

## Microstructure and Deformation Behavior of a Mg-RE-Zn-Al Alloy Reinforced with the Network of a Mg-RE Phase

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A new Mg-RE-Zn-Al alloy reinforced with the second phase of  $Mg_{12}(RE)$  has been developed to enhance mechanical properties at the elevated temperatures. When the alloy solidifies with a relatively high cooling rate under the pressure applied, an extremely fine  $\alpha$ -Mg phase with a completely closed network of the second phase of  $Mg_{12}(RE)$  is developed. The reinforcing network restricts grain boundary sliding during deformation, resulting in a high yield strength of 150 MPa at 150 °C. Furthermore, the refined alloy exhibits around 27 % elongation to failure at 150 °C. This indicates that the failure behavior cannot be affected by the effects of residual stresses induced during solidification and stress concentrations developed near the second phase during deformation.

**Keywords:** magnesium alloy, misch metal, network structure, mechanical properties

### 1. INTRODUCTION

A magnesium alloy, one of the most promising light-weight structural materials, has received an increasing amount of attention in the automobile industry [1]. While the magnesium alloy exhibits high specific strength (the ratio of strength to density) at room temperature, the industrial application of the magnesium alloy as a structural component has been limited because of a rapid decrease in strength at elevated temperatures. Thus, the improved mechanical properties of magnesium alloys at elevated temperatures have been achieved with the formation of thermally stable second phases located within the grains and/or along the grain boundaries which restrict grain boundary sliding during deformation [2-5]. In particular, an MEZ alloy (Mg-RE-Zn-Mn, where RE is rare earth elements) exhibits significantly improved creep resistance with the cooperation of the thermally stable second phase distributed in the grain boundary region [6]. However, the strength levels of the MEZ alloy at elevated temperatures are not so high (the yield strength is 78 MPa at 150 °C) [7]. While large amounts of RE elements must be added to obtain high strength in such an alloy, limited ductility has been overcome [8,9]. On the other hand, in the alloys that contain RE elements, the sluggish atomic movement of the

heavy RE elements in the melt significantly modifies the distribution of the second phase during solidification depending on the cooling rate and pressure applied on the melt [9].

In this study, large amounts of Ce-rich misch metal are added in the Mg-Zn-Al alloy system in order to achieve high strength at elevated temperatures up to 150 °C. The deformation behavior of the alloy is evaluated at room temperature and 150 °C. When the alloy contains misch metal higher than 10 wt.%, the  $\alpha$ -Mg phase is found to be mostly surrounded by the second phase, providing a network structure in the conventional casting route (gravity casting). Furthermore, the network of the alloy can be significantly modified to be refined through the die casting method, providing improved mechanical properties in both strength and ductility [10].

### 2. EXPERIMENTAL PROCEDURES

An alloy of nominal composition (wt.%),  $Mg_{84}RE_{11}Zn_4Al_1$ , was selected in this study. The alloy was prepared under a dynamic argon atmosphere by induction melting of metals, Mg (99.0 %), Zn (99.9 %), Al (99.9 %), and commercially available Ce-rich misch metal which contains 51.7 % Ce, 23.1 % La, 18.6 % Nd, and 6.5 % Pr (in mass.%). The master alloy was remelted in the electric resistance furnace and then poured into a rectangular cavity ( $60 \times 15 \times 100 \text{ mm}^3$ ) for gravity casting. Thin plate samples ( $90 \times 50 \times 2 \text{ mm}^3$ ) were

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fabricated by the die casting method with a fast cooling rate ( $\sim 10^2$  K/s) and pressure applied around 50MPa.

Scanning electron microscopy (SEM) was used to reveal the microstructure of the samples. Phase identification of the specimens was carried out using X-ray diffraction (XRD, Rigaku, CN2301) with  $\text{CuK}\alpha$  radiation. The chemical compositions of the respective phases formed in the alloy were analyzed using an energy dispersive X-ray spectrometer (EDX, Thermo Noran, 15 kV). The thermal properties of the alloy were measured by differential scanning calorimetry (DSC, Setaram TGA 92) during continuous heating at a heating rate of 0.333 K/s.

Uniaxial tensile tests were carried out on dog-bone specimens (gauge length: 10 mm) using an Instron-type machine under the constant cross-head speed conditions of an initial strain rate of  $10^{-4} \text{ s}^{-1}$  at room temperature and  $10^{-3} \text{ s}^{-1}$  at 150 °C, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Microstructure

Figures 1(a) and (b) show the microstructures of the  $\text{Mg}_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy fabricated by gravity casting and die casting, respectively. Significant variation of microstructure, depending on the fabricating condition, occurred. The primary  $\alpha$ -Mg (gray region) is mostly surrounded by a second phase (bright region), producing the network structure in gravity casting (Fig. 1(a)). On the other hand, for the sample fabricated by die casting with fast cooling under high applied pressure, the very fine  $\alpha$ -Mg phase with a completely closed fine network of the second phase was developed, as shown in Fig. 1(b). The average size of the  $\alpha$ -Mg phase is around 5  $\mu\text{m}$ , 10 times smaller than that produced by gravity casting. In general, the considerable undercooling caused by rapid solidification increases the nucleation sites of the  $\alpha$ -Mg phase [11,12] and the applied pressure restricts atomic movement in the melt [13], pro-

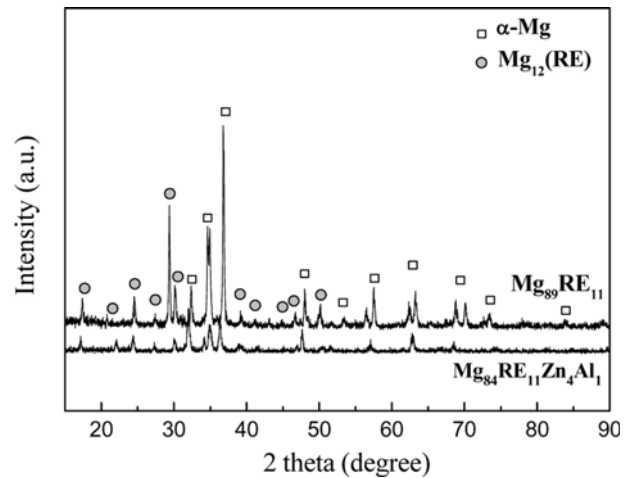


Fig. 2. X-ray diffraction pattern of the  $\text{Mg}_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy fabricated by die casting and Mg-RE alloy.

ducing such a refined microstructure.

Figure 2 shows the XRD patterns taken from the sample fabricated by die casting to identify the phases in the alloy. Since some peaks observed in the  $\text{Mg}_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy could not be identified, we prepared a  $\text{Mg}_{89}\text{RE}_{11}$  alloy for comparison that contained only two phases,  $\alpha$ -Mg and  $\text{Mg}_{12}(\text{RE})$ . Both alloys show similar peaks and any new peaks could not be observed in the  $\text{Mg}_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy. The zinc and aluminum contained in the alloy do not contribute to form any other phases. A similar XRD pattern is also detected for the sample fabricated by gravity casting (not shown). The EDX results are listed in Table 1. The  $\alpha$ -Mg phase was found to be nearly pure magnesium, and zinc and aluminum were mainly located in the  $\text{Mg}_{12}(\text{RE})$  phase due to the strong attraction effects of the RE elements contained in the alloy (Zn and Al have around 10 times higher negative values of heat of mixing with Ce, La, Pr and Nd than those with Mg [14]). Figure 3 shows the DSC trace of the sample fabricated by die casting in which

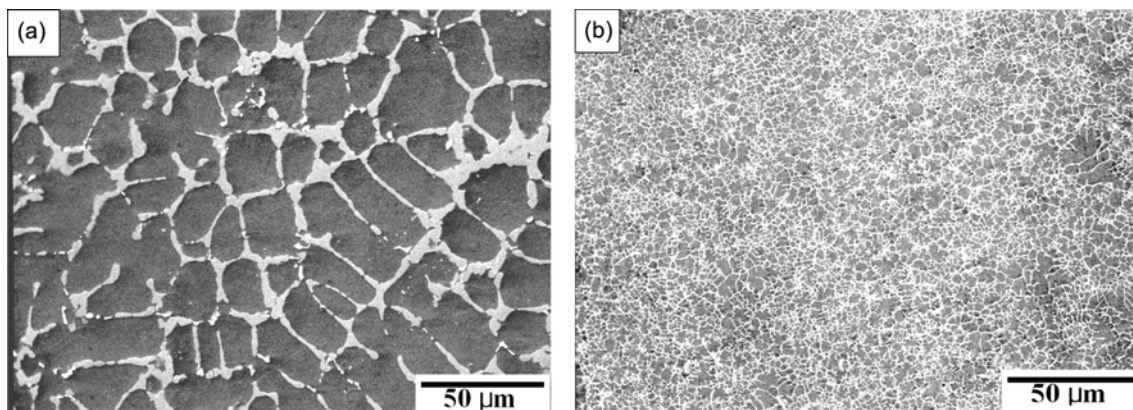
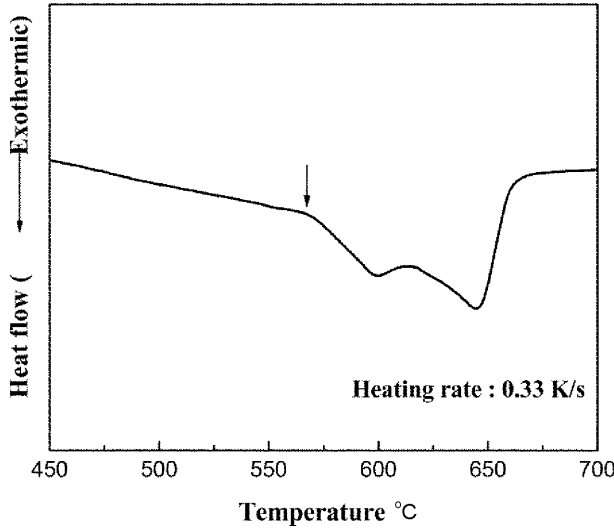


Fig. 1. SEM micrographs of the  $\text{Mg}_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy with the variation of (a) gravity casting and (b) die casting. All microstructures show the network structure of the secondary phase (bright region) which wraps the  $\alpha$ -Mg phase (dark region).

**Table 1.** Chemical compositions of the  $\alpha$ -Mg phase and the  $Mg_{12}(\text{RE})$  phase analyzed using EDX in the  $Mg_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy produced by die casting

Phase	Composition (wt.%)					Mg
	Ce	La	Nd	Zn	Al	
$\alpha$ -Mg	0.31	-	-	0.93	-	Balanced
$Mg_{12}(\text{RE})$	4.93	2.11	1.07	2.61	0.53	Balanced

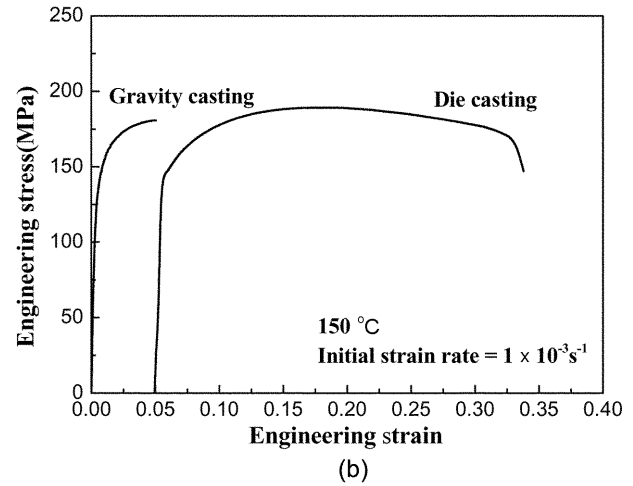
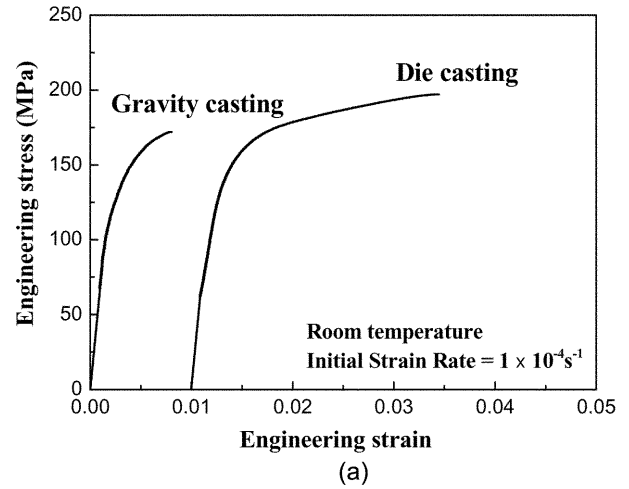


**Fig. 3.** DSC trace of the  $Mg_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy obtained during continuous heating at a heating rate of 0.33 K/s. The onset eutectic temperature is marked by an arrow.

the first endothermic peak appears at the temperature of 570 °C (marked by an arrow). This peak is recognized as the eutectic temperature of the alloy. Thus, the alloy does not show any phase transition in the temperature range up to 570 °C.

### 3.2. Deformation and fracture behaviors

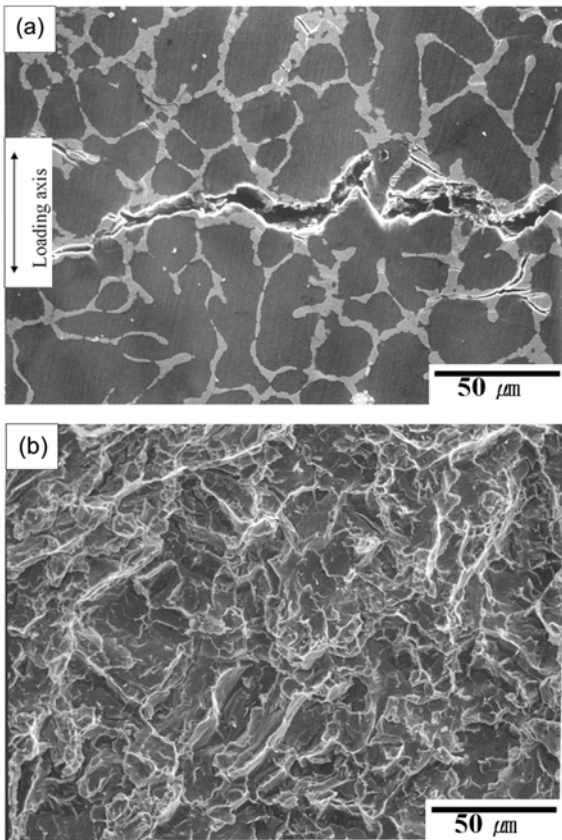
The engineering stress ( $\sigma$ ) versus engineering strain ( $\epsilon$ ) curves for the samples fabricated by gravity casting and die casting are given in Fig. 4 at (a) room temperature and (b) 150 °C, respectively. For the sample fabricated by gravity casting, the yield stress (at 0.2 % strain) is 160 MPa at room temperature with negligible elongation to failure and 142 MPa at 150 °C with elongation to failure around 3 %, as demonstrated in the alloys containing large amounts of RE elements [8,9]. The ratio of yield stress drops ( $\Delta\sigma = \sigma_{\text{room}} - \sigma$ , where  $\sigma_{\text{room}}$  is the yield stress at room temperature) to  $\sigma_{\text{room}}$ , ( $\Delta\sigma/\sigma_{\text{room}}$ ), at 150 °C is only 0.11, the value of which is significantly lower than that of 0.31 for AE42 alloy, 0.24 for AZ91 alloy, 0.24 for MRI 153 alloy, and 0.2 for MEZ alloy [2,5,7,15,16]. Although the alloy does not have any strengthening effect stemming from the presence of solutes or precipitates in the nearly pure magnesium matrix, the network frame of the  $Mg_{12}(\text{RE})$  phase is strong enough to



**Fig. 4.** Engineering stress-strain curves of the  $Mg_{84}\text{RE}_{11}\text{Zn}_4\text{Al}_1$  alloy fabricated by gravity casting and die casting under uniaxial tension at (a) room temperature and (b) 150 °C.

resist the plastic deformation of the alloy at the elevated temperature of 150 °C. Further enhancement of mechanical properties is achieved by refining the microstructure. The die casting sample exhibits a yield stress of 170 MPa at room temperature and 150 MPa at 150 °C (i.e.  $\Delta\sigma/\sigma_{\text{room}} = 0.11$ ). The stress levels are higher than those of the gravity casting sample mainly due to the much finer network structure [17]. In addition, much enhanced elongation to failures is observed at room temperature (2 %) and at 150 °C (27 %). We also recognize that the alloy may contain some inclusions such as oxides inevitably included during the solidification processes, which may act as opening sites of the cracks during deformation. However, the die casting sample shows the typical ductile failure behavior of the formation and growth of a neck at 150 °C.

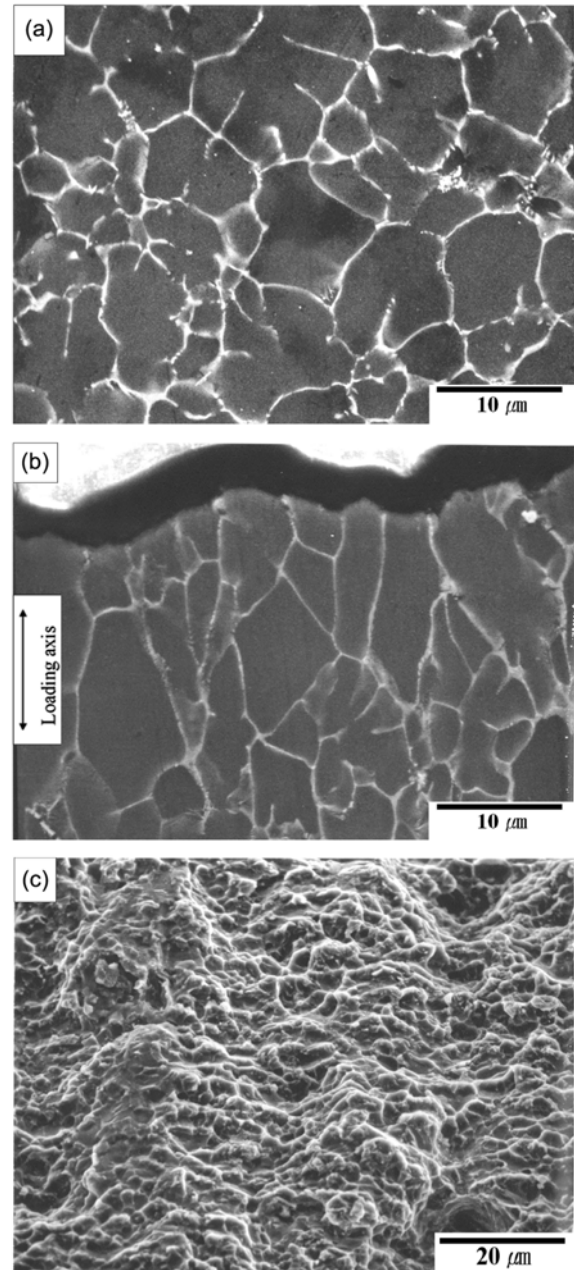
During solidification, the  $\alpha$ -Mg phase primarily solidifies, and then the secondary phase  $Mg_{12}(\text{RE})$  is formed near the  $\alpha$ -Mg phase boundaries, constructing the network



**Fig. 5.** SEM micrographs of (a) the deformed specimen and (b) the fracture surface after the test at 150 °C for the  $Mg_{84}RE_{11}Zn_4Al_1$  alloy fabricated by gravity casting. The crack propagates along the brittle  $Mg_{12}(RE)$  phase.

structure in the alloy. When the volume shrinkage occurring during solidification in the second phase is not fully accommodated by the  $\alpha$ -Mg phase, residual stresses are generally developed near the phase boundaries. The thicker second phase can develop a higher level of residual stresses. Eventually they will assist in initiating and propagating the cracks formed in the network during deformation, leading to the failure of the alloy [18,19]. Figure 5(a) shows a crack propagating along the  $Mg_{12}(RE)$  phase for the gravity casting sample at 150 °C. The sample fails in an almost brittle manner, showing a fracture surface (Fig. 5(b)) in which typical cleavage facets of the  $Mg_{12}(RE)$  phase are observed.

However, for the sample having a fine network, as shown in Fig. 6(a), after 27 % tensile elongation at 150 °C, both the  $\alpha$ -Mg phase and the network elongate along the loading axis, as shown in Fig. 6(b). This infers that grain boundary sliding is completely restricted by the network during deformation even at the elevated temperature. Second, no cracks are observed near the failed region. The thickness of the  $Mg_{12}(RE)$  phase constructing the network is so thin that stress concentration developed near the second phase dur-



**Fig. 6.** SEM micrographs of (a) the as-cast specimen and (b) the deformed specimen and (c) the fracture surface after 27 % elongation at 150 °C for the  $Mg_{84}RE_{11}Zn_4Al_1$  alloy fabricated by die casting.

ing deformation could not significantly influence on the formation of cracks. Furthermore, the level of residual stresses introduced during solidification must not be high to encourage the propagation of the cracks along the phase boundaries, as seen in Fig. 5(b). The fracture surface reveals very fine intragranular facets with dimples, as shown in Fig. 6(c). That is, the fracture mode is changed from an intergranular fracture to an intragranular fracture by the refinement of the microstructure.

#### 4. CONCLUSIONS

For the  $Mg_{84}RE_{11}Zn_4Al_1$  alloy, which consists of a  $\alpha$ -Mg phase and  $Mg_{12}(RE)$  phase, the deformation behavior of the alloy has been investigated with a relation of the microstructure at room temperature and 150 °C. The alloy does not show any phase transition in the temperature range up to 570 °C since the eutectic temperature of the alloy is very high around 570 °C. The microstructure of the alloy containing large amounts of heavy RE elements could be easily modified by the casting method. For the alloy fabricated by gravity casting, which contains the thick and coarse frame of the  $Mg_{12}(RE)$  network, the yield strength is about 142 MPa at 150 °C and is insensitive to the temperature up to 150 °C. However, elongation to failure is generally low since the propagation of cracks can occur along the thick frame. On the other hand, the alloy produced by die casting, which contains the thin and fine network which restricts grain boundary sliding during deformation, exhibits a high strength of 150 MPa at 150 °C. Furthermore, the alloy exhibits around 27 % elongation to failure at 150 °C and fails not by the formation of cracks in the network, but rather by necking after large elongation. Thus, the alloy that contains large amounts of RE elements can be modified to have improved mechanical properties in both strength and ductility through the refinement of the microstructure.

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