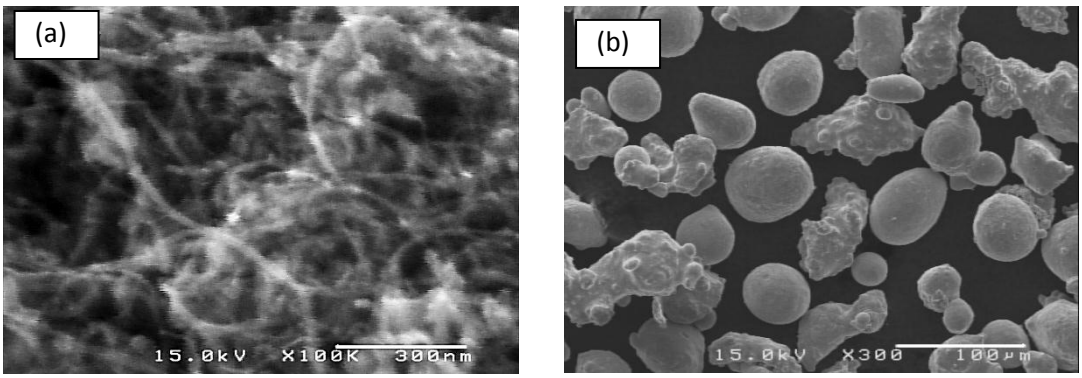

Fig. 1 Morphologies of starting materials, a) MWCNT, and b) pure Cu powder.

Results and discussion

Figure 2 shows the morphology evolution of powder mixtures during ball milling. After 3 h of milling both compositions lead to flake like powder particles with considerably increased particles size, which demonstrates the predominant welding mechanism during milling up to 3 h (Fig. 2- a and c).

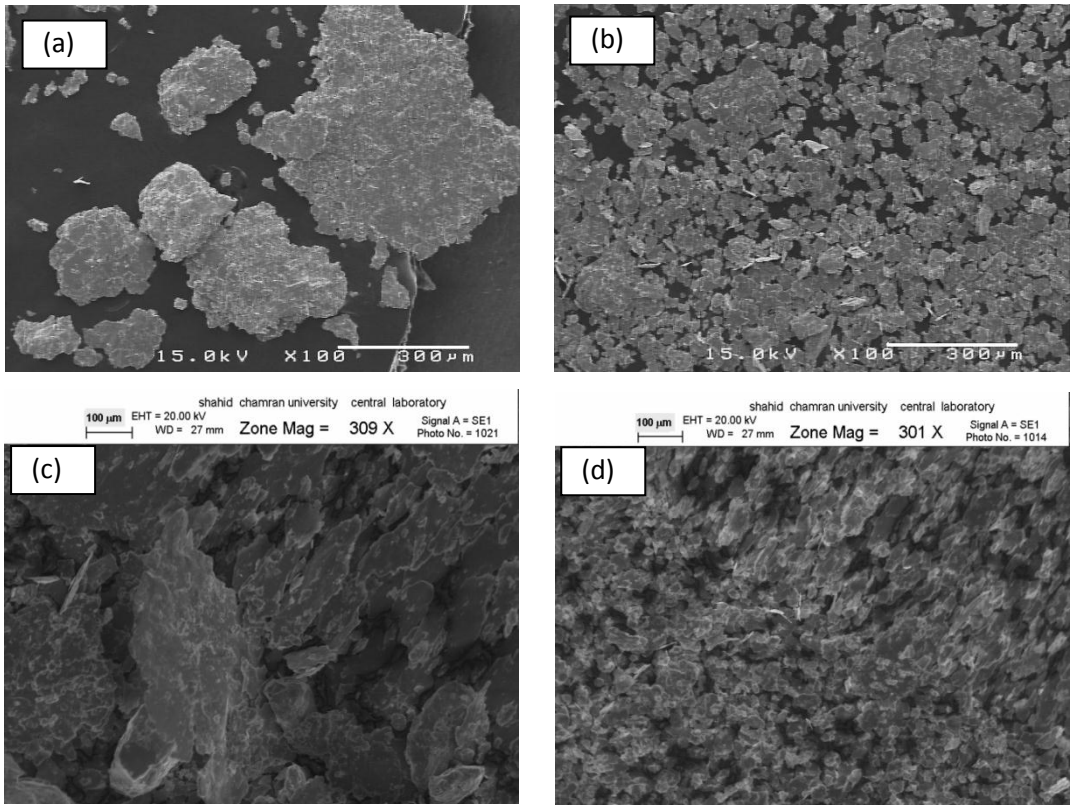

Fig. 2 Morphologies of milled powders, a) Cu-0.5 wt.% CNT after 3h milling, b) Cu-0.5 wt.% CNT after 15h milling, c) Cu-1 wt.% CNT after 3h milling, and d) Cu-1 wt.% CNT after 15h milling.

The flake like particles of CU- 1wt.% CNT powder mixture show a smaller size, in the range of about 15-120 μm, compared to that of Cu-0.5 wt. % CNT, having particle size in the range of 15-600 μm. The smaller size of the powder flakes in Cu-1 wt. % CNT can be attributed to CNT effect which tends to higher hardness and brittleness of powder particles. Therefore, it can be suggested that increasing the CNT proportion shortened the predominant welding period during the milling process.
After 15 h milling the size of powder particles decreased in both compositions but the shape of the particles remained flake like (Figs. 1- b and d). In most metallic alloys, milling for up to long times has been reported to result in semi sphere-shaped particles [10]. This response of Cu base composite to severe plastic deformation resulted from mechanical milling is reasonable due to the Cu lattice structure.
Figure 3 presents high magnifications of powder particles containing 0.5 and 1 wt.% CNT obtained from 3 h milling. In both compositions no evidence showing the agglomeration of CNTs on the surface or inter the Cu particles was perceived, even in after milling as short as 3 h. In previous studies some obvious amounts of agglomerated CNTs have been reported during the milling of Cu-CNT powder mixture [8, 11]. The addition of controlling agent to the starting material might have influenced the progress of fracture mechanism during the first stages of milling. This, together with predominant welding caused a more uniform distribution of CNTs in the powder.

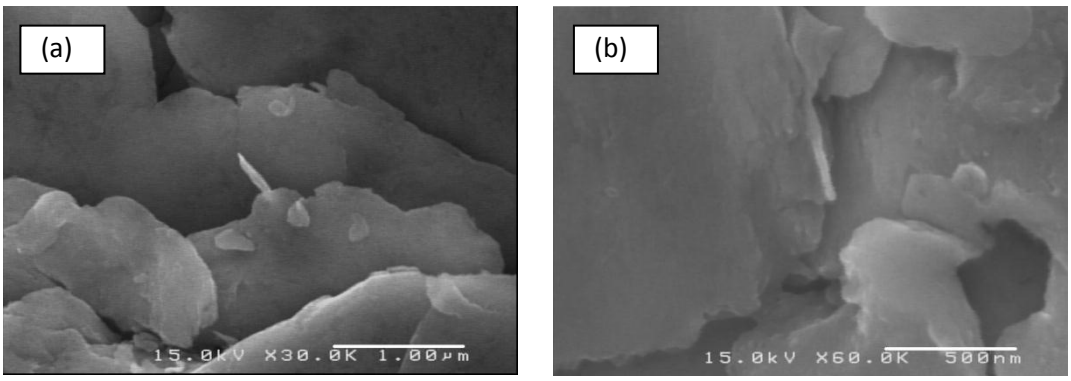

Fig. 3 High magnification FESEM image of powder morphologies after 3 h milling, a) Cu-0.5 wt. % CNT, and b) Cu- 1 wt. % CNT.

Microhardness measurements on the powder particles showed the increase of hardness from 50 to about 120 VHN after 3 h milling of Cu containing 0.5 wt. % CNT. For the hardness measurement on Cu- 1 wt. % CNT powder the problem was relatively small size of particles which caused a large deviation in measurements. It should be noted that even for Cu- 0.5 wt. % CNT a remarkable deviation in the measurements occurred. Considering the flake shape of the particles these deviations are understandable by the effect of underneath embedding material.
Pure Cu powder and Cu- 0.5 wt. % CNT milled for 15 h were sintered to study the influence of CNT existence and milling process on mechanical properties of material. By density measurements of the hot pressed samples, pure Cu showed a density of 8.88 g cm^{-3} which is 99% of the calculated composite theoretical density (8.94 g cm^{-3}). For Cu-0.5 wt. % CNT the density was measured to be 8.09, which is about 92% of the composite density. This finding implies the reduction in compressibility of the powder with the addition of CNT.
The hardness of pure Cu sintered sample was measured about 50 VHN while that of Cu-0.5wt.% CNT was determined to be about 130 VHN. Higher hardness of Cu-0.5 wt. % CNT can be explained by the presence of CNTs in Cu matrix as well as by the structural evolution of Cu matrix resulted from mechanical alloying. Typical stress- strain curves obtained from the hot pressed samples are shown in Figure 4. Cu-0.5 wt. % CNT showed a strength 1.3 order of that of pure Cu. However it is obvious from the curve related to Cu-0.5 wt. % CNT that the sample exhibited a brittle behavior in tensile testing and was fractured before yielding. Figure 4-b presents the typical macroscopic features of the samples showing the brittle fracture mode, without any evidence of necking for Cu-0.5 wt. %CNT.
Fractography of the fractured samples showed that the matrix performed a ductile manner at microscopic scale, resulting in the formation of dimples even in Cu-0.5 wt. % CNT (Fig. 5). Pure hot pressed Cu showed the typical fracture surface of ductile materials consisting dimples with a mean size of about 15 μm, while the maximum size of the dimples in Cu-0.5 wt.% CNT was about 500 nm. Such behavior has been reported for metal matrix nanocomposites previously [12]. At high concentrations of the second phase, this phenomenon has been attributed to clustering of the second phase [6]. No evidence showing the presence of agglomerated CNTs on fracture surface was observed in the fractured surface of Cu-0.5 wt. % CNT. Therefore, the brittle behavior may not be attributed to the uneven distribution of CNTs in the matrix.

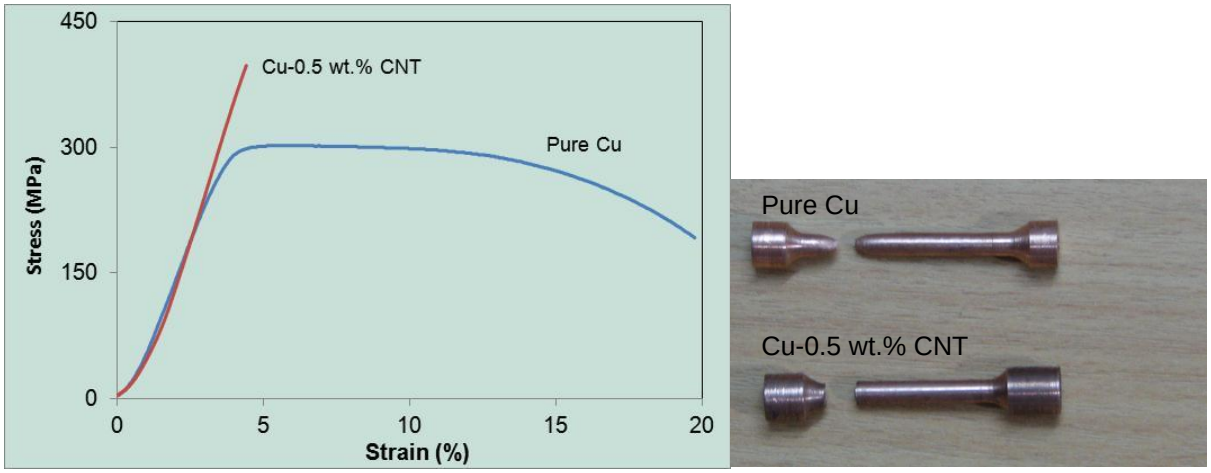

Fig. 4 a) Typical stress-strain curves obtained from the hot pressed samples, and b) fractured samples.

As shown in Figure 6 the hot pressed Cu-0.5 wt. % CNT contained a relatively high extent of very small pores as well as cracks. Higher magnification revealed the existence of lots of submicron pores and cracks. The distribution of submicron pores and cracks at the end of a growing crack can cause prompt propagation of the crack without a considerable plastic deformation. Submicron porosity is expected in bulk nanostructures metal matrix materials obtained from mechanically alloyed powders, resulted from severe work hardening and larger powder particle size [13]. Figure 7 shows the X-ray diffraction patterns obtained from the powders after milling. Peak broadening which is the characteristic of mechanical alloying of ductile materials has occurred even after 3 h of milling. Therefore, lower compressibility of the mechanically alloyed powder due to high strain induced structure is predictable. This can explain the presence of a nearly high content of submicron pores and cracks in the hot press sample. Even after sintering, Cu-0.5 wt. % CNT showed broader peaks compared to the sintered pure Cu (Fig. 8). The existence of CNTs in Cu-0.5 wt. % CNT might have resulted in resistance against grain growth during hot pressing, which tend to persist the broadened X-ray diffraction peaks.

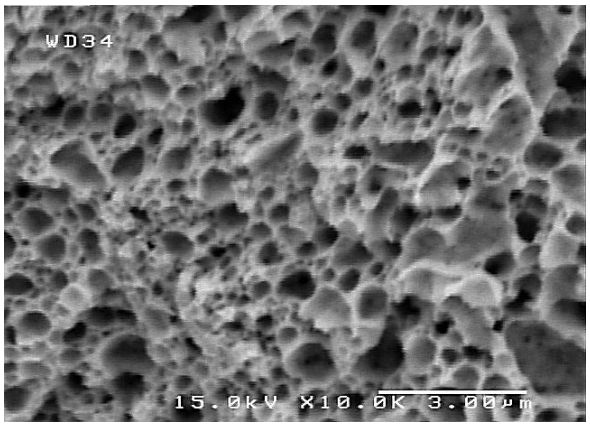

Fig. 5 Typical fracture surface morphology of Cu-0.5 wt.% CNT hot pressed sample.

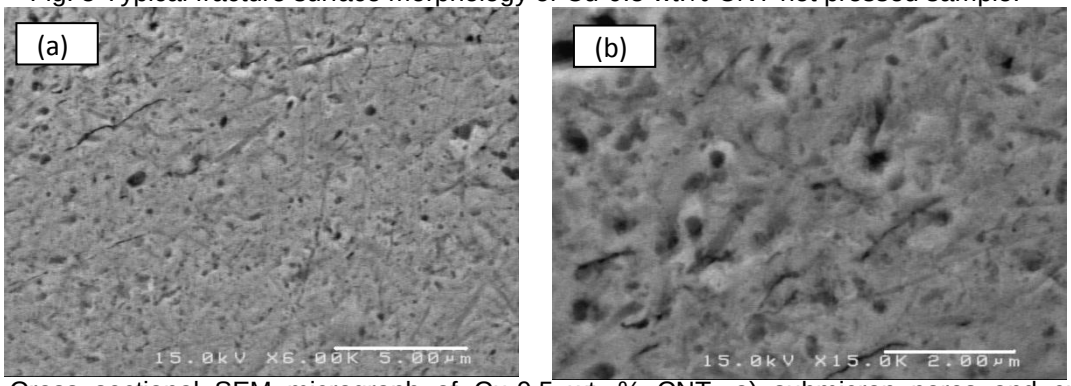

Fig. 6 Cross sectional SEM micrograph of Cu-0.5 wt. % CNT, a) submicron pores and cracks distribution, and b) higher magnification.

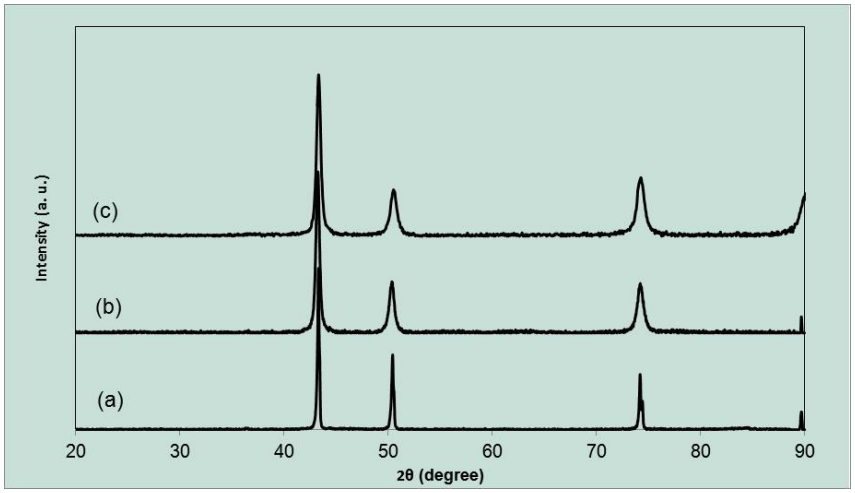

Fig. 7 X-ray diffraction patterns obtained from a) initial Cu powder, b) Cu-0.5 wt. % CNT milled for 3 h, and c) Cu-0.5 wt. % CNT milled for 15 h.

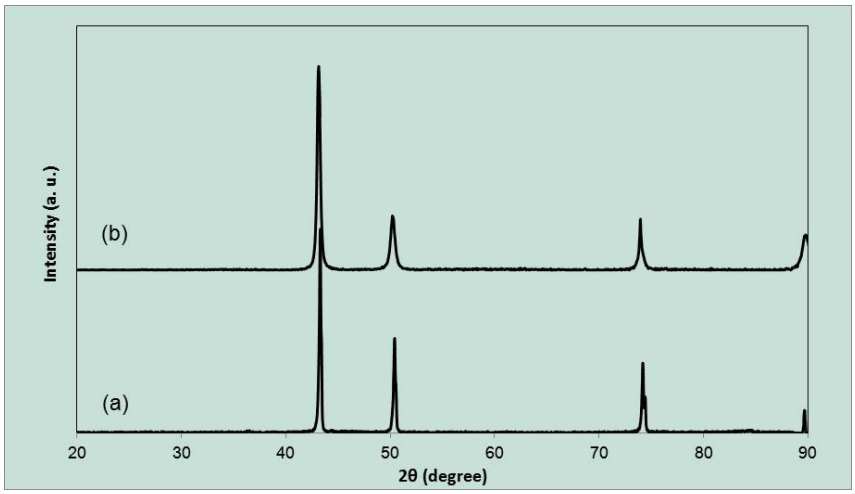

Fig. 8 X-ray diffraction patterns obtained from hot pressed materials a) Pure Cu, and b) Cu-0.5 wt. % CNT.

Conclusion

Cu-CNT nanocomposite was fabricated by mechanical alloying and hot press sintering without obvious agglomeration of CNTs. The resultant Cu-CNT presented improved tensile strength of about 360 MPa and relatively high hardness of about 130 VHN. The hot pressed Cu-CNT sample represented a brittle behavior which needs more investigation to reveal the fundamental reason.

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