Microstructures and Mechanical Properties of Mg-Zn-Y Alloys with LPSO Structure Produced by Rheo-squeeze Casting

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Abstract. Mg alloys reinforced with long period stacking ordered (LPSO) phase are a new type of structural materials due to their excellent mechanical properties. However, the coarse LPSO phase in the castings usually aggregates at grain boundaries. In this work, ultrasonic vibration (UV) and rheo-squeeze casting were applied on the Mg$_{99.9}$-$3x$-$Zn_x$-$Y_{2x}$-$Zr_{0.1}$ ($x=0.5, 1, 2$) alloys to refine the LPSO structure. The semisolid slurries of Mg-Zn-Y-Zr alloys were prepared by UV and processed by rheo-squeeze casting. The effects of UV, LPSO fraction and squeeze pressure on microstructure and mechanical of semisolid Mg-Zn-Y alloys were studied. The results revealed that the combination of UV and rheo-squeeze casting can refine the LPSO structure and the $\alpha$-Mg matrix, but the phase composition of LPSO structure was not changed. With the increase of LPSO fraction, the size of $\alpha$-Mg grains decreased while the refinement of LPSO became slight. When the squeeze pressure increased from 0 MPa to 400 MPa, the block LPSO structure was completely eliminated and the thickness of LPSO structure decreased. Mechanical properties of these semisolid Mg-Zn-Y-Zr alloys, especially the elongations, were significantly improved, compared with the gravity cast alloys.

Introduction

For the last decade, research has been focused on new kind of Mg alloys reinforced with long period stacking ordered (LPSO) phase due to their excellent mechanical properties. The yield strength of Mg$_{97}$Zn$_1$Y$_2$ alloy, produced by rapidly solidified powder metallurgy process, could achieve 610 MPa at ambient temperature [1]. This superior property arises from the presence of LPSO phase and the refinement of $\alpha$-Mg matrix. However, during the conventional casting process, the LPSO phase precipitates at the end of solidification and usually aggregates at grain boundaries as 3D networks.

Ultrasonic vibration (UV) is a simple method and has been extensively studied in refining the microstructure of Mg alloys. After UV treatment, the primary $\alpha$-Mg dendrites were refined to globular grains, and more importantly, the morphologies of second or eutectic phases can be modified [3]. Moreover, our recent investigations indicated that rheo-squeeze casting is an effective process to refine the second or eutectic phases in Al alloys [4, 5], and it has the potential to achieve refinement and uniform distribution of LPSO phase in Mg matrix combined with UV.

In this work, UV and rheo-squeeze casting was employed to refine the LPSO phase and $\alpha$-Mg matrix. UV was utilized to prepare semisolid slurries of Mg$_{99.9,3x}$-$Zn_x$-$Y_{2x}$-$Zr_{0.1}$ ($x=0.5, 1, 2$) alloys, and then the slurry was directly shaped by rheo-squeeze casting. Microstructure and mechanical properties of the semisolid Mg-Zn-Y-Zr alloys were investigated.

Experimental procedures

The installation of USV in reference [6] was employed for preparing semi-solid slurry of the Mg alloy in this experiment. In this research, the power of the ultrasonic generator was 1.8 kW, and the
vibrating frequency was 20 kHz.

Mg_{99.9-3x}Zn_{x}-Y_{2x}-Zr_{0.1} (x=0.5, 1, 2) alloys were synthesized using commercially available pure Mg, Mg-25wt.%Y, Mg-25wt.%Zr and pure Zn (99.99 wt.%) as raw materials. The raw material was melted in a mild steel crucible at 750 °C under mixed atmosphere of SF$_6$ and N$_2$ with the volume ratio of 1:99. About 300 mL (550 g) of the melt was poured into a metallic cup in the heating furnace which was preheated to 600 °C. Then the sonotrode was immersed into the melt 15 mm to 20 mm deep from the surface. The melt was treated by USV starting at 650 °C. After vibrated for 1 min, the liquid melt was converted into semi-solid slurry, poured into the steel mould preheated to 200 °C. Different squeeze pressures (0 MPa, 100 MPa, 200MPa and 400 MPa) were applied to the slurry from the top and bottom simultaneously and held for 1 min. Cylindrical samples with 30 mm in diameter and 80 mm in length were ejected from the mould. The samples were made into standard tensile specimens with 5 mm in diameter.

Microstructure of the samples were observed by optical microscope, SEM and TEM. The size of primary α-Mg particles was characterized by average particles diameter (APD). The shape coefficient of a primary α-Mg particle was defined as $S_F$. $S_F$ varies from 0 to 1, and when the value of $S_F$ is close to 1, the sectional shape of the particle approaches to a circle.

Results and Discussion

Microstructure of the rheo-squeeze cast Mg-Zn-Y-Zr alloys. Fig. 1 shows the typical microstructure of Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy under different casting processes. In rheocast alloy, the primary α-Mg phase was obviously refined and presented as two different grains in morphology and size, as shown in Fig. 1 (a) and (c). In gravity cast alloy, the primary α-Mg phase presented as equiaxed dendrites, with an average diameter of 230 μm and $S_F$ of 0.43, as shown in Fig. 1 (b) and (d). It is well known that two distinct solidifications occur during rheocasting [4, 5]. Solidification of the Mg alloy during slurry making process is named as the first solidification, and the primary α-Mg phase precipitated in this stage is referred to as the primary α$_1$-Mg phase. Then, solidification of the residual liquid during transportation and in the mold cavity is named as the second solidification. Under high squeeze pressure, solidification finish with a high cooling rate, resulting in fine grains referred to as the primary α$_2$-Mg phase. The APD and $S_F$ of the primary α$_1$-Mg and α$_2$-Mg phases were 57 μm and 23 μm, 0.72 and 0.55, respectively. The reduce in APD and increment in number of α-Mg (including α$_1$-Mg and α$_2$-Mg) lead to narrower grain boundaries and finer second phase in rheocast alloy.

All the second phase in the Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy connected as continuous bright networks at grain boundaries. For gravity casting alloy, the bright phase was not uniformly distributed; some coarse blocks were usually observed at the junctions. The average thickness of the networks was 13.2 μm. For rheocasting alloy, the bright phase was distributed more uniformly; coarse blocks at the junctions were almost eliminated. The networks were significantly refined under UV and high squeeze pressure, with an average thickness of 4.3 μm. The EDS results of bright phase in both rheocast and gravity cast alloy were similar, as shown in Fig. 1 (c) and (d), and the atomic ratio of Zn to Y in this phase was close to 1:1. The bright phase is considered to be LPSO structure.

TEM result of Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy are shown in Fig. 2. Fig. 2(a) is the bright-field image including α-Mg and LPSO structure, and these two phases in SEM images presented as gray matrix and bright phase, respectively. Fig. 2(b) is the corresponding SAED pattern of the fine LPSO phase. There are five diffraction spots between the brighter spots of Mg matrix. This characteristic confirms that the LPSO structures in rheocast are 18R type [7, 8]. It can be concluded that the combination of UV and rheocasting can significantly refine the LPSO structure in Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy, but it cannot change the phase compositions of the alloy or the type of LPSO phase.
Fig. 1 Microstructures of the Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy produced by different processes: (a) and (c) rheo-squeeze casting, (b) and (d) gravity casting.

Fig. 2. TEM images of (a) bright-field image and (b) SAED of LPSO structure in the rheocast Mg$_{96.9}$Zn$_1$Y$_2$Zr$_{0.1}$ alloy, with electron beam parallel to [1120].

Fig. 3 shows the optical microstructures of Mg-Zn-Y-Zr alloys subjected to varied squeeze pressures ranging from 0 to 400 MPa. It is obvious that as squeeze pressure increased, both $\alpha_1$-Mg and $\alpha_2$-Mg grains were refined, and the $\alpha_2$-Mg dendrites evolved into fine granular grains. It also can be seen that as the squeeze pressure reached to 200 MPa, the APD decreased remarkably and the grains became rounder. Beyond 200 MPa, both the size and morphology of the $\alpha$-Mg phase changed weakly. The influence of squeeze pressure on microstructure refinement can be apprehended from two aspects. On the one hand, the application of pressure on a solidifying alloy leads to an increase in alloys’ liquidus temperature, thereby inducing a higher degree of undercooling and stimulating nucleation [4]. On the other hand, the application of squeeze pressure is favorable for the improvement of heat transfer between the slurry and mould interface [5]. As the pressure increases, the casting is forced to keep in closer contact with the mold and heat transfer becomes faster. Thus, a
higher cooling rate is achieved in the slurry and finer \( \alpha_1 \)-Mg and \( \alpha_2 \)-Mg grains are generated. Consequently, the decrease in grain size of \( \alpha \)-Mg was insignificant as the squeeze pressure increased.

![Fig.3 Microstructures of the Mg-Y-Zn-Zr alloys produced by different squeeze pressures: (a)-(d) \( \text{Mg}_{98.4}\text{Zn}_{0.5}\text{Y}_{1}\text{Zr}_{0.1} \) alloy, (e)-(h) \( \text{Mg}_{96.9}\text{Zn}_{1}\text{Y}_{2}\text{Zr}_{0.1} \) alloy, (i)-(l) \( \text{Mg}_{93.9}\text{Zn}_{2}\text{Ya}_{4}\text{Zr}_{0.1} \) alloy; (a), (e) and (i) 0MPa; (b), (f) and (j) 100MPa; (c), (g) and (k) 200MPa; (d), (h) and (l) 400MPa.](image)

Fig. 4 shows the SEM micrographs of LPSO structure in rheocast Mg-Zn-Y-Zr alloy under different squeeze pressures. The volume fraction of LPSO phase in \( \text{Mg}_{98.4}\text{Zn}_{0.5}\text{Y}_{1}\text{Zr}_{0.1} \) alloy, \( \text{Mg}_{96.9}\text{Zn}_{1}\text{Y}_{2}\text{Zr}_{0.1} \) alloy and \( \text{Mg}_{93.9}\text{Zn}_{2}\text{Ya}_{4}\text{Zr}_{0.1} \) alloy are 7\%, 18\% and 33\%, respectively. It is obviously that the LPSO structure became finer as squeeze pressure increased. Under low squeeze pressure, the block LPSO structure was usually observed, as arrowed in Fig. 4 (a), (b), (e), (f), (i) and (j). When the pressure reached 200 MPa, the blocks were almost eliminated and the thin LPSO phase was uniformly distributed at the grain boundaries. The thickness of LPSO structure in rheocast Mg-Zn-Y-Zr alloy was decreased as pressure increased. For example, the thickness of LPSO structure in \( \text{Mg}_{96.9}\text{Zn}_{1}\text{Y}_{2}\text{Zr}_{0.1} \) alloy was sharply decreased from 9.8 \( \mu \)m to 4.5 \( \mu \)m as the pressure increased from 0 MPa to 400 MPa. It also obvious that the refinement of LPSO became slight as the increment of LPSO fraction. The refinement of LPSO structure can be attributed to the fine \( \alpha \)-Mg matrix and the high local cooling rate of the residual liquid. During the secondary solidification, the last residual liquid is split into innumerable small pools by the very fine \( \alpha_2 \)-Mg grains, and the precipitation of LPSO structure is restricted to small intergranular spaces. Meanwhile, the low temperature of semisolid slurry and the high squeeze pressure lead to a high local cooling rate in the confined spaces.

**Mechanical properties of the rheo-squeeze cast Mg-Zn-Y-Zr alloys.** Table 1 and Table 2 shows a comparison of mechanical properties of the Mg-Zn-Y-Zr alloys produced by different processing conditions. Compared with the gravity cast Mg-Zn-Y-Zr alloys, mechanical properties of the rheo-squeeze cast alloys were significantly improved, especially the elongations. From table 1, it can be seen that the tensile strengths of the alloys increased sharply when the pressure rose to 100 MPa, beyond which the increment was slightly. The increase of mechanical properties of the rheocast alloy results mainly from the fine microstructure and low casting defect. Microstructure refinement of the
α-Mg matrix (α<sub>1</sub>-Mg and α<sub>2</sub>-Mg grains) and LPSO structure, especially the LPSO structure, plays an important role in enhancing the tensile strength and elongation. The existence of LPSO structure in Mg-Zn-Y-Zr alloys can effectively hinder the basal slip under a stress. However, the block LPSO structure aggregating at the grain boundaries under low squeeze pressure, such as in Fig. 1(d), Fig. 3(a), Fig. 3(e) and Fig. 3(i), is apt to cause stress concentration and inhomogeneous deformation. For the rheocast alloy solidifying under higher squeeze pressure above 100 MPa, the strengthening effect of LPSO structure is exerted better. The thinner and uniformly distributed LPSO structure works as a denser skeleton. It is more powerful to resist tensile stress and exhibits better formability of the α-Mg matrix. In addition, squeeze pressure can effectively eliminate some casting defects including shrinkage pores and gas pores [5].

Fig. 4 SEM micrographs of the LPSO structure in rheocast Mg-Y-Zn-Zr alloys produced by different squeeze pressures: (a)-(d) Mg<sub>98.4</sub>Zn<sub>0.5</sub>Y<sub>1</sub>Zr<sub>0.1</sub> alloy, (e)-(h) Mg<sub>96.9</sub>Zn<sub>1</sub>Y<sub>2</sub>Zr<sub>0.1</sub> alloy, (i)-(l) Mg<sub>93.9</sub>Zn<sub>2</sub>Y<sub>4</sub>Zr<sub>0.1</sub> alloy; (a), (e) and (i) 0MPa; (b), (f) and (j) 100MPa; (c), (g) and (k) 200MPa; (d), (h) and (l) 400MPa.

Table 1 Mechanical properties of the rheocast Mg-Zn-Y-Zr alloys with different squeeze pressures.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Squeeze pressure/MPa</th>
<th>σ&lt;sub&gt;b&lt;/sub&gt;/MPa</th>
<th>δ/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg&lt;sub&gt;98.4&lt;/sub&gt;Zn&lt;sub&gt;0.5&lt;/sub&gt;Y&lt;sub&gt;1&lt;/sub&gt;Zr&lt;sub&gt;0.1&lt;/sub&gt;</td>
<td>0</td>
<td>190±7.3</td>
<td>12.3±0.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>203±6.6</td>
<td>15.0±0.6</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>208±7.7</td>
<td>18.4±0.7</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>210±8.3</td>
<td>19.3±0.7</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;96.9&lt;/sub&gt;Zn&lt;sub&gt;1&lt;/sub&gt;Y&lt;sub&gt;2&lt;/sub&gt;Zr&lt;sub&gt;0.1&lt;/sub&gt;</td>
<td>0</td>
<td>214±6.9</td>
<td>7.9±0.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>232±8.7</td>
<td>11.8±0.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>232±8.1</td>
<td>16.5±0.3</td>
</tr>
</tbody>
</table>
MgZnYSr alloy and the modification effect of Sr on X-Zn alloys [7]


Table 2 Mechanical properties of the gravity cast Mg-Zn-Y-Zr alloys without UV

<table>
<thead>
<tr>
<th>Alloy</th>
<th>σb/MPa</th>
<th>δ/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg98.4Zn0.5Y1Zr0.1</td>
<td>178±8.4</td>
<td>9.2±0.6</td>
</tr>
<tr>
<td>Mg96.9Zn1Y2Zr0.1</td>
<td>197±10.1</td>
<td>6.5±0.4</td>
</tr>
<tr>
<td>Mg93.9Zn2Y4Zr0.1</td>
<td>213±9.6</td>
<td>3.2±0.3</td>
</tr>
</tbody>
</table>

Summary

The combination of UV and rheo-squeeze casting can refine the LPSO structure and α-Mg in Mg99.9-3x-Znx-Y2x-Zr0.1 (x=0.5, 1, 2) alloys, but the phase composition of LPSO structure was not changed and remained as 18R type. With the increase of LPSO volume fraction, the size of α-Mg grains decreased while the refinement of LPSO became slight.

When the squeeze pressure increased from 0 MPa to 400 MPa, the block LPSO structure in rheo-squeeze cast Mg99.9-3x-Znx-Y2x-Zr0.1 (x=0.5, 1, 2) alloys was completely eliminated and the thickness of LPSO structure decreased.

Compared with the gravity cast alloys, mechanical properties of the rheo-squeeze cast Mg99.9-3x-Znx-Y2x-Zr0.1 (x=0.5, 1, 2) alloys were significantly improved, especially the elongations.

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References