

## Fabrication of carbon nanotubes reinforced AZ91D composites by ultrasonic processing

LIU Shi-ying(刘世英)<sup>1,2</sup>, GAO Fei-peng(高飞鹏)<sup>1,2</sup>, ZHANG Qiong-yuan(张琼元)<sup>1,2</sup>,  
ZHU Xue(朱 雪)<sup>1,2</sup>, LI Wen-zhen(李文珍)<sup>1,2</sup>

1. Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China;  
2. Key Laboratory for Advanced Materials Processing Technology of Ministry of Education,  
Tsinghua University, Beijing 100084, China

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**Abstract:** Magnesium matrix nanocomposite reinforced with carbon nanotubes (CNTs/AZ91D) was fabricated by mechanical stirring and high intensity ultrasonic dispersion processing. The microstructures and mechanical properties of the nanocomposite were investigated. The results show that CNTs are well dispersed in the matrix and combined with the matrix very well. As compared with AZ91D magnesium alloy matrix, the tensile strength, yield strength and elongation of the 1.5%CNTs/AZ91D nanocomposite are improved by 22%, 21% and 42% respectively in permanent mold casting. The strength and ductility of the nanocomposite are improved simultaneously. The tensile fracture analysis shows that the damage mechanism of nanocomposite is still brittle fracture. But the CNTs can prevent the local crack propagation to some extent.

**Key words:** carbon nanotube; magnesium alloy; composite; ultrasonic processing

### 1 Introduction

Due to the increasing demand on lightweight materials in automotive and aerospace applications, magnesium and its alloys have gained widespread attention in scientific research and commercial application. But the mechanical properties of magnesium limit its application at elevated temperatures. In order to cover the deficiencies in mechanical properties of magnesium, efforts have been made to develop Mg metal matrix composites due to their promising advanced properties[1–6].

Since the discovery by IJIMA[7] in 1991, carbon nanotubes (CNTs) have been the subject of intense research efforts aimed at both characterizing and understanding their remarkable mechanical, electrical and thermal properties. In recent years, there has been a steadily increasing interest in the development of CNTs reinforced composites. Polymer[8], ceramic[9], and metal[10–15] are favorably considered as matrix materials. The research efforts have focused on CNTs reinforced polymer based composites and only limited research has been done on CNTs reinforced metal

composites. CHOI et al[10] processed and characterized aluminum matrix composites with multi-wall carbon nanotubes as reinforcements. The tensile yield and ultimate strength of composite increased to 90% with 2% (mass fraction, the same below if not mentioned) addition of CNTs. SHIMIZU et al[11] fabricated 1.0% CNTs reinforced magnesium alloy composites by vacuum hot-press and extruding processes. GOH et al[12] and GEORGE et al[13] fabricated magnesium and aluminium composites using CNTs as reinforcement by powder metallurgy technique.

The main problems for CNTs reinforced metal composites are to disperse each of CNTs separately in the matrix and develop a tight interface between CNTs and the matrix. ZHANG et al[14] fabricated carbon nanotube/magnesium matrix composite by melt stirring. But the dispersion of CNTs in the Mg matrix was still uneven. LI et al[15] applied a two-step process to disperse CNTs in magnesium alloy. In the first stage, a block copolymer was used as a dispersion agent to pre-disperse CNTs on Mg alloy chips. Then, the chips with the well dispersed CNTs on their surface were melted and at the same time vigorously stirred. Using a two-step process can well disperse CNTs in the matrix,

but this technique is difficult to carry out. Accordingly, the primary aim is to obtain highly dispersive CNTs reinforced magnesium composites. Thus, composites have high mechanical properties. In this study, the mechanical stirring and high-intensity ultrasonic processing was used to fabricate 1.5%CNTs reinforced magnesium alloy composite. The microstructures and mechanical properties of the CNTs/AZ91D composites were investigated.

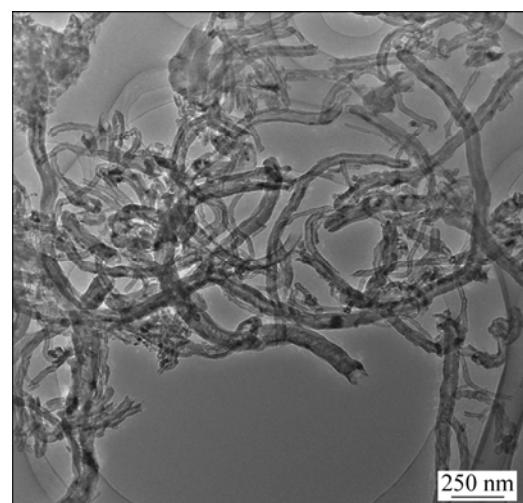
## 2 Experimental

The magnesium matrix composites with 1.5%CNTs were fabricated by mechanical stirring and high-intensity ultrasonic dispersion method. The matrix material was Mg-Al-Zn alloy ingot (AZ91D). The chemical composition of the matrix alloy is listed in Table 1. The reinforcement material was multi-wall carbon nanotubes with greater than 95% purity and outer diameter in the range of 20–40 nm and length in the range of 1–5  $\mu\text{m}$ . Fig.1 shows a transmission electron microscopy image of CNTs. The CNTs were not processed such as purification or surface coating. Steps involved and the procedure employed for the fabrication of composites are as follows: the melting was carried out using a resistance heating furnace. A clay-graphite crucible with 130 mm in inner diameter and 180 mm in height was used to melt magnesium alloy. About 2 kg AZ91D was melted in clay-graphite crucible. In order to avoid oxidation and burning of the magnesium alloy, the magnesium melt was protected by  $\text{CO}_2+0.2\%\text{SF}_6$  (volume fraction). When the alloy was completely melted, the mechanical stirring was applied and CNTs were added into the stirring vortex. The stirring speed was 300–500 r/min and the stirring time was about 2 min. In order to disperse better CNTs within the matrix, a high-intensity ultrasonic wave with a 20 kHz, a maximum 1.4 kW power output and a titanium alloy waveguide of 40 mm in diameter was used for processing CNTs/AZ91D melt. The ultrasonic processing time was 15 min and the ultrasonic probe was dipped into the melt for about 35 mm. After ultrasonic processing, the composite melt was heated to 700 then cast into a steel permanent mould (preheated to 250–300  $^{\circ}\text{C}$ ). For comparison, the samples without CNTs were prepared without mechanical stirring and ultrasonic processing.

**Table 1** Chemical composition of AZ91D Mg alloy (mass fraction, %)

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
8.5–9.5	0.45–0.9	> 0.17	0.05	0.015	0.001	0.04	Bal.

Both unreinforced AZ91D and 1.5%CNTs/AZ91D composite test bars in the as-cast state were cut into various specimens for the following analyses. The tensile tests were carried out by an SANS machine at a strain rate of 2 mm/min at room temperature. The distributions of the CNTs and individual elements in the composite phases were investigated with a scanning electron microscope (FEI Siron200 SEM), equipped with an EDS detector. The metallographic microstructures were observed with Zeiss Axio Imager A1m microscope. The samples were polished and etched at room temperature for 5 s using a solution of 0.5% glacial acetic acid, 75% ethanol and 24.5% distilled water (volume fraction). For TEM analysis, nanocomposite samples of 3 mm discs were cut, mechanically ground, and finally ion polished by Gatan 691 precision ion polishing system.



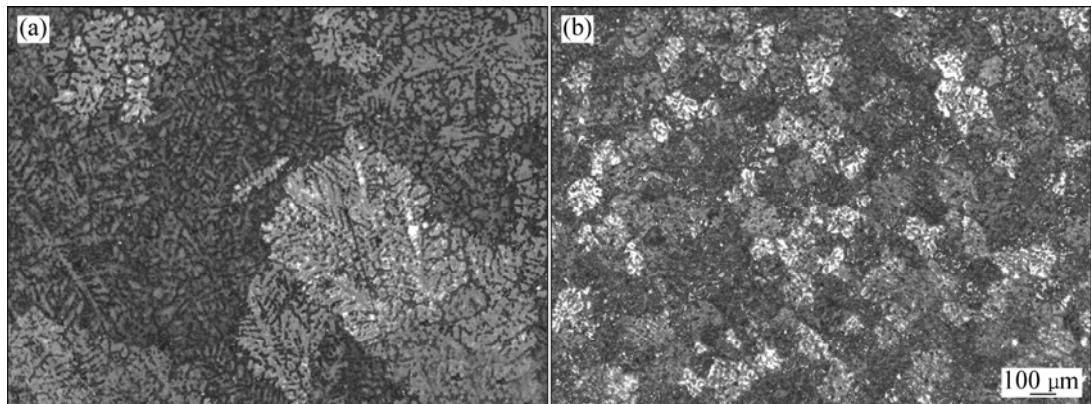
**Fig.1** TEM image of CNTs

## 3 Results and discussion

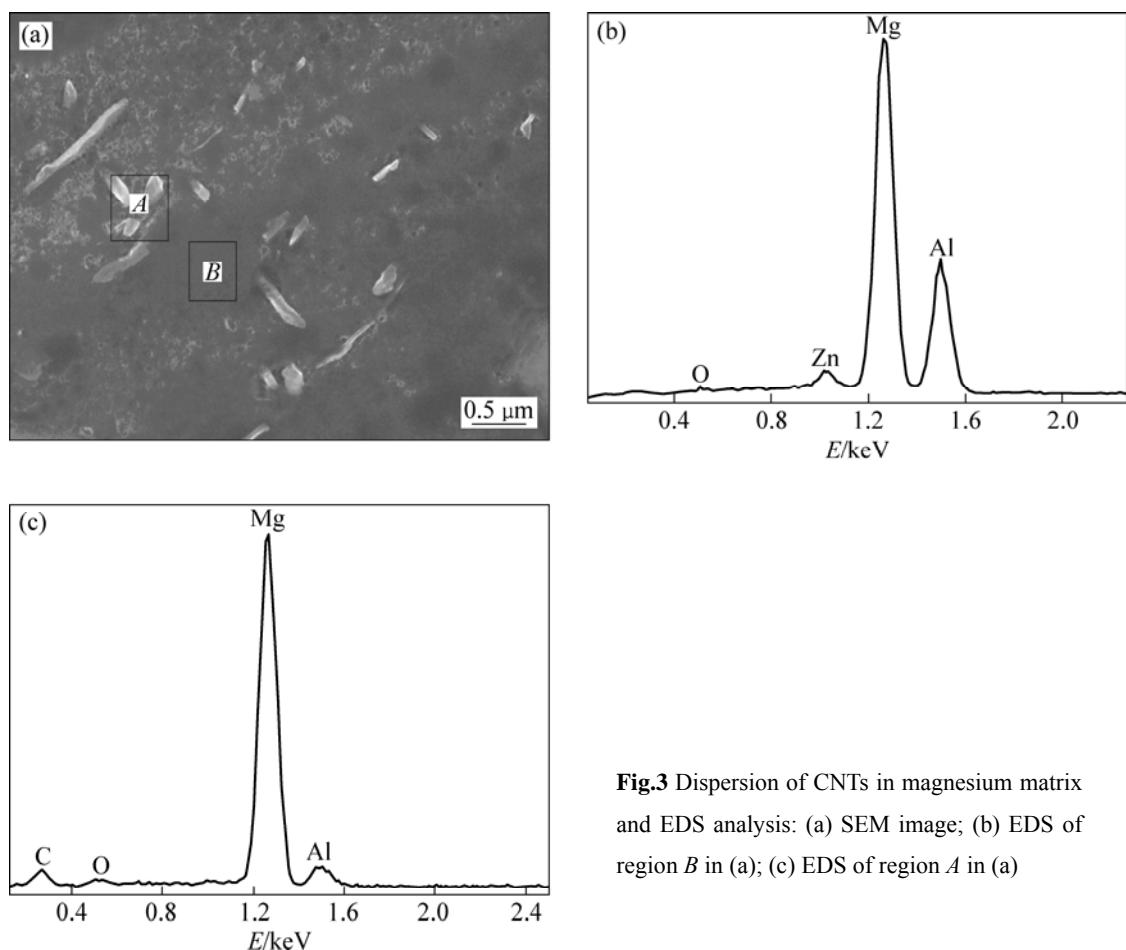
### 3.1 Microstructures

Fig.2 shows the typical microstructures of as-cast AZ91D and 1.5%CNTs/AZ91D composite. The granular structure is made visible by the color contrast between adjacent grains. The dendritic structure enclosed within grains is also revealed by etching[16]. It can be seen that the grain size of CNTs/AZ91D was refined due to the addition of CNTs. Compared with AZ91D alloy without ultrasonic processing, the average grain size of 1.5%CNTs/AZ91D is reduced by 72%. The microstructure of the as-cast AZ91D alloy consists of primary  $\alpha$ -Mg and eutectic phase  $\beta$ - $\text{Mg}_{17}\text{Al}_{12}$ , in which the large-sized  $\alpha$ -Mg dendrite will reduce the mechanical properties of alloy. After adding CNTs, however, the large-sized dendritic structure is obviously refined.

Fig.3(a) shows the distribution and dispersion of CNTs in the AZ91D matrix. It can be seen that CNTs are



**Fig.2** Microstructures of AZ91D (a) and 1.5%CNTs/AZ91D (b) (light micrograph using polarized light)



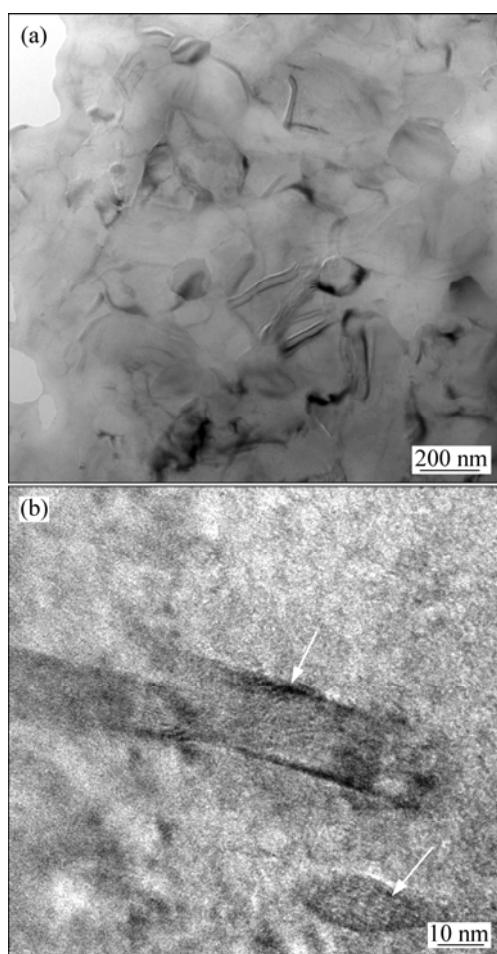
**Fig.3** Dispersion of CNTs in magnesium matrix and EDS analysis: (a) SEM image; (b) EDS of region B in (a); (c) EDS of region A in (a)

well distributed and dispersed without clusters in the matrix. The EDS was used to determine the chemical composition of regions *A* and *B*. In region *A*, the *C* peak can be seen clearly, which indicates that there are CNTs. The wettability is bad between molten magnesium and graphite, and the contact angle is larger than 90°[17]. It is difficult to add CNTs into magnesium melt. The effective range of high-intensity ultrasonic is limited due to its frequency and swing, and it is weak on the surface of melt. Therefore, in this study, mechanical stirring was

used to stir CNTs into magnesium melt. The homogeneous distribution and dispersion of CNTs may be attributed to the function of the high-intensity ultrasonic. The high-intensity ultrasonic can generate non-linear effects in melts, namely, acoustic cavitation and acoustic streaming. Acoustic streaming, a liquid flow due to acoustic pressure gradient, is very effective for stirring[5]. Acoustic cavitations can produce an implosive impact strong enough to destroy the solid surface[6]. Acoustic cavitations can break up the

clustered particles and disperse them more uniformly in the melts. So, the nanocomposite with CNTs homogeneously dispersed in the matrix is the result of cooperative effects of acoustic cavitations and high speed acoustic streaming in AZ91D alloy melt.

As shown in Fig.4(a), CNTs are dispersed well in the AZ91D matrix and no clusters of CNTs are found. Most of CNTs are embedded in the matrix and are stable, which can strengthen the composite. But the outer diameter and length of CNTs are not homogeneous. It can also be seen from TEM image of CNTs, as shown in Fig.1. Fig.4(b) shows the high magnification micrograph of the CNTs/AZ91D interface. CNTs bond well with matrix without forming an intermediate phase.



**Fig.4** TEM images of 1.5%CNTs/AZ91D: (a) Low magnification; (b) High magnification

### 3.2 Mechanical properties

It can be seen from Table 2 that CNTs bring out good strengthening effects on magnesium alloy. As compared with AZ91D magnesium alloy matrix, the tensile strength, yield strength and elongation of the 1.5%CNTs/AZ91D nanocomposite are improved by 22%, 21% and 42% respectively in permanent mould casting. The strength and ductility of the nanocomposite are

improved simultaneously. This is different from what is observed when using traditional reinforcements such as micro-sized particles and fibers[18]. In this study, CNTs are well dispersed in the matrix. The interface of them is stable without bad interface reaction and the interface bonding strength of them is high. High elastic modulus and good plasticity make CNTs cause elastic deformation in order to fit the deformation of matrix during stretching, which improves the strength and ductility of the nanocomposite.

**Table 2** Tensile properties of as-cast AZ91D and 1.5%CNTs/AZ91D at room temperature

Material	UTS/MPa	YS/MPa	E/GPa	$\delta/\%$
AZ91D	128.3	86.0	44.3	0.90
1.5%CNTs/AZ91D	157.0	104.0	64.3	1.28

The fracture surfaces of the matrix and 1.5%CNTs/AZ91D composite are shown in Fig.5. The fracture analysis of them reveals the intrinsic mechanisms governing failure to be essentially brittle. The whole tensile fracture surfaces are mixed into dimple and cleavage, as shown in Figs.5 (a) and (b). The fracture mechanism is controlled by defects in the material. The fracture type is decided by the production and growth of micro-cracks near defect. The dendrite can be seen in whole fracture and there are many gaps between the dendrite, which cannot bear the force when material is stretched.

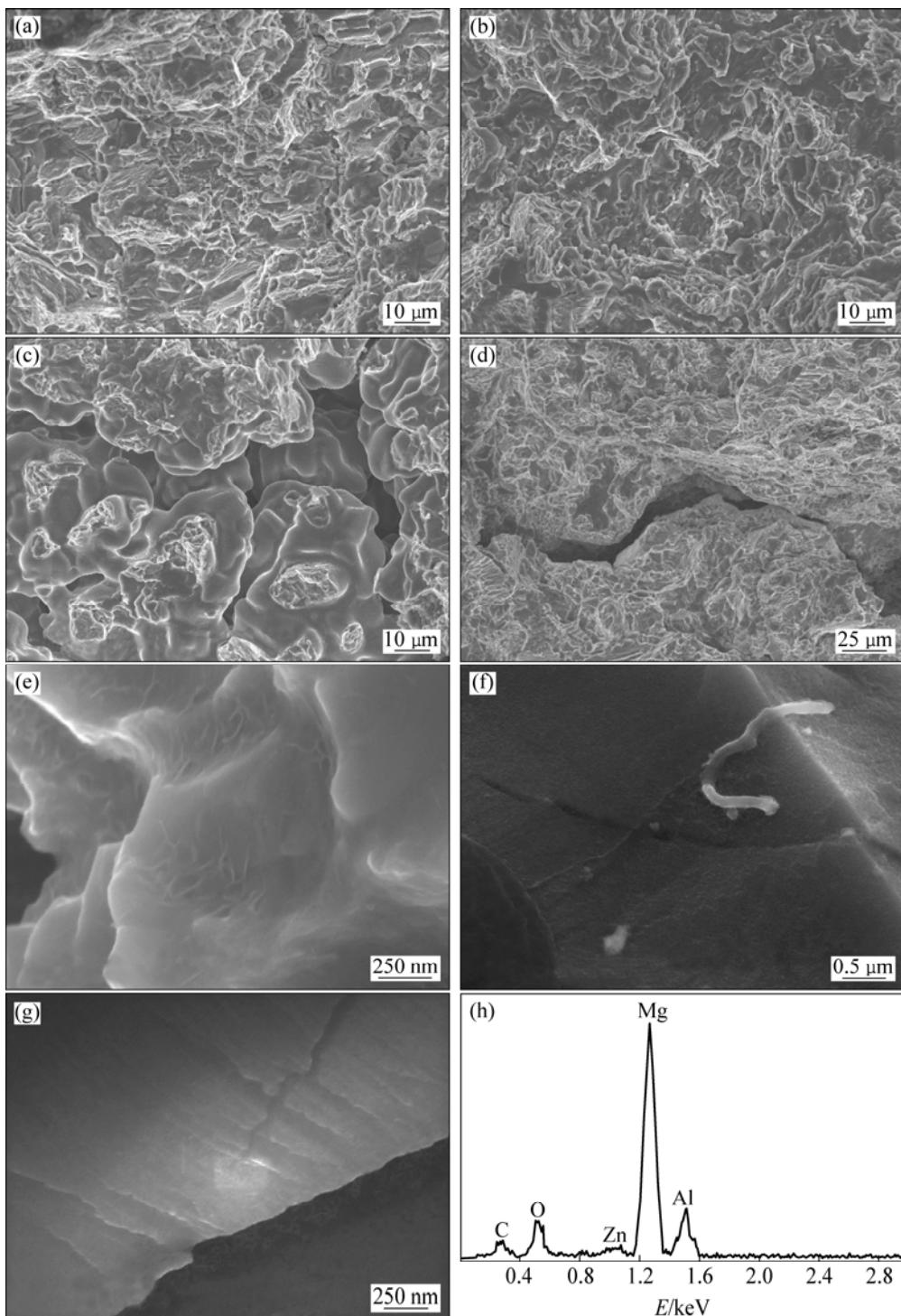
The CNTs added into the matrix can play bridging effects in crack, as shown in Fig.5(e), which can increase the resistance of crack propagation. The CNTs can prevent the local crack propagation to some extent, as shown in Fig.5(g). The CNTs bond well with the magnesium matrix and the interface of them can seldom separate during composite stretching. The dispersion of CNTs in the matrix is random and there is few pulled out and the pulled length is short, as shown in Fig.5(f).

## 4 Conclusions

1) The magnesium matrix composites containing 1.5%CNTs were fabricated by mechanical stirring and high-intensity ultrasonic dispersion method.

2) The microstructural analyses show that high-intensity ultrasonic wave can be used to disperse CNTs in matrix uniformly. And the grain can be refined to some extent. The CNTs combine with the magnesium matrix very well.

3) The mechanical properties can be significantly improved and the strength and ductility of the nanocomposites are improved simultaneously. The



**Fig.5** SEM images of fracture surface: (a) AZ91D; (b) 1.5%CNTS/AZ91D; (c), (d) Dendrite and crack on fracture surface; (e), (f) Dispersion of CNTs on fracture surface; (g) CNTs preventing local crack propagation; (h) EDS of (g)

tensile fracture analysis shows that the damage mechanism of nanocomposites is still brittle fracture. But the nano-sized reinforcements can prevent the local crack propagation to some extent.

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