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Effects of Ca addition on as-cast microstructure and mechanical properties of Mg–3Ce–1.2Mn–1Zn (wt.%) magnesium alloy

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ABSTRACT

The effects of Ca addition on the as-cast microstructure and mechanical properties of the Mg–3Ce–1.2Mn–1Zn (wt.%) alloy were investigated by using optical and electron microscopes, differential scanning calorimetry (DSC) analysis, and tensile and creep tests. The results indicate that the additions of 0.3–0.9 wt.%Ca to the Mg–3Ce–1.2Mn–1Zn alloy do not cause an obvious change in the morphology and distribution for the $Mg_{12}Ce$ phase in the alloy. However, the grains and secondary dendrite arm spacings of the Ca-containing alloys are refined, and an increase in Ca amount from 0.3 wt.% to 0.9 wt.% causes the grain size and secondary dendrite arm spacings to gradually decrease, respectively. In addition, the additions of 0.3–0.9 wt.%Ca to the Mg–3Ce–1.2Mn–1Zn alloy can effectively improve the as-cast tensile and creep properties of the alloy, and an increase in Ca amount from 0.3 wt.% to 0.9 wt.% causes the as-cast tensile and creep properties to gradually increase, respectively.

1. Introduction

Magnesium alloys are the lightest structural alloys commercially available and have great potential for applications in automotive, aerospace and other industries. At present, the widely used magnesium alloys are from the Mg–Al series alloys, such as AZ91 and AM60 alloys, but they are unsuitable for manufacturing parts operating at temperatures higher than 120 °C because of their poor creep resistance. Therefore, in recent years, improving the elevated temperature properties has become a critical issue for possible application of magnesium alloys in hot components. Previous investigations indicated that Mg–Ce–Mn–Sc alloys are considerably superior to WE alloys and exhibit high creep resistance at high temperatures over 300 °C [1–3]. However, due to the expensive Sc, the application of Mg–Ce–Mn–Sc alloys is limited. Since Zn can form intermetallic phases with Mg and/or RE as plates on basal planes of α-Mg matrix [4], the research of replacing expensive Sc by cheap Zn for Mg–Ce–Mn–Sc alloys has been carried out, and the results indicated that Mg–Ce–Mn–Zn alloys have similar mechanical properties at room temperature and 300 °C as compared with Mg–Ce–Mn–Sc alloys [4,5]. However, it is further reported that, similar to the quaternary Mg–Ce–Mn–Sc alloys, the grains of the quaternary Mg–Ce–Mn–Zn alloys also are relatively coarse, leading to the relatively poor mechanical properties [5,6]. Therefore, further enhancement in the mechanical properties for the quaternary Mg–Ce–Mn–Zn alloys by grain refinement needs to be considered. But up to now, the investigations about the effects of alloying and/or microalloying on the grain refinement and mechanical properties of Mg–Ce–Mn–Zn alloys are very rare. Although in the previous investigations [6] the authors of this paper found that minor Zr and/or Sr additions to the Mg–3Ce–1.2Mn–1Zn (wt.%) alloy can refine the grains thus leads to enhance the properties, it is not clear whether other additions such as Ca to Mg–Ce–Mn–Zn alloys have similar effects on the microstructure and properties as Zr and Sr. It is well known that Ca not only can behave as a grain refiner of magnesium alloys but also can form a stable Mg_2Ca compound with Mg [7]. Furthermore, Ca and Zn together with Mg may form the stable intermetallic compound $Ca_2Mg_6Zn_3$ [8]. In addition, Jun et al. [9,10] found that Ca addition to the Mg–4RE–3Zn (wt.%) alloy not only can refine the primary α-Mg grains but also increase the thermal stability of the Mg–RE phases in the alloy. Therefore, it is reasonable to expect that Ca addition possibly plays a beneficial role in the grain refinement and mechanical properties for Mg–Ce–Mn–Zn alloys. Based on the above mentioned-reasons, the present work investigates the effects of Ca addition on the as-cast microstructure and mechanical properties of the Mg–3Ce–1.2Mn–1Zn (wt.%) magnesium alloy.

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2. Experimental procedures

The Ca-containing Mg–3Ce–1.2Mn–1Zn (wt.%) experimental alloys were prepared by adding pure Mg and Zn, Mg–29.24 wt.%Ce, Mg–4.38 wt.%Mn, and Mg–19.7 wt.%Ca master alloys. The experimental alloys were melted in a crucible resistance furnace and protected by 2 wt.% RJ-2 flux additions (45 wt.% MgCl + 37 wt.% KCl + 8 wt.% NaCl + 4 wt.% CaF + 6 wt.% BaCl). After being held at 740 °C for 20 min, the melts of the experimental alloys were respectively homogenized by mechanical stirring of a stainless steel bar at 300 rpm and then poured into a permanent carbon-steel mould which was coated by a water based coatings (10 wt.% ZnO + 3 wt.% H_3BO_3 + 1 wt.% $CH_3(CH_2)_{10}CH_2$–OSO_3-Na + 2 wt.% Na_2SiO_3 + 84 wt.% H_2O (deionised-water)) and preheated to 200 °C in order to obtain a casting. The specimens as shown in Fig. 1 were fabricated from the castings for tensile and creep tests. Furthermore, the samples of the experimental alloys were subjected to a solution heat treatment (520 °C/24 h + water cooled) in order to reveal the grain boundaries and examine the microstructural stability at high temperatures. For comparison, the Mg–3Ce–1.2Mn–1Zn alloy without Ca addition was also cast and machined into the same dimensions and tested under the same conditions as the above samples. Table 1 lists the actual chemical compositions of the experimental alloys, which were inspected by inductively coupled plasma spectroscopy.

In order to analyze the solidification behavior of the experimental alloys, the differential scanning calorimetry (DSC) was carried out by using a NETZSCH STA 449C system equipped with platinum–rhodium crucibles. A 30 mg (±0.1 mg) sample of each examined specimens were heated in a flowing argon atmosphere from 30 to 700 °C for 5 min before being cooled down to 100 °C. The heating and cooling curves were recorded at a controlling speed of 15 °C/min.

The as-cast and solutionised samples of the experimental alloys were respectively etched in an 8% nitric acid solution in distilled water and a solution of 1.5 g picric, 25 ml ethanol, 5 ml acetic acid and 10 ml distilled water, and then were examined by an Olympus optical microscope and/or JEOL JSM-6460LV type scanning electron microscope equipped with Oxford energy dispersive X-ray spectrometer (EDS) with an operating voltage of 20 kV. The phases in the as-cast experimental alloys were also analyzed by D/Max-1200X type analyzer operated at 40 kV and 30 mA. The grain size was analyzed by the standard linear intercept method using an Olympus stereomicroscope. Based on the tensile test standards of metallic materials at ambient and elevated temperatures, which are GB/T 228.1-2010 [11] and GB/T 4338-2006 [12], respectively, the as-cast tensile properties of the experimental alloys at room temperature and 300 °C were determined from a complete stress–strain curve. Ultimate tensile strength (UTS), 0.2% yield strength (YS), and elongation to failure (Elong.) were obtained based on the average value of three tests under the strain rate of 0.1 s^{-1}. Based on the uniaxial creep test standard of metallic materials, GB/T 2039-2012 [13], constant-load tensile creep tests were performed at 300 °C and 30 MPa for creep extension up to 100 h. The minimum creep rates of the as-cast experimental alloys were measured from each elongation–time curve and averaged over three tests.

Table 1
Actual compositions of the experimental alloys, wt.%.

Experimental alloys	Ce	Mn	Zn	Ca	Mg
1# (Mg–3Ce–1.2Mn–1Zn)	2.76	1.08	0.92	–	Bal.
2# (Mg–3Ce–1.2Mn–1Zn–0.3Ca)	2.81	1.12	0.88	0.25	Bal.
3# (Mg–3Ce–1.2Mn–1Zn–0.6Ca)	2.79	1.10	0.94	0.58	Bal.
4# (Mg–3Ce–1.2Mn–1Zn–0.9Ca)	2.80	1.09	0.93	0.82	Bal.

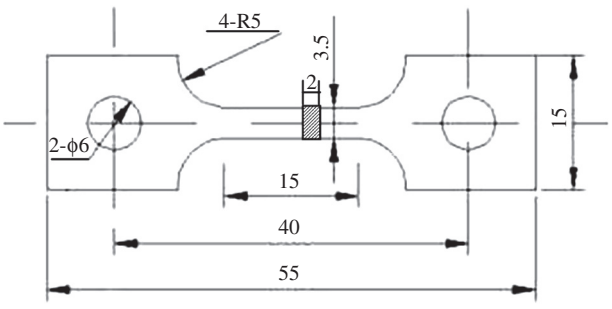

Fig. 1. Configuration of the samples used for the tensile and creep tests (unit: mm).

3. Results and discussion

3.1. Effects on as-cast microstructure

Fig. 2 shows the XRD results of the as-cast experimental alloys. As shown in Fig. 2, all the experimental alloys are mainly composed of α-Mg and $Mg_{12}Ce$ phases, and except the alloy with the addition of 0.9 wt.%Ca other Ca-containing alloys do not observe the peak of the Mg_2Ca phase which is generally found in Mg–Ca and Mg–Al–Ca alloys. The absence of the Mg_2Ca phase in the alloys with the additions of 0.3 wt.% and 0.6 wt.%Ca is presumably ascribed to the relatively small amount of Ca. Actually, the XRD results may be further confirmed by the DSC results of the as-cast experimental alloys. Fig. 3 shows the DSC cooling curves of the as-cast experimental alloys. It is found from Fig. 3 that all the DSC cooling curves of the experimental alloys are similar, with two main peaks at about 630 °C and 580 °C, respectively, corresponding to the α-Mg matrix solidification and second phase transformations. Based on the DSC results, it is preliminarily inferred that during the solidification of the experimental alloys the primary α-Mg phase first nucleates and grows until the temperature falls to about 580 °C where a binary eutectic reaction ($L_1 \rightarrow$ α-Mg + $Mg_{12}Ce$) occurs [14]. Accordingly, the final microstructures of the experimental alloys mainly consist of α-Mg and $Mg_{12}Ce$ phases. However, it is further found from Fig. 3 that a peak at about 510 °C is uniquely observed in the DSC cooling curve of the alloy with the addition of 0.9 wt.%Ca. This possibly corresponds to the binary eutectic reaction ($L_2 \rightarrow$ α-Mg + Mg_2Ca) [15], which is consistent with the above XRD results (seeing Fig. 2).

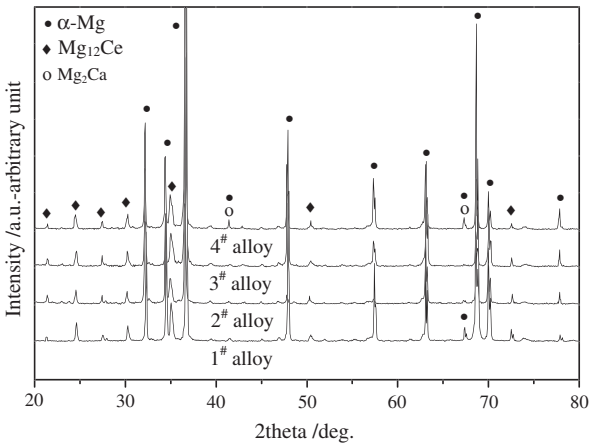

Fig. 2. XRD results of the as-cast alloys.