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Improving precipitation hardening behavior of Mg—Zn based alloys with Ce—Ca microalloying additions

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ABSTRACT

The precipitation hardening behavior of newly developed Mg—Zn—Ca—Ce alloys, with modified texture and improved ductility, is studied to delineate the microstructural characteristics that lead to effective hardening upon ageing treatments. Advanced electron microscopy and atom probe techniques are used to analyze the structural characteristics in relevance to the hardening potential. It has been found that the formation of a new basal precipitate phase, which evolves from a single atomic layer GP zone, and is finely distributed in both under-aged and peak-aged microstructures, has a significant impact in the improvement of the hardening response compared with the base Mg—Zn alloys. It has also been found that the β'_1 rod precipitates, commonly formed during ageing treatments of Mg—Zn alloys, have their size and distribution significantly refined in the Ca—Ce containing alloys. The role of alloy chemistry in the formation of the fine basal plate GP zones and the refinement in β'_1 precipitation and their relationships to the hardening behavior are discussed. It is proposed that Ca microalloying governs the formation of the GP zones and the enhancement of hardening, particularly in the under-aged conditions, but that this is aided by a beneficial effect from Ce.

1. Introduction

Despite the high potential for utilization of magnesium alloys as a lightweight material their use is limited by their generally low strength and poor ductility [1,2]. Two promising options to improve these properties are by increasing strength through precipitation hardening [3,4], and enhancing ductility by rare earth element additions [5–8]. Recent research has demonstrated that the precipitation hardening effect in magnesium alloys can be significantly improved by the additions of microalloying elements [3,9–11]. These are additional elements added to a base alloy in small amounts (typically <0.5 wt.%), which tend to enhance the hardening response by refining precipitation and increasing the precipitate number density [9,12–14], but in some cases microalloying additions are reported to alter the types of precipitates that form as well [11,12]. The continued development of precipitation hardening magnesium alloys through proper design of alloy chemistry and selection of cost-effective alloying, and microalloying elements has the potential to resolve the low strength issue exhibited by the common Mg alloys.

Among precipitation hardening magnesium alloys, the Mg—Zn system shows potential for alloy development, despite a low hardening response compared to Mg—Zn binary alloys [15–17]. The precipitates of interest for strengthening purposes in the Mg—Zn system are the metastable β'_1 and β'_2 precipitates (β'_1 also referred to as MgZn′) which have been found to be rods that lie with their long dimension perpendicular to the basal plane, and plates on the basal plane, respectively. Many reports on the β'_1 and β'_2 precipitates identified both phases as the hexagonal $MgZn_2$ laves-C14 phase, with β'_1 having an orientation relationship of $\{11\bar{2}0\}_{\beta'_1}||(0001)_{Mg}$, $[0001]_{\beta'_1}||\langle 11\bar{2}0\rangle_{Mg}$, and β'_2 having an orientation relationship of $(0001)_{\beta'_2}||(0001)_{Mg}$, $\langle 11\bar{2}0\rangle_{\beta'_2}||\langle 10\bar{1}0\rangle_{Mg}$ [11,14,18,19]. However, Gao and Nie [17] have reported the β'_1 phase to be monoclinic Mg_4Zn_7, with an orientation relationship of $\{630\}_{\beta'_1}||(10\bar{1}0)_{Mg}$, $[001]_{\beta'_1}||[0001]_{Mg}$. A more recent report by Rosalie et al. [20] has identified domains of both $MgZn_2$ and Mg_4Zn_7 phases within the β'_1 rods.

As noted in the early work of Clark [15], the number density of precipitates which form during ageing of binary Mg—Zn alloys tends to be low, which limits the amount of hardening. Therefore, a refinement of the precipitate microstructure by proper alloying element additions may result in an increased age hardening response for these types of alloys [10,12,13,21–27]. In particular, improved precipitation hardening response in Mg—Zn alloys with Ca addition in alloying or microalloying levels has been reported [11,14,21–24]. Generally, Ca addition to

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magnesium alloys is of significant interest, as it provides a multitude of processing and performance benefits to the alloys. These include a significant reduction in flammability and improvement in the oxidation and creep resistance, as well as grain refinement and biocompatibility [25–31].

Considering the other major drawback of most wrought magnesium alloys – their poor ductility – it is known that this can be exacerbated by strong textures which tend to form following bulk deformation processes (i.e. rolling, extrusion). These textures result in grains generally oriented with the basal pole either normal to the sheet plane in rolling, or normal to the extrusion direction, and arise as a consequence of the predominance of basal slip [32]. Improving the ductility of wrought magnesium is therefore possible by reducing the strength of the basal textures [33], which is noted by many recent studies to be achievable through the addition of RE elements [5–7,33–36]. The potential for development of wrought magnesium alloys with a good combination of ductility and strength may therefore be realized by improving ductility through RE addition to modify the alloy texture, and by strengthening through precipitation hardening. Among RE elements, Ce has been reported as one of the most potent in affecting texture [7], having an effect even when added at microalloying levels [36,37]. However, when added to the Mg—Zn system, the precipitation hardening response of the alloys has been unchanged or even reduced [38]. As the authors reported, combined Ce—Ca microalloying of the Mg—Zn system showed significant improvement of the texture and tensile ductility [39]. The following work focuses on the precipitation hardening effect of such alloys, and through a systematic experimental analysis shows that the combinational microalloying strategy is also successful in significantly improving the precipitation hardening response of the Mg—Zn system.

2. Experimental Methodology

The alloys of this study are based on the Mg—4Zn (wt.%) system, microalloyed with either Ce—Ca, or with Ce or Ca, as individual microalloying elements, as well as the base Mg—4Zn alloy. The compositions and designations of these alloys are listed in Table 1.

Alloys were prepared from pure Mg and Zn, while Ce/Ca rich master alloys were used for the microalloying elements. Ingots were produced by gravity casting in an Ar atmosphere, and homogenized for 6 h at 300 °C, then for 24 h at 400 °C [40]. The homogenized ingots were then sectioned into 3.0 mm thick pieces, and rolled at 400 °C to a final thickness of 0.5 mm with a reduction of approximately 0.25 mm/pass. Samples were annealed at 400 °C for 10 min between rolling passes, and at 400 °C for 30 min following the final pass. A full description of the hot rolling procedure, as well as the microstructures and properties of the rolled and annealed alloys has been reported in ref. [39]. For the purposes of age hardening, rolled samples were further sectioned and given a solutionizing heat treatment of 420 °C for 6 h, while packed in MgO powder in order to limit oxidation. Solutionizing was followed by water-quenching and artificial ageing at 180 °C, for times up to 240 h.

Microhardness testing was conducted on aged samples to evaluate the precipitation hardening response of the alloys. An MHT series LECO 200 Vickers microhardness tester and a 100 g load was used for this purpose. For each sample, a minimum of seven indentations were measured, with the reported values being the measurement averages after discarding the maximum and minimum measurements from the data. Error bars presented on the data points represent one standard deviation, assuming a normal distribution.

Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) and high-angle annular dark field scanning TEM (HAADF-STEM) were conducted to examine the precipitation characteristics of the aged samples. TEM foils were prepared by two methods. In the first method, aged samples were ground to a thickness of <0.075 mm, 3 mm discs were punched out, and those discs were electropolished to perforation at −50 °C and 50–90 V in a solution of 5.3 g lithium chloride (LiCl), 11.16 g magnesium perchlorate ($Mg(ClO_4)_2$), 500 ml methanol, and 100 ml butyl cellosolve. For the second method, 1.6 × 0.5 × 0.5 mm sections of aged samples were mechanically polished into wedges at an angle of 4°, using an Allied MultiPrep instrument and a 0.5 μm abrasive diamond film, with the wedges then fixed to a 3 mm diameter Mo ring using adhesive. All TEM foils were then thinned by ion-milling using a Gatan precision ion polishing system (PIPS) at 2.5–4 keV and 4–7° for 0.5–1 h at liquid nitrogen temperatures. TEM observations were made using a Philips CM12 microscope at 120 kV, and a JEOL 3010 microscope at 300 kV. HR-TEM and HAADF-STEM observations were made using an FEI Titan 80-300 LB microscope at 300 kV, and an FEI Titan 80-300 HB microscope at 200 kV.

Atom probe tomography (APT) was conducted to further analyze the precipitation characteristics of the ZEX 400 alloy. APT specimens were prepared by first mechanically grinding sections of the alloy into pillars, approximately 0.50 × 0.50 × 10 mm in dimensions. These pillars were subsequently made into fine nano-tipped needles by two-stage electro-polishing [41–43]. The first stage was done by repeatedly dipping one end of the pillar intro a solution of 25% perchloric acid (70%) in glacial acetic acid at 20 V-DC until a point was formed. The point was then refined by the second stage of electro-polishing, which used an electrolyte of 2% perchloric acid in 2-butoxyethanol and a potential of 15–20 V-DC.

APT testing was performed using a Cameca local electrode atom probe (LEAP) 4000X HR. Testing was performed at a temperature of ~55 K and under ultrahigh vacuum (~3.0×10^{-11} Torr). Evaporation was induced either by voltage pulsing, with a voltage pulse fraction of 20% and a pulse rate of 200 kHz, or by laser pulsing with a UV ($\lambda =$ 355 nm) laser at 90 pJ pulse energy and a 250 kHz pulse rate. Evaporation was set to target rates between 0.5% and 3% (0.005 to 0.03 ions/pulse).

All APT data was reconstructed using the Integrated Visualization and Analysis Software package (IVAS) v3.6.6 and established algorithms, with HCP-Mg crystal plane spacing values to spatially calibrate the reconstructions.

It is known that peaks in the APT mass spectrum may overlap when ions exhibit identical mass/charge ratios. For the Mg—Zn—Ce—Ca alloys, there is overlap between the most abundant Ce peak ($^{140}Ce^{2+}$, 88.45% isotopic abundance, 69.95 Da) and a low-abundance Zn peak ($^{70}Zn^{+}$, 0.631% isotopic abundance, 69.93 Da). While it is not possible to discriminate spatially between the two ions, it is possible to correct the ion count by decomposing the different peaks from each isotope, and checking their relative numbers against known values for natural isotope abundances. Reported composition values in this work are the result of performing a peak decomposition analysis in IVAS. Where composition values are reported, the standard error, s, is estimated as:

$$s = \sqrt{\frac{c^i\left(1-C^i\right)}{n_T}} \tag{1}$$

where C^i is the concentration of solute atoms in a given volume, and n_T is the total number of atoms detected in the volume [41].

Table 1
Compositions of experimental alloys, given in wt.% (at.%).

Alloy Designation	Mg	Zn	Ce	Ca
Z4	(Balance)	4.0 (1.52)	–	–
ZE40	(Balance)	4.0 (1.53)	0.1 (0.018)	–
ZX40	(Balance)	4.0 (1.53)	–	0.3 (0.19)
ZEX400	(Balance)	4.0 (1.53)	0.1 (0.018)	0.3 (0.19)