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Effect of mechanical alloying time and carbon nanotube (CNT) content on the evolution of aluminum (Al)–CNT composite powders

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Abstract One of the major obstacles to the effective use of carbon nanotubes as reinforcements in metal matrix composites is their agglomeration and poor distribution/dispersion within the metallic matrix. In the present work, we use mechanical alloying (MA) to mechanically mix CNT (2 and 5 wt.%) with Al powders. These powders would be used as precursors for subsequent consolidation to generate bulk CNT-Al composites. Hence controlling the initial powder characteristics prior to high temperature consolidation is important. Up to 48 h of milling was employed to investigate the effect of milling time on the particle size, morphology and CNT dispersions. The results show that particle size and morphology vary with milling time and CNT content. Also the addition of process control agents such as methanol can aid in controlling the powder characteristics.

Introduction

Metal matrix composites are important technological materials with applications that range from structural, thermal management, aerospace and automotive. With the recent realization of the outstanding properties of carbon nanotubes, the interest in using them as reinforcement for metals, ceramics and polymers has been growing significantly over the past few years. Reinforcements for Al have previously varied both in geometry and chemical composition, and include SiC, graphite and boron [1]. Defect-free carbon nanotubes have outstanding properties, for example, elastic modulii on the order of ~ 1 TPa and tensile strengths around 150 GPa [2–5]. They have therefore already been considered as new reinforcements for a number of material systems including polymeric [6, 7], metallic [8–10] and ceramic [11] matrices.

It is clear that successful dispersion of CNTs in metallic matrices is needed before we can realize any sort of significant benefits in terms of property gains in the composite. This paper investigates mechanical alloying (MA) as a means for dispersing CNTs in Al. MA (through the energetic ball milling of powders), involves continuous impact, welding, fracturing and re-welding of powders such that dispersions would be effectively and homogeneously distributed within the ductile particle matrix. It has previously been successfully used to produce homogeneous and well-dispersed distribution of reinforcements in a powder matrix. For example, SiC_p in Al-Li alloy powder [12], yttria in iron aluminides [13] and recently one of the authors studied the dispersion of nickel particles in Al powders [14].

Some work covered the ball milling of just CNT [15]. In a recent study [16], ball milling of a mixture of CNT and aluminum powder for 5 min was conducted in order to break down the CNT clusters. These authors limited the milling intensity to 200 rpm and the milling

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time to 5 min. Recently the current authors examined mechanical alloying as a mean of dispersing CNTs in Al [17]. In that work only 2 wt.% CNTs was used, and one of the findings is that the particle size becomes uncontrollably large with milling time. In the current paper we investigate the effect of CNT wt.% (2 and 5 wt.%) and the influence of milling time and process control agents on the size and morphology of the mechanically alloyed powders. The work may have significant implications for the processing of CNT–metal composites in general.

Experimental procedures

Al (99.7% pure,—75 μm) and multi-wall carbon nanotubes (MWCNT) (approximately 140 nm in average diameter and 3–4 μm in length, supplied by the MER corporation), were used in the present study (Fig. 1a, b). The starting materials were characterized by scanning electron microscopy (SEM) to determine (1) the Al particle size and morphology and (2) the MWCNT average diameter and length. Two compositions were used in the study, 2 and 5 wt.% CNT with the balance in each case being Al. Each composition was placed in 125 mL stainless steel mixing jars containing 25 stainless steel milling balls of 10 mm diameter (giving an initial ball-to-powder weight ratio (BPR) = 10:1). The jars were filled with argon and were then agitated using a Planetary ball mill (Retsch 400 MA) at 200 rpm for milling times up to 48 h. Samples were extracted from each batch at regular intervals for sieve analysis and analysis using a field emission scanning electron microscopy (FESEM) (LEO Supra 55 FESEM), to characterize the dispersion of the CNTs within the Al matrix, composite particle morphology and size.

Results and discussion

Initial experiments using conventional dry mixing of the CNT and Al powders resulted in CNT clustering/agglomeration due to the extremely small size (~140 nm) of CNTs used.

Figure 2 shows clustering of the nanotubes after dry mixing in a Turbula mixer at 22 rpm for 6 h. Similar clustering was observed for other mixing speeds and times with the minimum cluster size of about 20 μm reached when mixing at 46 rpm for 8 h or 67 rpm for 6 h.

The FESEM micrographs are presented in Fig. 3, which show the powder size/morphological evolution with milling time for both 2 and 5 wt.% CNT-Al powder mixtures.

It can be seen from Fig. 3 that for both CNT contents used, the aluminum particles were first flattened under the impact of the balls forming flakes. With prolonged milling time, the flakes started to weld together forming large particles with a rough surface (that became smoother as the milling continued for the 2 wt.% CNT–Al mixture). For the 2 wt.% CNT reinforced material, some particles reached a size approaching 3 mm after 24 h of milling with a very smooth surface. In MA there are two competing processes; one is work hardening of the powders, which should lead to a decrease in ductility and eventual fracturing of the particles, while the other is welding of particles which tends to increase the particle size [18]. Due to the overwhelming ductility of Al in the 2 wt.%

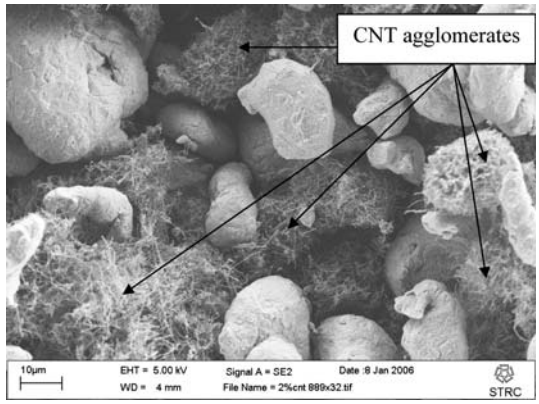


Fig. 2 Clusters on nanotubes after dry mixing in a Turbula mixer

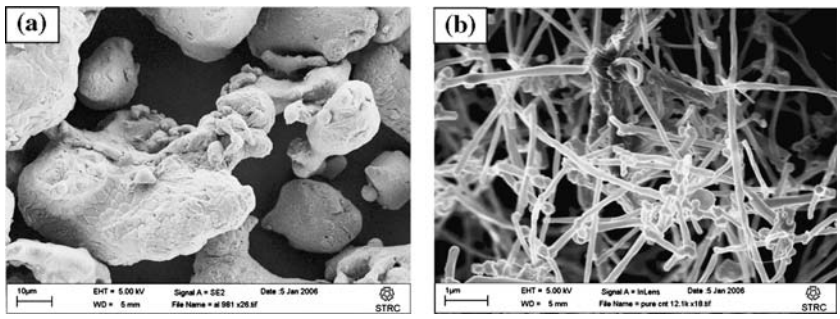


Fig. 1 (**a**) Al powders and (**b**) CNTs used in the present study

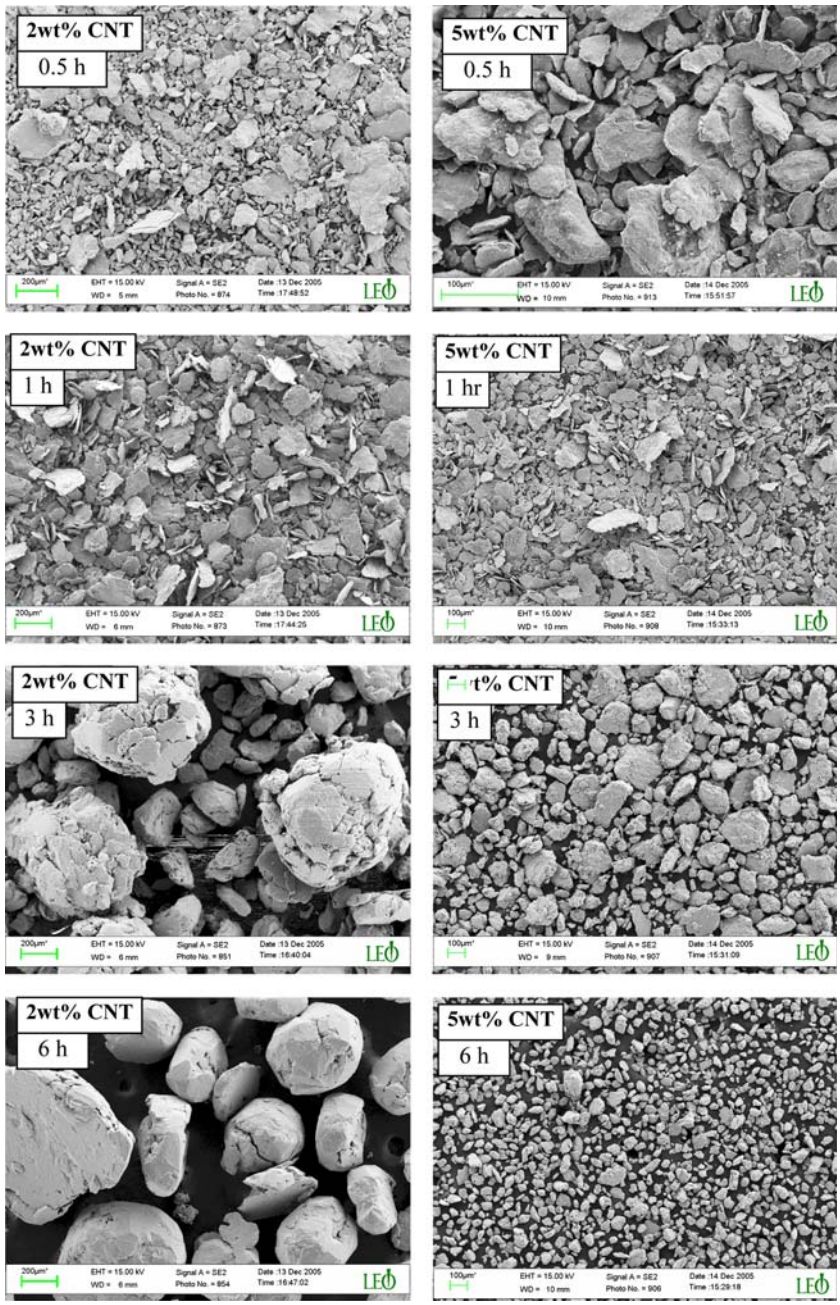
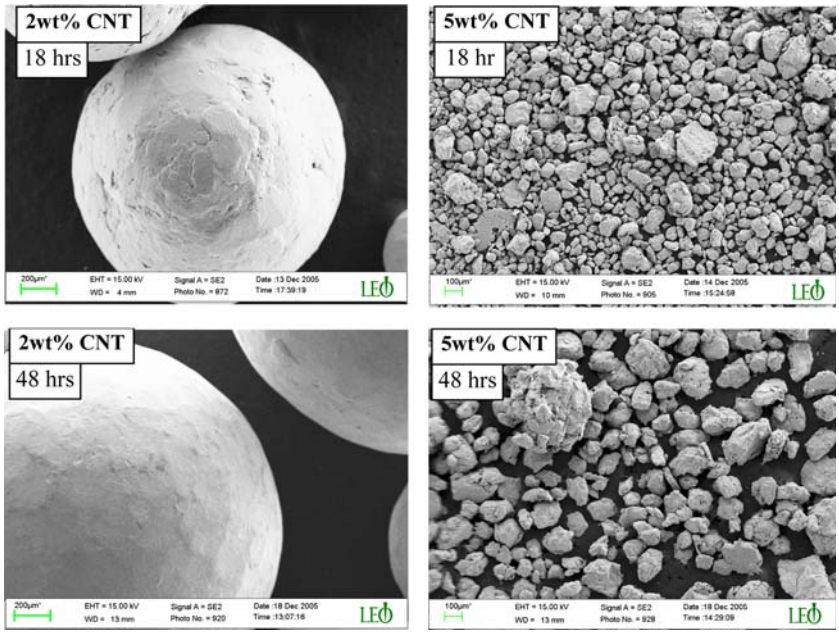


Fig. 3 SEM micrographs showing particle morphology and size change with mechanically alloying time for 2 and 5 wt.% CNT–Al powder composites

CNT–Al composite particles and possible dynamic recovery processes occurring, particle welding may be more pronounced, leading to the very large particles observed even after 48 h. This behavior was however not observed for the 5 wt.% CNT reinforced material, since in this case the composite particles are expected to be less ductile and hence much smaller particle sizes were obtained, and therefore more suitable for subsequent sintering processes. In contrast to the 2 wt.% CNT–Al mixture, the 5 wt.% CNT–Al mixture observed an initial increase in particle size followed by a decrease then increase again from 36 h milling to 48 h milling. Figure 4 shows a cumulative particle size distribution generated from the results of sieve analysis on the 5 wt.% CNT–Al mixture mechanically alloyed for 48 h. The median particle size (D_{50}) is shown to be 110 μm. Sieve analysis also revealed that as the milling time is increased from 36 to 48 h, the D_{50} also increases, for 2 wt.% CNT–Al (from 1.44 to 1.73 mm) and for 5 wt.% CNT–Al (from 90 to 110 μm).

For the 2 wt.% CNT–Al powders, investigation of the particle surface after various milling times revealed the presence of nanotubes—uniformly distributed—on the flakes' surfaces after 0.5 h of milling, as shown in Fig. 5. The same dispersed presence of nanotubes on the surface was observed for particles milled for 1 and

Fig. 3 continued



3 h. However, after 6 h, at which time smooth-surfaced large particles had been formed, no nanotubes were observed on the surface. It was assumed that by this stage the nanotubes were already embedded in between the welded particles. Deforming the large particles obtained after the maximum milling time of 48 h and then fracturing the particles to reveal the fracture surface confirmed this. High magnification FESEM analysis was conducted and revealed the presence of CNTs within the aluminum matrix as

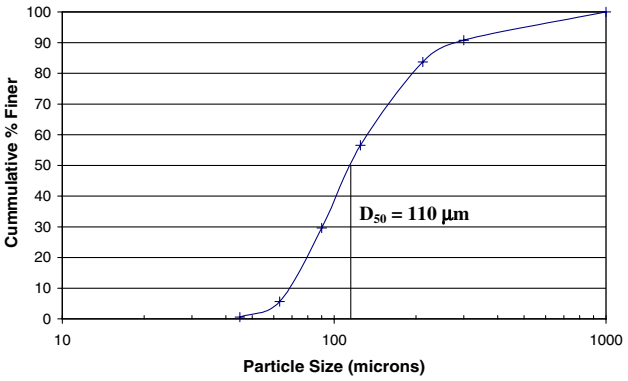


Fig. 4 Cumulative particle size distribution of 5 wt.% CNT–Al powders mechanically alloyed for 48 h

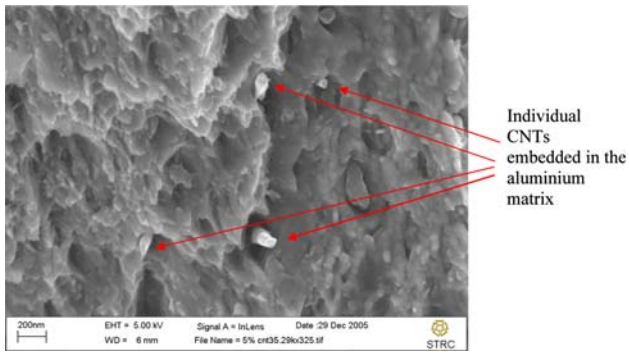
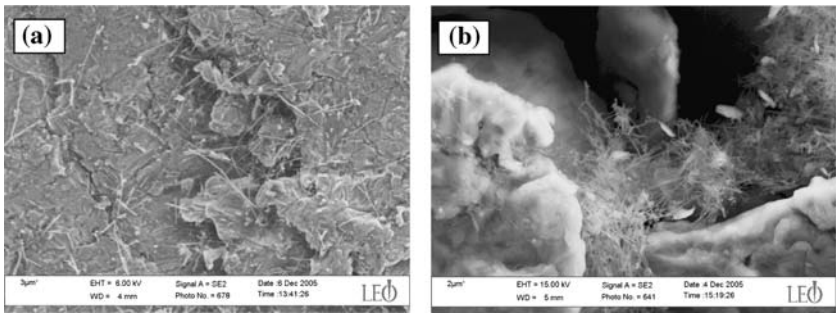


Fig. 6 Deformed and fractured particle of 2 wt.% CNT–Al (48 h MA), showing individual CNTs embedded in the aluminum matrix after the longest milling time of 48 h

Fig. 5 (**a**) CNTs dispersed on the surface of aluminum flakes after 0.5 h milling time of 2 wt.% CNT–Al powders, (**b**) after 0.5 h of milling 5 wt.% CNT–Al powders, some CNTs are still seen to be agglomerated/clustered



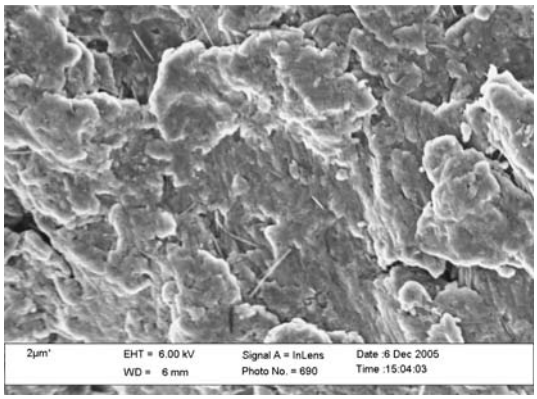


Fig. 7 Particle of 5 wt.% CNT–Al (3 h MA), showing individual CNTs embedded in it

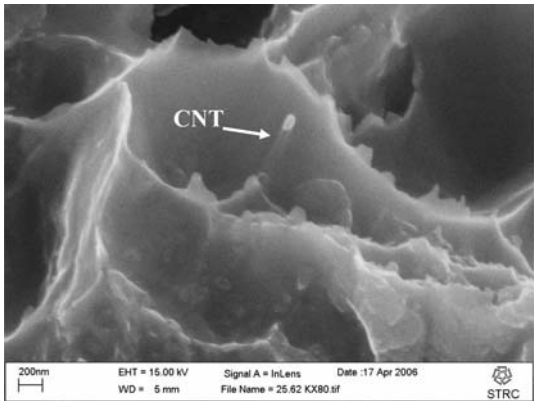


Fig. 8 Deformed and fractured particle of 5 wt.% CNT–Al (48 h MA), showing a CNT embedded in the aluminum matrix

shown in Fig. 6. It can be seen that the CNTs appear intact after being subjected to the MA process. For the 5 wt % CNT—Al mixture, some CNT clustering was observed after 0.5 h of milling, as shown in Fig. 5b. This disappeared after 1 h when the nanotubes became dispersed on the surface of the particles. With the re-welding of the aluminum particles after 3 h under the impact of the balls, individual nanotubes were observed on the surface of aluminum particles (Fig. 7). No nanotubes were detected on the surface as the milling time increased further. However, fracture of deformed particles after 48 h of milling confirmed the presence of CNTs embedded in the matrix, as shown in Fig. 8. For the 5 wt.% CNT-Al powders despite nanotube observation, it cannot be discounted that some nanotubes may have been destroyed in the ball milling process at the higher ball milling times.

The powder sizes obtained for the 2 wt.% CNT-Al mixture can be so large to exclude any possibility of sintering. One way to control this effect is through the addition of a process control agent (PCA). Figure 9 shows that after adding 0.7 wt.% of methanol as a PCA to the 2 wt.% CNT-Al mixture the particle morphology is predominantly that of flakes even after 12 h of milling. Here the methanol hindered the cold-welding process. When however 0.1 wt.% of methanol was used, more rounded particles where produced but with a much finer particle size than previously observed even after 12 h milling. Carbon nanotubes were observed being embedded between the aluminum particles that are being cold-welded, as demonstrated in Fig. 10. These results suggest that it is possible to

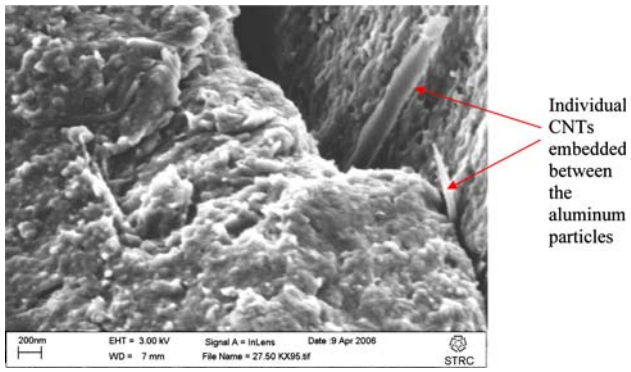


Fig. 10 2 wt.% CNT–Al (6 h MA with 0.1 wt.% PCA), showing individual CNTs being embedded between the aluminum particles

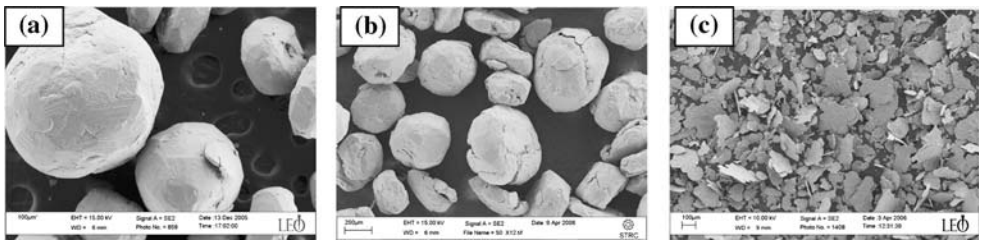


Fig. 9 2 wt.% CNT–Al after 12 h MA (**a**) with no PCA added, (**b**) with 0.1 wt.% PCA, (**c**) 0.7 wt.% PCA, showing flake morphology with addition of 0.7 wt.% PCA

control the particle size and morphology at low carbon nanotube contents, which is also the subject of ongoing research by the authors.

Conclusions

The results presented in this paper demonstrate that mechanical alloying is a promising technique for dispersing CNT in aluminum and controlling CNT–Al powder morphology and size. It also shows that MA time and CNT content can influence particle morphology and size. The use of process control agents such as methanol has been found to be beneficial in allowing reasonable particle sizes for low CNT content material to be attained with MA. The control of particle size is important for subsequent sintering/consolidation processes.

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