

Effect of cooling speed on microstructure of as-cast Mg-3.7Zn-0.6RE quasi-crystal alloy

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Abstract. By means of optical micrograph(OM), X-ray diffraction (XRD), scanning electron micrograph(SEM) and Energy Dispersive Spectrometer(EDS) analysis, the microstructure and phase compositions of Mg-3.7Zn-0.6RE alloys with different cooling speed were studied. All alloys had dendritic structure, the grain size and dendrite spacing had inverse relationship with the cooling speed of the ingots. quasi-crystal phases and W-phase were detected in all the alloys. The solidification process of the alloy was deduced by the results of the experiments above, and the peritectic reaction which could form the quasi-crystal phase was also confirmed in the investigations of the alloys which had the lowest cooling speed.

Introduction

Magnesium alloy is the lightest metal structure material. This advantage made it become the most indispensable material in aerospace and automobile industry[1]. Researchers are doing their best to strengthen the properties of magnesium alloys in order to extend its application domains[2]. In the last decade, magnesium alloy containing quasi-crystal became a new research hotspot[3]. Because the quasi-crystal is a new kind of structure which could bring it special properties what crystals do not have[4]. Moreover, the quasi-crystal phases in magnesium alloy could be prepared by conventional casting, which means this kind of alloy is suitable for industrial production[5].

However, in industrial production, the ingots should be large in order to improve production efficiency. When the ingots become larger, the microstructure of the ingots would be inhomogeneous, as the cooling speed in different parts of the ingots is different, and the microstructure will greatly affect the properties of the alloys in all machining processes. Thus, the effect of the cooling speed on microstructure and phase composition was studied, which could provide theoretical guidance for the industrial production.

Experimental details

The nominal composition of the alloy in this paper was Mg-3.7Zn-0.6RE(at.%), where the rare earth elements were Gd and Y, and the proportion of the Gd and Y was 1:1. The ingots were prepared in a electromagnetic induction furnace with steel crucibles (Φ 100mm×500mm), and the shield gas of Argon and R134a. All alloying elements were added as pure elements in different temperatures. When the alloying and impurity processes were completed, the crucibles were lifted out. Three cooling methods were carried out for the melts to cool down and solidify. One crucible was directly chilled into water, and this ingot was named Alloy 1; one crucible was placed in air, and this ingot was named Alloy 2; the last one was putted into a muffle furnace whose temperature was set to 600°C, then the power of the furnace was shut, and the ingot was cooled inside the furnace to room temperature, this ingot was named Alloy 3. Then, the top of the three ingots were cut to 10mm×10mm×10mm specimens for OM, SEM observations and EDS, XRD analysis.

Results and discussion

To observe the microstructure of the alloys visually, OM observation was carried out, as shown in Fig.1.

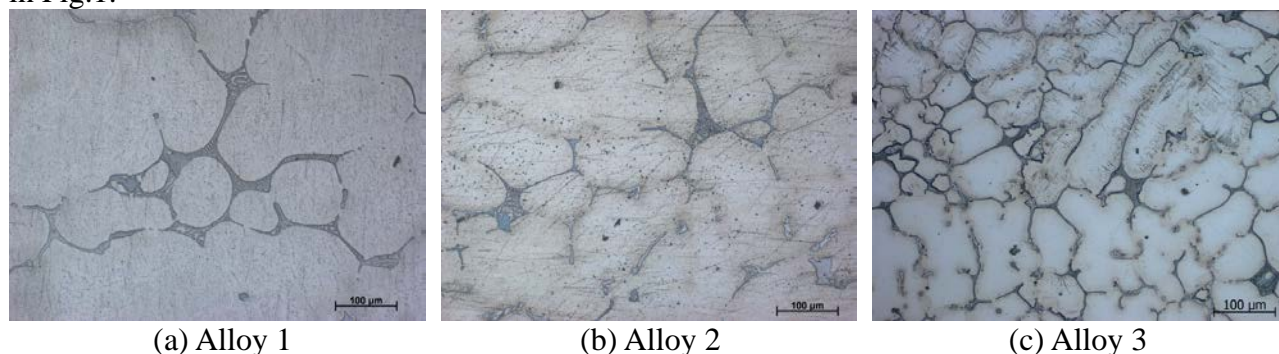


Fig.1 OM micrograph of the as-cast alloys

It could be seen that the microstructures of the three alloys were quite different. In Fig. 1 (a), alloy 1 had the coarsest structure, as there were thick eutectics and large equiaxed grains. A great number of precipitated particles emerged inside the grains, which made the contrast of the basis gray. In Fig. 1 (b), the OM micrograph was also coarse. Eutectic structure and bulk phase were observed. The areas which were near the second phases shown gray contrast; it might be the second precipitation zones. The alloying elements diffused out from the big second phases at high temperature and formed fine precipitations not far from the big second phases. For alloy 3 which was shown in Fig. 1 (c), the structure was much finer, dendritic structure could be clearly observed. The dendrite arm spacing was about 60μm. Besides, it could be obviously seen that there were two big grains in the micrograph, as the morphology after corrosion of the second precipitations were different in these two areas. The grain located at the upper half of the graph had more obvious precipitation zone. As comparison, the grain located at the bottom half of the graph had cleaner grains. Only misty precipitation areas with gray contrast were found between the dendrite arms. This phenomenon indicated that there were two big grains in the micrograph; these two grains had different orientation, which led to the disorientation of the second precipitations.

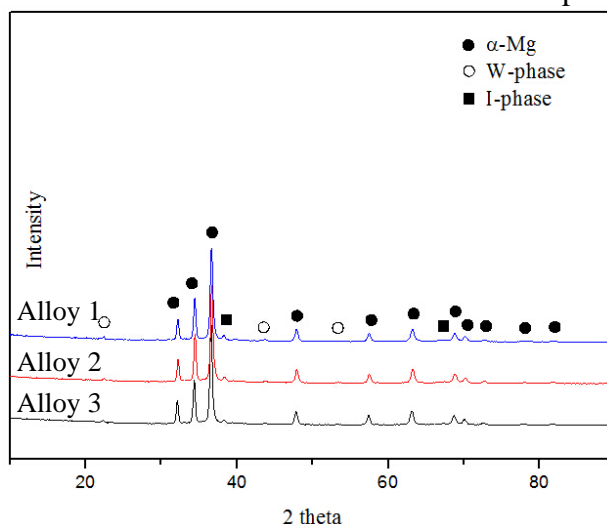
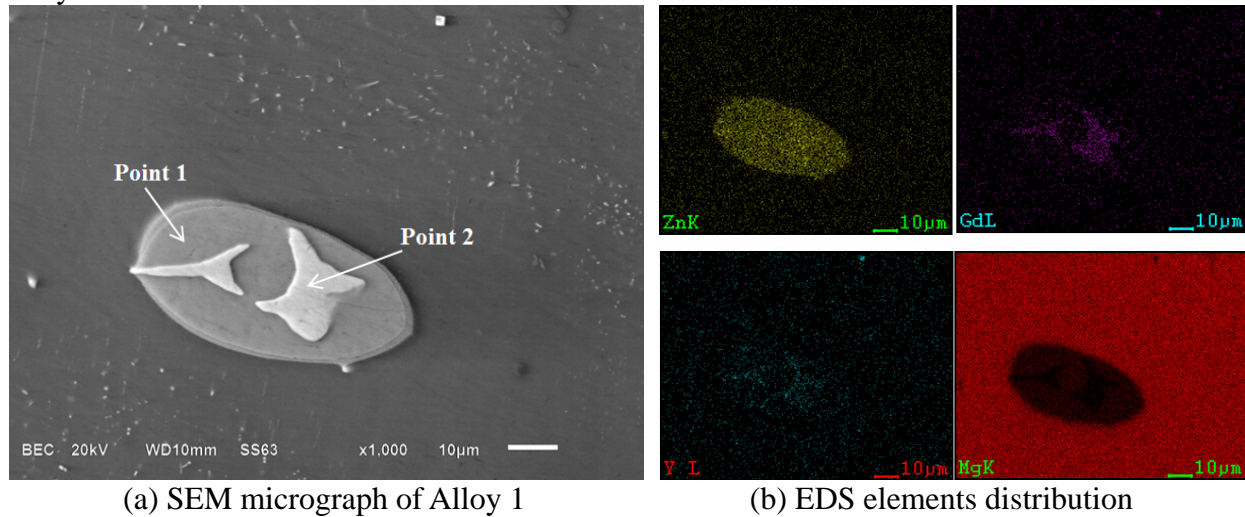


Fig.2 XRD patterns of the three alloys

To confirm the phase compositions of the alloys, XRD analysis was carried out, as shown in Fig. 2. All alloys were consisted of α -Mg basis, cubic structure W-phase and icosahedral quasi-crystal phase (I-phase). This result had some deviation with the theoretical result, especially with the ternary equilibrium phase diagram. In the diagram, the phase composition was determined by the content of the alloying elements. At the Mg-rich part of the diagram, the phase composition was controlled by the Zn/RE atomic ratio[6,7]. The chemical formula of the I-phase and W-phase were Mg_3REZn_6 and $\text{Mg}_3\text{RE}_2\text{Zn}_3$ respectively[8]. The atomic ratio of Zn and RE in these two phases

informed that if the atomic ratio of Zn/RE was 6, there should be only I-phase in the alloy in equilibrium state. If the atomic ratio was lower than 6, there would be not enough Zinc to form I-phase, thus, the precursor phase W-phase was remained. However, in this paper, the Zn/RE atomic ratio was bigger than 6, which should make the phase composition of the alloys are I-phase and Mg-Zn binary phase. But W-phase still existed in all three alloys, and Mg-Zn binary phase was not confirmed by the XRD patterns. This may because the Mg-Zn phase was the second precipitation, the content and size of which was too small to be detected by the XRD. Meanwhile, the main diffraction peaks of Mg-Zn binary phase were overlapped with the peaks of Mg-basis and W-phase. Synthesize the above results, the Mg-Zn binary phase could not be recognized in the XRD patterns clearly.



(a) SEM micrograph of Alloy 1

(b) EDS elements distribution

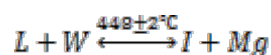
Fig. 3 SEM micrograph and EDS elements distribution of Alloy 1

In order to investigate the deviation between the realistic phase composition and the ternary phase diagram, the solidification process should be deduced. Therefore, SEM and EDS analysis for Alloy 1 was carried out, as shown in Fig. 3.

Fig. 3(a) presented an enfolded particle. The sensor source of this micrograph was backscattered electron, which means the contrast of the image could be associated with the atomic number of the phases. It can be clearly seen that the core of the particle was bright and the coat was gray, as indicated by the arrows, which meant they were different phases. EDS results shown that, the phase marked as point 1 was Mg-Zn binary phase. Because it did not contain rare earth elements, the atomic number was low, so the contrast was gray. The phase indicated by arrow 2 was the core of the particle. The Zn/RE ratio of the core was about 6:1, which meant it was I-phase. The contrast of the core was bright which also manifested it contained more alloying elements, especially rare earth elements.

Fig. 3(b)-(e) were the EDS elements distribution of Fig. 3(a). The distribution of the four alloying elements could be intuitively observed. The zinc covered the entire particle, including the coat and the core, and it was hard to distinguish the core from the coat. It might refer that the content of zinc in these two phases was nearly the same. Fig. 3(c) and (d) were the distribution of the rare earth elements. It could be clearly observed that the rare earth elements were mainly concentrated in the core, which meant the core was Mg-Zn-RE ternary phase.

Based on all the experimental results and analysis, it could be found that the differences between the three alloys were mainly caused by the diversity of the cooling speed, because the cooling speed was the only variable. According to the reference, it could be known that the solidification of the Mg-Zn-RE alloy was complicated. Though the quasi-crystal phase could be prepared by conventional casting, but it was not formed during the solidification. There was a peritectic reaction during the solidification[9,10]:



According to the reaction equation, the I-phase was transformed from the W-phase. The liquid phase should be rich in zinc, because the melt point of Mg-Zn binary phase was about 350°C, and

the I-phase had much more zinc than W-phase. When the melt started to freeze, primary crystal α -Mg crystallized first, and the dendrite structure was also formed. Liquid phase which was rich in alloying elements was squeezed to the areas between the dendrites and the dendrite arms, then W-phase crystallized. The remained liquid phase was rich in zinc and prepared for the peritectic reaction to form I-phase. However, the cooling speed was low, and the dendrites were still growing and spheroidizing. The liquid was squeezed away, which caused the zinc distributed uneven. This lead to the failure for some of the reaction, and the particle shown in Fig.3 (a) was covered by too much zinc. The cooling speed was lower, the uneven of alloying elements was more serious, and this made the difference of the three alloys.

Conclusion

Three Mg-3.7Zn-0.6RE alloys were prepared by conventional casting at different cooling speed. All alloys had the same phase compositions: α -Mg basis, W-phase and I-phase. Lower cooling speed made the structure coarser. The low cooling speed might cause the uneven distribution of the alloying elements, especially zinc, which lead to the existence of W-phase and MgZn-clad quasi-crystal particles.

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