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Magnesium nanocomposite via mechanochemical milling

L. Lü [a,*], M.O. Lai [a], W. Liang [b]

[a] Department of Mechanical Engineering, The National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore
[b] Taiyuan University of Technology, China

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Abstract

Nanocomposite Mg5wt%Al–10.3%Ti was synthesized via mechanochemical milling of elemental powders of Mg, Al and Ti with polyethylene–glycol. Formation of TiH_2 was observed after milling and the concentration of TiH_2 was found to further increase after sintering. The nanocomposite shows an improvement in yield strength and ductility compared to its counterpart fabricated using a conventional powder metallurgy (P/M) process. The increase in mechanical properties is associated with the ultra fine grain size and the presence of nano-dispersoids in the matrix.

Keywords: Nanostructured alloy

1. Introduction

Light-weight magnesium alloys have recently received much attention due to their attractive properties. Although Mg alloys are generally believed to possess relatively low yield strength and poor ductility [1], they can be strengthened by incorporating either intermetallics or ceramic particulates [2–4]. Currently, most Mg-based composites have been fabricated through casting routes for the reason of cost effectiveness in comparison to other process techniques [5–7]. However, microstructures obtained from traditional cast generally reveal coarse structures. In addition, reactions between the Mg matrix and the reinforcements cause degradation of the composites [8]. Another difficulty encountered in the processing of Mg composites by casting is the incorporation of fine ceramic particulates. In most cases, only large ceramic particulates with size in the range of a few micrometer to tenth micrometer particulates are practically applicable. Some attempts in using mechanical or mechanochemical millings have been introduced in the fabrication of extremely fine and/or nanostructured Mg-based composites [9–11]. It has been found that strength of nanostructured Mg-based composites can be increased but on the cost of ductility [12,13]. The cause of ductility decrease is mainly due to selection of reinforcements.

The present research focuses on the formation of nanocomposites with ultra-fine in situ TiH_2. Microstructure and mechanical properties of the composites are studied. Mechanisms of the formation of TiH_2 will also be discussed.

2. Experimental procedures

Mg alloys of nominal composition Mg5%Al–10.3%Ti were prepared via powder metallurgy and mechanochemical milling routes. Elemental powders of Mg of purity >98.5%, Al of purity 99.5% and Ti of purity >98% were used in the processes.

For the alloy prepared by powder metallurgy method, the powders were mixed in a V-blender at 45 rpm for 2 h. For the composite prepared by mechanochemical milling process, the Mg, 5%Al and 10.3%Ti powder mixture was milled using a Fritsch planetary ball mill operating at 250 rpm. Forty 15 mm diameter balls were employed. A ball-to-powder weight ratio of about 20:1 was maintained. Polyethylene–glycol ($H(OCH_2\text{-}CH_2)_nOH$) was added to the

* Corresponding author. Tel.: +65-6874-2236; fax: +65-6779-1459.
E-mail address: luli@nus.edu.sg (L. Lü).

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powder mixture with the purposes of prevention of agglomeration and excessive cold welding of the powders, and decomposition of it. To gain enough hydrogen, 6 wt% of polyethylene–glycol was used. Prior to mechanical alloying, powder mixtures were sealed with 99.9% pure argon gas in milling vials after evacuation with a vacuum pump.

After mixing and mechanochemical milling, the powders were isostatically cold-pressed at 400 MPa to cylinders of about 40 mm diameter and 50 mm length. The compacts were then sintered at 450 °C for 2 h in a vacuum furnace. Extrusion of the compacts with an extrusion ration of 25:1 was carried out at 400 °C using graphite as a lubricant. The extruded rods were subjected to post heat treatments at three different temperatures of 350, 400 and 450 °C for 5 and 8 h. Tensile specimens of 5 mm diameter and 25 mm gauge length which cut from middle of the extrude rods were machined in accordance to ASTM E8M-96. Tensile testing was carried out at strain rate of 1.0 mm/min using an automated servo hydraulic INSTRON machine. A clip-on extensometer with 25 mm gauge length was used to record the displacement.

X-ray diffraction (XRD) analysis was carried out using a Shimadzu Lab XRD-6000 X-ray diffractometer with Cu Kα $\lambda = 1.54056$ Å radiation. The crystalline size was evaluated by the Hall–Williamson equation and transmission electron microscope (TEM).

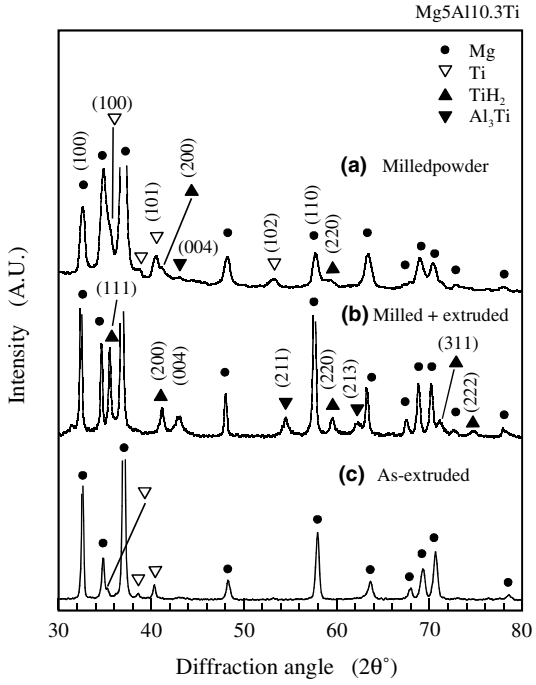

Fig. 1. X-ray spectra of mechanochemically milled powder mixture and extruded rods: (a) as-milled powder; (b) extruded rod after 20 h of milling; (c) as-extruded rod directly from powder metallurgically sintered compact.

3. Results and discussion

3.1. Structures

Fig. 1(a) shows the spectrum of the as-mechanochemically milled power mixture prior to any heat treatment process. Several features of the diffraction can be observed. Firstly, all the Mg and Ti diffraction peaks can be observed to be broadened indicating a reduction in grain size. Due to the broadening, (1 0 0) Ti peak completely overlaps with (0 0 2) Mg peak after the milling. In spite of the overlap, the rest of the Ti diffraction peaks, like (0 0 2), (1 0 1) and (1 0 2), can still be clearly identified. In addition, it is clear that some new structures have been formed after the milling as indicated by the presence of the new peaks at 40.80° and 59.00°. It is generally understood that the solubility of Mg in Ti or vice versa is very small and negligible. The solubility has been found to decrease sharply with addition of Al in Mg [12]. It has been reported that solubility of Mg in Ti can be increased by mechanical alloying. However, the increase in alloy addition would lead to a shift in diffraction peaks due to the change in the lattice parameters. Therefore, the formation of the new peaks must have been originated from the formation of new phases. Comparing the XRD spectrum of the milled specimens shown in Fig. 1(a) to that of the sintered and extruded specimen shown in Fig. 1(c), it can be seen that the diffraction peaks at 40.80° and 59.00° in the as-sintered specimen have become undetectable. The observation implies that the formation of the new phase is directly associated with the milling. Since polyethylene–glycol ($H(OCH_2CH_2)_nOH$) consists mainly of hydrogen and Ti is very sensitive to it, Ti hydride could directly be formed during mechanochemical alloying via the decomposition of $H(OCH_2CH_2)_nOH$ through:

$$(1+2n)\mathrm{Ti} + \mathrm{H(OCH_2CH_2)_nOH} \rightarrow (1+2n)\mathrm{TiH_2} + (1+n)\mathrm{CO} + (n-1)\mathrm{C}$$

If it is assumed that $n = 1$, it follows that

$$3\mathrm{Ti} + \mathrm{H(OCH_2CH_2)OH} \rightarrow 3\mathrm{TiH_2} + 2\mathrm{CO}$$

The carbon monoxide evaporates as gas. From the above analysis it is clear that the two new diffraction peaks at 40.80° and 59.00° are TiH_2 (2 0 0) and (2 2 0) at standard diffraction of 40.798° and 59.177°, respectively. From thermodynamic point of view, formation of TiH_2 is possible since the excess standard Gibbs free energy of formation of TiH_2 is −14.96 kJ/mol.

It is interesting to note from Fig. 1(b) that Ti (0 0 2), (1 0 1) and (1 0 2) peaks completely disappear from the extruded rod that has been sintered after 20 h of milling.