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Multi-walled carbon nanotube-reinforced magnesium alloy composites

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This study demonstrates the ability to fabricate lightweight, ductile but mechanically strong magnesium alloy (AZ91D) composites by introducing a small number of high crystalline multi-walled carbon nanotubes. It is demonstrated that 1% of relatively short and straight carbon nanotubes distributed homogeneously on the outer surface of magnesium powders act as an effective reinforcing filler to prevent deformation, thereby contributing to the enhanced tensile strength of magnesium alloy composites (e.g., from 315 to 388 MPa).

Keywords: Carbon nanotubes; Magnesium alloy; Powder processing; Mechanical property

There has been strong recent interest in developing lightweight and high-strength materials to improve energy efficiency through the weight reduction of automobiles and aircraft. For these purposes, magnesium alloys have attracted a lot of attention [1–3], as they have low density in their purest form and, in addition, they have been proved to have good mechanical properties through the incorporation of structural filler (e.g., silicon carbide whisker, aluminum and graphite particles, and carbon fibers) [4–7]. Within this context, dimensionally nano-sized, mechanically strong, electrically and thermally conductive carbon nanotubes [8–11], considered to be the ideal reinforcing filler in various composite systems [12–15], have been incorporated into magnesium matrix [16–19]. Recently, Goh et al. [19] reported a simple way of preparing nanotube-reinforced magnesium composite by powder–powder mixing and subsequent hot extrusion processes. However, low enhancement of (only 5%), or even a decrease in, tensile strengths in nanotube-reinforced magnesium composites (see Table 3 in Ref. [19]) could be explained by the presence of aggregated carbon nanotubes within a magnesium matrix. To exploit carbon nanotubes fully as a mechanical reinforcing filler in a magnesium matrix, optimized fabrication processes, including homogeneous dispersion of carbon nanotubes, must be developed to achieve high mechanical properties for their use in the major components of automotives.

This study reports an appropriate fabrication route for preparing high-density carbon nanotube-filled magnesium alloy composites through the suitable selection of filler and matrix alloy, followed by vacuum hot-press and extruding processes, and shows that such composites, reinforced by 1% of shortened linear carbon nanotubes, have moderate ductility and largely enhanced high tensile strength (e.g., from 315 to 388 MPa). The preparation process involved the mechanical shortening of long carbon nanotubes. Technical reasons for selecting short and straight carbon nanotubes are their high dispersibility in magnesium alloy matrix and their theoretically expected good reinforcing effect, similar to that for the long tubes [20]. This work also makes a detailed study of the interfacial state between nanotubes and magnesium matrix.

In preparing carbon nanotube-reinforced magnesium alloy composite, we first prepared AZ91D-type magnesium alloy (see Table 1) powders with diameter of 100 μm or less, using zirconia balls with a diameter of 10 mm in a triaxial vibrating-type ball miller

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Table 1. Chemical composition of AZ91D alloy (mass%)

Al	Zn	Mn	Si	Cu	Ni	Fe	Be	Mg
9.25	0.68	0.24	0.030	⩽0.001	⩽0.001	⩽0.001	⩽0.001	Bal.

(TKMAC-1200L) with a rolling rate of 800 rpm for 6 h in argon (Fig. 1a). The high-purity and high-crystalline multi-walled carbon nanotubes, prepared by the catalytic chemical vapor deposition method and subsequent high-temperature thermal treatment in argon [21,22], were mechanically shortened to have a length distribution of ~5 μm (Fig. 2b) using a high-speed blade cutting machine (Wonder Blender WB-1, Osaka Chemical Inc.). Then, magnesium powders and shortened carbon nanotubes (~20 g) were physically blended with zirconia balls (diameter 1 mm, 20 g) in a container (125 ml) using the same triaxial ball miller with a rolling rate of 800 rpm for 5 h in argon. The absence of aggregated carbon nanotubes for the magnesium alloy powder containing 1% carbon nanotubes indicates that short carbon nanotubes are homogeneously impinged on the near surface of magnesium alloy particles (see Fig. 1c). In the case of the magnesium alloy powders containing 5% carbon nanotubes, the observed aggregated carbon nanotubes are indicative of non-homogeneously distributed carbon nanotubes (Fig. 1d). Next, the magnesium powders containing 0.5–5% carbon nanotubes were hot-pressed in a molder to form a precursor at 823 K for 5 h by applying a pressure of 25.5 MPa in a vacuum <10 Pa. The carbon nanotube-reinforced magnesium alloy composites were finally obtained in the form of rods (Fig. 1e) (diameter 6 mm, length 120 mm) by extruding precursors at 723 K with an extrusion ratio of 9:1. There was no distinctive defect in appearance. For these extruded rods, solution treatment was carried out at 683 K for 15 min and artificial aging at 473 K for 15 h, respectively.

For these dumbbell-shaped specimens (gauge length 15 mm, diameter 4 mm), the mechanical properties were measured using an AG2501S (Shimazu) with a cross-head speed of 0.5 mm min^{-1}. Stress–strain curves for the pristine and nanotube-filled magnesium composites are shown in Figure 2, and their tensile properties and densities are summarized in Table 2. Note that the tensile property of the milled, consolidated and extruded AZ91D rod sample was used as a reference. The elastic modulus, tensile strength, and 0.2% proof stress for the carbon nanotube-filled composites increased with increase in the number of carbon nanotubes added, and they reached maximum values when 1–1.5% of carbon nanotubes were added. In particular, the tensile strength of magnesium alloy containing 1% carbon nanotubes was 388 MPa, which is comparable with that of the generally used mild steel in automobiles. Tensile properties greatly improved by introducing a small number of carbon nanotubes could be explained by the homogeneous distribution of short carbon nanotubes in the vicinity of magnesium grain boundaries, because short carbon nanotubes with an average length of 5 μm were believed to impinge on the near surface of magnesium alloy powders very homogeneously during a triaxial mixing process.

To confirm the above interpretation, the cross-sectional texture of the rods was observed by electron probe micro-analysis (EPMA, Shimadzu). As shown in Figure 3a–c, most of the carbon nanotubes were situated predominantly in the vicinity of magnesium grain boundaries. In addition, they were distributed in a singular fiber, which was confirmed by SEM (JEOL, JSM7000F) observation on the etched surface with 0.04% hydrochloric acid solutions for 40 s (Fig. 3d). As a result, the strengthened near-surface of the magnesium domains by a suitable coverage of carbon nanotubes is highly resistant to deformation, and thus contributes to the enhancement of tensile properties when a suitable number of carbon nanotubes are added. This interpretation is supported by the observation that the ductility was not extremely reduced (Table 2). Unfortunately, when the added numbers of carbon

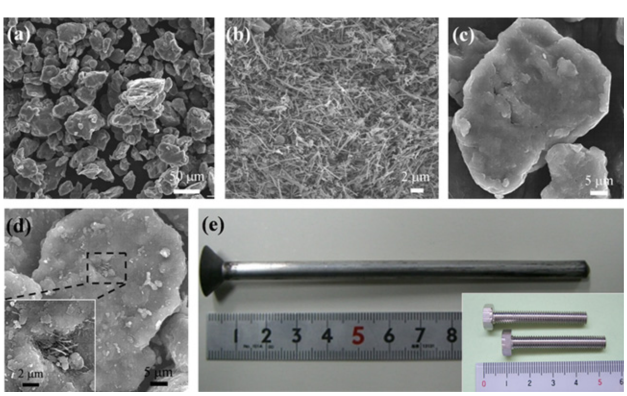

Figure 1. SEM images: (a, b) mechanically milled AZ91D-type magnesium powders with an average diameter of 100 μm and shortened carbon nanotubes with an average length of ~5 μm; (c, d) mechanically mixed magnesium powders containing 1% and 5% short carbon nanotubes, respectively. Note that the aggregated carbon nanotubes were observed in magnesium powders containing 5% of carbon nanotubes (inset is a magnified SEM image). (f) Photo of carbon nanotube-reinforced magnesium composite-based rod exhibiting clean appearance without any macro-morphological defects (inset is a photo of clean shining two volts fabricated from extruded rods).

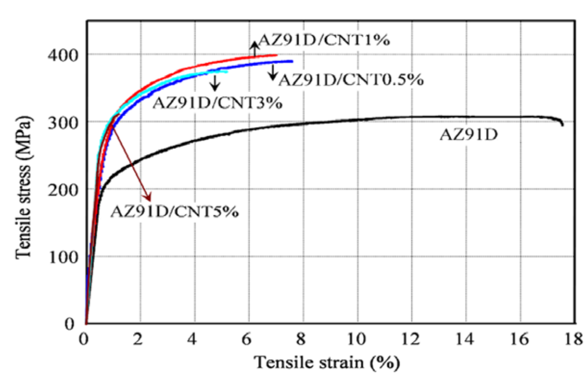

Figure 2. Stress–strain curves for the pristine and carbon nanotube-filled AZ91D magnesium alloy composites, respectively.