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Effect of Ca and RE (Y, Sm) on microstructure and mechanical properties of as-cast AZ91 magnesium alloy

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Abstract

AZ91 magnesium as a lightest structural material, of the alloying additions to magnesium to date, composite Ca, Y and Sm have not been studied. Herein, the effects of Ca and RE(Y, SM) on the microstructure and mechanical properties of as-cast AZ91 magnesium alloy were studied. The results showed that the addition of 1 wt% Ca into AZ91 magnesium alloy could effectively refine the grains, and change the second phase distribution as well. Based on that, the addition of Y and Sm can change the second phase distribution of as-cast AZ91-1Ca alloy. When the content of Y and Sm increased to 0.67 wt% and 0.33 wt% respectively, Al2Y, Al2Sm and Al2(Yx,Sm1-x) composite phases are introduced to refine the alloy grains, also change the size and distribution of the second phase (Mg17Al12, Al2Ca). Furthermore the mechanical properties of AZ91 magnesium Alloy can be improved by Ca and RE (Y, Sm), among which the comprehensive mechanical properties of AZ91-1Ca-0.67Y-0.33Sm alloy has the best presentation, Consequently, the yield strength and tensile strength reached the highest, which are 126 MPa and 198 MPa respectively due to the ensuring elongation. The fracture mode of magnesium alloy can be changed by composite addition of Ca and RE (Y, Sm).

1. Introduction

As the lightest structural material, magnesium alloy is widely applied in aerospace and automobile fields, because its characteristics of low density, high specific strength and high specific stiffness [1–3]. With the rapid development of science and technology, in order to meet the demands of different fields, various series of magnesium alloys have been gradually exploited, and among which AZ series magnesium alloys are widely applied in industrial fields for their low cost and moderate mechanical strength [4–6]. AZ91 magnesium alloy has been widely used due to its excellent machining properties, and commonly found in the automotive industry [7–9]. For the purpose of making this series of magnesium alloys more extensively satisfy the operational requirements, many scholars have conducted extensive research on them in recent years.

Yunus Turen [10] studied the effect of different content of Sn on the microstructure and mechanical properties of AZ91 magnesium alloy, and argued that 0.5 wt% Sn was beneficial to improve the mechanical properties of it. Sun et al [11] found that the addition of appropriate amount of Sm into AZ31 magnesium alloy will form Al-Sm composite phase, inhibiting the formation of Mg17Al12 phase, which can not only effectively refine the grains, but also improve the mechanical strength of AZ31 magnesium alloy. Furthermore, Hu et al [12] indicated that Sm preferentially segregates with Al, reducing the area fraction of Mg17Al12 phase and refining the grain size of AZ91 magnesium alloy. Jia et al [13] claimed that the appropriate amount of Y can obviously refine the grain size of AZ91 magnesium alloy and improve its corrosion resistance. On the other hand, Tong et al [14] reported the composite addition of Ca and Y also can refine the microstructure of as-cast AZ91 magnesium alloy, which can’t be realized by addition of single element. What’s more, the addition of Sm, Si and Ca elements into AZ91 magnesium Alloy Can effectively refine the grain structure and improve the mechanical its properties.
The results above all suggested that the composite addition of appropriate elements is beneficial to the improvement of microstructure and mechanical properties of AZ series magnesium alloys.

Given all that, although there was an amount of study done on the alloying of AZ91, but the composite addition of Ca, Y and Sm into AZ91 magnesium alloy has not been studied yet. Therefore in this experiment, Ca and RE (Y: Sm = 2:1) were added to AZ91 magnesium alloy to observe their effects on as-cast AZ91 magnesium alloy, and analyze the mechanism.

2. Experiment process

In this study, AZ91 magnesium alloy as master alloy were selected, Mg-Y, Mg-Sm and Mg-Ca alloys as element addition method were selected. The experimental alloy was completely melted in a graphite crucible with argon as protective gas at the temperature of 750 ℃, and then mechanically stirred for 5 min to disperse the components evenly. After fully reaction, quickly poured them into a metal mold preheated to 200 ℃, as shown in figure 1. The design compositions of the experimental alloy are listed in table 1.

The experimental process of the research on as-cast alloy specimens are presented in figure 1. The metallographic samples were prepared according to the standard procedures of grinding, polishing and etching (corrosive medium: alcohol 25 ml, picric acid 2.6 g, acetic acid 2.5 ml), and the microstructure was observed by optical microscope. The microstructure of the specimens was further studied by FEI-SIRION scanning electron microscope (SEM, EDS). X’pert PRO x-ray diffractometer (XRD) was used for phase analysis, and JEM-2100 transmission electron microscope (TEM) was used to analyze the second phase and calibrate the diffraction spots.

DNSI00 electronic universal testing machine was used to test the tensile mechanical properties of samples with different components at room temperature, with 1 mm min⁻¹ tensile speed, and the tensile test sample as shown in figure 1. The fracture morphology was observed by FEI-SIRION scanning electron microscope (SEM).

### Table 1. Design compositions of the experimental alloys (wt%).

| Alloy | Al | Zn | Mn | Ca | Y   | Sm | Mg   |
|-------|----|----|----|----|-----|----|------|
| A     | 9  | 1  | 0.2| —  | —   | —  | Bal. |
| B     | 9  | 1  | 0.2| 1  | —   | —  | Bal. |
| C     | 9  | 1  | 0.2| 1  | 0.33| 0.17| Bal. |
| D     | 9  | 1  | 0.2| 1  | 0.67| 0.33| Bal. |
| E     | 9  | 1  | 0.2| 1  | 1   | 0.5 | Bal. |

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3. Results and analysis

3.1. Microstructure

The optical microstructure of as-cast magnesium alloys as presented in figure 2. It can be seen from figure 2(a) that the microstructure of as-cast AZ91 magnesium alloy is mainly composed of massive-dendrite like α-Mg matrix and β-Mg17Al12 phase with network distribution, the average grain size of the Alloy A is about 193.07 μm, as shown in figure 2(f). According to figure 2(b), with the addition of Ca, the grain size of the alloy decreases significantly and so is the amount of β-Mg17Al12 phase with network distribution, the continuity reduces and the refinement phenomenon is conspicuous.

This is because that, Mg phase crystallizes and precipitates first during cooling, and except the small amount of Al in solid solution in the crystallization region, the rest of Al starts to transfer to the liquid phase, which causes the Al content in the liquid-solid front to increase, resulting in the supercooling of the composition and the formation of dendritic α-Mg phase. When the content of Al in the liquid phase reach the eutectic composition point, the β-Mg17Al12 phase begins to nucleate in it. It is known that the solid solubility of Ca in Mg is small and Ca is a surface active element of Mg, thus when 1 wt%Ca(Alloy B) is added into the alloy, the concentration of Ca in the liquid-phase region of the liquid-solid interface of the alloy increase continuously and adsorb on the surface of α-Mg, resulting in the supercooling of components and inhibiting the diffusion of solute elements, therefore the growth of alloy grains is hindered. In addition, the difference of electronegativity between Ca and Al is higher than that between Mg and Al (Ca = 1, Al = 1.61, Mg = 1.31) [16]. The melting point of Al2Ca is much higher than that of Mg17Al12, leading to the formation of Al2Ca phase preferentially by the Al in enrichment and Ca in liquid phase and thus the obvious decreasing of the formation of β-Mg17Al12 phase in the alloy. On the other hand, growth of the grain was inhibited due to formation of Al2Ca liquid region in magnesium.

Based on it, when 0.33 wt% Y and 0.17 wt% Sm (Alloy C) are added into the alloy, the grain size of Alloy C relative to Alloy B does not change conspicuously, and the second phase slightly reduces, as seen in figure 2(c). When the content of Y and Sm in the alloy increases to 0.67 wt% and 0.33 wt% respectively (Alloy D), the grain size is refined again, and the number of second phase decreases significantly, are presented figure 2(d), the average grain size of this component alloy was 155.98 μm as shown in figure 2(f). That is because of the increase of Y and Sm content, the formation of Al2Y and Al2Sm acted as the nucleation core of the alloy, and also, it restricted the grain growth, causing the shrink of grain size of magnesium alloy. The formation of Al2Y and Al2Sm will further consume the content of Al, resulting in the decrease of β-Mg17Al12 phase. Excessive Al2Y and Al2Sm gather, causing the increase of grain size and second phase size of magnesium alloy with the content of Y and Sm increasing to 1 wt% and 0.5 wt% (Alloy E), as shown in figure 2(e).

According to figure 3 that the XRD patterns of magnesium alloys with each components. Alloy A is composed of α-Mg phase and β-Mg17Al12 phase. When 1 wt% Ca was added into the alloy, Al2Ca phase was detected in Alloy B besides the above two phases. When 0.33 wt% Y and 0.17 wt% Sm (Alloy C) are added continuously, no Al2Sm phase is detected in Alloy C because of the small amount of RE added. The small drop of the number of the second phase in figure 2(c) is possibly caused by the consumption of some Al elements in the...
liquid phase by the formation of Al$_2$Y phase. And in Alloy D and alloy E, the number of diffraction peaks of β-Mg$_{17}$Al$_{12}$ phase is conspicuous decreased. Therefore, it is proved again that the addition of Y and Sm hinders the formation of β-Mg$_{17}$Al$_{12}$ phase.

Typical SEM images and EDS results of Alloy B and Alloy D are shown in figure 4. Regarding Alloy B, it can be found that Alloy B is composed of α-Mg matrix and bright white second phase with discontinuous network and lamellar structure. By EDS analysis, it is shown that the second phase with discontinuous network distribution at position I is Mg$_{17}$Al$_{12}$ phase, and a small amount of Ca is found in solid solution, while the lamellar structure at position II is Al$_2$Ca phase. In alloy D, the bright white second phase is significantly refined and distributed in discontinuous network along the grain boundary, and there are granular bright white second phase. EDS analysis shows that Al$_2$Ca phase is at position III and the circular phase at position IV is Al$_2$(Y$_x$,Sm$_{1-x}$) composite phase.

It can be seen from figure 5 that SEM images of magnesium alloys with different compositions. When 1 wt% Ca(Alloy B) is added to AZ91, the bright white second phase (β-Mg$_{17}$Al$_{12}$) with discontinuous network distribution is conspicuously refined and a lamellar structure(Al$_2$Ca) is formed (figure 5(b)). The formation of lamellar Al$_2$Ca phase consumes Al element in the liquid phase, thus the formation of Mg$_{17}$Al$_{12}$ phase is hindered, and so is to the size. When 0.33 wt% Y and 0.17 wt% Sm(Alloy C) are added, the second phase of the alloy reduces again because of the generation of Al$_2$Y phase, and the lamellar phase of Al$_2$Ca transforms into a slender fishbone like distribution in figure 5(c).
When the content of Y and Sm in the alloy is 0.67 wt% and 0.33 wt% respectively (Alloy D), the granular Al$_2$(Y$_{x}$Sm$_{1-x}$) composite phase increases drastically, the bright white Al$_2$Ca phase and β-Mg$_{17}$Al$_{12}$ was refined again, which is for the reason that the formation of Al$_2$Y, Al$_2$Sm and Al$_2$(Y$_x$Sm$_{1-x}$) composite phase further hinders the formation of Mg$_{17}$Al$_{12}$ phase. And the size of β-Mg$_{17}$Al$_{12}$ phase and Al$_2$Ca phase reduces again for the additional consumption of Al element (figure 5(d)). When the content of Y and SM in the alloy increases to 1 wt% and 0.5 wt% (Alloy E), the granular Al$_2$(Y$_x$Sm$_{1-x}$) composite phase was thicken, size of the second phase starts to increase.

The TEM micrograph of Alloy D shown in figure 6. It can be inferred from the above that Al-Sm phase appears in the alloy, and this compound is mainly distributed in the grain with the form of particles. With the calculation of diffraction spots, it is known that the phase was Al$_2$Sm phase.

Figure 7 depict the crystallization principle of Alloy D. Due to the existence of Y and Sm elements in Alloy D, granular Al$_2$(Y$_x$Sm$_{1-x}$) phase will be formed, and part of Al atoms (Area A) in the liquid phase will be consumed, thus the lamellar Al$_2$Ca (figure 5(b)) will disappear and the fishbone like Al$_2$Ca will be occurred. With the decrease of temperature to 650 °C, because Al$_2$(Y$_x$Sm$_{1-x}$) phase can be set as heterogeneous nucleation core of magnesium alloy, a part of primary Mg grains begin to adhere to Al$_2$(Y$_x$Sm$_{1-x}$) phase and nucleate. But due to
the existence of Al2(Yx,Sm1-x) and Al2Ca phase in the alloy, an impediment is provided to grain growth. When the temperature is decreasing, the secondary Mg grains grow on the primary Mg grains with attachment, while the Al concentration in the liquid phase increases gradually (Area B). And the Mg17Al12 phase begins to adhere to the Al2Ca phase to crystallize, causing the size of Mg17Al12 phase to shrink with the consumption of Al2(Yx, Sm1-x) and Al2Ca.

3.2. Mechanical properties and fracture morphology

The tensile properties of magnesium alloys at room temperature as shown figure 8. The results suggest that the yield strength and tensile strength of the alloy increase first and then decrease with the change of Alloy Composition, and reaching the optimal in AZ91-1Ca-0.67Y-0.33Sm (Alloy D), with yield strength and tensile strength at 126 MPa and 198 MPa respectively. However, the elongation of the alloy fluctuates in a small range and increases on the whole.

Figure 8 reveal the tensile fracture morphology of the alloys at room temperature. The results suggest that the fracture mode of Alloy A was brittle fracture. And noncontinuous cleavage steps can be observed at the fracture in figure 9(a), and the fracture was almost perpendicular to the tensile stress. Because of that the thick and continuous distribution of Mg17Al12 phase became the root reason of crack propagation, thus resulting in a brittle fracture of Alloy A. With the addition of 1 wt% Ca, a small amount of dimples and fluvial patterns can be observed in Alloy B, but the fracture mode of which was still mainly in brittle fracture, and right white stratiform structure can be found at the fracture, as what is shown in figure 9(b). It can be inferred from figure 8 that the
increase of Alloy B strength was related to the decrease of grain size on the one hand, and on the other hand, it was due to the formation of Al2Ca phase, which caused Mg17Al12 phase more refined, thus improving the strength of the alloy. The strength of Alloy C continued to increase for the variation of the second phase and the formation of Al2Y phase. From figure 9(c), a large number of dimples and a small amount of tear edges occurred at the fracture of Alloy C, therefore it can be inferred that the fracture mode of Alloy C began to transform from brittle fracture to ductile fracture, and for there is no bright white lamellar structure found on the fracture surface of Alloy C compared with Alloy B, which may be the reason for the change of alloy elongation in figure 7.

Figure 9(d) demonstrates there are a large number of dimples and a small amount of tear edges at the fracture of Alloy D. Therefore, it can be inferred that compared with Alloy C, the fracture mode of Alloy D did not change, which was still mainly in ductile fracture and supplemented by brittle fracture. Additionally, bright white granular hard brittle phase was also found at the bottom of the micro pit or at the height of the matrix in the fracture of Alloy D. Thus combined with the above, the crack propagation will be blocked by these white granular hard brittle phases (Al2Y, Al2Sm, Al2(YxSm1-x) composite phase) in a certain extent, and the grain size of the alloy will be refined and the distribution of the second phase will be improved by the formation of these phases, therefore increasing the strength of the alloy. The second phase in Alloy E was enriched at the grain boundary due to the excessive addition of Y and Sm elements, resulting in the reduction of yield strength and tensile strength. However, there were still a large number of dimples and a small amount of tear edges in the fracture morphology, indicating that the fracture mode of which did not change compared with Alloy D (figure 9(e)). Besides, the number of small cracks on the fracture of Alloy E increased, which may be the reason for the decreasing of mechanical properties.

4. Conclusion

(1) The composite addition of Ca and RE (Y, Sm) can effectively refine the grain size and improve the second phase distribution of as-cast AZ91 magnesium alloy. Among them, the grain size of AZ91-1Ca-0.67Y-0.33Sm alloy (Alloy D) is the smallest and the second phase distribution of which is the most uniform.

(2) The composite addition of Ca and RE (Y, Sm) can significantly improve the strength of as-cast AZ91 magnesium alloy. The comprehensive mechanical properties of AZ91-1Ca-0.67Y-0.33Sm alloy (Alloy D) is the best, the yield strength and tensile strength of which reach 126 MPa and 198 MPa respectively, based on ensuring elongation.

(3) The fracture mode of magnesium alloy can be changed by composite addition of Ca and RE(Y, Sm).

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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