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Role of manganese on the grain refining efficiency of AZ91D magnesium alloy refined by Al_4C_3

Shengfa Liu*, Yuan Zhang, Hui Han

School of Materials Science and Engineering, Wuhan University of Technology, 205 Luoshi Road, Wuhan 430070, China

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ABSTRACT

A novel Mg–50% Al_4C_3 (hereafter in wt.%) master alloy has been developed by powder in situ synthesis process, the role of manganese on the grain refining efficiency of AZ91D magnesium alloy refined by this master alloy has been investigated. X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) results show the existence of Al_4C_3 particles in this master alloy. After addition of 0.6% Al_4C_3 or combined addition of 0.6% Al_4C_3 and 0.27% Mn, the average grain size of AZ91D decreased dramatically from 360 μm to 210 μm, and from 360 μm to130 μm, respectively. However, no further refinement of grain size was achieved with additional amount of Mn exceeding 0.27% for AZ91D alloy refined by 0.6% Al_4C_3 in the present investigation. Al–C–O–Mn–Fe-rich intermetallic particles with an Al–C–O-rich coating film, often observed in the central region of magnesium grains of the AZ91D alloy treated by the combination of Al_4C_3 and Mn, are proposed to be the potent nucleating substrates for primary α-Mg.

1. Introduction

Over the past two decades, the consumption of magnesium alloys in the automobile industry has been increasing rapidly owing to adopting more and more light materials for energy conservation and emission reduction [1,2]. However, the applications of magnesium alloys are restricted due to their low absolute strength and poor workability [3–5]. Thus, in order to improve the mechanical properties and further increase the industrial applications of the magnesium alloys, grain-refining treatment is urgently needed. Among all those available grain refining methods at present, such as superheating [6,7], carbon inoculation [8–11], and addition of alloying elements [12–15], and so on, carbon inoculation is known to be the most effective one for operating at a low temperature and less fading with long-time holding [3,5]. It is widely accepted that the grain refining effect of carbon inoculation on the Mg–Al based alloy is attributed to the formation of Al_4C_3 particles which could act as the nuclei for Mg grains [8–11].

It is well known that commercial Mg–Al alloys contain relatively high contents of Fe and Mn elements, and Mn plays a critical role in the development of them as an iron remover [16]. What is more, the grain refining efficiency of carbon inoculation is associated with the presence of these impurity elements (Fe, Mn). Earlier research by Tamural et al. [17–19] on the influence of minor impurity elements on the grain refinement of high purity Mg–Al alloys, led to a conclusion that Fe and/or Mn were inhibiting elements for grain refinement by transforming Al–C–O into Al–C–O–Fe (Mn). However, Pan et al. [20] held a different opinion. After the study of the role of Fe in grain refinement of an AZ63B magnesium alloy by Al–C master alloy, they suggested that grain refinement by carbon addition is mainly due to the heterogeneous nucleation on the Al-, C-, O-, Fe- and Mn-rich particles and Fe plays an important role in the formation of the nucleating particles rather than an inhibiting element. Subsequent work by Cao et al. [21] on the effect of manganese on grain refinement of Mg–Al based alloys found that manganese is a grain refiner for high purity Mg–Al based alloys when introduced in the form of an Al–60% Mn master alloy splatter, proposed that a hexagonal close-packed ε-AlMn phase act as the nuclei of Mg grains. Du et al. [22] had also devoted their energies to the research of the effect of Mn and carbon inoculation on the grain refinement of Mg–3Al alloy, they suggested the Al–C–O–Mn compounds as the potent nuclei for Mg grains and proposed a new hypothesis that the particles of Al–Mn compounds with Al_4C_3 coating film can act as potent nuclei for Mg grains. Most recently, Han et al. [23,24] investigated the effect of manganese on the microstructure of Mg–3Al alloy and duplex nucleation in Mg–Al–Zn–Mn alloys with carbon inoculation, found that Al–Mn phase has low nucleation efficiency on primary Mg while Al_4C_3-coated $Al_{0.89}Mn_{1.11}$ and Al_4C_3-coated Al_8Mn_5 act as the duplex nucleation sites in carbon-treated AZ31 and AZ63, respectively.

In this paper, the effect of Mn on the grain refining efficiency of commercial AZ91D magnesium alloy refined by a novel Mg–Al_4C_3 master alloy has been investigated. The grain refinement mechanism in relation to the effect of manganese and Al_4C_3 is discussed.

* Corresponding author. Tel.: +86 27 87664610.
E-mail address: liusfa@163.com (S. Liu).

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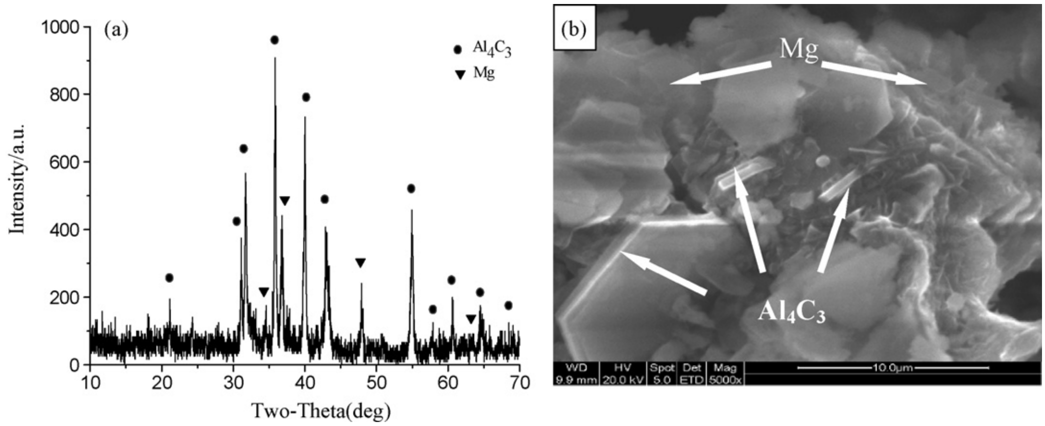

Fig. 1. Characteristics of Mg–50% Al_4C_3 master alloy: (a) XRD diffraction pattern of the Mg–50% Al_4C_3 master alloy and (b) SEM image of the Mg–50% Al_4C_3 master alloy.

Table 1
Chemical composition of AZ1D magnesium alloy (wt.%).

Al	Zn	Mn	Fe	Si	Cu	Ni	Mg
8.6895	0.6691	0.2300	0.0021	0.0426	0.0023	0.0002	Bal.

2. Experimental procedures

A commercial AZ91D magnesium alloy was used for grain refinement tests in the present study and its chemical compositions are listed in Table 1. The new Mg–50% Al_4C_3 (Mg–37.5% Al–12.5% C) master alloy was fabricated by powder in situ synthesis process in a vacuum sintering furnace at about 973 K for 120 min, and a commercial ZS-Mn75 produced by Sichuan Lande Industry Co. Ltd. was used as Mn additive. The alloy was melted in an electrical furnace using a mild steel crucible under the protection of about 1% RJ-2 flux (chemical compositions: w(KCl) = 35–45%, w(CaF_2) = 5–8%, w($MgCl_2$) = 40–50%, w(NaCl + $CaCl_2$) = 5–8%). Mg–50% Al_4C_3 master alloy and Mn additive were added into the melt at 750 °C. The melt was held for 10 min and then poured into a mild steel mold preheated to 200 °C with a size of Ø50 mm × 100 mm. Samples were sectioned from 15 mm from the edge of the ingots, then subjected to heat treatment in a sulfur atmosphere at 415 °C for 10 h followed by quenching into cold water in order to reveal the grain size. Characterization of the grain size and qualitative analysis were conducted on selected specimens using a Leica MEF4 M optical microscope (OM) and a JSM-5600LV scanning electron microscope (SEM) with an energy dispersive X-ray (EDS) spectrometer (Oxford Instruments). The mean linear intercept method was used to measure the average grain size.

3. Results and discussion

3.1. Characteristics of Mg–50% Al_4C_3 master alloy

Fig. 1(a) shows the XRD pattern of the new Mg–50% Al_4C_3 master alloy. It can be seen that the master alloy is composed of Al_4C_3 and Mg phases. The microstructure is illustrated by SEM in Fig. 1(b). The Al_4C_3 particles are characterized with well defined boundary, regular lamellar structure and rod-shaped, distributed in the master alloy and easy to distinguish from the Mg matrix. The thickness of the lamellar Al_4C_3 is about 0.5 μm.

3.2. Grain refining efficiency

Fig. 2 shows the typical grain morphologies of the AZ91D magnesium alloy with different addition of Al_4C_3 and Mn. The commercial AZ91D magnesium alloy contains about 0.23% Mn initially,

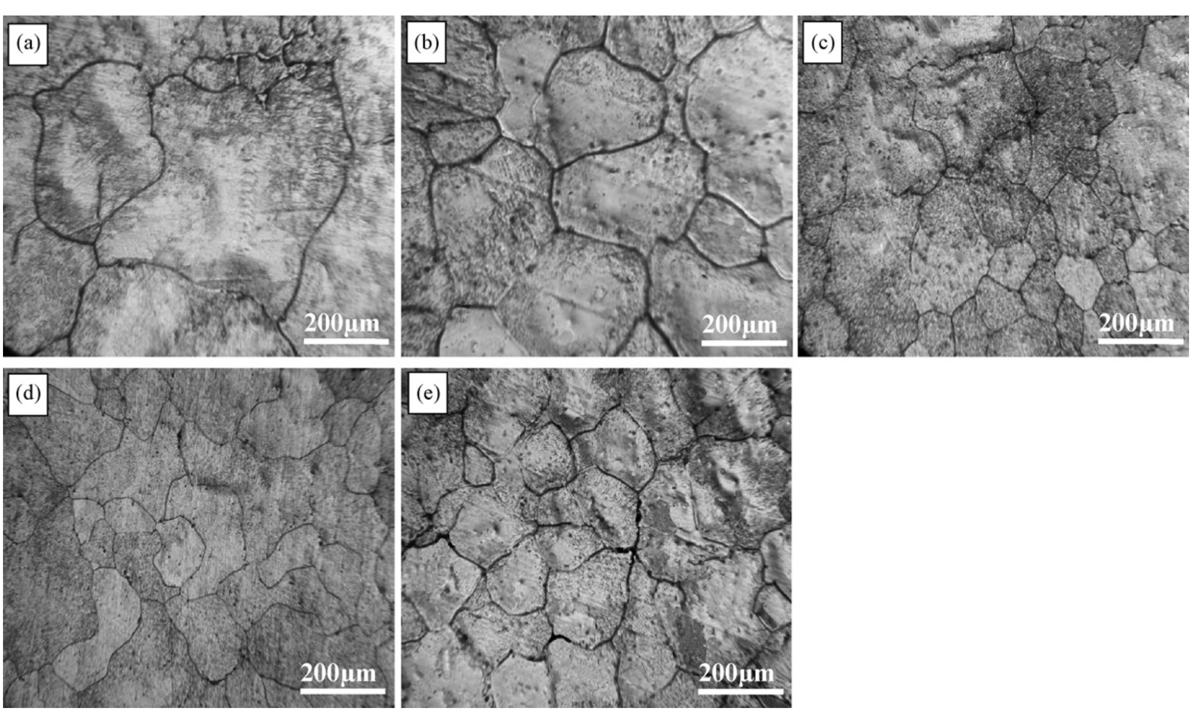

Fig. 2. Microstructure of heat-treated AZ91D alloy: (a) without any treatment, (b) treated by 0.6% Al_4C_3, and (c)–(e) treated by 0.6% Al_4C_3 with the combination of 0.27%, 0.47% and 0.67% additional Mn.