New practical method of homogeneous dispersion of multi-walled carbon nanotubes (MWCNTs) into Mg matrix composites

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Abstract. It is difficult to disperse multi-walled carbon nanotubes (MWCNTs) into Mg matrix composites homogeneously due to the high specific surface energy between MWCNTs. This would affect the mechanical properties of magnesium matrix composites reinforced by MWCNTs tremendously. The key is to overcome MWCNTs aggregate together, and gain the homogeneous dispersion of MWCNTs. Moreover, the density difference of Mg matrix and MWCNTs is another problem which prevents MWCNTs from dispersing homogeneously into Mg matrix composites. In order to solve these problems, a new practical method of homogeneous dispersion of carbon nanotubes into Mg matrix composites was presented basing on combination the tow step ball milling and ultrasonication dispersion methods. First, a certain amount of MWCNTs was ball-milled in ethanol solution contain 5 wt.% sodium stearate at various rotation speeds (100 rpm-300 rpm) and ball-milled times (0.5 H-2 H) to break MWCNTs hard aggregation. Second, MWCNTs which were subjected to the ball-milling were dispersed further in ethanol solution containing (SDS, DBS) using ultrasonication method. Third, the Mg powers were mixed with good dispersion of carbon nanotubes solution and ball-milled for 1 H to make MWCNTs coated uniformly on the surface of the magnesium substrate. The results were mainly examined by field emission scanning electron microscopy (SEM). It was found that MWCNTs were dispersed well and some of these MWCNTs had directional arrangement. Furthermore, MWCNTs were homogeneously dispersed into Mg matrix composites. These results suggest that this method has good application for magnesium matrix composites reinforced by carbon nanotubes.

Keywords: MWCNTs, Mg matrix composites, dispersion, tow step ball milling

1. Introduction
The investigations for Mg matrix composites reinforced by MWCNTs have been carried out extensively on the account of its remarkable mechanical properties [1-3]. Although, the mechanical properties of composite materials are improved, there is great difference between experiment and expected results. The main reasons for this phenomenon are the aggregation of MWCNTs and non-uniform distribution of MWCNTs into Mg matrix. In order to overcome these problems, some researchers try to apply powder metallurgy method to disperse MWCNTs into metal matrix which is a more conventional method to prepare desired ratio materials [4-7], and other researchers used the
solution containing zwitterionic surfactant isopropyl alcohol to transfer CNTs onto the powders surface [8]. However, single process couldn’t meet the demand of dispersion MWCNTs uniformly into Mg matrix. Thus, multi-step methods such as mechanical stirring and high-intensity ultrasonic dispersion methods were taken into consideration by some researchers [9-10]. Unfortunately, a little achievement has been obtained on the uniform dispersion of MWCNTs into Mg matrix because of higher specific surface energy between MWCNTs clusters and the density difference between Mg matrix and MWCNTs. Consequently, the homogeneous dispersion of high volume fractions of MWCNTs into Mg matrix has not been achieved yet.

Ball milling is effective way to break the hard agglomeration of MWCNTs with the aid of grinding agent in semi-wet environment [11-12]. In this paper, a practical method was developed which combined semi-wet ball milling and ultrasonic dispersion methods with the aids of dispersing agent (SDS, SDBS) in absolute ethyl alcohol environment, then the dispersed MWCNTs were adsorbed onto the surface of Mg powers uniformly by secondary ball milling process in absolute ethyl alcohol environment. Moreover, the effect of dispersing agent (SDS, SDBS) and ball milling condition( ball-milled time and rotation speed) on the dispersion of MWCNTs were investigated and discussed basing on the analysis of dispersion characteristics of MWCNTs by field emission scanning electron microscopy (SEM).

2. Experiment
Multwall carbon nanotubes (MWCNTs) with 40-60 nm in diameter, 97% in purity and 5-μm in length were supplied by Shenzhen Nanotech Port Co Ltd. The surfactant agents of sodium dodecyl sulfate sodium salt (SDS), sodium dodecyl benzene sulfonate(SDBS) and the grinding-aids of sodium stearate which are analytical purity were used to prevent MWCNTs from aggregating, magnesium powders is also analytical purity (99.5%, 100μm).

2.1. MWCNTs dispersion procedure
0.5g MWCNTs mixed with 5 wt.% sodium stearate were placed in 200 ml nylon mixing jars which contained 20 zirconia balls and 20 ml absolute ethyl alcohol. The diameter of balls is 4, 8, 10 mm respectively, and the number of different diameter balls is 4, 6, 10 accordingly. The mixtures were ball milled by planetary ball mill (BXQM-2L, Nanjing, China) at 100-300 rpm for milling time changing from 0.5 H to 2 H. The samples were ball-milled for 2 min at 2 min intervals in order to prevent absolute ethyl alcohol from volatilizing during ball milling process. Subsequently, further dispersion treatment of ball-milled MWCNTs was performed using ultrasonic dispersion method at a frequency of 40 KHz for 1.0 H in absolute ethyl alcohol containing certain mount of SDS (0.5 g/L) and SDBS (0.5 g/L) respectively.

2.2. MWCNTs dispersion in Magnesium matrix procedure
For the purpose of dispersion MWCNTs homogeneously into magnesium matrix, magnesium powder was ball-milled with the dispersed MWCNTs in anhydrous ethanol environment on condition of the ball milling rotary speed of 100 rpm and milling time of 1 H. Then, the samples were compacted into 20 mm diameters and 10 mm height under the pressure of 20 MPa by a cold isostatic press. Moreover, the homogeneous dispersion of MWCNTs and MWCNTs into magnesium matrix were mainly characterized by field emission scanning electron microscopy (SEM) analysis.

3. Results and discussion
The original morphology of MWCNTs which were used in this paper is shown in figure 1(a). It can be observed that smaller and larger diameters of MWCNTs are tangled around each other. In order to break the MWCNTs hard aggregation, carbon nanotubes were subjected to medium energy level ball milling with the ball milling rotary speed of 100-300 rpm and milling time of 0.5-2 H in absolute ethyl alcohol environment containing 5 wt.% sodium stearate. It can be seen that MWCNTs were dispersed further. In addition, the length of MWCNTs was shortened when the ball milling rotation speed was
Figure 1. (a) original carbon nanotubes; (b), (c), (d) are the dispersion of MWCNTs with the ball-milled condition of 100, 200, 300 rpm, and the milling time of 0.5 H in absolute ethyl alcohol containing 5 wt% sodium stearate respectively; (e), (f) are the dispersion of MWCNTs with the ball-milled condition of 200 rpm, and the milling time of 1.0, 2.0 H in absolute ethyl alcohol containing 5 wt% sodium stearate respectively.

up to 200 rpm which are shown in figure 1(b)-1(c), the diameter of MWCNTs become larger, and aggregated together again as the ball milling rotation speed up to 300rpm which is shown in figure 1(d). This suggested that moderate ball milling rotation speed is required for ball milling process of MWCNTs dispersion. Moreover, it is interesting to observe that some MWCNTs have directional alignment which is shown in figure 1(b). Figure 1(e) and figure 1(f) show the morphology of MWCNTs variation along with ball milling time, longer ball milling time could increase the diameter of carbon nanotubes and lead to MWCNTs aggregation again. Therefore, short ball milling time process is more effective on carbon nanotubes dispersion in absolute ethyl alcohol environment containing 5 wt% sodium stearate.

Figure 2 shows the effect of ball milling on the dispersion of MWCNTs in liquid environment containing 5% sodium stearate + absolute ethyl alcohol, SDS (0.5g/l) + absolute ethyl alcohol and
SDS (0.5g/l) + deionized water respectively. It can be seen that some MWCNTs show oriented distribution, and it is evidently observed that MWCNTs were dispersed well. This means that ball milling could break the hard agglomeration of MWCNTs with the aid of 5% sodium stearate + absolute ethyl alcohol. The reason for this could be that the specific surface energy of the carbon nanotubes was reduced due to the adsorption of sodium stearate in absolute ethyl alcohol environment [13]. Obviously, single ball milling process couldn't meet the complete dispersion of carbon nanotubes.

In order to obtain homogeneous dispersion of MWCNTs which were ball-milled by the above process were dispersed further using ultrasonic dispersion method. As figure 3 shown, ball milling rotary speed and disperse agents have different effects on MWCNTs dispersion. Compared with the rotation speed of 200 rpm and 300 rpm, there was no aggregation phenomena when the rotation speed was 100 rpm during ultrasonic dispersion process in absolute ethyl alcohol solution which are shown in figure 3(a), figure 3(b), and figure 3(c) respectively. Similar results were observed during ultrasonic dispersion process in absolute ethyl alcohol + SDS (0.5 g/l) solution, which are presented in figure 3(d), figure 3(e) and figure 3(f) respectively. However, the difference is that MWCNTs were distributed more uniformly when the rotation speed was 100 rpm in absolute ethyl alcohol + SDS (0.5g/l) solution as figure 3(a) and figure 3(d) shown. The main reason for this may be that the specific surface energy of MWCNTs was decreased because of the absorption of SDS on the surface of MWCNTs [15]. It was found that some of the MWCNTs were shortened and intertwined together once more obviously on the account of higher rotation speed of 300 rpm which are shown in figure 3(c) and figure 3(f).

SDBS was used for better dispersion of MWCNTs on the condition of 300 rpm. Figure 4 shows the effect of SDBS on the dispersion of MWCNTs which were subjected to ball milling process on the ball-milled condition of 300 rpm, and 0.5 H-2 H in 5% sodium stearate + absolute ethyl alcohol solution and then were ultrasonic dispersed in absolute ethyl alcohol + SDBS (0.5g/l) solution. It suggested the re-aggregation of MWCNTs were completely broken up with the aids of SDBS. Furthermore, some MWCNTs present oriented distribution which is shown in figure 4(c).

Based on the above dispersion treatment of MWCNTs, homogeneous dispersion MWCNTs have been obtained, secondary ball milling process was carried out for the mixture of MWCNTs into
magnesium powder with the ball milling rotation speed of 100 rpm and ball mill time of 1 H in absolute ethyl alcohol environment. It is evidently found that MWCNTs were uniformly distributed into Mg matrix composites with the content of MWCNTs up to 2 wt.% which are shown in figure 5(a) and figure 5(b). The present results would provide a promising way to prepare Mg matrix composites reinforced by MWCNTs with higher content of MWCNTs.

Figure 3. The dispersion of MWCNTs with the ball-milled condition of 100, 200, 300 rpm, and the milling time of 0.5 H in absolute ethyl alcohol containing 5 wt% sodium stearate, ultrasonic dispersion time is 1.0 H in absolute ethyl alcohol in (a), (b), (c); and ultrasonic dispersion time is 1.0 H in absolute ethyl alcohol containing SDS (0.5g/l) in (d), (e), (f) respectively.

The dispersion mechanism of carbon nanotubes is discussed as follows: first, sodium stearate was completely dissolved in alcohol and adsorbed onto MWCNTs which may lead to reduce the zeta potential of MWCNTs [13]. Then, the surfactant agent SDS or SDBS were adsorbed onto MWCNTs to overcome van der Waals force between carbon nanotubes for MWCNTs dispersion furtherly [14]. Due to the adsorption of surfactants onto the surface of MWCNTs, the bind energy between MWCNTs was also decreased with the respect to the adsorption density of SDS increasing [15]. This may result in the orientation arrangement of MWCNTs which are shown in figure 2(b), figure 3(a), figure 3(d) and figure 4(c). Therefore, It is reasonable to concluded that the dispersion of MWCNTs was greatly improved by the adsorption of sodium stearate and surfactants (SDS or SDBS), which are evidently observed in figure 3(d) and figure 4.
4. Conclusions
A practical method have been developed to disperse MWCNTs into Mg matrix composites homogeneously with higher content of MWCNTs by combining two step high-energy ball milling and ultrasonic dispersion processes in wet environment. The following conclusions were obtained:

The aggregation of MWCNTs was completely broken up by wet-ball milling in 5% sodium stearate + absolute ethyl alcohol environment on the ball-milled condition of 100 -200 rpm and the milling time of 0.5 H. The dispersing agents (SDS, SDBS) have great effect on the further dispersion of MWCNTs in absolute ethyl alcohol using ultrasonic dispersion method. Furthermore, some of MWCNTs present oriented arrangement. The secondary wet ball milling process was contributed to obtain Mg matrix composites containing higher mass fraction of MWCNTs.

Acknowledgements
Thanks are given to the Dr. Start-up fund of Xi’an University of Science and Technology (2014QDJ067), and the Scientific research cultivated fund of Xi’an University of Science and Technology (201602).

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