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Partition of Er among the constituent phases and the yield phenomenon in a semi-continuously cast Mg–Zn–Zr alloy

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This paper describes an increased partition of a rare earth element Er to the Mg matrix in a semi-continuously cast Mg–1.5Zn–0.6Zr alloy, resulting in a significant increase in elongation, as well as a refined grain size and a higher yield strength in the extruded Er-containing alloys compared with the Er-free alloy. Yield phenomena with distinct upper and lower yield points were also observed, caused by the strong interaction between solute atoms and dislocations as a result of Er addition.

Keywords: Magnesium alloys; Rare earth; Yield phenomena; Solidification microstructure

With a relatively high specific strength, magnesium alloys are desirable for many applications in the microelectronics, aerospace and automobile industries. However, the potential use of magnesium alloys in wrought forms, such as sheets and extrusions, are seriously limited due to their poor ductility and workability. The poor ductility at room temperature is attributed to the fact that there are only two independent basal $(0001)\langle 11\bar{2}0\rangle$ slip systems available in hexagonal close-packed (hcp) Mg and its alloys, since the critical resolved shear stress (CRSS) for the basal slip is much lower than those for the non-basal (prismatic and pyramidal) slip systems. Furthermore, strong deformation texture, $\{0\,0\,0\,1\}$ basal texture, readily exists in rolled or extruded products, which is detrimental to post-processing performance and service. Recent research [1–8] on Mg alloys have shown that rare earth alloying can improve their hot workability and room temperature ductility.

Mg–Zn–Zr alloys (known as ZK alloys) are the most commonly used commercial alloys for their high strength and lower cost. The effects of rare earth addition on the mechanical properties of ZK alloys have been widely explored. Rare earth additions [9–14] were found to form largely thermally stable intermetallic particles with Zn and Mg. The volume fraction of these particles increases with the rare earth content, resulting in only a negligible increase in the concentration of the rare earth element in solid Mg. It is suggested that these rare earth and Zn bearing second-phase particles influence recrystallization and hinder grain growth [5,15], due to their dispersion strengthening effect [14–17]. However, recent studies show that it is the dissolved rare earth element in the Mg matrix that enhances ductility and formability by facilitating non-basal slip and cross-slip of screw dislocations [3,4]. This is made possible because the dissolved rare earth element can either reduce the c/a ratio or increase the stacking fault energy, leading to favorable texture modification [6]. Furthermore, excessive second-phase particles are detrimental to plasticity [17,18]. Therefore, it is of great interest to explore the possibility of maximizing the solute concentration of the rare earth element in the Mg matrix for a given rare earth content, while still maintaining a sufficient number of particles to stabilize the microstructure, so as to optimize the beneficial effect of the rare earth element on the mechanical properties and deformation behavior.

In this paper, we report an increased partition of a rare earth element Er to the matrix in a semi-continuously cast Mg–1.5Zn–0.6Zr magnesium alloy, resulting in a significant increase in elongation of the alloy. Yield phenomena with apparent upper and lower yield points were also observed, caused by the strong interaction between the solute atoms and dislocations as a result of Er addition.

The nominal composition of the experimental alloys was Mg–1.5Zn–0.6Zr (wt.%) or Mg–0.6Zn–0.2Zr

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(at.%) containing systematic additions of 0, 0.5, 1, 2 and 4 wt.% Er or 0, 0.075, 0.15, 0.3 and 0.6 at.% Er. The alloys were prepared from commercial high purity Mg (>99.9%) and Zn (>99.95%) and master alloys Mg–31 wt.% Zr and Mg–30 wt.% Er. All the materials added were melted in a steel crucible inside an electrical resistance furnace. The molten metal was mechanically stirred during melting and held at 750 °C for 30 min. The melt was then cooled down to around 720 °C and cast into ingots 85 mm in diameter by semi-continuous casting under a $(SO_2 + CO_2)$ protective gas mixture with water cooling. The ingots were then homogenized for 12 h at 410 °C and cooled in a furnace. Small samples for microstructure observation and hardness inspection were also heat treated with the same isothermal holding as the ingots, followed by quenching in water at about 70 °C to retain the high temperature microstructures.

The ingots were then skinned and heated to 420 °C for 1 h before extrusion. The extrusion die was also heated to 420 °C. Extrusion was conducted on a XJ-500 horizontal extrusion machine made in China. The extrusion ratio was 25 with a ram speed of 2–2.4 mm s^{-1}. After extrusion the alloys were cooled in open air.

Cylindrical samples of 60 mm in gauge length and 10 mm in gauge diameter were machined from the extruded bars for tensile tests at room temperature under a cross-head speed of 3 mm min^{-1}. The tension axes were parallel to the extrusion axis. Brinell hardness testing was conducted using a 0.5 kg load.

Microstructural characterizations were carried out by optical microscopy, as well as scanning electron microscopy (SEM) using a Tescan Vega2 scanning electron microscope equipped with an INCA Energy 350 energy dispersive X-ray spectrometer (EDX). Phase constitutions were determined by a Rigaku D/max 2500PC X-ray diffractometer with the use of CuKα radiation. DSC analysis was carried out with a Netzsch STA449C system. In DSC testing samples of 30 mg sectioned from the as cast and as homogenized ingots were heated to 700 °C for 5 min and then cooled at a controlled speed of 15 K min^{-1} under flowing argon.

Figure 1 shows the SEM micrographs (secondary electron images) of the as cast Mg–1.5Zn–0.6Zr alloys with different Er additions. The Er-free alloy contained only a few non-equilibrium Mg–Zn binary compounds. With increasing Er content the volume fraction of secondary intermetallic particles increased, forming a nearly continuous network along the grain boundary in the alloy with 4 wt.% Er. It should be noted that the background intensity at and near the grain boundaries was higher. The varying background intensity was supposed to be due to variations in the backscattered electron signal, indicating a higher concentration of heavier elements in the grain boundary region. EDX analysis indicated that these particles were Er- and Zn-bearing compounds. The average Zn/Er atomic ratios of the particles in the alloys are also provided in Figure 1, which were separately analyzed for particles of different morphologies, i.e. interior spherical particles within grains and grain boundary striped or blocky particles, which were formed during different stages of solidification. It shows that these compounds were in a Zn-rich phase, with the Zn/Er ratio falling in the range 2–4.2. The grain boundary particles were of a lower Zn/Er ratio than the interior particles, implying that Er segregates more to the grain boundary region than Zn during solidification.

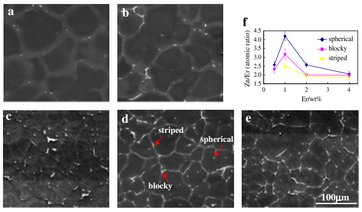

Figure 1. SEM micrographs (secondary electron images) of as cast Mg–1.5Zn–0.6Zr–Er alloys with Er contents of (a) 0, (b) 0.5, (c) 1, (d) 2 and (e) 4 wt.%. The average Zn/Er atomic ratios of particles (*y*-axis) of different morphologies, determined by EDX measurements, in the Er-containing alloys (*x*-axis) are given in (f).

XRD patterns of the as cast and as homogenized alloys (not shown here) revealed that only the α-Mg phase was detected in the Er-free alloys. New diffraction peaks appeared after addition of Er. Moreover, with increasing Er addition both the number and intensity of the peaks increased, indicating an increasing volume fraction of the second phase, which is consistent with the microstructural observations. The phases were identified to be $(Mg, Zn)_4Er$ and $(Mg, Zn)_6Er$ in the as cast and as homogenized alloys, respectively. Both are hexagonal phases with lattice parameters $a = 14.185$ Å, $c = 13.957$ Å and $a = 8.9079$ Å, $c = 9.2687$ Å, respectively, which were identified by Li et al. [19], with approximate compositions $Z_{n70.8}Mg_{10.6}Er_{18.6}$ and $Z_{n61.9}Mg_{24.1}Er_{13.9}$, respectively. These two phases show similar XRD patterns and are structurally related [19]. It is conceivable from the present work that the $(Mg, Zn)_4Er$ phase is the non-equilibrium form of the $(Mg, Zn)_6Er$ phase. The stoichiometric $(Mg, Zn)_4Er$ phase possesses a Zn/Er ratio of 3.8, lower than that of the $(Mg, Zn)_6Er$ phase at ~4.4. Er is supposed to segregate more than Zn, especially at regions that solidify last, thus resulting in a lower Zn/Er ratio in the compounds formed during solidification. On homogenization, since the solubility of Er in Mg increases rapidly with temperature, being ~5.3 at.% at 400 °C [20], excess Er will diffuse out of the compounds, leading to an increased Zn/Er ratio. The Mg–Zn–Er ternary phase diagram, to the best of our knowledge, has not yet been established. However, DSC measurements showed that besides the endothermic peak corresponding to melting of the Mg matrix, there was no additional peak in the heating curves of either the as cast or the as homogenized alloys from room temperature to 700 °C. These findings suggest that the $(Mg, Zn)_6Er$ ternary phase was thermodynamically stable under the experimental conditions.

It was noted that the XRD peaks of α-Mg were somewhat shifted from the standard positions for all the alloys. This was clearly associated with dissolution of Er and Zn in the Mg lattice. The lattice parameters of the Mg matrix for homogenized alloys were calculated using the Jade software developed by Materials Data Inc. The results are given in Table 1. Zn has a smaller atomic radius than Mg, at 1.39 Å and 1.60 Å, respectively, thus the dissolution of Zn in Mg causes lattice contraction, as reflected in the decrease in lattice cell volume in