Effects of rare earth elements on microstructure and high temperature mechanical properties of ZC63 alloy

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Magnesium (Mg) alloys have gained a considerable attention from automobile and aerospace industries due to their low density (1.74 g/cm^3), good weldability, high specific solidity, good damping properties, and excellent castability [1]. However, relatively inferior high temperature strength and creep properties of the Mg alloys have limited their commercial utilization, thus, principal challenges to widespread use of the Mg alloys have focused on the enhancement of their mechanical properties at elevated temperature [2–5].

Rare earth (RE) metals such as Cerium (Ce), Lanthanum (La), Neodymium (Nd), Yttrium (Y), and Gadolinium (Gd) are well known to improve high temperature properties of the Mg alloys by formation of Mg-RE compounds possessing high thermal stability. Accordingly, RE containing Mg casting alloys such as WE43, WE54, EZ33, ZE41, and ZE63 *et al*. have been developed and used for high temperature applications. Most of these alloys except for ZE41, however, contain expensive RE elements above 2% in weight, which eventually leads to rise in production cost [6–9].

As a basic research for the development of cheaper heat resistant Mg alloy with small RE content, the influences of RE on microstructure and high temperature mechanical properties were studied in ZC63 (Mg-6.0%Zn-2.7%Cu-0.25%Mn) casting alloy. For this investigation, cheaper Ce-rich misch metal (Mm) consisting of ∼55% of Ce, ∼22% of La, ∼18% of Nd, and ∼5% of Praseodymium (Pr), was used as RE elements and its amount was limited to ∼1%.

The three ZC63 + RE alloys containing RE in a range of 0–1.0% (in weight) were prepared by melting 99.8%Mg, 99.99%Zn, 99.9%Cu, 99.9%Mn, and 99%Mm under a protective $SF_6 + CO_2$ atmosphere and casting into a metallic mould. From these ingots, various specimens for microstructural observations, X-ray diffractometry (XRD), and tensile tests were prepared by machining. All specimens were solution-treated at 440 °C for 8 hr followed by an artificial aging at 200 °C for 16 hr, in accordance with the recommended T6 condition for the ZC63 alloy [10]. The chemical compositions of experimental alloys are listed in Table I.

Tensile tests were performed at 175 and 250 °C with a fixed initial strain rate of 2×10^{-3} s^{-1} on an Instron-type tensile testing machine. ASTM subsize specimens with a gauge length of 25 mm were used. Phase constituents of the alloys were identified by XRD (Rigaku CN-2200) using a Cu-Kα radiation. The microstructural analyses were carried out using optical microscopy (OM, Olympus CK-40 M) and scanning electron microscopy (SEM, Hitachi S-2700) equipped with energy dispersive X-ray spectrometry (EDS) system. Samples for optical and SEM microstructures were chemically etched with an Acetic picral solution (5 ml acetic acid + 6 g picric acid + 10 ml H_2O + 100 ml ethanol) [11]. The hardness of the specimens was measured by means of a MicroVickers hardness tester (Matsuzawa MXT-α) with a load of 100 g.

XRD patterns for the T6-treated ZC63 + RE alloys are given in Fig. 1. In view of a previous report [12] that much of Cu atoms in Mg-Zn-Cu ternary system are incorporated into Mg-Zn eutectic phases, it is reasonable to designate Mg-Zn phases as Mg(Zn,Cu) and $Mg(Zn,Cu)_2$ rather than MgZn and $MgZn_2$ in the present study. The addition of 0.5%RE introduces two peaks corresponding to $Mg_{12}RE$ phase between 25 and 30°, as shown in Fig. 1b, and their intensities become greater with further RE addition. It is noted in Fig. 1c that MgRE phase peaks are observed around 52° when the RE content is 1.0%.

Fig. 2 shows the optical microstructures of T6-treated ZC63 + RE alloys. The microstructure of ZC63 alloy is distinctively characterized by dendritic grains of Mg solid solution surrounded by discontinuous Mg(Zn,Cu) or $Mg(Zn,Cu)_2$ eutectic phases along the grain boundaries. The addition of 0.5%RE effectively refines the grains of ZC63 alloy from ∼75 to ∼39 μm, but no remarkable change is seen by further RE addition. It is noticeable that the number density of the eutectic phases appears to become higher as the RE content is increased. Secondary electron (SE) image of the ZC63 + 1.0RE alloy and chemical compositions of the eutectic phase (A) and spherical precipitate (B) inside the eutectic phase determined by EDS analyses are given in Fig. 3 and Table II, respectively. The phases A and B show the compositions of $Mg_{33.1}Zn_{58.7}Cu_{8.2}$ and $Mg_{85.5}RE_{8.2}Zn_{4.8}Cu_{1.5}$, indicative of $Mg(Zn,Cu)_2$ and $Mg_{12}RE$ compounds, respectively. The fact that most of $Mg_{12}RE$ particles are observed within the eutectic phase strongly implies that during solidification, Mg-RE particles act as nucleants of the eutectic phase, resulting in the increased number density of the

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TABLE I Chemical compositions of experimental alloys

	Chemical composition (wt.%)				
Alloy designation	Zn	Cu	Mn	Mm	Mg
ZC63 (Mg-6%Zn-2.7%Cu-0.2%Mn)	5.12	2.37	0.07	–	Bal.
ZC63 + 0.5RE	5.21	2.46	0.12	0.38	Bal.
ZC63 + 1.0RE	5.29	2.51	0.13	1.18	Bal.

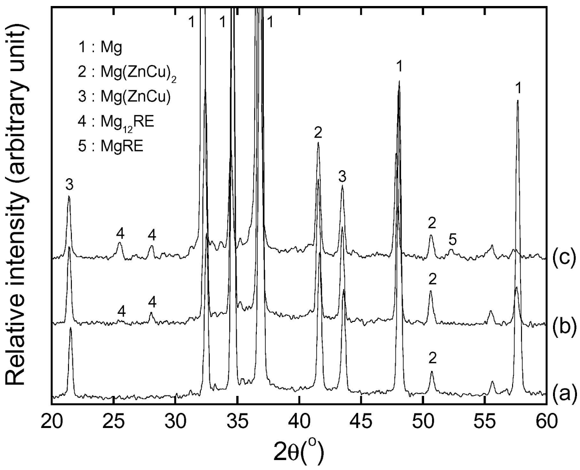

Figure 1 X-ray diffraction patterns of the T6-treated ZC63+RE alloys: (a) ZC63, (b) ZC63+0.5RE, (c) ZC63+1.0RE.

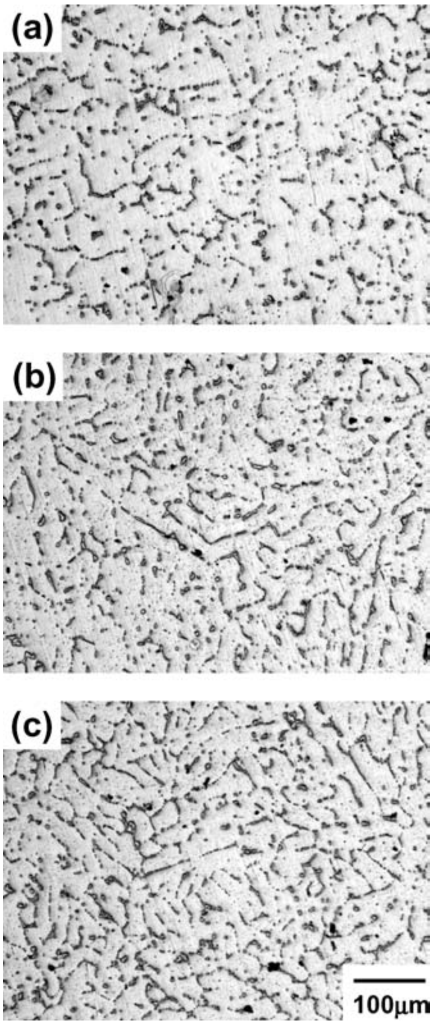

Figure 2 Optical microstructures of the T6-treated ZC63+RE alloys: (a) ZC63, (b) ZC63+0.5RE, (c) ZC63+1.0RE.

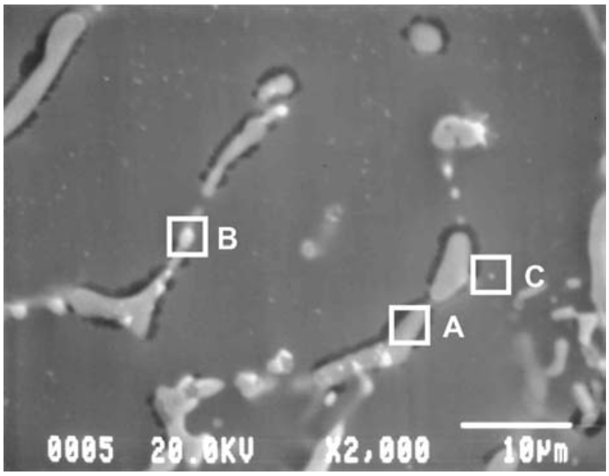

Figure 3 Secondary electron image of the T6-treated ZC63+1.0RE alloy.

discontinuous eutectic phases. The small particles inside the grains (C) are assumed Mg-RE compounds, although compositional data could not be obtained owing to the resolution limit of EDS analysis.

The addition of RE into ZC63 alloy gives rise to the increase in hardness in T6-treated state from 56Hv (ZC63) to 63Hv (ZC63 + 0.5RE) to 71Hv (ZC63 + 1.0RE). Taking microstructural features in Figs 1–3 into consideration, this may well be ascribed to the following three factors : (i) grain refinement, (ii) increased number density of Mg(Zn,Cu) and Mg(Zn,Cu)$_2$ eutectic phases and (iii) precipitation of Mg-RE compounds such as Mg$_{12}$RE and MgRE.

The mechanical properties at 175 and 250 °C for the T6-treated ZC63 + RE alloys are listed in Table III. The higher the RE content, the greater the yield strength (YS) and ultimate tensile strength (UTS) values with a gradual decrease in elongation. The improved YS and UTS at elevated temperatures for the ZC63 + RE alloys over ZC63 can be explained by three reasons for the increase in hardness addressed previously. The UTS and YS of ZC63 + 1.0RE alloy at 250 °C are superior to those of ZE41 alloy

TABLE II Chemical compositions of precipitates A and B determined by EDS

Precipitate	Chemical composition (at.%)
A	$Mg_{33.1}Zn_{58.7}Cu_{8.2}$
B	$Mg_{85.5}RE_{8.2}Zn_{4.8}Cu_{1.5}$

TABLE III High temperature mechanical properties of the T6-treated ZC63 + RE alloys

	175 °C			250 °C		
Alloy	YS (MPa)	UTS (MPa)	El. (%)	YS (MPa)	UTS (MPa)	El. (%)
ZC63	86	143	10.8	71	78	16.1
ZC63 + 0.5RE	95	151	9.3	77	88	10.5
ZC63 + 1.0RE	123	164	5.4	105	119	7.8

($\sim$70 MPa of YS and $\sim$100 MPa of UTS at 250 °C) [12] with similar amount of RE, and are comparable to those of EZ33 or ZE63 alloys with higher RE contents [12]. This result demonstrates that small amount of RE addition around 1.0% is very effective in improving high temperature mechanical properties of ZC63 alloy.

In summary, the small amount of RE addition into ZC63 alloy gives rise to the refinement of grains, precipitation of $Mg_{12}RE$ and MgRE compounds, and increase in number density of Mg(Zn,Cu) and $Mg(Zn,Cu)_2$ eutectic phases, resulting in improvement of high temperature strength for the ZC63 + RE alloys. The UTS and YS values of ZC63 + 1.0RE alloy at 250 °C are better than those of ZE41 alloy, and are comparable to those of EZ33 and ZE63 alloys with higher amount of RE. This result indicates that around 1% of RE addition is effective to improve high temperature mechanical properties of ZC63 alloy.

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