ENHANCED DUCTILITY WITH SIGNIFICANT INCREASE IN STRENGTH OF AS-CAST CNTs/AZ91D NANOCOMPOSITES

Rongyu Feng[1], Lin Zhu[2], Wenzhen Li[1]

[1]School of Materials Science and Engineering (Tsinghua University, Beijing100084, China)
[2]Tsinghua-Foxconn Nanotechnology Research Center (Tsinghua University, Beijing 100084, China)

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Abstract

This paper was focused on significantly increasing the ductility and strength of as-cast CNTs/AZ91D nanocomposites by solid solution (T4) and aging treatment (T6). The CNTs/AZ91D nanocomposite fabricated by permanent gravity casting assisted with ultrasonic processing was subject to as-cast, T4 and T6 treatment and the mechanical properties were tested. The results showed that the ductility and the tensile strength of the nanocomposites after T4 treatment were increased by 23.8 percent and 82.8 percent compared with the as-cast properties. After T6 treatment, the tensile strength and especially the yield strength of the nanocomposites was increased by 26.2 and 17.6 percent, while its ductility was still increased by 20.7 percent. The strengthening and toughing mechanisms of the nanocomposites were discussed based on the microstructure characterization results.

Introduction

Stir casting is an effective way for batch production of magnesium matrix nanocomposites. However the as-cast strength and toughness of magnesium matrix nanocomposites produced using this method are usually unsatisfactory. Though better performance can be achieved by subjecting the cast magnesium matrix nanocomposite to heavy plastic deformation [1], this method only applies to those parts having simple shapes. The existed studies have given little attention to whether heat treatment can be used to strengthen and toughen the magnesium matrix nanocomposites. In this paper, the stirring casting and high-energy ultrasonic dispersion method were used to prepare the as-cast AZ91D composite reinforced with CNTs and the research was focused on increasing the ductility and strength of as-cast CNTs/AZ91D nanocomposites by solid solution (T4) and aging treatment (T6). The strengthening and toughing mechanisms were analyzed through microstructure characterization.

Experimental Procedures

Preparation and Heat Treatment of CNTs/AZ91D Composites

AZ91D magnesium alloy was selected as matrix alloy with composition of 8.0-9.0wt.%Al, 0.50-0.90wt.%Zn, 0.15-0.40wt.%Mn and balanced Mg. The 1.5wt%CNTs with the mean diameter of 40 nm was used as reinforcing filler. The CNTs/AZ91D composites were prepared using semi-solid mechanical stirring and high intensity ultrasonic composite dispersion method as the processing

described in other work [2].

The box-type resistance furnace with temperature control was used for heat treatment. For solid solution treatment (T4), the composite samples were heated to 688K and held for 24 hours, and then quenched in 343K hot water. For artificial aging (T6), the T4 treated composite samples were heated to 473K and held for 16 hours, then air-cooled to room temperature. The sample for heat treatment was 4 mm-thick rectangular tensile test specimen machined in accordance with GB/T228-2002, and the heat treatment was conducted with the protection of CO_2 gas.

Mechanical Property Test and Microstructure Characterization

The tensile tests were done on the SANS 4105 electronic universal testing machine. The gage length, width and thickness of rectangular specimen are 25 mm, 6 mm and 4 mm respectively. The tensile speed was set at 0.5 mm/min. Each group of data was obtained by testing five pieces of tensile test specimen and then averaged the measured values.

Metallographic specimen was ground and polished on the Buehler automatic grinding and polishing machine, and then eroded with 1vol.% nital. The Zeiss-Axio Imager.A 1m optical microscope (OM) was used to observe the microstructure at the different processing conditions. The FEI-Siron200 field emission scanning electron microscopy (FESEM) with energy disperse spectroscopy (EDS) was used to show the effects of CNTs on the morphology of precipitates after heat treatment. The TECNAI G2 F20 transmission electron microscopy (TEM) was used to characterize the interface and distribution of CNTs and the deformation mechanism of the nanocomposites.

Results and Discussions

Mechanical Properties of CNTs/AZ91D Composites after Heat Treatment

After the solid solution treatment (T4), the tensile strength and elongation after fracture of CNTs/AZ91D were improved by 23.8% and 82.8% to 260MPa and 10.6%, respectively, compared with the composites in their as-cast condition. After the aging treatment (T6), the yield strength and tensile strength of composites were further improved. In contrast to the solid solution state (T4), the elongation after fracture decreased, but remained greater than that in the as-cast condition. After the aging treatment (T6), the yield strength, tensile strength and elongation after fracture of CNTs/AZ91D were improved by 17.6%, 26.2% and 20.7% to 140MPa, 265MPa and 7.0%, respectively, compared with those in the as-cast condition (see Figure 1).

Microstructure of CNTs/AZ91D Composites after Heat Treatment

The XRD results shows that the structure of composites in the as-cast condition was mainly composed of two phases - α-Mg and β-$Mg_{17}Al_{12}$; after the solid solution treatment (T4) of composites, the eutectic phase β-$Mg_{17}Al_{12}$ in the gravity casting condition was almost dissolved into α-Mg completely and the single supersaturated α-Mg solid solution phase was then formed; after the aging treatment (T6), the β-$Mg_{17}Al_{12}$ which had been dissolved in solid solution during T4 treatment was precipitated again to form the precipitated phase (see Figure 2).

The grain images of AZ91D and CNTs/AZ91D composite after solid solution treatment (T4) were obtained through OM under polarized light. The grains of composites with CNTs after T4 treatment was significantly decreased (see Figure3). The MIAPS software attached to Zeiss

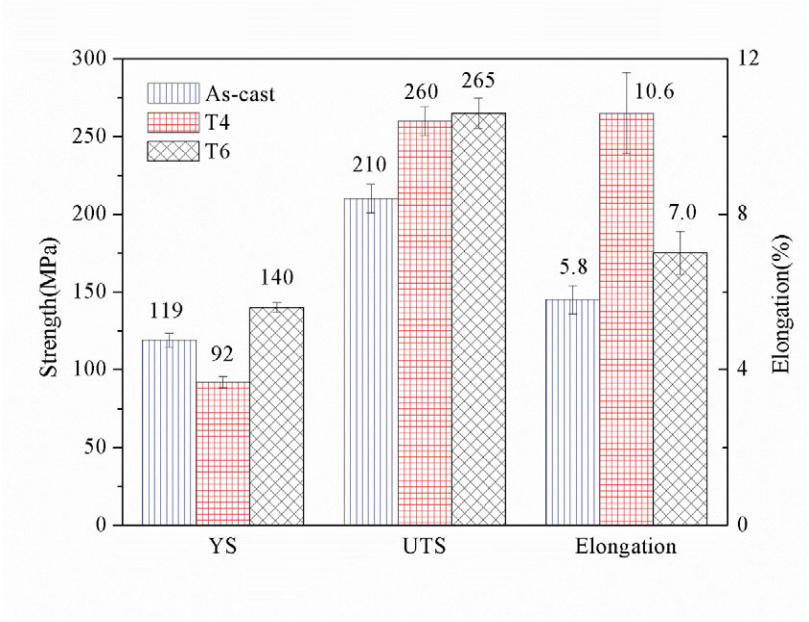

Figure 1. Mechanical properties of CNTs/AZ91D composite at different heat treatment conditions

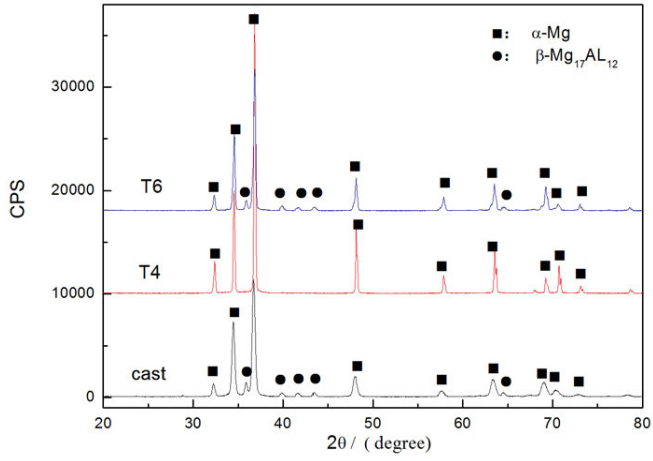

Figure 2. XRD patterns of CNTs/AZ91D composites at different heat treatment conditions.

microscope was applied to measure the grain size. The results showed that the grain size of AZ91D was 205μm (see Figure 3 (a)) while that of CNTs/AZ91D was 75μm (see Figure 3 (b)).

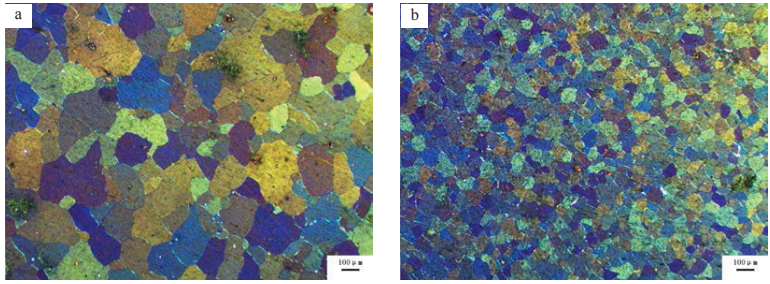

Figure 3. OM images of AZ91D-T4 (a) and CNTs/AZ91D-T4 (b)

The microstructures of CNTs/AZ91D composites after the aging treatment (T6) were analyzed with SEM (see Figure 4). The discontinuous lamellar or cellular β-$Mg_{17}Al_{12}$ was precipitated near the grain boundary, and the continuous precipitation of β-$Mg_{17}Al_{12}$ phase occurred inside the grain (see Figure 4 (a)). The initial stage of aging was dominated by discontinuous precipitation. Lamellar β-$Mg_{17}Al_{12}$ phase was first precipitated and grew at grain boundary. In the later stage of aging, the precipitation mainly occurred inside the grain, and the β-$Mg_{17}Al_{12}$ phase was continuously precipitated. In the areas with fewer secondary-precipitated phase of β-$Mg_{17}Al_{12}$, some slender, white and strip-shaped substances were found in the α-Mg matrix, as indicated by the arrow in Figure 4(b). Principal component analysis of EDS showed that besides the peak of Mg, Al and Zn elements, the peak of C element also appeared at the arrowed place and was identified as CNTs.

The distribution of CNTs and the morphology of precipitated phase inside the grain were analyzed. The precipitated β-$Mg_{17}Al_{12}$ was mainly the dispersed cellular structure with the size of 100-200 nm. CNTs were also uniformly distributed around the precipitated phase of cellular β-$Mg_{17}Al_{12}$, the diameter of the CNTs was about 50nm and their length was 200nm-500nm, as indicated by the arrow in Figure 4 (c). A contrast experiment was conducted to show the morphology and distribution of the precipitated phase of β-$Mg_{17}Al_{12}$ inside the grain of mono AZ91D alloy after the same heat treatment process (see Figure 4 (d)). It clearly indicates that the CNTs/AZ91D composites had precipitated fewer phase of β-$Mg_{17}Al_{12}$ than the mono AZ91D alloy without CNTs.

The discontinuous precipitation of β-$Mg_{17}Al_{12}$ occurred near the grain boundary and the morphology of the precipitated phase of β-$Mg_{17}Al_{12}$ was mostly lamellar. The thickness of lamella was 100-150 nm and the length was 5-10 μm (see Figure 4 (e)). The majority of lamellas were distributed in some order and in parallel in a certain direction. A small amount of cellular precipitated phase with the size of 100nm-150nm was also distributed between lamellar β-$Mg_{17}Al_{12}$ phases. Besides, some white and strip-shaped CNTs were dispersed between lamellar precipitated phases, as indicated by the arrow in Figure 4 (e).

The precipitation of secondary phase near the grain boundary of AZ91D alloy was also found after the same heat treatment process (see Figure 4(f)). By comparing Figure 4(e) and Figure 4(f), it was found that the precipitated phase of the composites with CNTs at grain boundary was mainly lamellar β-$Mg_{17}Al_{12}$ after the aging treatment (T6), together with very few cellular β-$Mg_{17}Al_{12}$, and the distance between lamellar precipitated phases was relatively large; in contrast, lamellar and cellular precipitated phase of β-$Mg_{17}Al_{12}$ coexisted near the grain boundary of AZ91D matrix, and the precipitated phase had a relatively large size and was densely distributed. The above analysis indicates that in the composites with CNTs after T6 heat treatment, CNTs has an influence on the morphology of precipitated phase of β-$Mg_{17}Al_{12}$. When CNTs were uniformly distributed in AZ91D, a coherent or semi-coherent relation was developed between CNTs and α-Mg interfaces. CNTs generated a very strong stress field which can inhibit the nucleation of β-phase effectively and hinder the growth of grain. As a result, the precipitated phase was more diffusely distributed and its size was finer, thus contributing to the precipitation strengthening effect of precipitated phase.

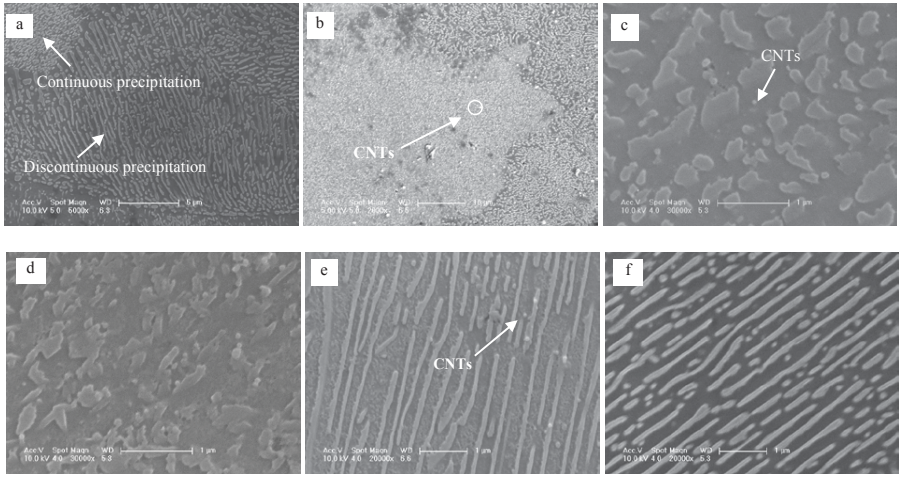

Figure 4. Morphology of β-$Mg_{17}Al_{12}$ secondary precipitation and distribution of CNTs in the composite matrix after T6 treatment. (a) Morphology of secondary precipitation in the grain and at the grain boundary, (b) CNTs nanoparticles distributed at grain boundary, (c) CNTs nanoparticles distributed in grain, (d) no CNTs nanoparticles distributed in grain for AZ91D alloys, (e) CNTs nanoparticles distributed between the lamellar β-$Mg_{17}Al_{12}$, (f) no CNTs nanoparticles distributed between the lamellar β-$Mg_{17}Al_{12}$ for AZ91D alloys.

The distribution of CNTs in the composite and the interface between the CNTs and the matrix alloy were analyzed with TEM (see Figure 5). The results showed that CNTs were tightly combined with matrix in the as-cast composites and no significant gaps were found, but there were obvious boundaries at joints (see Figure 5 (a)). After T4 and T6 treatment, CNTs were well combined with matrix all the time and the interfaces between CNTs and matrix were relatively

fuzzy (see Figure 5 (b) and (c)), which may suggest that the combination between CNTs and matrix be further improved after heat treatment.

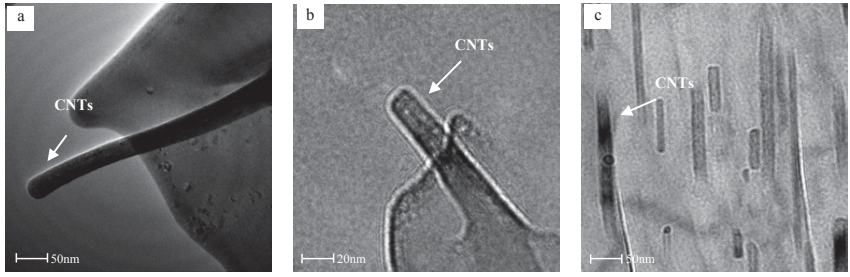

Figure 5. TEM images of CNTs in composites at different heat treatment conditions: (a) As-Cast, (b) T4, (c) T6.

Analysis of Strengthening and Toughing Mechanism

Strengthening Mechanism of Grain Refinement. According to the results of the grain size analysis, the grain size of AZ91D was 205μm while that of CNTs/AZ91D was 75μm. It suggests that the alloy grain was significantly refined after the addition of CNTs. Based on the classic Hall-Petch formula [3]:

$$\sigma_y = \sigma_0 + k_y d^{-\frac{1}{2}} \tag{1}$$

Where σ_y is the yield strength, σ_0 and k_y are material-related constants, and d is the average grain diameter. Finer grain indicates higher yield strength. The refinement of grain improves both the strength and the plasticity of composites. In this work the grain size of AZ91D was 205μm while that of CNTs/AZ91D was 75μm (see Figure 3). Therefore the grain refinement due to CNT addition significantly enhance the strength and ductility of the composites.

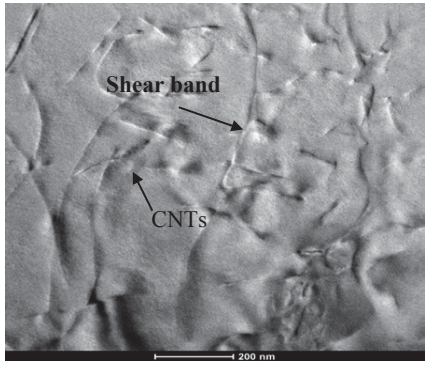

Figure 6. The effect of load transfer of the CNTs in composite materials

Strengthening Mechanism of Load Transfer. CNTs have excellent mechanical properties. The tensile strength and axial elasticity modulus of CNTs are up to 800GPa and 1TPa, respectively, and the elastic strain is up to 12% [4]. In the magnesium matrix composite reinforced by CNTs, the CNTs can bear partial deformation under load in matrix. As shown in Figure 6, CNTs were distributed in composites after the solid solution treatment (T4). They all had a complete shape, no fracture of CNTs was found, and a large number of shear bands arranged in a certain direction were identified in the matrix, suggesting that CNTs bore the shearing force on materials. Therefore, the strengthening of load transfer is one of the important strengthening mechanisms of CNTs/AZ91D composites.

Mechanism of Ductility Enhancement. Magnesium alloy can be deformed by means of slippage. Slippage occurs usually along a certain slip plane and the direction in the close-packed plane, which is related to crystal structure. When a crystal material starts to slip, there must be a critical shear stress. In the deformation of magnesium the critical shear stress for basal slip at room temperature should be much lower than that for the slip plane of prism. Therefore, the slip system of magnesium in close-packed hexagonal crystal structure at room temperature is $\{0001\}\langle 11\bar{2}0\rangle$ [5-6].

After the T4 treatment of CNTs/AZ91D composites, TEM analysis was used to observe the slipping deformation plane in the tensile test sample of composites, as shown in Figure 7 (a). It can be seen that many groups of parallel lines appeared in the composites with CNTs after the T4 treatment, showing obvious slip traces. They should be considered as (0001) basal slip line. Figure 7 (b) shows the high definition image of slip line at 50 nm scale. Moreover, the TEM images also show that a lot of dislocations lines were produced at the two ends of the slip lines. It suggests that in the composites with CNTs after the T4 treatment, obvious slippage occurred, and a lot of dislocations were generated and the plasticity was improved. The more detailed analysis will be done in the future research.

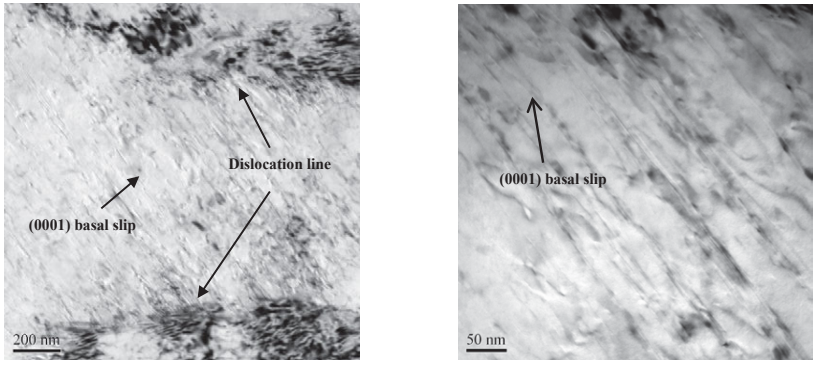

Figure 7. Dislocation and slip lines of CNTs/AZ91D-T4 after tensile test
(a)(0001) slip line; (b) high magnification image of slip line

Conclusions

The stirring casting and high-energy ultrasonic dispersion method were used to prepare the as-cast AZ91D composite reinforced with 1.5wt% CNTs and the solid solution and aging treatment were used to improve the ductility and strength of as-cast CNTs/AZ91D nanocomposites.

- The ductility and the tensile strength of the T4-treated nanocomposites were increased by 82.8 percent and 23.8 percent compared with the as-cast ones, which were 10.6 percent and 260MPa respectively. After T6 treatment, the tensile strength and especially the yield strength of the nanocomposites was increased by 26.2 and 17.6 percent to 265MPa and 140MPa respectively, while its ductility was still increased by 20.7 percent.
- The addition of CNTs to the matrix had an obvious effect on grain refinement and resulted in significant improvement of the strength and ductility of CNTs/AZ91D nanocomposites. The load transfer is another important strengthening mechanism.
- During the tensile deformation process of the T4-treated nanocomposites CNTs contributes to the increase of dislocation lines and slip lines. This might be the reason of the strengthening and toughening CNTs/AZ91D nanocomposites.

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