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Grain refining mechanism of Al-containing Mg alloys with the addition of Mn–Al alloys

Gaowu W. Qin*, Yuping Ren, Wei Huang, Song Li, Wenli Pei

Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Wenhu Road 3-11, Heping District, Shenyang 110004, Liaoning Province, China

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ABSTRACT

The effect of manganese on grain refinement of Al-containing AZ31 Mg alloy has been investigated by designing a series of Mn–Al alloys composed of either pure ε-AlMn, γ_2-Al_8Mn_5 or both of them using optical microscopy and X-ray diffraction. It is experimentally clarified that the grain refinement of the AZ31 Mg alloy is due to the existence of the ε-AlMn phase in the Mn–Al alloys, not the γ_2-Al_8Mn_5 phase. The grain size of AZ31 Mg alloy is about 91 μm without any addition of Mn–Al alloys, but remarkably decreases to ∼55 μm with the addition of either Mn–34 wt% Al or Mn–28 wt% Al. With a minor addition of 0.5 wt% Mn–28Al alloy, the grain size of AZ31 alloy decreases to ∼53 μm, and the Mn–28Al alloy can be active as grain refiner for holding time up to 60 min for the melt AZ31 alloy at 750 °C.

1. Introduction

Grain refining of as-cast Mg alloys is one important issue to improve their deforming behavior, allowing to get wide sheets by rolling and to get complicated profiles by extrusion. Generally, Zr is an effective grain refiner for Al-free Mg alloys while research progress is very limited so far for Al-containing Mg alloys. As one of the most important alloying elements, manganese is usually added into most of Mg-based alloys to remove impurity elements, such as Fe, and thus the corrosion resistance can be improved [1]. More than 60 years ago, Tiner [2] found that Mn was also an effective grain refiner of Mg alloys, however, Nelson [3] gave a negative conclusion later. Recently, Tamura et al. [4] confirmed that the average grain size of Mg–9 wt% Al alloy increased from about 40 μm to 160 μm due to the formation of Al–C–O–Mn quaternary intermetallics when the Al–10 wt% Mn master alloy was added, which was generally consistent with Nelson [3]. More recently, Byun et al. [5] proposed that $Al_8(Mn, Fe)_5$ particles could act as the nucleus in the AZ91 alloy containing 0.23–0.45 wt% Mn, however, which was not supported by the result obtained by calculating the oriented relationship between the HCP structured α(Mg) matrix and $Al_8(Mn,Fe)_5$ phases [6]. Subsequently, the effect of the Al–60 wt% Mn and Al–70 wt% Mn master alloys on the grain size of the AZ31 Mg alloy was investigated by Cao et al. [7] and Li and co-workers [8], and they proposed that the ε-AlMn phase played a critical role in the grain refinement. However, both the γ_2-Al_8Mn_5 and ε-AlMn phases existed in the two Al–Mn master alloys they used. Therefore, it was hard to give a solid conclusion that which phase determines the grain refinement effect of AZ31 Mg alloy and how efficiently they act as grain refiners for the Al-containing Mg alloys.

The purpose of this work is to prepare a series of Mn–Al master alloys containing either γ_2-Al_8Mn_5 or ε-AlMn phase, or both of them, respectively, to clarify which compound plays a role in the grain refinement of Al-containing Mg alloys, and the general characteristics of grain refining behavior of AZ31 Mg alloy, a model Al-containing Mg alloy, will be addressed.

2. Experimental procedure

Three kinds of Mn–38Al, Mn–34Al, and Mn–28Al (in wt%) alloys were prepared by arc melting with pure metals of 99.9% Mn and 99.99% Al in the argon atmosphere. And then these alloys were heat treated at 1000 °C for 72 h, finally quenched in water. These alloys were further mechanically crushed and milled into powders with a diameter less than ∼50 μm. The refining treatment was carried out in an electrical furnace by using a graphite crucible and protected by the mixing gas of N_2 and SF_6. In this study, AZ31 alloy was chose as a model alloy of Al-containing Mg alloys. When the melt temperature of AZ31 alloy reached 750 °C, the 0.5–2.5 wt% Mn–38Al, Mn–34Al and Mn–28Al alloy powders were added into the melts, respectively, thereafter holding for another 10–60 min. The melts were then poured into a permanent mould with the size of ϕ 25 × 100 mm. The microstructure observation was performed at the cross section which was cut 25 mm away from the ingot bottom end. All specimens of the treated AZ31 alloys were annealed at 400 °C for 2 h so that the grain boundaries could be clearly observed.

All samples mentioned above were mechanically polished, etched by the solution of 5 g picric acid, 1 mL acetic acid, 1 mL nitric acid and 100 mL alcohol, and then observed by using OLYMPUS GX71 optical microscope. The grain size was measured

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* Corresponding author. Tel.: +86 24 83683772; fax: +86 24 83686455.
E-mail address: qingw@smm.neu.edu.cn (G.W. Qin).

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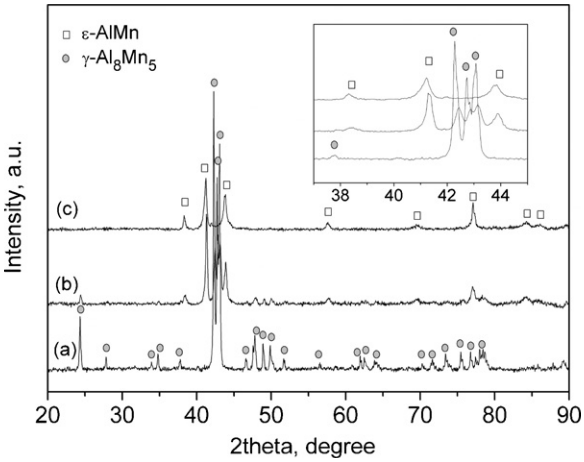

Fig. 1. X-ray diffraction patterns of the Mn–Al alloys held at 1000 °C for 72 h: (a) Mn–38Al; (b) Mn–34Al; (c) Mn–28Al.

by the standard linear intercept method. The phases in the Mn–Al master alloys were also analyzed by Philips PW3040/60 diffractometer with Cu Kα irradiation, and a high tension of 40 kV and 40 mA.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of the Mn–Al master alloys treated at 1000 °C for 72 h. There only exists the γ_2-Al$_8$Mn$_5$ in the treated Mn–38Al while the ε-AlMn phase in the Mn–28Al master alloys. In contrast, the annealed Mn–34Al master alloy is composed of the γ_2-Al$_8$Mn$_5$ and ε-AlMn phases. It is very important to determine which intermetallic compound plays a critical role in the grain refinement of AZ31 Mg alloy.

Fig. 2 shows optical microstructures of the AZ31 Mg alloy with the addition of either Mn–38Al, Mn–34Al or Mn–28Al master alloys. All the alloys demonstrate typical equiaxed grains. For the AZ31 Mg alloy with or without addition of the Mn–38Al master alloy (pure γ_2-Al$_8$Mn$_5$ phase), grain sizes in the both cases are very similar (~85 μm) with a large size distribution, as shown in Fig. 2a and b, suggesting that the γ_2-Al$_8$Mn$_5$ phase be less effective in grain refinement of AZ31 Mg alloy. In contrast, the average grain size remarkably decreases, together with a smaller size distribution, when the Mn–28Al master alloy (pure ε-AlMn phase) is added, as shown in Fig. 2c. It clearly implies that the ε-AlMn intermetallic compound can act as the heterogeneous site of α-Mg phase during the solidification of the AZ31 Mg alloy, but not the γ_2-Al$_8$Mn$_5$ intermetallic compound. This experimental result is well consistent with the calculated result by Zhang et al. [6]. It is very interesting to find that the grain size of AZ31 Mg alloy with the addition of Mn–34Al master alloy (ε-AlMn + γ_2-Al$_8$Mn$_5$ phases) is basically equivalent to that with the Mn–28Al master alloy (pure ε-AlMn phase), as shown in Fig. 2d. That is to say, the grain refinement of AZ31 Mg alloy is not largely affected by the content of the ε-AlMn phase in the Mn–Al master alloys, at least in the studied volume fraction range of this work. Fig. 3 summarizes the observation results above. It is worthy to note that this observation is different from the prediction of Cao et al. [7], where a Mn–Al master alloy containing a large amount of the ε-AlMn phase will be able to produce more effective grain refinement.

Fig. 4 shows the effect of holding time on the grain size of AZ31 Mg alloy conducted at 750 °C when 1 wt% Mn–28Al master alloy is added. The grain size slightly changes from ~63 μm at 10 min to ~49 μm at 60 min, which confirms that the refinement efficiency does not deteriorate with holding time prolonged to 60 min although the ε-AlMn phase is stable only above 840 °C [9]. It implies that the metastable ε-AlMn phase at 750 °C does not disappear after

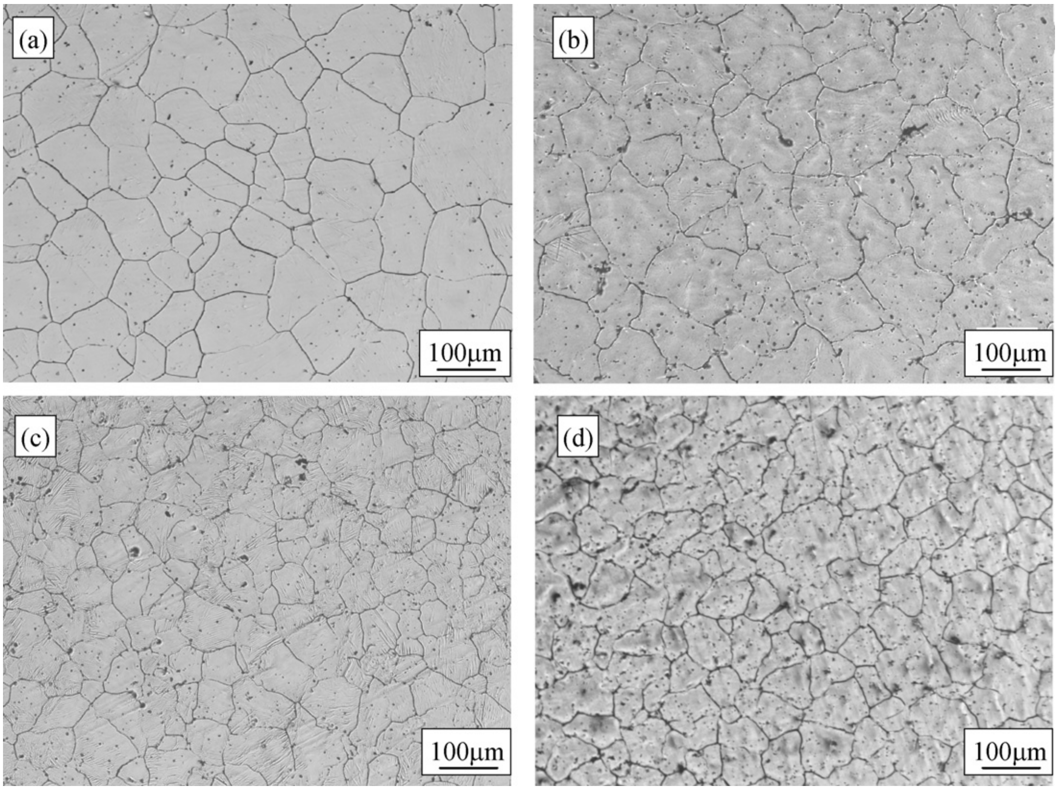

Fig. 2. Optical microstructures of the AZ31 alloys with or without the addition of different Mn–Al master alloys melt at 750 °C for 40 min: (a) without Mn–Al master alloy addition; (b) 1 wt% Mn–38Al; (c) 1 wt% Mn–34Al; (d) 1 wt% Mn–28Al.

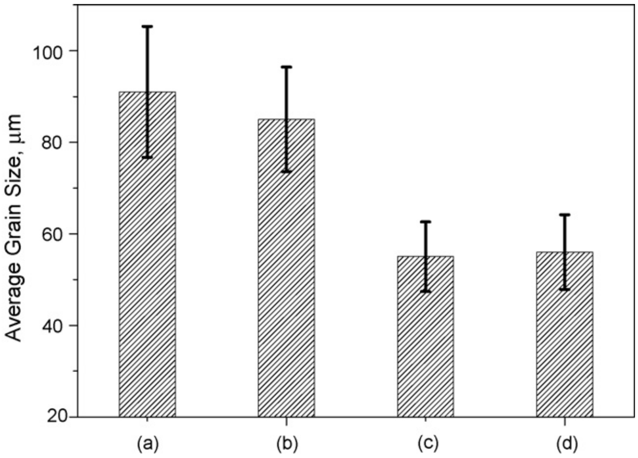

Fig. 3. Average grain size of the AZ31 alloys with or without the addition of different Mn–Al master alloys melt at 750 °C for 40 min: (a) without Mn–Al master alloy additions; (b) 1 wt% Mn–38Al; (c) 1 wt% Mn–34Al; (d) 1 wt% Mn–28Al.

holding for 60 min, which is consistent with the Cao and Stjohn's result [10,11].

Fig. 5 shows the effect of the addition amount of Mn–28Al alloy on the grain refinement of AZ31 Mg alloy. Compared to the original AZ31 Mg alloy, the grain size is markedly refined by the addition of 0.5–2.5 wt% Mn–28Al alloy. Even with 0.5 wt% Mn–28Al alloy, the grain refinement is very clear. This result is summarized in Fig. 6. It is interesting to find that the refinement efficiency is not further improved with the more addition amount of the Mn–Al master alloy. The reason remains unknown at present time, and it possibly implies that the effect of Mn on the grain refinement of the AZ31 Mg alloy depends on whether the ε-AlMn intermetallic phase exists or the phase formed in the melts. In any case, the fact is very important for industrial application that a small amount grain refiner addition can produce obvious grain refinement.

In summary, our experiments clearly confirm that the refining mechanism of AZ31 Mg alloy is due to the existence of ε-AlMn intermetallic phase, not γ_2-Al_8Mn_5 phase, which supports the crystallographically calculated results [6]. It is thus suggested that the grain size of Al-containing Mg alloys can be effectively refined if the ε-AlMn phase alloy is added, or *in situ* formed in the melts of Mg alloys. The former conclusion is also confirmed by that of Cao et al. [7], Li and co-workers [8], Stjohn et al. [11] and Tamura et al. [4]. That is, the effective grain refinement can be obtained with the addition of Al–60Mn, or Al–70Mn master alloys into Mg alloys [7,8], but not the Al–10Mn alloy which possibly contains the Al_6Mn phase. For the latter case, the formation of ε-AlMn phase depends on the superheating temperature and holding time, alloy composition and minor additions of other elements since the thermal stability of ε-AlMn phase is above 840 °C [9]. Tamura et al. argued that these Al–Mn(–Fe) particles are effective nucleus for α-Mg phase during the solidification processing because these particles can be often observed when the superheating melt at 900 °C was cooled to the pouring temperature of 700 °C [12]. These particles should be probably the ε-AlMn phase formed at 900 °C with a minor Fe element. At the same time, the superheating conditions and alloy compositions perhaps lead to the contrary results obtained by Tiner [2] and Nelson [3] although both of them used $MnCl_2$ as the Mn additive. It thus suggests that the phase diagrams of the Mg–Al–Mn and Al–Mn–X (X = minor elements such as Fe, C) systems at elevated temperatures should be studied to get a clearer phase relation, and it is thus allowed to use superheating process to facilitate the grain refinement processing of Al-containing Mg alloys.

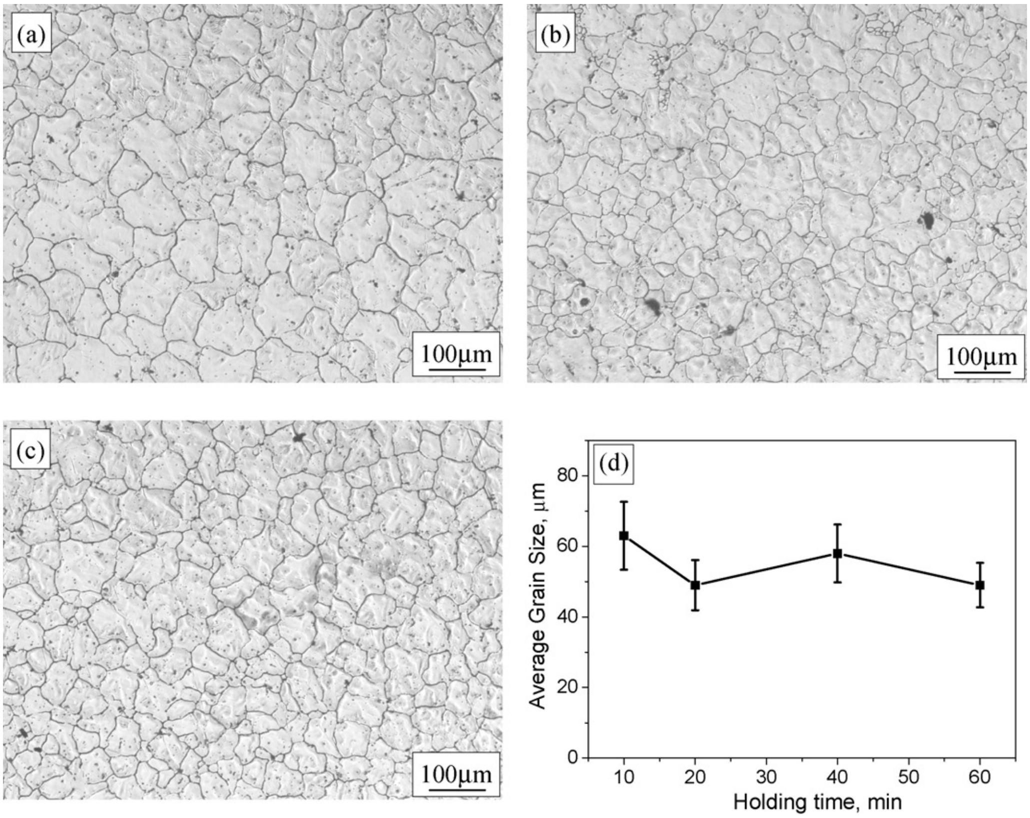

Fig. 4. Optical microstructures of the AZ31 alloys with 1 wt% Mn–28Al master alloys at 750 °C for different times: (a) 10 min; (b) 20 min; (c) 60 min and (d) summary of holding time effect.

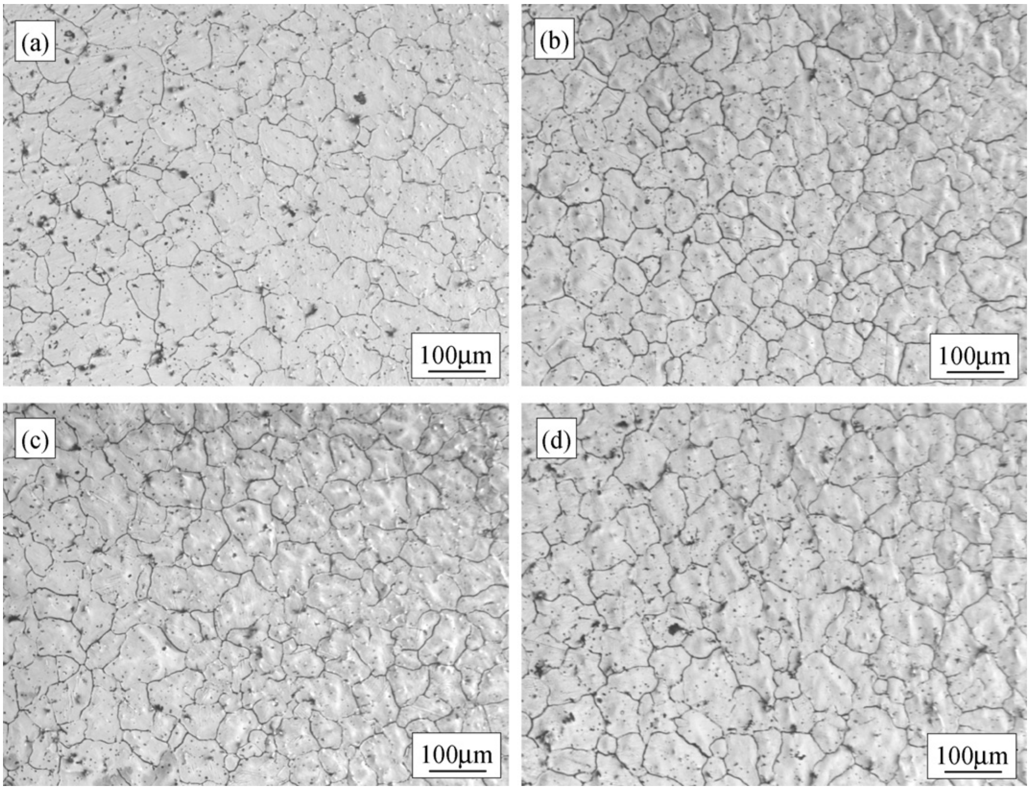

Fig. 5. Optical microstructures of the AZ31 alloys with the different addition amount of Mn–28Al master alloy melt at 750 °C for 40 min: (a) 0.5 wt%; (b) 1.5 wt%; (c) 2.0 wt%; (d) 2.5 wt%.

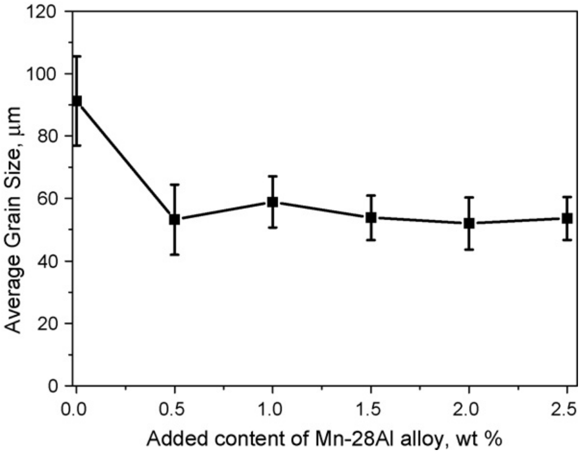

Fig. 6. The effect of addition amount of the Mn–28Al alloy on the average grain size of the AZ31 alloys melt at 750 °C for 40 min.

4. Conclusions

It is experimentally clarified that it is ε-AlMn phase that acts as the heterogeneous nucleus of α-Mg phase during the solidification of the AZ31 Mg alloy, not the γ-Al_8Mn_5 phase. The average grain size of AZ31 Mg alloy is ~91 μm, and drastically decreases to ~55 μm with addition of 1 wt% Mn–34Al (γ_2-Al_8Mn_5 + ε-AlMn) or Mn–28Al (pure ε-AlMn). The grain refinement effect is very clear with the addition of only 0.5 wt% Mn–28Al alloy and does not deteriorate up to the holding time of 60 min.

Acknowledgements

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