Grain Boundary and Intragranular Reactions during Aging in Mg-Al System Alloys Poured into Sand and Iron Molds

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1. Introduction

The body of electronic equipment and automobile parts has expanded with the increased use of Mg-Al system alloys. This is because they have been adjusted to be light-weight, save resources and energy, have an excellent balance between strength and ductility, die-casting property and corrosion resistance. To improve the property of magnesium without gain in weight by alloying, aluminum is the most suitable element. In addition, there is a large misfit strain based on the difference between atom radius of magnesium and aluminum. It is reported that the improvement of 0.2% proof stress and tensile strength by dispersion strengthening by beta Mg₁₇Al₁₂ phase, castability and corrosion resistance. It is well-known that magnesium alloy containing aluminum more than 6 mass% has remarkable age hardenability.

Magnesium has poor workability at room temperature due to its crystal structure. Alloying and grain refinement were proposed to improve the workability. Using the alloying, workability was improved by the action of non-basal plane including c+a slip with the addition of yttrium to magnesium. The workability of magnesium at room temperature was improved by the addition of lithium in order to change the crystal structure from hcp with a high crystal anisotropy to bcc structure with a different crystal symmetry. In grain refinement, it is suggested that the severe plastic deformation for the fabrication of bulky materials with nanometer grain size. On the other hand, the refinement of cast structure induced by increasing the cooling rate during solidification is proposed as the fundamental method for improving the workability by the control of cast structure. Eutectic phase crystallized in the grain and cell boundaries of primary alpha magnesium and beta phase precipitated just below the solidus temperature and are dispersed in Mg-Al system alloys. Therefore, it is thought that the form and volume fraction of second phase is closely related to the workability of materials in the as cast condition. However, the relation between cooling rate and cast structure in magnesium alloys has not been found.

In the present study, the microstructure evolution of AM60 magnesium alloy cast into sand and iron molds during age hardening process after solution and aging treatments was investigated by the microstructure observation and hardness measurement.

2. Experimental Procedure

2.1 Material

Target composition of castings is 6 mass%Al, 0.3 mass%Mn and 0.002 mass%Be containing magnesium alloy. In order to prevent the molten metal combustion, a small amount of beryllium was added. The Mg₂Si equivalent is about 0.8 mass% in 0.5 mass%Mg containing alloy and about 1.3 mass% in 0.8 mass%Mg containing alloy. Pure magnesium, pure aluminum, pure manganese and Al-2.5 mass%Be with industrial purity were used for the ingot fabrication.

2.2 Casting procedure

An electric furnace was used to melt the casting ingots. The iron made mold with Y-shaped cavity was prepared as shown in Fig. 1. Titanium oxide was spread on the mold as mold wash. The temperature of mold and the center part of castings was measured with K-type thermocouple with the
diameter of 0.2 mm. Based on the target composition, pure magnesium ingots were put into a SUS430 crucible, and were melted in the electric furnace at 1023 K in a SF₆ and CO₂ mixed gas atmosphere. After the melting of magnesium ingots, dross was removed from the surface of the molten metal. Moreover pure aluminum, pure manganese and Al-2.5 mass%Be alloy ingots were added sequentially to the molten metal and the temperature of electric furnace was lowered to 993 K. Pouring was initiated when the temperatures of molten metal and mold were lowered to 953 K and 453 K respectively. After the pouring, the castings were released from the mold falling down to 473 K of castings temperature. The dimension of sample part in castings was 100 mm length, 12 mm width and 30 mm height, and a hot top with reverse trapezoid form was located on the sample part. The chemical composition of castings used in this investigation is listed in Table 1. The cooling rate during the solidification was measured by C-tigation is listed in Table 1. The cooling rate during the solidification was measured by CT scanning. The plate sample with the dimension of 10 mm width, 12 mm height and 2 mm thickness was cut from the sample part of castings.

Table 1 Chemical composition in mass% of AM60 magnesium alloy cast into sand and iron molds.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Si</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAND</td>
<td>5.88</td>
<td>0.075</td>
<td>0.005</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>0.003</td>
<td>bal.</td>
</tr>
<tr>
<td>IRON</td>
<td>6.19</td>
<td>0.038</td>
<td>0.005</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>0.002</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Vickers hardness was measured by a micro hardness test machine under an indentation load of 0.98 N and the time of 20 s with an average of twelve readings was reported. The microhardness of each primary alpha magnesium phase consisting of the matrix and intragranular precipitates, and cellular precipitation including alpha magnesium and beta Mg₁₇Al₁₂ intermetallic compound was measured under the load of 0.098 N.

2.5 Microstructure observation

The aged sample was applied to microstructure observation. Following the polishing operation, the etching of polished sample was done using the 1%HNO₃-C₂H₅OH solution. The microstructure was observed using an optical microscope (OM). The volume fraction of alpha magnesium and cellular precipitated alpha and beta phases was measured from the microstructures using image processing and computer calculation. In addition to the foregoing microstructure observation, the sample was mechanically ground and finally polished using a diamond paste. After the polishing operation, microstructure observation in high magnification and elementary analysis were carried out using the transmission electron microscope (TEM). The TEM samples were cut and thinned by a focus ion beam (FIB). FIB was carried out using a commercially available FIB system HITACHI FB2100 with a Ga⁺ ion beam accelerated by the voltage of 40 kV. TEM observation was performed by TOPCON EM-002B using the acceleration voltage of 120 kV.

3. Result and Discussion

3.1 As cast condition

The as cast microstructure of AM60 magnesium alloy cast into (a) sand and (b) iron molds is shown in Fig. 2. Both microstructures were composed of primary crystallized alpha magnesium phase and eutectic phase consisting of alpha magnesium and beta Mg₁₇Al₁₂ intermetallic compound. The eutectic phase was divided to none-equilibrium crystallized phase and precipitated phase with different hardesses. The non-equilibrium crystallized phase has 96.2% and 3.8%, respectively, in the sand mold castings. Also, there is 96.6% and 4.4% in the iron mold castings. The diameter of equivalent circle calculated by the image processing was 12 μm for crystallized phase and 6 μm for precipitated phase in sand mold castings. The diameter of equivalent circle of these phases in the iron mold castings was half in the sand mold castings. The grain size of as solution-treated at 688 K for 86.4 ks was 147 μm for sand mold castings and 6 μm for iron mold castings.

3.2 As age-treated condition

3.2.1 Sand mold castings

The Solution treatment was performed at 688 K for 86.4 ks prior to age hardening treatment. The second phases were fully diffused and solutionized in the alpha matrix by the solution treatment. The isothermal age hardening curve of
sand mold castings aged at 473, 498 and 523 K is shown in Fig. 3. Hardness increased with the aging time in under-age region and up to the maximum hardness, and then fell down in the over-age region. The maximum hardness increased when the aging temperature was lower, and the time to peak hardness increased. Its aging behavior corresponds to the typical dependence of aging temperature on aging hardness in age hardenable materials.

Figure 4 shows the microstructure change with the aging time at 473 K aging, the beginning of aging for 43.2 ks, under-aging for 86.4 ks, peak aging for 345.6 ks and over-aging for 1036.8 ks. In cellular precipitates which are grown from the grain boundary to the intragranular region with grain boundary movement is observed in Fig. 4(a). In Fig. 4(c), cellular precipitates grow more toward the intragranular. The volume fraction of cellular precipitates was significantly increased between 2% of Fig. 4(a) and 60% of (d) with aging time. However, the volume fraction of intragranular precipitates is very small about 10% even in the over-age condition, so it has no influence on the age hardening of sand mold castings.

It is found from Fig. 5, the pre-precipitation area is observed even in sand mold castings peak-aged at 473 K for 345.6 ks. There is a significant difference in hardness between the pre-precipitation area and intragranular precipitates, the hardness change with aging time has same tendency and almost constant. It can be found in Fig. 5 that intragranular precipitates are just partially formed around the grain boundary. Pre-precipitation area is unique phenomenon in AM60 magnesium alloy sand mold castings.14)

TEM analysis was performed to observe the pre-precipitation area in the sand mold castings over-aged at 493 K for 691.2 ks (Fig. 6). The existence of precipitates has not been observed in the pre-precipitation area using SEM and TEM yet. Aluminum concentration in the pre-precipitation area was analyzed to determine approximately 6 mass% from Fig. 6(c). If precipitates were formed in this area, aluminum concentration and hardness would most likely decrease drastically. To inspect the cause of pre-precipitation area in sand mold castings, further observation and analysis is needed.

In order to investigate the dependence of cellular and intragranular precipitates on the age hardening behavior, the hardness of existing phases were separately measured. Variations of Vickers hardness in sand mold castings were shown in Fig. 7 for isothermal aging at 473 K. It is found from this figure, the hardness of alpha magnesium phase is about 58 HV and that of intragranular precipitates is about 68 HV. On the other hand, the hardness of cellular precipitates is obviously decreased with the aging time. From these results, it is supposed that the hardness variation with aging time in sand mold castings mainly depends on the hardness of cellular precipitates. In the case of 493 K aging in Fig. 8 and 523 K aging in Fig. 9, the tendency of hardness variation of cellular precipitates with aging time is similar to the case of 473 K aging.

To examine the dependence of cellular precipitates on the aging behavior, volume fraction of cellular precipitates is measured through the image processing. The general composite rule in hardness is applied with the following equation;

$$HV_{cal} = HV_{a} \cdot Vf_{a} + HV_{CP} \cdot Vf_{CP}$$

where $HV_{cal}$ is calculated hardness by composite rule, $HV_{a}$ and $HV_{CP}$ are hardness in alpha magnesium phase and cellular precipitates, $Vf_{a}$ and $Vf_{CP}$ are volume fraction of alpha magnesium phase and cellular precipitates. Figure 10 shows the calculated hardness based on the composite rule and measured average hardness in 473, 498 and 523 K.
of aging temperature on aging hardness in age hardenable materials.

Figure 12 shows the microstructure change with the aging time at 523 K aging, the beginning of aging for 5.4 ks, under-aging for 21.6 ks, peak-aging for 86.4 ks and over-aging for 691.2 ks. Cellular precipitates of discontinuous type were generated along the cell boundary inside the grain from the beginning of aging. Volume fraction of cellular precipitates is 2%. In the peak-age condition, volume fraction of cellular precipitates is slightly increased to 20%, but the volume fraction of intragranular precipitates is obviously increased. In the over-age condition, the microstructure is wholly replaced by the intragranular precipitates and cellular precipitates with the volume fraction of 26%.

Figure 13 shows the variation of hardness within cellular precipitates and alpha magnesium phase including intragranular precipitates as compared to the measured average hardness. The hardness of cellular precipitates is larger than the measured average hardness by about 10 HV from the beginning of aging to over-age conditions. Also, a tendency of hardness variation in cellular precipitates is obviously different with that in the measured average hardness. On the other hand, the hardness of alpha magnesium phase including intragranular precipitates agreed with the measured average hardness. The tendency of hardness variation with aging time applies to the case of iron mold castings aged at 473 and 498 K. To examine the dependence of alpha magnesium phase including intragranular precipitates on the aging behavior, general composite rule in hardness is applied the same as the case of sand mold castings. Relationship between calculated and measured hardness is shown in Fig. 13. Volume fraction of cellular precipitates slightly increased
with the aging time. Variation of calculated hardness with the aging time was similar to that of measured hardness. It shows that AM60 magnesium alloy iron mold castings hardens due to the intragranular precipitates generated from the reaction inside the grain.\textsuperscript{15}

4. Conclusion

Grain boundary and intragranular reactions during aging in AM60 magnesium alloy poured into sand and iron molds were investigated by microstructure observation and hardness measurement. From the results of the investigations, the following conclusions have been obtained.

(1) Microstructure of AM60 magnesium alloy sand and iron mold castings in the as-cast condition was composed of primary crystallized alpha magnesium phase and eutectic

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure6}
\caption{(a) OM, (b) SEM and (c) TEM images of pre-precipitation area in AM60 magnesium alloy sand mold castings over-aged at 498 K for 691.2 ks.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure7}
\caption{Variation of Vickers hardness for structure phases in AM60 magnesium alloy sand mold castings isothermal-aged at 473 K.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure8}
\caption{Variation of Vickers hardness for structure phases in AM60 magnesium alloy sand mold castings isothermal-aged at 498 K.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure9}
\caption{Variation of Vickers hardness for structure phases in AM60 magnesium alloy sand mold castings isothermal-aged at 523 K.}
\end{figure}
phase consisting of alpha magnesium and beta Mg\textsubscript{17}Al\textsubscript{12} intermetallic compound.

(2) Fine cellular precipitates and intragranular precipitates obviously occur at the lower aging temperature in AM60 magnesium alloy sand and iron mold castings.

(3) Pre-precipitation area exits in AM60 magnesium alloy sand mold castings at the over age condition.

(4) AM60 magnesium alloy sand mold castings hardens by the cellular precipitates generated from the grain boundary reaction, on the other hand, iron mold castings hardens by the intragranular precipitates generated from the reaction inside the grain.

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Fig. 10 Comparison between measured and calculated hardness in AM60 magnesium alloy sand mold castings isothermal-aged at 473, 498 and 523 K.

Fig. 11 Isothermal age-hardening curve of AM60 magnesium alloy iron mold castings aged at various temperatures.

Fig. 12 Progress of precipitation reactions with aging time in AM60 magnesium alloy iron mold castings isothermal-aged at 523 K for (a) 5.4 ks, (b) 21.6 ks, (c) 86.4 ks and (d) 691.2 ks.
Fig. 13 Comparison between measured and calculated hardness in AM60 magnesium alloy iron mold castings isothermal-aged at 473, 498 and 523 K.

REFERENCES