Research on alloying technique of yttrium on AZ91D magnesium alloy

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Abstract. Effect of alloying techniques of dollop-like yttrium, as-cast and extruded Mg-Y master alloy in AZ91D magnesium alloy on microstructure and the efficiency of alloying was studied by optical microscopy, scanning electron microscopy, XRD and inductively-coupled plasma (ICP) spectroscopy. The as-cast AZ91D-1.2wt.%Y alloys were prepared and yttrium was added by different way at 750°C . The results showed that the efficiency of alloying achieved less than 50% within 60 minutes when dollop-like yttrium was added. When yttrium was added by as-cast and extruded Mg-25wt. %Y master alloy, the efficiency of alloying was 71.3wt. % and 78.3wt. %, respectively. The efficiency of alloying was improved because the Mg-Y master alloy could melt easily down at casting temperature. The Mg-Y phases were formed in the Mg-Y master alloys. After the as-cast Mg-Y master alloy was extruded, the decrease in Mg-Y particle size and increase in the number of nucleating sizes for Mg led to the microstructure of the as-cast AZ91D-1.15wt. %Y alloy was refined.

Introduction

The magnesium alloy is the lightest constructional material, which has lower density, higher specific strength, higher specific stiffness, better electric conductivity, better cast characteristics than steel and aluminum alloys. The application of magnesium alloy in the automobile lightweight design is becoming more and more important [1,2]. However, the high working temperature of power train components can cause serious problems for traditional magnesium alloy application. AZ91D alloy cannot meet the demands of temperature beyond 120°C and high stress load [3,4]. It was reported that rare-earth metal Y could improve the heat resistance of magnesium alloy, because the high-melting point compounds Al_2Y was formed and the grain was refined [5,6]. When the rare-earth metal Y added to as-cast Mg-Zr-Zn alloy, the grain was refined and Mg-Y phase was formed so that the mechanical property of magnesium alloy was improved at the elevated temperature [7,8].

For the AZ91D alloy, the typical die-casting temperature range of cold chamber die-casting machine is 650～680°C , and that of hot chamber die-casting machine is 620~640°C [9]. Due to the melting point of yttrium up to 1522°C , yttrium is difficult to dissolve in the ordinary casting temperature. Therefore, in this work, the alloying techniques of yttrium in AZ91D were studied at conventional casting temperature, and the preparation technique of the Mg-Y master alloy was investigated. The efficiency of alloying was calculated when yttrium was added into magnesium alloy by the different way. The microstructure of magnesium alloy containing yttrium was observed by optical microscopy, scanning electron microscopy and XRD.

Materials and experimental

The raw materials used were commercial-grade AZ91D, industrial pure yttrium ingots and pure magnesium ingots.

The as-cast Mg-Y master alloys were prepared by the conventional casting method. The magnesium ingot was melted in a high-frequency melting furnace. Yttrium was added when the temperature of the molten was about 750°C . Then the melt was refined by RJ-2 flux and cast into a permanent mould with a cavity of size Φ90 mm ×250 mm. Furthermore, a part of the as-cast Mg-Y master alloy was extruded by the extrusion machine after aging treatment carried at 550°C for 4h. The microstructure of as-cast and extruded Mg-Y master alloy was analyzed by optical microscopy and XRD.

The AZ91D magnesium alloy was melted in the crucible resistance furnace, using RJ-1 flux covering protection, and the crucible was heated to 750°C . The surface of the dollop-like yttrium was polished smooth, and the weight of each one was 1.2% (mass percentage) of the melt. The dollop-like yttrium, as-cast and extruded Mg-Y master alloys were added, respectively. The melt was held at 750 °C for 10 min and then poured into a permanent mould with a cavity of size Φ90 mm ×250 mm. When the dollop-like yttrium was added, the melt was held for 30 min, 60 min, 90 min, and 120 min, respectively. The content of yttrium in master alloys determined by inductively-coupled plasma (ICP) spectroscopy is shown in table 1.

The microstructure of the part of the ingot in the middle and bottom sampling was observed. The advantages and disadvantages of different alloying methods were studied by the microstructures' analysis and component analysis.

The microstructure of alloys was characterized by the optical microscopy (Carl Zeiss Axiovert 200) and the scanning electron microscopy (HITACHI - S4800) equipped with an energy dispersive spectrometer (Oxford). The phases in the as-cast AZ91D containing yttrium were analyzed by D/Max-1200X type X-ray diffraction (XRD).

Results and discussion

Efficiency of alloying at 750°C

Table 1 summarized the efficiency of alloying when yttrium was added into AZ91D by different ways at 750°C . The results show that the efficiency of alloying achieved less than 50% when the dollop-like yttrium was added into the melt held for 120 min. The efficiency of alloying reached to 10.8%, 19.2%, 24.4% and 37.5% when the dollop-like yttrium was added into the melt held for 30 min, 60 min, 90 min and 120 min, respectively. So it is difficult to achieve the desired alloy composition by directly adding dollop-like yttrium. However, the efficiency of alloying was around 71.3% and 78.3% when yttrium was added and held for 10 min by as-cast and extruded Mg-Y master alloy, respectively.

Table 1 contents of yttrium of alloys

Nominal alloys	Y [mass%]	Efficiency of alloying [%]	Addition type of Y	Melt holding time [min]
AZ91D-1.2%Y	0.13	10.8	Dollop-like	30
AZ91D-1.2%Y	0.23	19.2	Dollop-like	60
AZ91D-1.2%Y	0.29	24.2	Dollop-like	90
AZ91D-1.2%Y	0.45	37.5	Dollop-like	120
AZ91D-1.15% Y	0.82	71.3	As-cast master alloy	10
AZ91D-1.15% Y	0.90	78.3	Extruded master alloy	10

Dollop-like yttrium was difficult to melt down at 750°C because yttrium melts at 1522°C . The yttrium was dissolved by the diffusion or chemical reactions that produced the Mg-Y intermetallic compounds with the lower melting point. When the master alloy was added into the molten, the Mg matrix molten down and the Mg-Y phases with the higher melting point became some solid sphere of radius (*r*) that accelerated downward under the influence of gravity. However, there were two addition forces, both acting upward: the constant buoyant force and a velocity-dependent retarding force given by Stokes' law. When the sum of the upward forces was equal to the gravitational force, the sphere traveled with a constant speed (V), called the sink rate. By Stokes' law, the sink rate is given by the relation

$$\mathrm{v}=\frac{\mathrm{g}(r_S-r_{\mathrm{L}})\mathrm{r}^2}{9h}\,. \tag{1}$$

Where r_S and r_L are the densities of the solid and liquid, respectively. The sink rate was influenced by solid sphere of radius *r*. Extruded Mg-Y master alloy has resulted in significant refinement in Mg-Y phase size so that the sink rate decreased, and the reaction or diffusion time was increased. The efficiency of alloying was improved.

Microstructure of Mg-Y master alloy as-cast and extruded

Figure 1 shows the microstructure of the Mg-25wt%Y master alloys. The microstructure of as-cast Mg-Y master alloy was the primary α-Mg and (α-Mg+β-$Mg_{24}Y_5$) eutectic structure, as shown in figure 1(a). There was different shaped intermetallic phase, net-worked and isolated. The microstructure of extruded master alloy was shown in figure 1(b) and (c). The Mg matrix was stretched along the direction of extrusion stress. The Mg-Y phases were broken up.

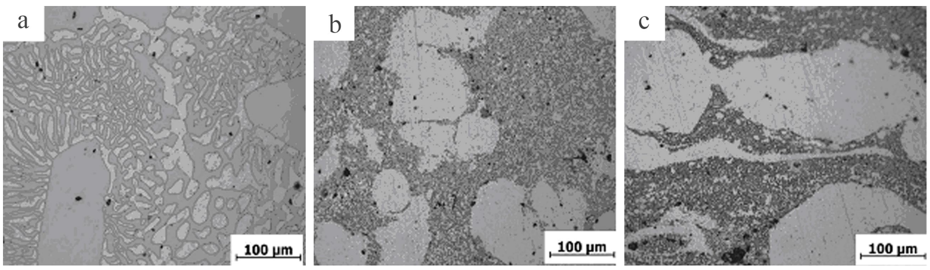

Fig. 1 Microstructures of Mg-25wt. %Y master alloy; (a) as-cast; (b) extruded, transverse; (c) extruded, longitudinal

From the analysis results of XRD, the phase composition of the as-cast Mg-Y master alloy was composed of primary α-Mg phase and β-$Mg_{24}Y_5$ phase.

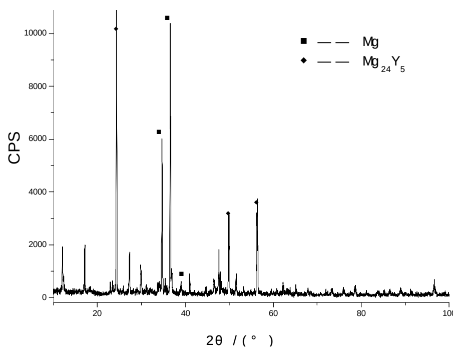

Fig. 2 XRD pattern of As-cast Mg-Y master alloy

When the master alloy was added into the molten, the Mg matrix molten down and yttrium elements in solid solution in the α-Mg dissolved in the melt. Meanwhile, the phase diagram of the Mg-Y alloy shows that the $Mg_{24}Y_5$ phase will decompose in about 605ºC and the Mg_2Y phase with higher melting point will be generated, the reaction equation is as follows [10]:

$$Mg_{24}Y_5(s) \rightarrow L_1 + Mg_2Y(s) \quad \text{the reaction temperature is } 605^{\circ}\text{C}. \tag{2}$$

The L_1 represents the liquid phase. As can be seen from the phase diagram, the content of yttrium in the liquid phase (L_1) is about 35%. When the $Mg_{24}Y_5$ phase decomposed into Mg_2Y phase, the yttrium element dissolved into the melt.

The AZ91D melts contains about 9wt. % of the Al element. Yttrium element preferentially reacts with Al to generate the Al-Y phase because the difference in electronegativity between yttrium and Al is greater than that between yttrium and Mg [11].

The Mg_2Y phase became solid particles floating in the melt, and gradually sank in magnesium melt.

Microstructures of AZ91D with addition of yttrium in various ways

The microstructures of as-cast AZ91D with addition of dollop-like yttrium are shown in Fig. 3. In this experiment, the AZ91D alloy melts and holds 30 min at 750ºC and the dollop-like yttrium was added into. It can be seen from figure 3(a) that the dollop-like yttrium didn't dissolved completely. In figure 3(a), the area of the A was the yttrium not molten, the area of the B was mainly composed of cluster compounds, the area of the C was mainly composed of α-Mg matrix and a large number of polygons Al-Y compound particles and the area of the D was composed of the α-Mg matrix, the fine dispersed $Mg_{17}Al_{12}$ and a large number of Al-Y compounds. Adding the dollop-like yttrium directly into the cast smelting furnace, the Al-Y compound particle was coarse and uneven distribution, which resulted the mechanical properties of magnesium alloy to reduce.

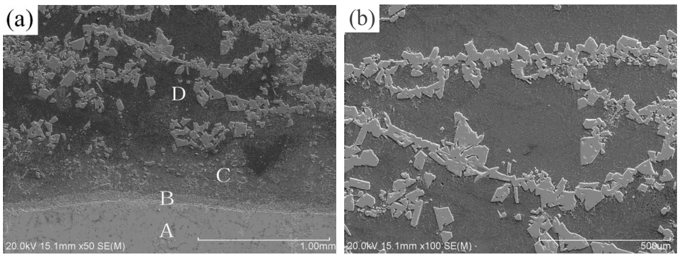

Fig. 3 Microstructures of as-cast with addition of dollop-like yttrium (a) General morphology; (b) D zone morphology

The microstructures of as-cast AZ91D with addition of the as-cast Mg-Y master alloys are shown in Fig. 4. It can be seen that as-cast AZ91D-0.82%Y alloy was composed of $Mg_{17}Al_{12}$ compounds and Al_2Y phase, as shown in Fig.4 (b). The Al_2Y particles dispersed in Mg matrix without apparent aggregation phenomenon.

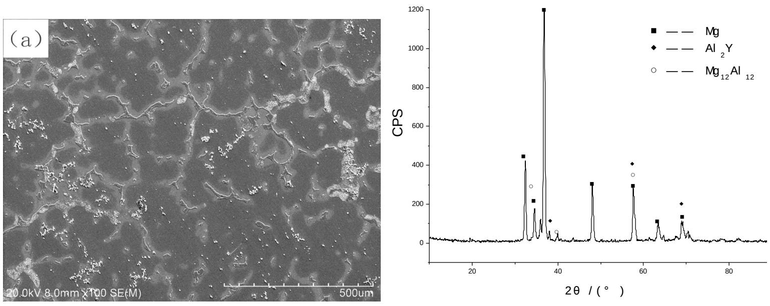

Fig. 4 Microstructures of as-cast AZ91D with addition yttrium by as-cast master alloy;(a) SEM picture of as-cast AZ91D-0.82%Y; (b) XRD of as-cast AZ91D-0.82%Y

The microstructure of the as-cast AZ91D with addition of the extruded Mg-Y master alloys is shown in Fig. 5. It can be seen that the microstructure of as-cast AZ91D-0.90%Y alloy with addition of the extruded Mg-Y master alloy was similar to that of as-cast AZ91D-0.82%Y alloy with addition of the as-cast Mg-Y master alloy. Compared with the as-cast Mg-Y master alloy, the Mg-Y particle in the extruded master alloy was finer. Therefore, the large compound particle didn't be observed in the microstructure of AZ91D-0.9%Y alloy.

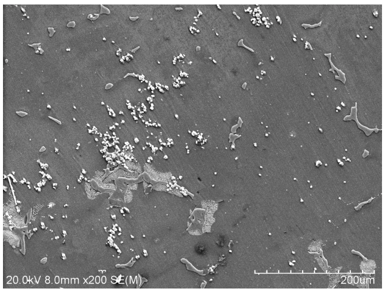

Fig. 5 SEM morphology of as-cast AZ91D with addition yttrium by extruded master alloy

Conclusions

(1) When AZ91D alloys were melted in an electric resistance furnace and the dollop-like yttrium was added to the melt held for 60 min at 750ºC , the efficiency of alloying achieved less than 50%.

(2) The Mg-25wt. %Y master alloy was prepared by permanent mould casting and then was extruded into the bars. The microstructure of as-cast Mg-25wt. %Y master alloy was composed of α-Mg matrix and $Mg_{24}Y_5$ phase. After hot extrusion deformation, the $Mg_{24}Y_5$ phase was fractured and formed into fine particles, which resulted in an increase in the number of nucleating sites for Mg.

(3) When the melting temperature was 750ºC , the as-cast and extruded Mg-25wt. %Y master alloy was added into the AZ91D melt and the efficiency of alloying was 71.3% and 78.3%, respectively. The reason is that the Mg matrix of the master alloy was dissolved, firstly, and $Mg_{24}Y_5$ phase dispersed into the melt and was decomposed into Mg_2Y phase. After extrusion, $Mg_{24}Y_5$ phase was broken into smaller particles. The finer the particle size was, the slower the settling velocity, and the efficiency of alloying of yttrium was increased.

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