Influence of rapid solidification on the mechanical properties of Mg-Zn-Ce-Ag magnesium alloy

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Received 19 September 2006; received in revised form 26 November 2006; accepted 27 November 2006

Abstract

This paper presents the differences in microstructure and mechanical properties between the conventional casting and rapidly solidified Mg-Zn-Ce-Ag alloy. The experimental results showed that the mechanical properties of rapidly solidified alloy are enhanced, which can be attributed to the changes of the microstructure significantly. The grain was refined and homogeneously distributed. High cooling rate refined the microstructure and changed the morphology of divorce eutectic phase. The mechanical properties of rapidly solidified alloy are high and variable. Microporosity appeared to degrade affect the mechanical properties of magnesium alloys.

Keywords: Magnesium alloy; Mechanical properties; Microporosity; Microstructure

1. Introduction

Magnesium and its alloys are among the lightest metallic structural materials (\( \rho = 1.74 \text{ g/cm}^3 \)) and especially attractive for structural automotive applications where weight saving and consequent increase in fuel efficiency are important [1–4]. However, only little research has been carried out on magnesium alloy as compared with aluminum alloy, and its applications are also limited [5]. Principal reasons for this situation are the relatively poor mechanical properties of magnesium alloy at room and elevated temperatures [6]. Therefore, developing magnesium alloys with excellent mechanical properties are crucial for its application.

Recently, it has been reported that the addition of Zr increases the strength and ductility of Mg-Zn-Ce alloy, due to the effect of grain refinement [7]. In current research, rapid solidification was carried out on Mg-Zn-Ce-Ag alloys. The results indicate that high cooling rate has strong effects on both microstructure evolution and mechanical properties of magnesium alloy.

2. Materials and experimental procedure

Nominal chemical composition of the studied alloy is listed in Table 1. For conventional casting (CC) method, the alloy was melted in a graphite crucible by induction in Ar atmosphere. Melts were stirred for about 5–10 min and air cooled. For rapidly solidified (RS) method, the alloy was remelted in quartz tube and injected into a cylinder-shaped copper mould with a cavity of 4 mm diameter and 60 mm length under Ar atmosphere.

Alloys were etched by 5% Nital solution. Microstructure was observed using an optical microscope (OM, LEICA MEF-4) and scanning electron microscope (Hitachi S-3400N) with an accelerating voltage of 25 kV. Phase analysis was performed using X-ray diffractometer with a resource of Cu K\( \alpha \) radiation. Microhardness was measured using Vickers pyramid indenter with the load of 100 g. Compression tests were carried out using a MTS810 Material Testing System at a strain rate of \( 2.5 \times 10^{-4} \text{ s}^{-1} \). The compressive specimens were 4 mm in diameter and 6.5 mm in length.
Table 1
Nominal chemical composition of Mg-Zn-Ce-Ag

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Ce</th>
<th>Ag</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>At%</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>96</td>
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</tbody>
</table>

3. Results and discussion

3.1. Microstructure

XRD spectrum (Fig. 1) shows that the main phases in Mg-Zn-Ce-Ag alloy are \( \alpha \)-Mg and \( \beta \)-Mg\(_{12}\)Ce. It can be clearly seen that the peaks of rapid solidification samples are broader than that of the CC samples. The effect can be attributed to the grain refinement. One finds that the peaks of Mg\(_{12}\)Ce are different between CC and RS alloys. Solid solution of Zn and Ag in Mg\(_{12}\)Ce phase may lead to the change of lattice constant. Although the lattice constant is different between the phase of CC and RS alloys, they belong to the same phase.

Fig. 2 shows the change of microstructure with increasing cooling rate. Fig. 2a shows the typical microstructure of CC alloy. The black dendrite phase is primary Mg. Bulk eutectic (Mg+Mg\(_{12}\)Ce) phase exists in the grain boundary in the form of network. CC alloy has a typical dendrite structure. Well developed primary \( \alpha \)-Mg dendrites with secondary dendrite showing sixfold symmetry are clearly visible. Comparing Fig. 2a with Fig. 2b, it can be inferred that high cooling rates lead to the morphological change of primary phase from well developed dendrite to refined rosette-shaped dendrite. In addition, Mg\(_{12}\)Ce phase also becomes finer and its distribution is more uniform than that for conventional casting alloy. The grain size, volume fraction of eutectic structure, and secondary dendrites arm spacing (SDAS) of the two alloys are summarized in Table 2. Table 2 indicates that with the increase of cooling rate, the grain size and SDAS decrease accordingly but the volume fraction of the secondary phase increases. Both CC and RS alloy have a very fine eutectic structure which can be resolved at low magnification (Fig. 2). The eutectics are shown more clearly at higher magnification (Fig. 3) with SEM. These two eutectics differ in shape and distribution. In CC alloy, the morphology of divorced eutectic phase is characterized by ‘islands’ of eutectic \( \alpha \)-Mg within Mg\(_{12}\)Ce, but bulks of \( \alpha \)-Mg are outside of Mg\(_{12}\)Ce particle. It is a partially divorced eutectic morphology (Fig. 3a). In RS alloy, a fully divorced eutectic structure (Fig. 3b) is that two eutectic phases are completely separated.

3.2. Mechanical properties

The typical stress-strain curves of Mg-Zn-Ce-Ag alloy with different casting method are shown in Fig. 4. The results of the compression tests are summarized in Table 3 [7,8]. The compressive strength of RS alloy is higher than that of CC alloy. It improved to values as high as 480 MPa.

<table>
<thead>
<tr>
<th>Grain size</th>
<th>SDAS</th>
<th>Volum fraction of eutectic regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC alloy</td>
<td>500 ( \mu )m–2 mm</td>
<td>45–65 ( \mu )m</td>
</tr>
<tr>
<td>RS alloy</td>
<td>10–40 ( \mu )m</td>
<td>About 6 ( \mu )m</td>
</tr>
</tbody>
</table>
Fig. 3. SEM microstructure of the alloys: (a) CC alloy and (b) RS alloy.

As following is a classical Hall-Petch formula:

$$\sigma_{0.2} = \sigma_0 + k d^{-1/2}$$

where $d$ is the grain size in $\mu$m. It is widely accepted that the microstructure of casting can be refined by increasing the number of potential nuclei in the melt and the thermal and constitutional under cooling at the advanced solid/liquid interface [9,10]. High cooling rate can produce more nuclei frequency in the melt, therefore leading to a refined microstructure. Grain refinement is one of the important practices to improve the properties of casting [11]. It is essential and fundamental approach since grain size significantly influences the mechanical properties of the casting. Grain refinement accounts for the mechanical properties difference between the RS alloy and CC alloy. The increase in mechanical properties observed on RS samples should attribute to grain refinement and homogeneous distribution of secondary phase [12,13]. The higher strength is also related to other factors, such as the decrease of SDAS, the increase of volume fraction of eutectics

![Fig. 4. Strain-stress curves of CC alloy and RS alloy.](image)

![Fig. 5. Strain-stress curves of four RS samples.](image)

Table 3

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Compressive strength (MPa)</th>
<th>Yield strength (MPa)</th>
<th>Elongation (%)</th>
<th>Hv (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC alloy</td>
<td>270</td>
<td>150</td>
<td>10</td>
<td>727</td>
<td></td>
</tr>
<tr>
<td>RS alloy</td>
<td>480</td>
<td>250</td>
<td>10</td>
<td>923</td>
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<tr>
<td>Mg-1.5%Ce-0.6%Zr (Ref. [8])</td>
<td>297.6</td>
<td></td>
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</tr>
<tr>
<td>Mg-2.8%Ce-0.7%Zn-0.7%Zr (Ref. [7])</td>
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<td></td>
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</tr>
<tr>
<td>Mg-2.8%Ce-0.7%Zn-0.7%Zr as-cast</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>124.8</td>
</tr>
<tr>
<td>Mg-2.8%Ce-0.7%Zn-0.7%Zr extrusion</td>
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<td>257.8</td>
</tr>
</tbody>
</table>
Fig. 6. Optical micrograph of RS alloy before etching.

Fig. 7. SEM fractograph of the fracture surface of compressive test specimen depicting porosity.

and the difference of texture tropism. Fine $\text{Mg}_12\text{Ce}$ precipitates homogeneously distributes along grain boundaries (G.B.). These particles would prevent G.B. from sliding and increase hardness.

Fig. 5 shows the stress-strain curves of four RS samples. The mechanical properties of RS alloy are high and significantly variable. RS alloy contains a considerable amount of microporosity. Microporosity and other casting defects appear to negative affect the mechanical properties of casting magnesium alloys and may lead to significant variability in their mechanical properties [14].

RS alloy has a significant microporosity as illustrated in Fig. 6 which shows unetched sample. There were more micro pores and pores were somewhat larger in the center of samples than towards the samples surface. Fig. 7 shows a typical SEM image of compressive fracture surface. The fracture surface contains shrinking porosity as well as gas (air) porosity. In these fracture surfaces, the porosity can be detected due to the presence of unfractured dendrites below the pores. The cause of microporosity in magnesium alloy has been studied by Baker in 1940s [15]. Much debate has occurred concerning which variables contribute to the formation of microporosity, e.g. solidification shrinkage, grain size, cooling rate and gas dissolution [15]. The porosity can be identified in the fracture surface due to the presence of intact dendrites below the pores. Thus, all the regions of the fracture surface that contain intact dendrites are essentially the areas occupied by either shrinkage pore or gas pore. One such region is designed by arrow in Fig. 7.

4. Conclusions

Rapidly solidified Mg-Zn-Ce-Ag alloy with a diameter of 4 mm was obtained by copper mould casting. Rapid solidification refined microstructure. The dendrites can be broken and nucleation sites can be increased for primary $\alpha$-Mg, which refine grain size and decrease the SDAS. The variability of mechanical properties in rapidly solidified samples occur with application of copper mould, which resulted from the presence of microporosity.

Acknowledgement

The authors gratefully acknowledge the financial support from the Ministry of Science and Technology of China (Grants No. 2006CB65201, 2005DFA50860), the National Natural Science Foundation of China (Grant No. 50471077).

References