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Dispersion of Carbon Nanotubes in Cu-Cr Matrix Nano-composite by Wet Milling

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Abstract

The preparation of Cu-2wt%Cr-5wt%CNT nano-composite powder by wet ball milling was investigated. The lattice parameter and mean crystallite size were calculated by X-ray diffraction technique. Also, the microstructure was characterized by field emission scanning electron microscopy and transmission electron microscopy. The results showed that, the CNTs were dispersed more homogeneously by wet milling and minimum damages were introduced on them. The mechanical properties of powders were investigated by microhardness test and the results were consistent with microstructural results. The mean crystallite size of wet milled powders was 46 nm.

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Keywords: Carbon nanotube; Wet milling; Copper; Nano-composite.

1. Introduction

Cu-Cr/CNT hybrid nano-composites have favourable properties, namely good mechanical properties, high electrical and thermal conductivity due to the presence of copper as matrix and carbon nanotubes (CNTs) as reinforcements. Among copper matrix composites Cu-Cr is an in situ composite. Cr has a small solid solubility in Cu matrix because of its positive heat of mixing which its formation results from decomposition of supersaturated Cu-Cr solid solution, Jin et al. (1998), Sheibani et al. (2010). Due to valuable properties of CNTs, in particular high stiffness, ultimate strength and excellent resilience, they are good candidates to be used as reinforcements in Cu matrix nano-composites, Jian (2004), Tsai and Jeng (2013). Among different approaches for producing Cu-based nano-composites, mechanical alloying is a promising way to reach a homogeneous dispersion of reinforcement

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particles in Cu matrix, Prasad Yadav et al. (2012), Tsai and Jeng (2013). Despite this advantage, agglomeration and defects that are introduced on CNTs during ball milling will affect their morphology, mechanical and physical properties, Tao et al. (2004). Wet milling in presence of a liquid phase has been used to enhance the dispersion of CNTs, Kim et al. (2012), Sotoudehnia and Paúl (2014), Zhou et al. (2013). Although relatively few studies has been directed towards of CNTs dispersion in metal matrix composites through wet mechanical milling, there were no detailed study that was carried out on the comparison of dry and wet ball milling in Cu-Cr/CNT hybrid nano-composite. In this work, the preparation of Cu-2wt%Cr/5wt%CNT hybrid nano-composite by dry and wet ball milling was compared.

2. Experimental procedure

Starting materials used in this research were commercially pure Cu (99.5%, <75μm), Cr (99.5%, <75μm) and multi-walled CNTs with purity of about 90% (~10μm length, and 10-30 nm diameter). It should be mentioned that CNTs were sonicated in ethanol for 90 minutes, to break up the CNTs agglomerates. In the first step, the nominal composition of Cu-2wt%Cr was mechanically milled in a planetary ball mill with hardened steel vial and balls under argon atmosphere. The ball-to-powder weight ratio and milling speed were 30:1 and 300 rpm, respectively. 1wt% of toluene was used as a process control agent. Milling was conducted up to 40 h. In the second step, Cu-Cr solid solution alloy together with 5wt% of CNTs was wet milled for 5 h in 10 ml of ethanol with purity of 99.7%. In this step, the ball-to-powder weight ratio and milling speed were 30:1 and 300 rpm, respectively. The milled samples were dried on hotplate for about an hour at 80^{o}C to evaporate the ethanol.

The structural evolution in the powder during milling was investigated by XRD using a Philips PW3170 X-ray diffractometer with Cu-K_{α} radiation. The lattice parameters were calculated from XRD data, Correia et al. (1997). The mean crystallite size was determined according to the Williamson-Hall plot, Williamson and Hall (1953). The microstructure was evaluated by field emission scanning electron microscope (FESEM) (CamScan MV2300) and transmission electron microscopy (TEM) (Philips CM30). Vickers microhardness of mounted and polished powders was evaluated by WOLPERT-WERKE GMBH D-6700 test machine. The measurement was performed with a load of 100 g for 15 s. The test was measured from the center to the edge of pressed powder mixture, in shape of a disc for 10 points.

3. Results and discussion

Figure 1 (a and b) show XRD patterns of Cu-2wt%Cr powder mixtures after different milling times. It can be seen that compared to initial powder mixture, the Cu peaks broadened on increasing milling time up to 40 h since the continuous deformation of powder particles during the milling process results in crystallite refinement and formation of structural defects. The absence of Cr peaks in the XRD patterns could be explained by the fact that the Cr content is very small to be detected by XRD technique. Also, a shift of the Cu peak to lower angles is observed, which is due to the increase of the lattice parameter, Suryanarayana (2001). Then, 5wt% CNTs were added to 40 h milled sample and milling was continued up to 45 h. Fig.1c shows XRD pattern of 45h wet milled Cu-2wt%Cr-5wt%CNT sample. It should be noted that XRD pattern of wet milled Cu-2wt%Cr-5wt%CNT powder mixture do not show an obvious change, and similar results are obtained.

In order to understand the formation of the Cu-Cr solid solution, the copper lattice parameter was determined. Table 1 shows Cu lattice parameter after different milling times. It can be seen that with increasing milling time from 0 to 40h, a large increase in lattice parameter of Cu happens suggesting that alloying between Cu and Cr may takes place in this period of time. Cu Lattice parameter calculation confirmed that the lattice parameters are approximately constant an about 0.3613 nm in wet milled sample. This indicates that CNTs do not significantly affect the solubility of Cr in Cu lattice in wet milling process. Also, it can see that the mean crystallite size reached to 51 nm after 40 h of milling due to the crystallite refinement and formation of structural defects during high energy ball milling. According to the Williamson-Hall calculation, it is found that the average mean crystallite size of wet milled Cu-2wt%Cr-5wt%CNT nano-composite powder is 46 nm.

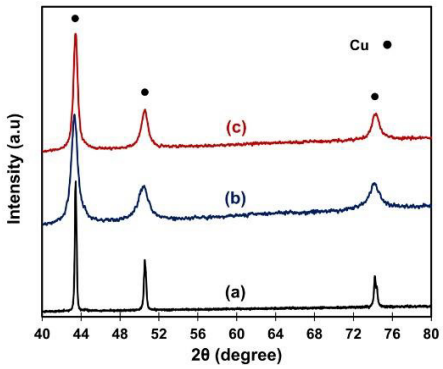

Fig. 1. XRD patterns of (a) initial Cu-2wt%Cr powder mixture; (b) 40 h milled Cu-2wt%Cr powder mixture; (c) 45 h wet milled Cu-2wt%Cr-5wt%CNT powder mixture.

Table 1. Cu lattice parameter and mean crystallite size of different samples.

Powder mixtures	Lattice parameter (nm)	Mean Crystallite size (nm)
Initial Cu-2wt%Cr	0.3505	-
40 h milled Cu-2wt%Cr	0.3612	51
45 h wet milled Cu-2wt%Cr-5wt%CNT	0.3613	46

Figure 2 shows the TEM image of initial CNTs which is used in this study. CNTs with 10μm length and 10-30 nm diameter can be seen in this image. For more detailed study on CNTs dispersion in the Cu-Cr solid solution matrix, the microstructure of milled samples was investigated by FESEM. Fig.3a shows the FESEM image of 40 h milled Cu-2wt.%Cr sample. The figure shows Cu-Cr alloyed particles with irregular morphology and average diameter of about 20 μm after 40 h milling. Since, the cold welding overcomes fracturing during 40h of milling, the relatively large particles are formed. Fig. 3b shows FESEM images of 45h wet milled Cu-2wt.%Cr-5wt.%CNT sample. It can be concluded that while powders are wet milled in the presence of ethanol, CNTs are dispersed homogeneously in the matrix. It should be noted that agglomerated CNTs cannot be observed in this sample.

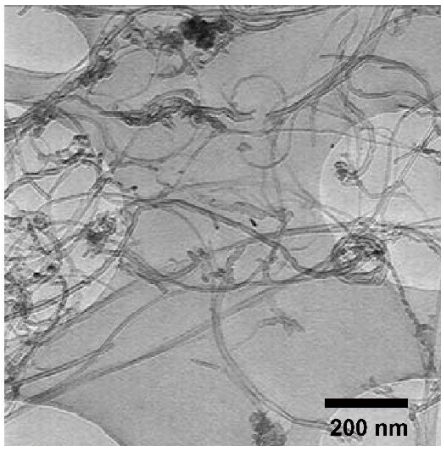

Fig. 2. TEM image initial CNTs.

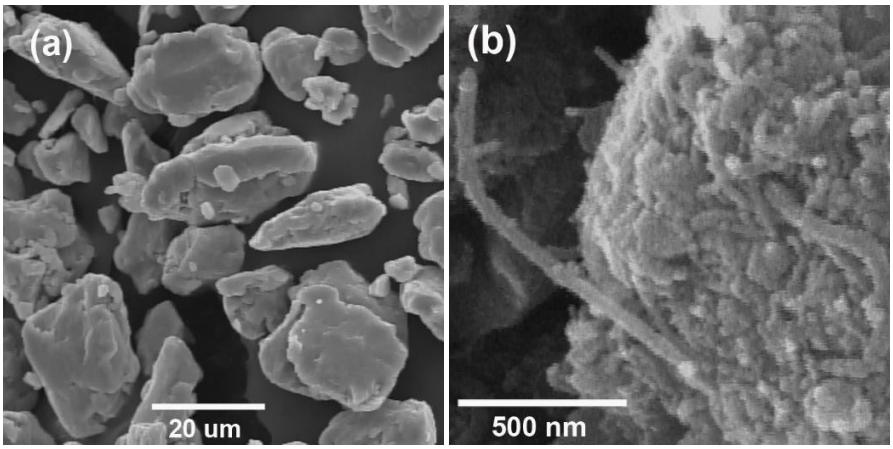

Fig. 3. FESEM images of (a) 40 h milled Cu-2wt.%Cr powder mixture; (b) 45 h wet milled Cu-2wt.%Cr-5wt.%CNT powder mixture.

Figure 4 shows microhardness results of different samples. It can be seen that the microhardness of 40h milled Cu-2wt.%Cr sample (fig. 4a) is lower than that of Cu-2wt.%Cr-5wt.%CNT sample (fig. 4b). This is related to effectiveness of adding CNTs and enhancement of microhardness. Additionally, fig. 4b shows narrow range of difference in microhardness values. This indicates that improved dispersion of CNTs and less damage introduced on them are effective on microhardness of composite samples. The microhardness results of samples are consistent with microstructural results.

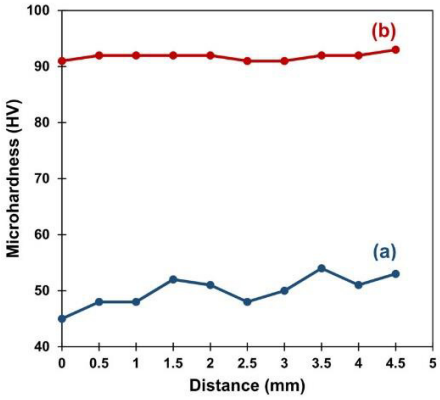

Fig. 4. Microhardness results of (a) 40h milled Cu-2wt.%Cr; (b) 45h wet milled Cu-2wt.%Cr-5wt.%CNT samples.

4. Conclusion

Cu-2wt.%Cr matrix nano-composite powder reinforced with 5wt%CNTs was fabricated via wet milling by 45 h mechanical milling. Microstructural analysis and mechanical properties of samples indicated that wet milling can be considered a better method for dispersing CNTs in the matrix and CNTs would undergo minimum damage. These results were in agreement with SEM images of samples which showed tightly embedded CNTs in the matrix.

Acknowledgements

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