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Effect of Ca Addition on Microstructure of Semi-Solid Al-Zn-Mg Al Alloys During Reheating

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In order to solve coarsened grain during reheating process, Calcium was added in these alloys. Calcium was anticipated that the formed intermetallic compounds such as Al_2Ca and Al_4Ca performed grain-boundary pinning and reduced grain growth during reheating process. Therefore, in this study, semi-solid Al-Zn-Mg billets contained calcium(0, 0.4, 0.6 and 0.9 wt.%) were fabricated by cooling plate method. Reheating behavior for microstructure was examined at 620°C. Primary α grain size of semi-solid Al-Zn-Mg-(0, 0.4, 0.6 and 0.9wt.%)Ca billets were 150, 133, 130 and 120μm and shape factor value was 0.68, 0.75, 0.74 and 0.74, respectively after holding 30min at 620°C. As adding calcium, the grain became more small and spherical. Also, solid fraction decreased because calcium elements increased in grain boundary.

Keywords: *Al-Zn-Mg alloy, thixo-forming, Ca addition, semi-solid state, reheating process*

1. Introduction

According to the tendency of the light weight fuel efficient vehicles with lower emission all over the world, the demand has been increased for new material with light and high strength in vehicle industry. Al-Zn-Mg alloy, one of the aluminum alloys, is suitable for these requirements because of highest strength property among aluminum series and approximately 60% lighter than steel. However, Al-Zn-Mg alloy causes high pressure due to their high strength when Al-Zn-Mg alloy was formed. Consider conventional extrusion for example, the extrudability for 6063 Al wrought alloy is to be 100. Especially, the extrudability index of 7075 Al wrought alloy was 316 [1]. Thus, Al-Zn-Mg alloy was limited by their extrudability for conventional extrusion. To solve this problem, there are semi-solid processes [2]. Thixo-forming, one of the semi-solid processes, has several advantages such as, prolonged die life, low forming effort and manufacturing near net shape component. Thixo-forming process has been studied extensively, presently. But, it has a problem which grain growth during reheating process. It is affecting mechanical property and formability of the alloy. Therefore, in order to prohibit coarsened grain during reheating, calcium was added in aluminum alloy. Calcium was anticipated that the formed intermetallic compounds such as Al_2Ca and Al_4Ca performed grain-boundary pinning and reduced grain growth during reheating process.
The aim of this study is to prevent grain growth and investigate variation of microstructure as adding calcium in semi-solid Al-Zn-Mg alloy during reheating process.

2. Experimental procedures

2.1 Fabricate semi-solid Al-Zn-Mg-(Ca) billets

Al-Zn-Mg alloy was cut about 1.3kg melts in a graphite crucible and a resistance furnace. The melting temperature was 720 °C. The cooling plate method was adopted to prepare semi-solid billets. After degassing, holding and deslagging, Ca-Al master alloy(Al 9.67%, Mg 0.31%, Cu 0.05%, Mn 0.05% and Ca balanced, wt.%) was added into the melt at the temperature of 680 °C, and then the melt was poured into the preheated steel mold through inclined cooling plate as designated conditions(pouring temperature : 650°C, angle of cooling plate : 30°, length of cooling plate : 250mm, steel mold temperature : 600 °C). The inclined cooling plate was coated with boron nitride to prevent adhesion between the alloy and the copper plate. The mold was then water quenched. The chemical compositions of fabricated semi-solid Al-Zn-Mg-(Ca) billets were shown in table 1.

Table 1. Chemical compositions of semi-solid Al-Zn-Mg-(Ca) alloys. (wt.%)

Alloys	Zn	Mg	Cu	Mn	Si	Ti	Fe	Ca	Al
Ca free	6.25	2.65	0.47	0.33	0.05	0.04	0.18	0	Bal.
0.4wt.%Ca	6.47	2.68	0.49	0.34	0.09	0.03	0.21	0.44	Bal.
0.6wt.%Ca	6.37	2.72	0.49	0.35	0.07	0.03	0.22	0.64	Bal.
0.9wt.%Ca	6.09	2.59	0.47	0.34	0.06	0.03	0.20	0.92	Bal.

2.2 Reheating process

For the reheating, the billets were machined into 10mm x 10mm x 10mm. A hole of 1mm was drilled into the center in order to insert a K-type thermocouple and observe the temperature of the samples during reheating process. The samples were reheated in a resistance furnace with isothermal temperature at 620^{o}C. After soaking and holding time from 0min to 30min, the samples were water quenched. Diagram for reheating conditions is indicated as shown in figure 1.

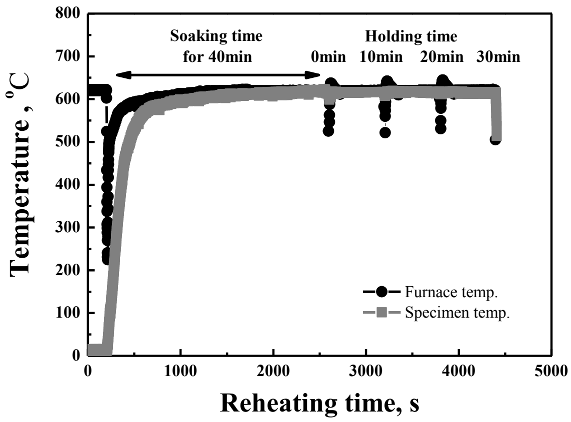

Fig. 1 Diagram for reheating conditions.

2.3 Microsturcture examination

All specimens for microstructure observation were polidshed with SiC papers from 400 mash to 2000 mash and alumina powder from 1μm to 0.3μm, cleaned in ethanol, dried with warm air and etched in modified Dix-keller reagent(3ml hydrochloric acid + 5ml nitric acid + 4ml hydrofluoric acid + 190ml distilled water). The specimens were analysed by means of optical microscope (OM), X-ray diffraction (XRD) and electron probe micro anlyzer (EPMA).

The microstructural characteristics were decided by image analyzer, IMT(VT) IA model, for grain size and shape factor as given equation 1 and 2.

$$D = \sqrt{\frac{4A}{\pi}} \tag{1}$$

$$F = \frac{4\pi A}{P^2} \tag{2}$$

Where A and P are the area and perimeter of each grain.

3. Results and discussion

Figure 2 shows structural evolution of semi-solid Al-Zn-Mg-(Ca) billets with increasing reheating time at 620^{o}C as adding different amount of calcium. Microstructures of Al-Zn-Mg-(0, 0.4wt.%, 0.6wt.% and 0.9wt.%)Ca billets consist of rosette phases and inter-dendrite eutectic phases and each microstructure is very similar from calcium free to calcium added. As increasing reheating and holding time, The grains of every Al-Zn-Mg-(Ca) billets grew obiously because of the coalescence of rosette grains and inter-dendrite eutectic phases. Liquid phase was increasing after increasing holding time. Compared with the grain of calcium free billet, the grain of calcium added billets became more spherical and small than calcium free billet.

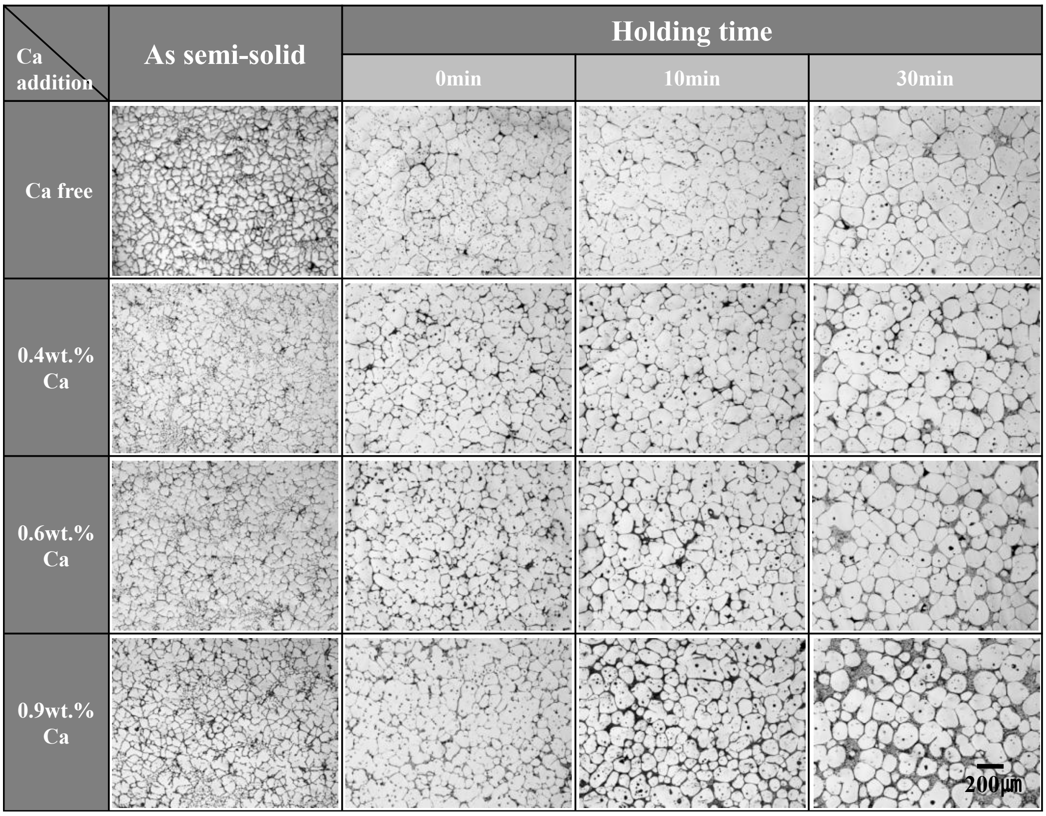

Fig. 2 Structural evolution of semi-solid Al-Zn-Mg-(Ca) billets with increasing reheating time at 620^{o}C as adding different amount of calcium**.**

Microstructure was analyzed by image analyze. These results that primary α grain size of as semi-solid Al-Zn-Mg-(0~0.9wt.%Ca) billets was 67, 71, 74 and 70μm, respectively. Primary α grain size of semi-solid Al-Zn-Mg-(0~0.9wt.%Ca) billets was 124, 108, 102 and 96μm after holding 10min. In the case of holding 30min, primary α grain size of semi-solid Al-Zn-Mg-(0~0.9wt.%Ca) billets became 150, 133, 130 and 123μm, respectively. Compared with primary α grain size of calcium free, primary α grain size of 0.9wt.% calcium added was smaller about 30μm than primary α grain size of calcium not added after holding 30min.

X-ray diffraction patterns of semi-solid Al-Zn-Mg-(Ca) billets after holding 10min were carried out. Al_4Ca peaks were confirmed in the XRD analysis of semi-solid Al-Zn-Mg-(0.9wt.%)Ca billet. However, Al_2Ca peaks were not observed because it is likely that Al_2Ca particle was very fine and intensity was low. The Al_4Ca and Al_2Ca have a high melting point(699^oC and 1079^oC) leading to incompletely dissolve into the these alloys during the reheating process. During the process of reheating, Al_4Ca and Al_2Ca still existed as solid particles distributing along grain boundaries. For this reason, thermally stable Al_4Ca and Al_2Ca particles seem to prohibit grain growth owing to grain boundary pinning effect during initial stage of reheating process.

Change of shape factor and solid fraction for semi-solid Al-Zn-Mg-(Ca) billets as increasing holding time was investigated by using image analyze, IMT (VT) IA model. If shape factor value is 1, its mean is perfectly spherical to grain. Shape factor value of as semi-solid Al-Zn-Mg-(0~0.9wt.%Ca) billets was 0.65, 0.61, 0.62 and 0.63, respectively. Shape factor value was sharply increasing after reaching holding 0min. In the case of holding 30min, shape factor value was 0.68, 0.75, 0.74 and 0.74, respectively. Solid fraction was measured by image analysis in samples quenched from semi-solid state [3]. As increasing holding time from 0 to 30min, the solid fraction of semi-solid Al-Zn-Mg-(Ca) billets decreased. And, according to increasing amount of calcium added, solid fraction was decreasing dramatically. During the reheating of semi-solid Al-Zn-Mg-(Ca) billets, the eutectic region at the grain boundary remelted firstly and formed liquid phase. The solute element was moved at the solid/liquid interface due to greater difference of solute concentration such as the elements Zn, Mg and Cu et. Also, calcium elements located in grain bounday due to less than 0.05 at.%Ca at the eutectic temperature(616^oC) in Al [4]. As increasing calcium elements in the grain boundary, grain boundary remelted more fast. This evidence can be confirmed through EPMA.

4. Conclusions

The purpose of this study was to prevent the grain growth of semi-solid Al-Zn-Mg billets during reheating process as adding different amount of calcium. The results are:

1. Primary α grain sizes of semi-solid Al-Zn-Mg-(0, 0.4, 0.6 and 0.9wt.%)Ca billets were 150, 133, 130 and 123μm, respectively after holding 30min at 620^oC. Primary α grain size of Al-Zn-Mg-(0.9wt.%)Ca billet was lowest. It seems that thermally stable Al_2Ca and Al_4Ca particles impede the grain boundary movement during reheating process.
2. As increasing amount of calcium, solid fraction of semi-solid Al-Zn-Mg-(0, 0.4, 0.6 and 0.9wt.%)Ca billets has been different and became 90, 88, 85 and 80% after holding 30min. It was sure that the eutectic region at the grain boundary remelted more rapidly, as increasing amount of calcium elements in alloys.

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