Grain refinement of cast zinc through magnesium inoculation: Characterisation and mechanism

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ABSTRACT

It was previously found that peritectic-forming solutes are more favourable for the grain refinement of cast Al alloys than eutectic-forming solutes. In this work, we report that the eutectic-forming solute, Mg, can also significantly grain refine cast Zn. Differential thermal analysis (DTA) of a Zn–Mg alloy, in which efficient grain refinement occurred, evidenced an unexpected peak that appeared before the nucleation of η-Zn grains on the DTA spectrum. Based on extensive examination using X-ray diffraction, high resolution SEM and EDS, it was found that: (a) some faceted Zn–Mg intermetallic particles were reproducibly observed; (b) the particles were located at or near grain centres; (c) the atomic ratio of Mg to Zn in the intermetallic compound was determined to be around 1/2. Using tilting selected area diffraction (SAD) and convergent beam Kikuchi line diffraction pattern (CBKLDP) techniques, these faceted particles were identified as $MgZn_2$ and an orientation relationship between such grain-centred $MgZn_2$ particles and the η-Zn matrix was determined. Hence, the unexpected peak on the DTA spectrum is believed to correspond to the formation of $MgZn_2$ particles, which act as effective heterogeneous nucleation sites in the alloy. Together with the effect of Mg solute on restricting grain growth, such heterogeneous nucleation is cooperatively responsible for the grain size reduction in Zn–Mg alloys.

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1. Introduction

Through the addition of efficient grain refiners into metal melts, the formation of fine, equiaxed and uniform grain structures can be enhanced. Such grain-refined microstructures deliver casting soundness and improved mechanical properties, further facilitating subsequent mechanical processing and therefore the service performance of polycrystalline metallic materials [1–3]. Zinc is favoured as an engineering material for many industrial applications due to its low melting temperature, good atmospheric corrosion resistance and sound dimensional tolerance [4]. Wrought Zn products are mainly used in four forms: flat-rolled products, wire-drawn products, extrusions and forged products [5]. To improve the formability and mechanical properties of these Zn products, the starting cast Zn ingots need to be grain refined [6–8]. Krajewski and co-workers comprehensively investigated the grain refinement of cast high-aluminium zinc alloys and the relationship between grain refinement and mechanical properties [6,8]. Recently, two peritectic-based master alloys (Zn–10 wt.% Ag and Zn–18 wt.% Cu) and two eutectic-based master alloys (Zn–60 wt.% Mg and Zn–6 wt.% Al) have been developed as grain refiners for cast Zn [9]. The grain refining mechanism of cast Zn through Ag/Cu inoculation has already been investigated and reported [10]. However, it still remains unclear why

the eutectic-forming solutes Mg/Al can also lead to significant grain refinement in cast Zn [9].

Over the past six decades, research on grain refinement of cast metals/alloys has been extensively conducted in Al, Mg and their respective alloys [2,11–16], and the most significant grain refiners have mainly been found in the peritectic-based alloy systems. This includes the Al–Ti system [17,18] (or Al–Ti–B [19]), the Mg–Zr system [14,20], the Mg–Al–Y system [21,22] and the Zn–Ag system [10]. In the early 1950s, Crossley and Mondolfo [17,18] first proposed the peritectic theory to elucidate grain refinement in Al and Al-based alloys. In the middle of the 1960s, Emley [14] re-introduced the peritectic theory to explain grain refinement of Mg–Zr alloys. Recently, Wang and co-workers found that the peritectic-forming solute elements (V, Zr and Nb) have much higher grain refining efficiencies than the eutectic-forming solute elements (Cu, Mg and Si) in cast Al when the solutes are added at levels over their individual maximum solid solubility (C_m) [15,23]. However, Qian and StJohn [20,24] suspected the contribution of peritectics in the grain refinement of Mg, because notable grain refinement can be achieved at levels far below C_m. Therefore, the question of whether peritectics are essential for the grain refinement of cast metals/alloys remains controversial, particularly for Zn.

The present authors previously found that peritectic-forming solutes, Ag and Cu, substantially reduce the grain sizes of cast Zn even at concentrations below C_m [9]. Ag contributes to the grain refinement of cast Zn through a strong growth restriction effect and the in-situ

formation of pro-peritectic nuclent particles that have favourable nucleation crystallography [10]. However, they also reported [9] that addition of the eutectic-forming solute, Mg, can produce significant grain refinement in cast Zn. Thus, several questions arise: (1) What are the grain refining mechanisms of Mg in cast Zn? (2) Does any enhanced heterogeneous nucleation occur in this eutectic alloy? (3) If so, what are the potent nuclent particles? (4) What are the dominant factors that govern the grain refining efficiency in cast metals?

2. Experimental procedure

2.1. Materials and cast process

In order to add Mg into liquid Zn, a master alloy (Zn–60 wt.% Mg) was first prepared using super-high-purity Zn ingots (99.995 wt.%) and Mg ingots (99.95 wt.%) that were melted together at 750 °C in a steel crucible coated with boron nitride in an electrical resistance furnace. This melting process was carried out using a protective cover gas (1.0% SF_6, 49% dry air and 50 vol.% CO_2). Eight binary Zn–Mg alloys, containing 0.03%, 0.06%, 0.10%, 0.20%, 0.30%, 0.45%, 0.60% and 0.74 wt.% Mg respectively, were then produced through weighed additions of the master alloy into Zn melts at 600 °C. Unless specified otherwise, all chemical compositions in the work are described in weight percent. After isothermally holding the melts of binary Zn–Mg alloys at 600 °C for 20 min, removing the surface dross and stirring, the melts were then cast into cylindrical graphite moulds (30 mm in diameter and 40 mm in length) that were preheated to 600 °C. An N-type thermocouple was used to measure the average solidification cooling rate. The cooling method developed by Backerud and Shao [25] was used in the present work. Using such a cooling method, the average cooling rates in the casting moulds were determined to be around 1 °C/s. Chemical compositions of both the master alloy and the Zn–Mg alloys were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are listed in Table 1. In order to investigate the potential phase transformation associated with the solidification of Zn–Mg alloys, differential thermal analysis (DTA) was also carried out on pure Zn and the Zn–Mg alloys using a Netzsch DTA 402 C system at a cooling rate of 0.08 °C/s.

2.2. Microstructural characterisation

Metallographic samples were sectioned at a position about 10 mm from bottom of the cylindrical ingots and were then ground and polished using Struer® equipment. To highlight the grain boundaries, the metallographic specimens were etched with Gennone–Kersey solution (84% distilled H_2O, 15% H_2SO_4 and 1 vol.% HF). These specimens were firstly examined using a Leica polarised optical microscope (OM) equipped with a Spot 32 image analysis software. The average grain sizes were measured using the linear intercept technique (ASTM 112–10). In samples where the addition level exceeded 0.2 wt.% Mg, due to the insufficient contrast, it was hard to distinguish the adjacent grains using optical microscopy. Therefore, electron backscattered diffraction (EBSD) was used to examine the microstructure of these alloys. In order to identify phase constituents, the binary Zn–Mg alloys were examined using X-ray diffraction (XRD) in a Bruker D8 diffractometer. XRD was operated at 40 kV with Cu-K_α radiation (wavelengths is $\lambda_{k\alpha1} = 1.54056$ Å).

In order to investigate the possibility of heterogeneous nucleation occurring in the Zn–Mg binary systems, the grain-refined alloys were also examined with transmission electron microscopy (TEM) to identify the heterogeneous nucleation particles (also called nuclents). The nuclents were located within the grains. Because the size of the grain-centred particles is small (1–6 μm) compared with the average grain size (≥100 μm), it was extremely difficult to find such particles in TEM using the thin foils prepared by the conventional TEM preparation methods (i.e. twin-jet polishing, precision ion polishing system (PIPS) and tri-pod grinding). Focused-ion beam (FIB) milling remains as a unique method for site-specific TEM specimen preparation [26–30]. However, FIB cannot be directly employed on the ion beam-sensitive Zn alloys due to severe ion beam damage. Thus, a modified FIB-TEM method was developed to prepare site-specific TEM specimen for the ion beam-sensitive Zn alloys in this paper. The conventional process of FIB-TEM sample preparation consists of: (1) depositing a protective Pt layer using an ion beam to preserve the target area; (2) subsequent rough milling; (3) lifting-out; and (4) post-thinning. The modified method combines the electron beam-induced (EBI) deposition process with the ion beam-induced (IBI) deposition process to produce two consecutive Pt layers before follow-up FIB thinning. Fig. 1 shows one typical site-specific FIB-TEM specimen which was prepared using this modified method. More details of the modified method are given in Appendix A. The EBI Pt layer provides protection of the target area from ion beam damage, and the subsequent IBI process can then more efficiently deposit a Pt layer over the initial EBI layer, thereby reducing the time consumed in the whole process. Site-specific TEM specimens were milled out from a bulk sample by Helios Nanolab 600 dual beam SEM/FIB, and an in-situ lift-out procedure was used to secure the TEM foil on an Omniprobe® TEM grid. All the TEM specimens were then examined in a JEOL 2100 TEM operated at 200 kV.

3. Results

3.1. Microstructures of the Zn–Mg alloys

Fig. 2 presents typical optical micrographs of some selected cast Zn–Mg alloy microstructures. Addition of 0.03 wt.% Mg fully converted the columnar grain structure of pure Zn into equiaxed grains, as shown in Fig. 2a–b. Further increases in Mg content led to significant grain refinement, as illustrated in Fig. 2c–f. In the plot of average grain size versus Mg content in Fig. 3, it can be seen that the grain size decreases sharply from 1878 to 224 μm with only 0.1 wt.% Mg addition (note: the maximum solubility (C_m) of Mg in Zn is 0.1 wt.%). A further increase in the Mg content causes a continual reduction in the average

Table 1
Contents of major solute elements in the as-cast master alloy, and the difference of Mg concentrations between nominal and determined addition levels in the eight Mg–Zn alloys.

Master alloy Zn–60 wt.% Mg	Solute concentrations determined using ICP-AES (all in wt.% unless specified otherwise)										
	Zn	Mg	Cu	Al	Fe	Ni	Sn	Mn	Cr	Pb	Cd
	.Bal	60.05 ± 0.15	.002	.002	.002	.001	.001	.024	.001	.001	.001
Grain-refined specimens	Specimen no.			Nominal addition				Determined content			
	1			0.03 Mg				0.023 Mg			
	2			0.06 Mg				0.044 Mg			
	3			0.10 Mg				0.067 Mg			
	4			0.20 Mg				0.150 Mg			
	5			0.30 Mg				0.260 Mg			
	6			0.45 Mg				0.410 Mg			
	7			0.60 Mg				0.570 Mg			
	8			0.74 Mg				0.730 Mg			