Original Research

Enhanced ductility of Mg–3Al–1Zn alloy reinforced with short length multi-walled carbon nanotubes using a powder metallurgy method

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Abstract

Mg–3Al–1Zn–CNTs composites, with different weight fractions (0.25–1.0 wt%) of carbon nanotubes (CNTs) were successfully fabricated via a powder metallurgy method. The processing parameters were adopted in such a way to have uniform dispersion of short length CNTs without any damage, as well as refined and dissolved $\beta$ phases structures throughout the composite matrix. The composite exhibited impressive increase in microhardness (about +23%) and tensile failure strain value (about +98%) without significant compromise in tensile strength, compared to the un-reinforced Mg–3Al–1Zn alloy. The synthesized composites can be used in automotive and aerospace industries due to their low density and high specific strength.

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1. Introduction

Metal matrix composites (MMCs) employing carbonaceous materials fillers have attracted significant attention in research society due to their improved mechanical and electrical properties [1–6]. MMC have wide spread applications in automobile industry because of their low density and high specific strength. MMCs are commonly used in automobile oscillating engine parts including connecting rod, valve system, piston pin, cylinder head, motor block and cylinder liner. In addition, magnesium, aluminum alloys and iron pistons are synthesized using a powder metallurgical technique which can afford the loads at high temperature [7–10]. Furthermore, MMCs revealed high thermal conductivity and are widely used in our industrial components. According to up-to-date research, several researchers have attempted to fabricate magnesium composites reinforced with CNTs. Wei et al. [11] used a disintegrated melt deposition technique to fabricate Mg–CNTs composites with different weight fractions of CNTs. The microstructural and mechanical characterization of extruded materials revealed simultaneously increase in strength and ductility. Later in 2011, Habibi et al. [12,13] used the powder metallurgy technique to fabricated Mg–Al–CNTs composites. The extruded composites exhibited significant increase in microhardness, tensile and compression strength at the expense of ductility loss. Moreover, CNTs were also used to enhance the mechanical strength of magnesium alloys i.e. ZK60 [14,15], AZ31 [16,17], AZ61 [18,19], and AZ91 [20,21], via powder metallurgy method and stir casting techniques. The mechanical testing results revealed that addition of CNTs into alloy matrices exhibited improved tensile and compression strengths. However, ductility of developed composites was lower than pristine matrix.

Generally, morphology of CNTs and processing routes has great influence on dispersion of CNTs in composite matrix,
which affects the mechanical strength of resulting composites. It was found that CNTs with small diameter and large length are bent/entangled and difficult to disperse in composite matrix. On the other hand, CNTs with large diameter and short length are stiffer/straight and are found to be easily dispersed in the matrix [22]. Another important issue of CNTs in composites is structural integrity. The structure of CNTs may be damaged during ball milling process and CNTs may agglomerate (due to van der Waals forces) during disintegrated melt deposition/stir casting process. Hassan et al. [23] investigated the effect of CNT’s integrity on mechanical behavior of CNTs reinforced aluminum composites. Recently, Li et al. [24] attempted to fabricate magnesium composites with uniform distribution of CNTs via a improved stir casting technique. The integrity of CNTs was examined in magnesium matrix. However, rare attempt was made to fabricate CNTs reinforced magnesium composites with un-damaged CNTs structure using the powder metallurgy technique. Therefore, it is noteworthy to develop a new method to keep balance between uniform dispersion and maintenance of the structural integrity of CNTs.

In this work, wet-process was used to achieve uniform distribution of short length MWCNTs in Mg–3Al–1Zn matrix, followed by cold pressing, vacuum sintering and extrusion techniques. Since a wet process was free of ball milling, the CNTs structure was maintained without any damage as proved by Raman spectroscopy and mechanical testing. The Mg–3Al–1Zn–CNTs composites revealed impressive increase in fracture strain without significant compromise in tensile strength.

2. Experimental procedure

Short length multi-walled CNTs with average length and diameter of 40 nm and 2 µm respectively, were supplied by Nanjing Xian Feng Nano-Material Technology Co., Ltd. Jiangsu, China. Fig. 1 shows transmission electron microscopic (TEM) images of as received CNTs. Short length multi-walled CNTs were dispersed in ethanol using a ultra-sonication process for 1 h. At the same time, Mg, Al and Zn powders (with particle size of 74 µm) were dissolved in ethanol to make slurry of Mg–3 wt%Al–1 wt%Zn. In next step, 0.25 wt% CNTs dispersion was added drop wise into Mg–3 wt%Al–1 wt%Zn powder slurry with vigorous mixing using mechanical agitator at 1500 rpm. The mixing process was continued for 1 h to obtain uniformity. Later composite mixture slurry was filtered and vacuum dried at 65 °C for 10 h to obtain Mg–3Al–1Zn–0.25CNTs composite powders. The composite powder was placed in a stainless steel die and pressed under 550 MPa pressure to make solid compact of \( \phi 82/\phi 20 \) mm. To further consolidate, the solid compact was sintered at 630 °C for 2 h in a furnace under highly purified argon gas. The compacts with composition of Mg–3Al–1Zn–0.5CNTs, Mg–3Al–1Zn–1.0CNTs, and Mg–3Al–1Zn were also prepared using above method. The sintered compacts were heated to a temperature of 400 °C for 1 h and hot extruded with a ram speed of 1 mm/min. The extrusion ratio of 1:9 was used to obtain the extrude bars of 9 mm diameters.

3. Results and discussion

Raman spectroscopy was used to characterize the structural integrity of CNTs in the composite powders as shown in Fig. 2(a). The CNTs and composite samples exhibit D (defect related), G (graphite related) and 2D bands at 1332 cm\(^{-1}\), 1587 cm\(^{-1}\), and

![Fig. 1. Transmission electron microscopic image of as received CNTs.](image)

![Fig. 2. Raman spectroscopy (a) of pristine CNTs and composite powders, and x-ray diffraction patterns (b) of extruded Mg–3Al–1Zn alloy and its composites.](image)
It can be observed that as the received CNTs possess significant D band, which means that there are several defects in as received CNTs. The ratio between D-band intensity and G-band intensity provide information about quality of the internal CNTs [25]. It can be observed from Fig. 2(a) that $I_D/I_G$ of pristine CNTs is about 1.488 and that for composites are 1.473, 1.467, and 1.479. The $I_D/I_G$ of pristine CNTs is almost equal to that of composites which indicated that the CNT graphite structure was not damaged during an adopted mixing process. Fig. 2(b) shows the x-ray diffraction (XRD) patterns of Mg–3Al–1Zn alloy and its composites taken perpendicular to extrusion direction. The peaks for magnesium matrix and intermetallic phase $\text{Mg}_17\text{Al}_{12}$ were recognized in all samples. Aluminum carbide or peak related to CNTs were not traced which is due to low weight fractions of aluminum and CNTs in composite matrices. It can be observed that the intensity of $\text{Mg}_17\text{Al}_{12}$ peak at two theta equal to 36.18° decreases as content of CNTs increases, which means that $\text{Mg}_17\text{Al}_{12}$ intermetallic phase production was prevented in composite samples. The suppression of $\text{Mg}_17\text{Al}_{12}$ intensity in composite samples confirmed the existence of CNTs.

Scanning electron microscopic analysis revealed that eutectic $\beta$ ($\text{Mg}_17\text{Al}_{12}$) phases along cell boundaries and discontinuous $\beta$
precipitates around eutectic β phases were detected in Mg–3Al–1Zn alloy as shown in Fig. 3(a). On the other hand, composite samples shows dissolved and finer β (Mg17Al12) phases (Fig. 3 (b)–(d)). The length of β phases was reduced to several micrometers in composites samples. Thus, CNTs particles prevent the production of β phases, as evident from XRD results. Numerous investigators reported the formation of carbide, Al4C3 [26] and Al2MgC2 [27]. In order to confirm the carbide formation, transmission electron microscopy (TEM) was carried for Mg–3Al–1Zn–1.0CNTs composite as shown in Fig. 3(e) and (f). It can be seen that most of CNTs lattices are embedded inside the β phases, thus serve to dissolve the intermetallic β phases in present composites. However, in pristine Mg alloys the solution treatment and aging techniques are performed to dissolve the β (Mg17Al12) phases.

Fig. 4. Energy dispersive spectroscopy of Mg–3Al–1Zn–1.0CNTs composite showing elemental mapping of magnesium, aluminum, zinc, carbon, and oxygen.

Fig. 5. (a) Tensile properties of Mg–3Al–1Zn alloy and its composites, (b) Schematic demonstration of β phase formation in pristine Mg–3Al–1Zn alloy and role of CNTs to dissolve β phases in composite matrix.
phases [28]. The TEM images confirm the absence of voids and carbide formation in Mg–3Al–1Zn–1.0CNTs composite [29,30]. The Energy dispersive spectroscopy (EDS) confirms the homogeneously distributed Al, Zn and CNTs elements as shown in Fig. 4(a)–(f).

The Vickers Hardness of samples was analyzed by an automatic digital micro hardness tester under a load of 100 g and 15 s dwell time. The results of microhardness measurements revealed a significant increase in hardness value of Mg–3Al–1Zn alloy with the addition of CNTs and an increasing amount of CNTs particles. The hardness values of alloy and its composites were 55, 57, 66, and 68, respectively. The mechanical strength of the extruded materials was measured under tensile loading parallel to extrusion directions with strain speed of $1 \times 10^{-3} \text{ s}^{-1}$ using round samples with gauge length and diameter of 15 and 3 mm respectively. The tensile properties are shown in Fig. 5(a). It can be observed that tensile fracture strain for CNTs reinforced composites increased with increase in CNTs contents, without significant compromise in yield and ultimate tensile strength. The 1.0 wt % CNTs reinforced composite exhibited tensile strength of 288 MPa and fracture strain of 17.9%.

So far, there have been two reports on the mechanical properties of AZ31–CNTs composites [16,17]. Kondoh et al. [16] reported a tensile strength of 375 MPa and an elongation of 5% from AZ31B-type magnesium matrix reinforced with 0.95 vol% of CNTs via the powder metallurgy method. In another work, Paramsothy et al. [17] examined a tensile strength of 296 MPa and fracture strain of 12.2% for AZ31 alloy reinforced with 1.0 vol%CNTs + 0.079AA5052 via a stir casting method. It can be noticed that composites developed in the present work are enough strong (tensile strength of 288 MPa), and furthermore, they showed impressive fracture strain value (17.9%) compared to previously reported AZ31–CNTs composites. The increased fracture strain and microhardness of composite is attributed to homogeneous distribution of short length CNTs in the vicinity of $\beta$ phases. As a result, CNTs (with an average length of 2 mm) impinged into/near $\beta$ phases helps to dissolve the $\beta$ phase particle size from several hundred microns to several microns as shown in Fig. 5(b). The refined $\beta$ phases do not adversely affect the ductility of composite matrices. In addition, basic strength mechanisms i.e. (a) dislocation generation due to coefficient of thermal expansion (CTE) and elastic modulus mismatch between reinforcements and matrix [31], (b) Orowan looping [32], (c) load transfer mechanism, and (d) geometry of reinforcements, also play vital role [33]. In addition, the significant enhanced fracture strains of developed composites were compared with earlier reports, where different matrices i.e. AZ31, AZ61, AZ81, and AZ91 were reinforced with CNTs, Al2O3 and Cu particles (Table 1) [18,19,21,34–36]. It can be noticed that the composites fabricated in present work exhibited superior fracture strain values, compared to previously developed composites, and thus revealed the significance of short length CNTs and adopted processing method [37,38].

4. Conclusions

In summary, we have successfully developed the Mg–3Al–1Zn–CNTs composites with excellent mechanical properties i.e. fracture strain. The composites fabricated by the PM method exhibited microhardness, tensile strength and fracture strain (% of 68Hv, 288 MPa, and 17.9 respectively. The micro-structural evaluation reveals that the short length CNTs was uniformly dispersed in composite matrix. The CNTs helps to dissolve the brittle Mg17Al12 intermetallic phases throughout composite matrix, which leads to high fracture strain of resulting composites. Comparison with previous reports reveals the superiority of the developed composites in this study due to the selection of appropriate CNTs morphology and processing techniques.

Acknowledgments

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<table>
<thead>
<tr>
<th>Materials</th>
<th>Synthesis methods</th>
<th>Fracture strain (%)</th>
<th>%Increase(+) or %Decrease(-)</th>
</tr>
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<tr>
<td>Mg–3Al–1Zn [Present work]</td>
<td>PM + Extrusion</td>
<td>9</td>
<td>–</td>
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<tr>
<td>Mg–3Al–1Zn–1 wt%CNTs [Present work]</td>
<td>PM + Extrusion</td>
<td>17.9</td>
<td>+98%</td>
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<td>AZ61 [18]</td>
<td>PM + Extrusion</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>AZ61–0.74 vol%CNTs [18]</td>
<td>PM + Extrusion</td>
<td>11</td>
<td>–31.25%</td>
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<tr>
<td>AZ61 [19]</td>
<td>PM + Extrusion</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>AZ61–0.71 vol%CNTs[19]</td>
<td>PM + Extrusion</td>
<td>12</td>
<td>–25%</td>
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<tr>
<td>AZ91D [21]</td>
<td>PM + Extrusion</td>
<td>14</td>
<td>–</td>
</tr>
<tr>
<td>AZ91D–0.5 vol%CNTs [21]</td>
<td>PM + Extrusion</td>
<td>6</td>
<td>–57.14%</td>
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<tr>
<td>AZ81 [34]</td>
<td>Stri-casting + Extrusion</td>
<td>7.9</td>
<td>–</td>
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<tr>
<td>AZ81–1.5 vol%CNTs [34]</td>
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<td>13.7</td>
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<td>11.8</td>
<td>–</td>
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<td>Stri-casting + Extrusion</td>
<td>8</td>
<td>–</td>
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<td>AZ31–1.5 vol%Al2O3–1.0 vol%Cu [36]</td>
<td>Stri-casting + Extrusion</td>
<td>12.1</td>
<td>+51.25</td>
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PM: Powder metallurgy method.
and 2011FU125Z07) and Chongqing Science and Technology Commission (CSTC2013JCYJC60001).

References