Effect of Cooling Rate on Mg$_{17}$Al$_{12}$ Volume Fraction and Compositional Inhomogeneity in a Sand-Cast AZ91D Magnesium Plate

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Mg$_{17}$Al$_{12}$ compound is a hardening phase in AZ91D alloy. Moreover, the concentration of Al and Zn has been found to be closely related to the corrosion performance of the magnesium alloy. The aim of this work was to study the effect of cooling rate on distribution of Mg$_{17}$Al$_{12}$ compound and compositional inhomogeneity in an AZ91D magnesium sand-cast plate (200 $\times$ 140 $\times$ 20 mm$^3$). A copper chill block, which was placed at the end of mold cavity, was used to increase the cooling rate during solidification. A sand-cast plate was also produced, where no chill block was mounted at the end of mold cavity. The “with chill block” plate showed a rapid increasing in cooling rate with respect to distance from riser, as compared to the “without chill block” plate where almost no cooling rate fluctuation occurred. The volume fraction of Mg$_{17}$Al$_{12}$ ($\beta$ phase) in the “without chill block” plate was higher than that in “with chill block” plate. In the “without chill block” plate, volume fraction of Mg$_{17}$Al$_{12}$ was about 13.9 vol% (near the riser) to about 19.3 vol% (close to the end of the plate). However, the “with chill block” plate was solidified in a higher cooling rate, leading to low volume fraction of the $\beta$ phase (13.4 vol%). Higher cooling rate also resulted in more severe compositional inhomogeneity in the sand-cast plate. The Al and Zn concentration in the “with chill block” plate showed a concave downward dependence against the distance to riser. Moreover, in the “with chill block” plate, concentrations of Al and Zn did not enrich at the position near chill face. Instead, the Al and Zn contents near the chill surface were well below the average value. This finding is in disagreement with previous studies.

1. Introduction

As the lightest structural materials, magnesium alloys are found increasing applications in various industries. The main commercial cast magnesium alloys are based on the Mg-Al-Zn series, especially AZ91D (Mg-9 mass% Al-1 mass% Zn). The AZ91D alloy covers the majority of magnesium applications due to its high castability, acceptable corrosion resistance and favorable mechanical characteristics. Alloyming element and their concentration decisively determine the performance of the AZ91D alloy. For instance, the addition of aluminum improves strength and corrosion resistance. Aluminum in the magnesium alloy leads to the formation of Mg$_{17}$Al$_{12}$ ($\beta$ phase). This intermetallic compound is the main second-phase particle that strengthens the AZ91D alloy at room temperature. Both of the volume fractions and morphology of Mg$_{17}$Al$_{12}$ $\beta$-phase substantially influence the mechanical properties of AZ91D alloy. The addition of zinc reduces the solid solubility of Al in magnesium matrix. Hence, Zn can increase the alloy’s strength by increasing the volume fraction of this intermetallic phase.

Homogeneity of the alloying element within casting is difficult to attain, since solute redistribution is inevitable during solidification. The macrosegregation of the alloying element in the cast structure can induce variations of physical and mechanical properties. Cho et al. studied the surface compositional inhomogeneity in the thin-walled AZ91D plate formed by hot-chamber die casting. The fluctuations of the alloying elements concentrations exhibit an increasing tendency with respect to locations on the plate along the melt filling sequence. On the other hand, sand casting process is one of the conventional methods to produce magnesium alloys castings. The advantages of the sand casting over the high pressure die casting are the complexity of producing components, and contained a relatively lower level of porosity. For the sand casting process, chill block is used extensively to promote progressive or directional solidification of the casting. Casting solidification rate can be increased locally by the use of metallic chill block to help in producing an optimal solidification pattern in the casting. However, the concentrations of the alloying elements near a chill block for the sand-cast AZ91D alloy were briefly explored. Bakke et al. investigated inhomogeneous distribution of major alloying elements that the AZ91D ingots were cast in open cast iron moulds. In the preceding report, the Al and Zn concentrations in the region near mould wall were higher than those in the central regions. This phenomenon is explained by inverse segregation as the melt enriched in alloying elements tend to be drawn outwards to colder regions. As the above mentioned, a chill block is often used to change the cooling rate of a local region in sand casting process. Currently, the studies concerning the sand casting of the Mg-Al-Zn alloy during solidification with and without chill block are limit. Moreover, there are no reports to elucidate the concentration profiles of alloying elements regarding the distance to the chill end. Therefore, this work reports on the macrosegregation of Al and Zn in sand-cast Mg-Al-Zn alloy. The dimensions of the sand-cast plate were 20 $\times$ 40 $\times$ 145 mm$^3$. The intermetallic compound, Mg$_{17}$Al$_{12}$, which is the main second phase that dominates dispersion strengthening of this alloy, will be examined for its volume

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fraction with respect to the distance from the chill end of the sand-cast plate.

2. Experimental

Table 1 shows the chemical composition of the molten AZ91D alloy. The molten metal was prepared in mild steel crucible under a protection of mixed gas of 99.8% (by volume) dried air and 0.2% SF6. Rectangular plate castings were used in this experiment (see Fig. 1(a)). The dimension of the plate was shown in Fig. 1(b). A copper chill block (20 mm thick by $40 \times 145$ mm$^2$ area) could be placed at the end of the mold cavity opposite the gate (Fig. 1(a)). Two castings were made, the first plate (designated as “without chill block” hereafter) had no chill block placed at the end of mold cavity, the second plate (designated as “with chill block”) had copper chill block. Silica sand of AFS No. 100 was employed to prepare the CO$_2$ molds, using 7 mass% sodium silicate as a binder. Eight chromel-alumel (K-type) thermocouples were placed in the mold (see Fig. 1(a) for illustration). The positions of the thermocouples with respect to the distance from riser were 10, 60, 80, 110, 130, 160, 180 and 200 mm. The tips of those thermocouples were located about half of the thickness of the casting plate. The CO$_2$ sand molds were baked at 120 °C for 12 hours to exclude remaining water. The pouring temperature was controlled at $700 \pm 5$ °C, and care was taken when filling the pouring basin to ensure steady and smooth flow of the melt.

For the thermal analysis of AZ91D samples, cooling curve during solidification were obtained using a data acquisition system (GW Instruments Inc., USA) at a sampling rate of two data points per second. A computer with Microsoft Excel spreadsheet software was used for data acquisition and processing. The cooling rate, $\varepsilon$, is defined as $\varepsilon = (T_L - T_E)/\Delta t$. $T_L$ is the liquidus temperature, which is obtained from the cooling curves. $T_E$ (437 °C) is the equilibrium eutectic temperature of AZ91D alloy. $\Delta t$ is the elapsed time between $T_L$ and $T_E$.

The concentrations of aluminum and zinc in AZ91D magnesium cast plate was determined by glow discharge optical emission spectrometry (GD-OES). The compositions of the molten AZ91D alloy (see Table 1) was taken with an appropriate iron mold and analyzed by GD-OES, as compared with sand-cast plate. Positions at the interior of the sand-cast plate were selected for the GD-OES analysis. The positions were located about half of the thickness of the casting plate, but with respect to the distance from the riser. The etchant 10 mL HNO$_3$, 30 mL acetic acid, 40 mL H$_2$O and 120 mL ethanol was used to reveal intermetallic phase (Mg$_{17}$Al$_{12}$). Point counting method was carried to estimate volume fractions of the intermetallic phase (Mg$_{17}$Al$_{12}$) as a function of the distance from the riser. The test grid was placed as a plastic overlay on the OM micrographs. The magnification is sufficiently high to discern the location of the test points in relation to the structural elements. X-ray diffraction experiment was conducted to examine the preferred orientation in casting plate. The X-ray data were collected by emitting copper K$_\alpha$ radiation on the sample surface parallel to chill surface. An X-ray scanning speed of 1° per minute was used.

3. Results and Discussion

The top plot of Fig. 2 indicates a schematic lateral view of the sand-cast plate. Hereafter, the casting process, which was done with a copper chill block placed at the end of the mold cavity, was named as “with chill block”. The casting process with no chill block placed at the end of mold cavity was designated as “without chill block”. Figure 2 showed the cooling rate during solidification in the “with chill block” and “without chill block” plates. The plate without chill block, as presented in Fig. 2, had the cooling rate between

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mg</th>
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<tr>
<td>Mass%</td>
<td>8.84</td>
<td>0.65</td>
<td>0.18</td>
<td>0.01</td>
<td>0.0017</td>
<td>0.0021</td>
<td>0.0006</td>
<td>Bal.</td>
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![Fig. 1](image-url)
squeezing casting. 23) The volume fraction in AZ91D sample which were produced by squeezing casting magnesium alloy were only about 12.2 vol%. Squeezing casting is a casting process that forces molten metal to be solidified within a permanent mold in a high cooling rate. 24) Since sand casting process enforced a much slower cooling rate than squeeze casting. The volume fraction of Mg17Al12 (β phase) in the sand-cast plate was higher than that in squeezed-cast bar. According to Yu and Uan, 5 high cooling rate will keep more Al in α-Mg matrix to form α-Mg-Al-Zn solid solution during solidification. The volume fraction of Mg17Al12 compound is therefore reduced. 25 Since the “with chill block” plate was solidified in higher rate (see Fig. 2 for comparison), as shown in Fig. 3, the volume fraction of β phase in the plate was less than that of “without chill block” plate.

During the cooling of an Mg-9 mass% Al-1 mass% Zn alloy melt, part of eutectic liquid tends to solidify into irregular eutectic β phase (Mg17Al12). 20) According to Cao and Wessen, 21) the volume fraction of the Mg17Al12 particle in Mg-Al-Zn alloy was constantly lower than results obtained from calculations using thermodynamic software. This means that the formation of the Mg17Al12 phase is due to non-equilibrium condition during solidification. Volume fractions of the β phase (Mg17Al12) as a function of the distance from riser were depicted in Fig. 3. The variation of Mg17Al12 volume fraction in the “with chill block” plate was a flat tendency; each position in the plate had similar volume fraction of Mg17Al12, about 13.4 vol%. For comparison, the β phase volume fraction in the “without chill block” plate was also indicated in Fig. 3. The β volume fraction in “without chill block” plate was higher than that in the “with chill block” plate. Maximum volume fraction of the β phase within the “without chill block” plate was about 19.3 vol%, which occurred at the position near the end of plate. In the “without chill block” plate, the volume fraction of the β phase increased with the distance from riser (see Fig. 3). Also as seen in Fig. 3, the volume fraction of the β phase under equilibrium solidification was calculated from Mg-Al phase diagram. 22) The data was shown as a dashed line in Fig. 3, which presented the β volume fraction to be about 20 vol%. 22) The dotted line in Fig. 3 represented the β phase volume fraction in AZ91D sample which were produced by squeezing casting. 23) The β phase volume fraction in the
Zn content showed rapid decreasing tendency. However, for the position approaching the riser, their Al and 200 mm showed the same profile of Al (see Fig. 5(a)). The Zn content (Fig. 5(b)) in the region between 70 to flat tendency of Al content. In the “without chill block” plate, distance from the riser between 70 to 200 mm had a relatively diffuse to form Mg\textsubscript{17}Al\textsubscript{12} (see Table 1); (b) Zn, the dotted line presents the Zn content of the original molten alloy (~0.65 mass%). The top plot in the figure indicates the plate of lateral view in the sand mold. The chill block was placed at the end of mold cavity.

was about 0.62 mass% near the chill block. Maximum concentration of Zn in the “with chill block” plate occurred at 100 mm distance from the riser. For the position toward riser, the Zn content finally went down to 0.48 mass%. The low-end limit of ASTM standard for Zn content in AZ91D alloy was 0.45 mass%. Figure 5 showed the concentration profiles of the alloying elements (Al and Zn) in the “without chill block” plate as a function of the distance from riser. Again, the dotted line in Fig. 5(a) presented the Al concentration (~8.84 mass%) of the original molten alloy. The distance from the riser between 70 to 200 mm had a relatively flat tendency of Al content. In the “without chill block” plate, the Zn content (Fig. 5(b)) in the region between 70 to 200 mm showed the same profile of Al (see Fig. 5(a)). However, for the position approaching the riser, their Al and Zn content showed rapid decreasing tendency.

Aluminum is a key element to form Mg\textsubscript{17}Al\textsubscript{12} intermetallic compound in the AZ91D magnesium alloy. The “without chill block” plate was solidified in a low rate (0.22–0.32°C/s) (Fig. 2). Aluminum had more time to diffuse to form Mg\textsubscript{17}Al\textsubscript{12} compound during solidification. According to Wei and Dunlop,\textsuperscript{26} the total amount of Mg\textsubscript{17}Al\textsubscript{12} β-phase increased with Al content. In the “without chill block” plate (see Fig. 5(a)), there was a decreasing tendency of the Al concentration profile from the end of the plate to the riser. Therefore, the volume fraction of β phase in the “without chill block” plate (Fig. 3) from the end of the plate to the riser showed a gradual decreasing tendency.

Compositional inhomogeneities in an AZ91D ingot have been observed by Bakke et al.\textsuperscript{16} The ingot was cast in open cast iron mold. Alloying elements content (i.e., Al, Zn and Si) were more concentrated close to mold surface than in center regions. For example, the position near mold surface has 10 mass% of Al, but only 7 mass% of Al in the center region of the ingot.\textsuperscript{16} Composition profile of variation in Al content from surface to center in high pressure die-cast AM50 magnesium bars has been elucidated.\textsuperscript{27} The Al content decreased from about 5 mass% at chill surface to about 2.5 mass% in center. Similar experimental results were explored by Nakatsuigawa et al.\textsuperscript{28} where enrichment of Al content in the vicinity of surface was found at die-cast and thixomolded specimens. The preceding studies\textsuperscript{16,27,28} reported that an enrichment of alloying element occurred in the region near the mold wall where cooling rate was higher than the interior position of the casting. However, the present study illustrated the experimental results of compositional inhomogeneities, which were different from those of previously known.\textsuperscript{16,27,28} Figure 2 had confirmed that there existed cooling rate gradient across the casting plate from the chill block surface to the riser. In the “with chill block” plate, the cooling rates with respect to the distance from riser had a rapid increasing
tendency. The highest cooling rate was 0.93 °C/s at the region near chill block, as indicated in Fig. 2. In Fig. 4, the composition profile in the "with chill block" plate showed that the Al and Zn concentrations (8.39 and 0.62 mass%) were not concentrated at the position close to the chill surface. Instead, the highest-cooling-rate position had less Al and Zn concentrations than the positions where their cooling rates were a little lower. Maximum concentration of Al and Zn (9.02 and 0.66 mass%) within the plate occurred at the position about 100 mm distance from riser. Figure 6 presents the X-ray data of the samples which were taken from the positions 80 to 190 mm distance from the riser. Each sample corresponding position (i.e., 80, 110, 130, 160, 180 and 190 mm distance from the riser) was also schematically denoted.

The positions of solidification away from chill surface (Fig. 6). In the beginning the liquid melt had 8.84 mass% of Al and 0.65 mass% of Zn. When solidification started, the liquid melt close to the chill face solidified first. The primary solid phase in the vicinity of the chill face grew predominately along the (0002) axis (Fig. 6) and was in opposite direction of heat flow. Since alloying elements (e.g., Al and Zn content in AZ91D magnesium alloy) have less solubility in solid phase than in the liquid melt, as shown by phase diagram.29,30 The solutes (e.g., Al and Zn in AZ91D) in the primary solid are drawn outward to the residual liquid, leading to solute enrichment of liquid and lower solute concentration in the primary solid.31 Therefore, as the solidification proceeded, the Al and Zn content accumulated progressively into the residual liquid, leading to maximum Al and Zn concentration (Fig. 4) at the position close to central location, where almost no (0002) preferred orientation occurred (Fig. 6).

Figure 7 presents as-cast microstructure in the “with chill block” plate, following the distance from riser. Figs. 7(a), (b), (c) and (d) showed the typical microstructures of the positions 10, 60, 110 and 190 mm distance from the riser, respectively. Each microstructure's corresponding positions in the casting was schematically denoted in the upper plot of Fig. 7. As indicated in the photographs, intermetallic compound Mg17Al12 (β phase) were observed as a dark phase at interdendritic spacing. Most of the β phases were irregularly shaped. Some arrows also noted that the phase close to β phase was eutectic α phase (Fig. 7). The phase with bright color was α-Mg grain. At the position of 190 mm from the riser (Fig. 7(d)), where cooling rate was highest, and the β phase was revealed as discrete particles. Figure 8 shows the as-cast microstructure in the “without chill block” plate, following the distance from riser. The typical microstructures at positions from the riser (10, 60, 110 and 190 mm) were illustrated in Fig. 8. The morphology of the Mg17Al12 (β phase) for the microstructures in the casting was not similar, depending on the position within the casting. As denoted by arrows, the β phase had irregular shape, locating at interdendritic positions. Some eutectic α phase in the vicinity of the β phase was also observed in Fig. 8. At the position about 190 mm from the riser (Fig. 8(d)), Mg17Al12 (β phase) tended to become irregular particle. The Mg17Al12 volume fraction measurement (Fig. 3) showed that the fraction up to about 19.3% was observed at the position close to the end of the “without chill block” plate. The micrograph of Fig. 8(d) illustrates a consistent result that there is high density of particles in that position. In comparison with the microstructure near to chill surface (Fig. 7(d)), Fig. 8(d) evidently shows more particles distributing in matrix. The aluminum concentration near to the end of the “without chill block” plate was about 8.85 mass% (Fig. 5(a)), while the similar position in the “with chill block” plate was only about 8.35 mass% of aluminum (Fig. 4(a)). Moreover, the “without chill block” plate was solidified in a relatively low cooling rate (Fig. 2), as compared to the “with chill block” plate. Since aluminum in liquid melt has relatively sufficient time to form Mg17Al12 particle during solidification, and high Al content will lead to high volume fraction of β phase, the position at the end of the “without chill block” plate had microstructure...
with higher volume fraction of \( \beta \) particles (Figs. 3 and 8(d)), as compared to the microstructure at the similar position in the “with chill block” plate (Fig. 7(d)).

4. Conclusions

The following conclusions can be drawn from the preceding results and discussion:

(1) An evident cooling rate gradient with respect to distance from riser during solidification in a sand-cast AZ91D plate was obtained via putting a chill block at one end of the mold cavity. However, almost no cooling rate fluctuation occurred in the plate without the chill block.

(2) The volume fraction of \( \text{Mg}_17\text{Al}_{12} (\beta \text{ phase}) \) in the “without chill block” plate was higher than that in the “with chill block” plate. An increasing in variation of the \( \beta \) phase volume fraction across the “without chill block” plate was observed from 13.9 vol\% (near to riser) and finally up to 19.3 vol\% near the end of the plate. However, a flat tendency of the \( \beta \) phase volume fraction in the “with chill block” plate where each position in the casting has similar volume fraction of \( \text{Mg}_17\text{Al}_{12} \) compound, about 13.4 vol\%.

(3) Compositional inhomogeneity with respect to distance from riser occurred in the sand-cast AZ91D plate. For the plate with chill block placed at the end of the mold cavity, Al and Zn profiles showed a concave downward tendency as a function of the distance from the riser. The Al and Zn were not concentrated near the chill face even the highest cooling rate was observed at this region, which is an experimental result that exhibits disagreement with previous work. In both two plates (i.e., “with” and “without” the chill block to be placed at the end of mold), for the positions toward the riser, the Al concentration decreased rapidly and the content was even less than the low-end limit of ASTM B93 standard.
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