Materials and Design 58 (2014) 204–208

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

# Effect of solidification on microstructures and mechanical properties of carbon nanotubes reinforced magnesium matrix composite

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ARTICLE INFO

*Article history:*
Received 21 October 2013
Accepted 5 January 2014
Available online 23 January 2014

*Keywords:*
Carbon nanotubes
Microstructure
Mechanical properties
Solidification
Push
Capture

ABSTRACT

A novel approach was successfully developed to fabricate bulk carbon nanotubes (CNTs) reinforced Mg matrix composites. The distribution of CNTs in the composites depends on the solidification rate. When the solidification rate was low, CNTs were pushed ahead of the solidification front and will cluster along grain boundaries. When the solidification rate was high, CNTs were captured by the solidification front, so the CNTs remained inside the grain. Moreover, good interfacial bonding was achieved in the composite under high solidification rate. Meanwhile, compared with the matrix alloy, the ultimate tensile strength (UTS) and yield strength (YS) of the composite were significantly improved. The mechanical properties of the composite under higher solidification rate are better than composite under low solidification rate and the alloy. Moreover, most CNTs on the fracture surfaces were directly pulled out from the matrix. The Kelly–Tyson formula agreed well with the experimental tensile value in the composite under higher solidification rate, and the load-transfer efficiency is almost equal to 1.



## 1. Introduction

Carbon nanotubes (CNTs) are paid more attention as the ideal reinforcements for composites due to their extremely high Young's moduli and strength as well as low density. Their densities can be as low as 1.3 g/cm$^3$ and their Young's moduli are superior to all carbon fibers with values greater than 1 TPa [1]. The highest measured strength for a carbon nanotube was 63 GPa [2]. In the past decades, the main research efforts were focused on the CNT reinforced polymer matrix composites, and works on CNT reinforced metal matrix composites have been relatively rare, especially for magnesium [3,4]. Mg alloys are currently receiving considerable attention as structural materials in automotive, railway and aerospace industries because of their low density, high specific strength and stiffness [5]. The addition of CNTs not only can improve the mechanical properties of matrix, but also can maintain the low density of matrix [6–9]. Thus, it is very interesting to study CNTs reinforced Mg matrix composites.

To obtain good properties, it is important that the CNTs are well distributed and dispersed in the metal matrix composites. However, it is extremely difficult to disperse CNTs in metal melt since the CNTs can easily form clusters due to their high surface energy [10]. In addition, even if the CNTs distribute homogeneously in the melts, the clusters may be formed during the solidification process. Solidification process can significantly influence the CNTs distribution in the solidified composites. Solidification process influences the "push" and "capture" effect of the solidification front on the CNTs. The "push" effect of the solidification front on reinforcements causes the clusters at grain boundaries in the solidified composites even if CNTs distribute homogeneously in the melts. If the CNTs are captured inside grains during solidification, the solidified composites maintain the distribution of CNT in the melt. Therefore, it is necessary to control solidification process to eliminate or reduce the clusters in metal matrix composites. Some researchers have tried to capture these dispersed nanoelements into solidified grains [11,12]. However, most papers focus on the particles reinforced metal matrix composites, and few researches have been conducted on CNTs capturing during solidification of metal materials (including magnesium).

Therefore, the aim of the present work is to investigate the influence of solidification on the microstructures and mechanical properties of the CNTs reinforced magnesium matrix composites. Furthermore, the relationship between microstructure and strength of the composites is also discussed.

## 2. Experimental procedures

The Pure Mg ingot and pure Zn ingot were used as the starting materials. CNTs were synthesized using CVD by Chengdu Organic Chemistry Co. Ltd., China. The external diameter of the CNT is about 40–60 nm, and the length is below 2 μm. Moreover, the CNTs are seriously entangled together in the formation of clusters, as shown in Fig. 1.

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0261-3069/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.matdes.2014.01.015

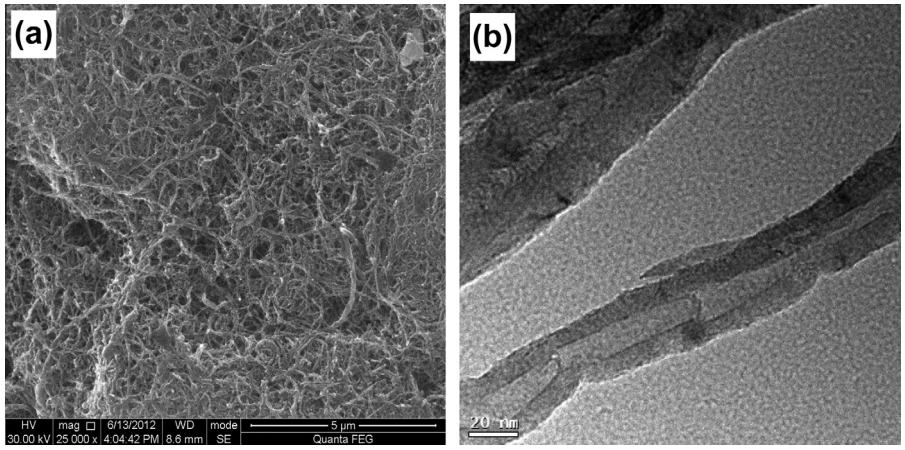


**Fig. 1.** (a) SEM image of raw CNTs. (b) TEM image of raw CNTs.

The chemical dispersant TNADIS (Chengdu Organic Chemistry Co. Ltd., China) was first dissolved in ethanol in a small beaker. Then CNTs (1.0 vol.% of the metal matrix, mass ratio to the organic dispersant 8:1) were added to the as-prepared solution. This mixture was put at room temperature into an ultra-sonic bath for 15 min. Then it was stirred for 30 min at 250 rpm. After adding 300 g magnesium chips, the suspension was further stirred at 250 rpm inside a fume cupboard to evaporate ethanol and homogenize the mixture.

About 640 g magnesium ingot was melted at 720 °C in $CO_2$ + $SF_6$ protective atmosphere, and then 60 g zinc ingot was added into the crucible. And then the melt was cooled down to 600 °C at which the matrix alloy was in semisolid condition. As the Mg chips coated with CNTs were quickly added into the semisolid alloy the melt was stirred in the protective atmosphere of $CO_2$ and $SF_6$ to avoid oxidation. The stirring rate was 800–1200 r/min and the stirring time was 10 min. After semisolid stirring for 10 min, the mixture of the melt and CNTs were rapidly reheated to 690 °C, and then the melt was ultrasonically processed at 500 W power level for 20 min before the ultrasonic probe was removed from the slurry. After the ultrasonic vibration, the mixture melt of the CNTs and the matrix alloy was poured into a preheated steel mold (375 °C) and allowed to solidify under 100 MPa pressure to obtain the composite ingots without porosity. The solidification rate is controlled by changing the thickness of the steel mold. The melt with the thicker mold will solidify faster than with the thinner one. The composite solidified at low rate was marked as A, while the one with the higher solidification rate was marked as B.

Scanning electron microscopy (SEM) (Quanta 200FEG, FEI Co.Ltd., USA) and transmission electron microscopy (TEM) (HR-TEM, Tecnai $G^2$ F30, USA) were used to study the microstructure of the matrix and the composite. The specimens for microstructure analysis were prepared by the conventional mechanical grinding, polishing and etching in the nitric acid. The specimens for TEM tests were prepared by grinding–polishing to produce a foil of 50 μm thickness and followed ion beam thinned. Tensile test was carried out at a tensile rate of 0.5 mm/min by Instron-1186 tension machine. The tensile properties of the samples were determined in accordance with ASTM: E8/E8M-13a standards. For each material, three samples with standard dog-bone shape were tested.

## 3. Results and discussion

### 3.1. Microstructures

Fig. 2 shows scanning electron microscopy (SEM) images of composite A. As shown in Fig. 2, it was found that most CNTs distributed along grain boundaries, moreover, individual CNTs and small clusters (white arrows) were observed. It should be noted that most CNT distributed along the grain boundaries.

Fig. 3 shows SEM images of the composite B. As shown in Fig. 3a and b, many "white spots" were observed at low magnification inside grains, and the "white spots" distributed uniformly. In addition, CNTs clusters were not observed. At the higher magnification, it was found that the "white spots" were composed by CNTs (white arrows), as shown in Fig. 3c. This proved that most CNTs were captured inside grains, and the distribution was homogeneous.

The distribution of reinforcement in cast composite is important because it influences the mechanical properties significantly. Subsequent deformation processes may modify the distribution, but the more uniform the reinforcement is in the initial as-cast billet, the more homogeneous will be the final composite will be.

Whether the distribution of CNTs in cast composites keep the distribution in the melt largely depends upon the interaction between CNTs and the solid/liquid interface of Mg matrix during solidification. During the solidification course of the Mg melt containing dispersed CNTs, a CNT will either be captured or pushed by the solid/liquid interface. In general, if the solid/liquid interfaces pushed the CNTs, CNTs tended to aggregate in the last solidified regions, such as grain boundaries, as shown in Fig. 2. If the solid/liquid interfaces captured CNTs, the as-cast composites can

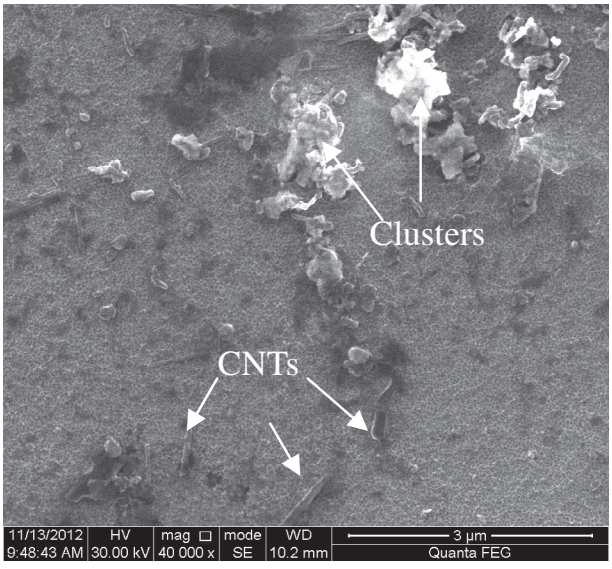


**Fig. 2.** SEM images of the CNT distribution in sample A.