Growth of Primary α Phase in the Semi-Solid State Mg–Zn–Ca–Zr Alloy

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The coarsening of the primary α phase in a Mg–6.0%Zn–2.0%Ca–1.5%Zr alloy in the semi-solid state temperature range was investigated to establish the necessary processing conditions for the semi solid state forming processes. The growth of the primary α phase was found to be influenced by the sample heating and holding duration. In addition, the growth rate was observed to be rather high for a lower holding temperature. These phenomena were discussed based on the experimentally measured distance between the grains in the semi-solid state.

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1. Introduction

With concerns on the recent energy crisis and environmental contamination, magnesium alloys have been recognized as ecologically compatible structural materials because of their high specific strength and potential for recycling. Although explosive oxidation of these alloys during melting and casting has been a critical obstacle for their wide-spread industrial application of the alloys, the addition of calcium with zirconium can effectively prevent the oxidation.¹⁾ The fracture elongation and toughness of the alloys have been improved significantly by refining the grain size. Various methods have been attempted to refine the grain size, including superheating,²⁾ carbon addition,²⁾ iron chloride addition²⁾ or zirconium addition.^{2,3)} Among these methods, zirconium addition was found to be most effective in Mg–Zn alloys (ZK) because the zirconium does not affect the solubility of zinc in magnesium. A Mg–Zn alloy with zirconium and calcium content higher than 1% was observed to have grains of approximately 20 μm in diameter.⁴⁾

Semi-solid state forming processes (SSF)⁵⁾ have recently attracted considerable attention for manufacturing complicated structural parts. Their several potential benefits include reduced energy for processing, extension of die life due to low injection temperature, and the improvement in ductility resulting from decreased shrinkage and porosity in the material. The application of SSF processes has also been attempted to produce near-net shape magnesium products.

After the SSF processing of the Mg–Zn alloys with Ca and Zr additions, the tensile properties of the alloys were found to be affected sensitively by their microstructure, which also has a significant influence on the fluidity, the handability and the deformability of the ingot in the semi solid state.⁶⁾ The ripening of the primary α phase, in particular, was observed to have a detrimental effect on the strength of the alloy.^{7,8)} Thus, in this study, the ripening characteristics of primary α phase in the Mg–Zn–Ca–Zr alloy in the semi solid state was

investigated to establish processing conditions of magnesium alloys with better mechanical properties via the SSF.

2. Experimental Procedure

2.1 Preparation of material

Mg–Zn–Ca–Zr alloy was prepared by melting ingots of pure magnesium (99.9 mass%), pure calcium (99.5 mass%), and pure zinc (99.9 mass%), together with a Mg–65%Zr master alloy. At 1073 K, the melt was poured into a mold preheated to 573 K and squeeze-cast under an applied pressure of 25 MPa. The plunger speed was 22 mm/s. Based on the results of the previous study,⁴⁾ the compositions of the ingot were selected as Mg–6.0 mass%Zn–2.0 mass%Ca–1.5 mass%Zr. Small 10 $\times$ 10 $\times$ 20 mm³ dimension specimens were cut from the ingot and used for semi solid quenching experiments. The specimens were heated to a specific temperature (623, 868, 883, 898 and 903 K) in 1.8 ks. After the sample reached the specific temperature, it was kept at the temperature for 0, 1.2, 2.4 and 5.4 ks followed by quenching into brine water.

2.2 Microstructural analysis

The microstructures of the ingot and quenched samples from the semi solid state were examined with an optical microscope (OM). Image analysis of the microstructure was conducted to determine the solid fraction, the size of primary α phase, and the distance between primary α phases. In this study, it was considered that primary α phases satisfied with the condition of $X > N/2$ as shown in Fig. 1 coalesced and were treated as a primary α phase. The distance between primary α phases is defined as shown in Fig. 2. The distance between centers of primary α phases, D_1 , is defined as $D_1 = \pi R/4Fs$, and the distance between edges of primary α phases, D_2 , is obtained from $D_1 - R$, where R is the diameter of primary α phase and Fs is the solid fraction. After tensile testing of the samples produced by the SSF process, the samples were electropolished to observe slip lines on the primary α phase.

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Fig. 1 Coalesced primary α phase defined in this study.

Fig. 2 Definition of the distance between centers, D_1 , and the distance between edges, D_2 , of two primary α phases.

3. Results

3.1 Initial microstructures

Typical microstructures of the ingot as well as those ingots heated to 868 K and kept at that temperature for 2.4 ks followed by quenching are shown in Fig. 3. The ingot consists of spherical grains with an average size of 23 μm . The white particles in the cast structures are the primary α -Mg phase, while the black continuous phase around the primary α phase is the eutectic structure. The microstructure of the specimen heated to the temperature followed by quenching consists of the ripened primary α phase, the remelted and resolidified α phase, and the eutectic compound that was liquid in the semi solid state. The resolidified α phase appeared as fine equiaxed grains in the eutectic area. The eutectic compound was identified as $\text{Mg}_6\text{Ca}_2\text{Zn}_3$.⁴⁾

3.2 Growth of primary α phase in semi solid state

Figure 4 illustrates the variation of the solid fraction as a function of the heating and holding time. The solid fractions of the ripened primary α phase in the semi solid state were approximately 90%, 70%, 65%, 40% and less than 25% at the temperatures of 623 K, 868 K, 883 K, 898 K and 903 K respectively. At all temperatures except 623 K, the solid

Fig. 3 Microstructures of Mg-Zn-Ca-Zr alloys cast (a) and quenched from the semi-solid state of 868 K (b).

Fig. 4 Variations of the solid fraction during heating and holding.

fraction decreased significantly until 1.2 ks. After the heating time, the solid fractions remained almost the same until 1.8 ks.

The sizes of primary α phase during heating and holding duration are shown in Fig. 5. The size of primary α phase increased with the heating time and the growth rate was higher at higher temperatures. The growth rate at temperatures exceeding 868 K, however, became saturated with increasing time but kept increasing with heating time at temperature of 868 K.

The size of the ripened primary α phase also increased with

Fig. 5 Variations of the size of primary α phase during heating and holding.

holding time as shown in Fig. 5. The growth rate, however, was lower at higher holding temperatures. The size of the primary α phase with a solid fraction exceeding 70% was observed to increase drastically with holding time. The size of the resolidified α phase, however, did not change with holding time, as reported previously.⁷⁾

The size distributions of the primary α phase of the samples kept at 868 and 903 K for 0 or 2.4 ks are shown in Fig. 6. The radius of primary α phase, r , was normalized by $r^*(t)$, which is the average radius of the primary α phase at the time, t . The size distribution of the primary α phase at 868 K was slightly broadened after being held at the temperature for 2.4 ks. The size distributions at 868 K were also broader than at 903 K.

The distance between centers of primary α phases and the distance between edges of primary α phases are shown in Figs. 7 and 8 as a function of the heating and holding time. D_2 has been considered to represent the characteristics of the growth behavior in the semi-solid state temperatures, rather than D_1 . At temperatures of 623, 868 and 883 K, D_1 and D_2 increase slightly during heating. The distances increased drastically with holding time at temperatures of 898 and 903 K. At 868 K, D_2 was only about 90 μm after holding for 5.4 ks, while at 898 K, it was 150 μm after only 2.4 ks.

4. Discussion

The difference in the growth behavior of the primary α phase during the heating period might be explained as follows. After being heated for 0.3 ks, all the specimens should include a solid fraction exceeding 60% as shown in Fig. 3. Under this condition, most of the primary α phases should contact each other, and the growth should occur by coalescence ripening. The distance between the primary α phases, however, becomes greater with increasing heating time due to the decreased solid fraction as noted in Figs. 7 and 8. This phenomenon should be more distinguished at higher temperatures such as 898 and 903 K, and that should lead to the decreased growth rate. At lower temperatures such as 623 and 868 K, the growth should continue at a higher rate as the solid fraction is not significantly changed with the heating time.

In Fig. 5, the primary α phases coarsened during holding and the growth rate was affected by the holding temperatures. At a low holding temperature (868 K), in particular, the growth rate was much larger than that at temperatures higher

Fig. 6 Distribution of normalized primary α phase size in Mg–6.0%Zn–2.0%Ca–1.5%Zr alloy after isothermal ripening at 868 and 903 K.

Fig. 7 Variations of the distance between centers of primary α phases during heating and holding.

Fig. 8 Variations of the distance between edges of primary α phases during heating and holding.

than 883 K. The growth rate decreased with holding time at 898 and 903 K. The different coarsening behavior might also be rationalized by the solid fraction at the processing temperature. At 868 K, the primary α phases should contact each other since the solid fraction is approximately 70%. At higher temperatures, the primary α phases are too far apart to be ripened by coalescence. The solid fractions at 898 and 903 K are approximately 40 and 25% respectively. The size distribution of the primary α phases kept at 868 K for 2.4 ks was

Fig. 9 Optical micrographs of Mg-Zn-Ca-Zr alloy quenched after holding at 868 K for 5.4 ks followed by tensile testing.

broader than that at 903 K. Takajo *et al.*⁹⁾ have shown that even a small contribution from coalescence ripening broadens the distribution significantly compared to that by ostwald ripening. These results indicate that the characteristics of the growth behavior at different holding temperatures are determined by the distance between the primary α phases rather than the size. Also, the coalescence ripening predominates the growth of the primary α phase with a high solid fraction.

Figure 9 shows the micrographs of the electropolished Mg-Zn-Ca-Zr alloy after the tensile test. The slip-lines in the individual primary α phases were observed to align in different directions (Fig. 9(b)). If two primary α grains coalesced together perfectly, the slip lines that pass through the contacting neck area should be observed.

Contacts between grains are induced by gravity, thermal motion, and settling. Several mechanisms are known to operate for contact formation. These include grain boundary migration by solid state diffusion, grain boundary migration by diffusion across an intermediate thin liquid layer, grain rotation to eliminate the grain boundary, or solution-precipitation from the smaller to the larger grains.¹⁰⁾ Once the contact forms, the driving force for coalescence is the reduction in the surface free energy of the system. In the semi-solid state, contacts form after the liquid appears and there is a probability that the contact forms a low angle grain boundary. Additionally, coalescence is generally favored when a large grain contacts a smaller one. Thus, it is reasonable that the small grains disappear first after contacting larger grains. In the samples used in this study, however, the grain size was approximately 22 μm in diameter and was very uniform throughout the sample as shown in Fig. 3(a). As the contacting grains are similar in size, the grain boundary should have been stable as the curvature was similar. In this case, the growth should be limited by the holding time.

In Fig. 9, there were small grains in the contacting neck area (see the arrows) rather than was slip line passing through the area. From these results, the growth process seems to proceed in the following steps. The primary α phases of similar size contact each other after the liquid phase appears. As the differences in the sizes of contacting primary α phases are small, the boundary should be stable since the driving force for diffusion across the boundary is small. The flattening pro-

cess of the boundary accompanies the solution-precipitation process. Thus, as the reprecipitation occurs at the boundaries between the primary α phases, new grains with a low orientation mismatch could be resulted at the boundary. The newly formed grains could grow via diffusion through the primary α phase.

5. Conclusions

The growth characteristics of primary α phase in a semi-solid state Mg-6.0%Zn-2.0%Ca-1.5%Zr alloy have been investigated. The results obtained are summarized as follows:

(1) The fraction of solid phase of the Mg-6.0%Zn-2.0%Ca-1.5%Zr alloy was 90%, 70%, 65%, 40%, and 25% at 623, 868, 883, 898 and 903 K respectively. The primary α phase ripened during the heating as well as holding durations. At the temperatures of 898 and 903 K, the growth rate of the primary α phase was small, but the rate was significant at 868 K.

(2) The size distribution of the primary α phase held at 868 K was broader than that at 903 K and was slightly broader after holding for 2.4 ks at that temperature.

(3) The distance between centers of primary α phases and the distance between edges of primary α phases increased with the heating time to the semi-solid state temperature and the holding time at that temperature. At 868 K, the distance between edges of primary α phases was only about 90 μm after holding for 5.4 ks while the distance exceeded 150 μm at temperatures above 898 K.

(4) It was observed that the distance between edges of primary α phases plays an important role in the ripening the primary α phase. The growth via the coalescence ripening occurred mainly when the fraction of the solid phase was high as much as 70%.

(5) The slip line did not pass through the contacting neck area between the coalesced primary α phases, and newly formed grains were observed in the contacting neck area.

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