Liquid Solubility of Manganese and Its Influence on Grain Size of Mg-Al Alloys*1

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We conducted this study to clarify the relationship between manganese solubility and grain sizes of Mg-Al alloys. Mg-5%Al, Mg-9%Al, and Mg-11%Al alloys were prepared using high-purity magnesium (>99.99%) and aluminum (99.99%). These alloys were melted at 1123 K by adding electrolytic manganese (99.99%) and solidified as alloy ingots after continuous stirring for 21.6 ks. The alloy ingots were then remelted at 933, 998, and 1073 K, and held statically at each of these temperatures for 21.6 ks. By this process, the excess Mn that existed over its liquid solubility precipitated and sedimented to the bottom of the melt. Thus, the solubility of Mn in liquid Mg-Al alloys was determined by analyzing the upper surface of the ingots quenched from each holding temperature. Consequently, the following equations were derived as experimental formulae for determining solubility of Mn in liquid Mg-Al alloys at different temperatures:

\[
Y = 1.79 - 6.22 	imes 10^{-2} X \quad (1073 \, K),
\]

\[
Y = 1.28 - 4.41 	imes 10^{-2} X \quad (998 \, K),
\]

and

\[
Y = 0.90 - 3.35 	imes 10^{-2} X \quad (933 \, K),
\]

where X is the concentration of Al (mass%) and Y is solubility of Mn (mass%). Mg-9% Al alloys containing 0 to 3% Mn were prepared in order to investigate the influence of Mn on grain sizes, and microscopic observations of these alloys were carried out with and without superheating of the specimens. The grain diameter of high-purity Mg-9% Al alloys (0% Mn) is approximately 40 μm, which is finer than that of the commercial AZ91E magnesium alloy with superheating. Therefore, high-purity Mg-9% Al alloys have an essentially fine-grained structure. An increase in the Mn content tended to coarsen the grain structure of Mg-9% Al alloys that contain 0.02 to 2.27% Mn; however, the coarse-grained structure can be refined by superheating. Superheating plays a role in resetting the coarse-grained structure to a high-purity structure (initially fine-grained) when Mn is added. Further, it is clarified that the solubility of Mn in liquid Mg-Al alloys exhibits no relationship with either the grain size or the superheating effect. [doi:10.2320/matertrans.47.1968]

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**Keywords:** high-purity, grain refinement, manganese, magnesium-aluminum alloy, solubility

1. Introduction

Magnesium (Mg) has high specific strength and rigidity, and it can be an excellent material for lightweight and high-quality products. By reasoning from an environmental viewpoint, it is considered that the production of lighter transport machinery can be increased by using Mg. This will contribute to a decrease in the emission of CO₂.

Mg-Al system alloys are inexpensive and have standard mechanical properties. To date, the demand for these alloys has been greater than that for any other Mg alloy. Therefore, this study focuses on Mg-Al alloys.

Iron (Fe) is always present in Mg as an impurity, thereby decreasing its corrosion resistance.1) Therefore, the Fe content in Mg alloys is restricted. During the production of Mg-Al alloys, manganese (Mn) is added to the molten alloy in order to remove Fe and reduce its content below an acceptable level. In Mg-Al alloys, Mn forms intermetallic compounds with Fe and Al. These compounds sediment because their specific gravity is greater than that of the molten alloy. Therefore, Fe is physically removed from the alloy during production.2,3) In commercial alloys, the final Mn content is adjusted to improve the corrosion resistance.

Mn also plays an important role in the control of the microstructure. For example, it influences the crystal grain size in the solidification structure and the grain refining response, such as superheating, and prevents abnormal germination, which occurs during solution heat treatment.3-5)

However, in Mg-Al alloys, Mn is mainly added to improve their corrosion resistance. Therefore, the effects of Mn on the microstructure have not been studied in detail.

The solubility of Mn in the molten Mg-Al alloy is low,6) and it forms various intermetallic compounds in the alloy. The solidification process and phase equilibrium can vary depending on a minor change in the Mn content. Not only the Mn content but also the abovementioned factors must be considered to clarify the relationship between crystal grain refinement and the Mn content. In fact, the mechanism of grain refinement3-5) by superheating has been discussed in relation to the solubility of Mn and the formation of its compounds. The solubility of Mn provides the most basic data for analysis; however, the solubility data obtained by various researchers differs to some extent.

In this study, the solubility of Mn in molten Mg-Al alloys is clarified. The effects of Mn on the grain size in the cast structure of Mg-Al alloys and on the superheating treatment are also discussed.

2. Experimental Methods

2.1 Mn solubility in Mg-Al alloys

The solubility of Mn in Mg alloys containing 5–11 mass% Al was investigated since this study is related to cast alloys. Mg-6 mass%Al, Mg-9 mass%Al, and Mg-11 mass%Al were prepared by using high-purity Mg (>99.99 mass%) and Al (>99.99 mass%). (Hereafter, “mass%” will be referred to as “%.”) A magnesia crucible coated with MgO powder (99%) was used for melting. Fluxless melting was carried out carefully by using a mixed gas (SF₆ + CO₂) in order to prevent the entainment of impurity elements.

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Table 1 lists the results of a chemical analysis; they indicate that it is possible to achieve the targeted alloy compositions.

When Mn is added to the molten Mg-Al alloy, Al-Mn compounds are formed. Therefore, when excess Mn is added, the Al content of the molten alloy gradually decreases because of the formation of Al-Mn compounds. Since a long time is required to reach equilibrium, the following experiment is conducted.

The Mg-Al alloy mentioned in Table 1 was remelted, and electrolytic Mn (99.99%) was introduced into it followed by stirring at 1123 K for 21.6 ks. Immediately after stirring, the molten alloy was poured into a mold with dimensions of 20 × 70 × 115 mm and a Mg-Al-Mn alloy ingot was obtained. This method was used to produce the following alloys at different holding periods: Mg-5.7%Al-Mn, Mg-8.7%Al-Mn, and Mg-11.7%Al-Mn; the Mn content of these alloys exceeded the solubility. Subsequently, a piece with dimensions of 15 × 15 × 100 mm was cut out from the center of the alloy ingots. Each piece was processed with a lathe into a round bar 10 mm in diameter and 80 mm in length. The bar was inserted into a Ti pipe (outer diameter: 12 mm, inner diameter: 10 mm, length: 100 mm) coated with MgO. Both ends of the pipe were then closed, and the alloy was remelted. The remelted alloys were maintained at 933, 998, and 1073 K for 3.6, 10.8, and 21.6 ks, respectively. The Mn content of the alloys obtained by adding Mn at 1123 K was greater than the saturation solubility at each holding temperature (933, 998, and 1073 K). Therefore, when the molten alloys were maintained at their holding temperatures, Mn crystallized in the form of Al-Mn compounds. These compounds sedimented when the molten alloys were allowed to stand. After holding at each temperature for the given period, the entire pipe was immediately quenched with water, and the sample was removed from the pipe. The upper portion of the sample was chemically analyzed and the Mn solubility was determined.

### 2.2 Superheating treatment

Alloys with different Mn contents were newly produced. Each alloy listed in Table 2 was superheated, and grain refinement was investigated. The superheating treatment was performed at 1123 K for 900 s (cooling from 1123 to 973 K in air). At 973 K, the molten alloy was immediately cast into a room temperature mold (diameter: 20 mm, length: 125 mm).

### 2.3 Metallographic examination and analysis

Metallographic examination and analysis were performed by using an optical microscope (OM), a scanning electron microscope (SEM), an electron probe microanalyzer (EPMA), and an X-ray diffractometer (XRD). The SEM observation was conducted at an accelerating voltage of 15 kV and a beam current of 3 × 10⁻⁸ A. The XRD analysis was performed with CuKα radiation at an applied potential of 40 kV and a current of 200 mA.

3. Results and Discussion

Mn was added to each alloy listed in Table 1 at 1123 K. The alloys were maintained at 933, 998, and 1073 K for 3.6, 10.8, and 21.6 ks, respectively. Therefore, the undissolved Al-Mn compound was separated by sedimentation. Vertical cross-sectional microstructures of the specimens obtained by rapid solidification before sedimentation are shown in Figs. 1(a)–(c). Microstructures of the specimens obtained by rapid solidification after sedimentation are shown in Figs. 2(a)–(c). Before sedimentation, undissolved Al-Mn intermetallic particles were dispersed throughout the specimens. However, after the melt was maintained for 3.6 ks, the intermetallic particles sedimented to the bottom of the molten alloy and formed clusters. Backscattered electron images of the bottom and top sections of the alloy after maintaining it in the molten state are shown in Fig. 3. Undissolved Al-Mn compounds cannot be identified in the top section. In the Mg-8.7%Al-Mn alloy (1073 K), phases corresponding to Al-Mn compounds are observed, as indicated by arrow. It is considered that they crystallized during solidification, as described later. According to the Stokes equation, when convection is ignored, particles with a size of less than 1 μm do not sediment because of the viscosity of the molten alloy. However, as shown in Fig. 3, particles with a size of less than 1 μm that were initially isolated in the molten alloy aggregated with each other and sedimented by the long-held molten state.

Figure 4 shows an Al-Mn compound observed in the top section. Its morphology clearly differs from that of the sedimented aggregate clusters, and it forms a long dendrite. This suggests that the compound crystallized during rapid cooling through free solidification. Therefore, it is assumed that an Al-Mn compound that crystallizes only during solidification is present in the top section of the specimen solidified by rapid cooling.

Results of a quantitative EPMA analysis of the Al-Mn compounds that sedimented to the bottom are listed in Table 3. In this case, the average composition of five particles are shown. The compositions of the Al-Mn compounds vary depending on the Al content, while they are independent of the holding temperature. The compounds are identified by using the XRD. Figure 5 shows the XRD patterns of the alloys. Based on an analysis of the results listed in Table 3 and those obtained using the XRD, Mg, Al₂₇Mn₃, and Mg₁₁Al₁₂ are identified in the Mg-5.7%Al-Mn alloy and Mg, Al₂₇Mn₃, and Mg₁₁Al₁₂ are identified in the Mg-8.7%Al-Mn and Mg-11.7%Al-Mn alloys. The XRD patterns are independent of the holding temperature. Figure 6
shows the results of an EPMA linear analysis of each particle where scattering was not observed in the distribution of the constituent.

The phase equilibrium at the Mg-rich corner of the Mg-Al-Mn ternary phase diagram has not been clarified sufficiently. However, it is generally considered that at the Mg-rich corner, only $\beta$-Mn is in equilibrium with the liquid phase in a wide range of compositions. Simensen et al. solidified Mg-0.8 mass%Al, Mg-4.7 mass%Al, and Mg-10 mass%Al alloys by the melt-spin method through rapid cooling at temperatures of 943–1023 K. They demonstrated the existence of Al$_8$Mn$_5$ and Al$_{11}$Mn$_4$ in addition to $\beta$-Mn in equilibrium with the molten alloy. In this study, the existence of Al$_8$Mn$_5$ was confirmed in the composition range reported by Simensen et al. As in the case of the melt-spin method, the stable phase at the quenching temperature was considered to
remain at room temperature due to water quenching. The top section of each specimen maintained in the molten state was analyzed microscopically and chemically. The obtained Mn content was considered as the saturation solubility of Mn in the molten Mg-Al alloy.

In this study, almost no change was observed in the contents of Al and Mn after 21.6 ks. The average results of chemical analyses at each holding temperature are shown in Table 4. In all cases, the Al content decreases considerably due to the addition of Mn. Because a greater amount of the Al-Mn compound dissolves when the temperature increases, the contents of both Al and Mn exhibit an increasing trend, although only slightly. For example, in the case of the Mg-8.7%Al-Mn alloy, when the temperature increases from 933 to 1073 K, the Al content increases from 8.21 to 8.46% and the Mn content increases from 0.62 to 1.26%. In Fig. 7, the Al and Mn contents listed in Table 4 are plotted against each other. In the range of the targeted Al content, the relationship between the Al and Mn contents fits a linear regression line, as shown in Fig. 7. The decreasing trend of the Mn solubility with an increase in the Al content is in good agreement with that reported previously.

From Fig. 7, alloys (No. 1–6) containing Mn shown in Table 2 were prepared. Figure 8 shows the cast grain size of the alloy. The grain size increases with the Mn content. Figure 9 shows the microstructure of the solidified alloy obtained after the superheating treatment. When we compare Figs. 8 and 9, the effect of the superheating treatment can be recognized for the alloy with structures that have become larger by manganese. Figure 10 shows the relationship between the Mn solubility in the Mg-9.0%Al alloy, Mn content, and grain size. The grain size of the alloy increases rapidly with the Mn content in the range of 0%–0.013%; thereafter, it exhibits a mild increasing trend. When the
superheating treatment is performed on the alloy whose grain size increases due to the addition of Mn, the size of its grains reduces again. However, the grains of a high-purity alloy that does not contain Mn are the smallest. This fine structure (average grain size: ca. 40 μm) cannot be obtained even when the superheating treatment is performed on the commercial alloy AZ91. The authors predict that when the Al-Mn compound crystallizes before Mg, the grains become coarse. However, as shown in Fig. 10, no relationship is observed between the Mn solubility and the grain size. Mn increases the recrystallization temperature of Mg and suppresses the grain growth of the Mg-Al alloy; however, Mn is assumed to be a disturbing factor of the nucleation of Mg during solidification.

The temperature-solubility nucleation theory is known to be the most general mechanism of grain refinement by superheating. According to this theory, a compound derived from Fe, Mn, etc., crystallizes in the molten alloy because of a change in its solubility and forms nucleation sites for Mg. Tiner stated that grain refinement by superheating does not occur in a high-purity Mg-Al alloy. He also stated that the Al-Mn compound should crystallize before Mg in order to achieve grain refinement by superheating. For example, he reported that the Mn solubility was ca. 0.1% at the starting point of the solidification of the Mg-8%Al alloy. Further, the effect of superheating was not observed in the alloy containing 0.02% Mn but in that containing more than 0.16% Mn. The Mn solubility determined in the present study was significantly greater than that estimated by Tiner, and it was greater than 0.16% even near the solidification point. In addition, it was not reported that the grain size of the high-purity alloy decreases, and he concluded that the superheating effect could not be produced in this alloy. On the other hand, Nelson reported the following: crystal grains of the high-purity AZ92 alloy are inherently small, and grains of alloys containing 0.09%–0.35% Mn are also relatively small. Since these crystal grains are originally small, it is difficult to determine the effect of superheating on these alloys. In many respects, these results are in good agreement with those of the present study. However, it was also reported that when the Mn content is greater than 1%, the superheating treatment is not effective. In the present study, this phenomenon was not observed.

In addition to the temperature-solubility nucleation theory, it is considered that some stable compounds are formed in the molten alloy in a certain temperature range. This concept is based on the process in which the molten alloy is superheated once to a predetermined temperature, rapidly cooled to the casting temperature, and poured into the mold. The compounds generally include MnAl₆ (less than 988 K), MnAl₄ (1123 K), and MnAl₃ (greater than 1123 K). Among these compounds, MnAl₄, which exhibits a hexagonal crystal structure similar to that of Mg, is formed in the superheated temperature range. This compound is considered to be effective in the nucleation of Mg. However, the Mn solubility determined in the present study indicates that these compounds are absent before the nucleation of Mg. In addition, in the present results and the Mg-Al-Mn ternary phase diagram, MnAl₆ and MnAl₄ are not observed as primary crystals in the Mg-Al-Mn alloy. In the present study, it is confirmed that Al₃Mn₅ can stably exist in the Mg-9%Al molten alloy at 1023 K.

The authors consider that the fine crystal grains of the high-purity Mg-9%Al alloy are produced because of the formation of an Mg-Al-C-O compound. A recent report[11]
states that grain refinement by superheating is not affected by Mn but by a trace of carbon inherently present in the metal. In the superheating treatment, Mn is generally required for the nucleation of Mg. According to the present study, the presence of Mn apparently increases the grain size, while superheating decreases it. When 0.02%–2.27% of Mn is added, the maximum increase in the grain size is 75 μm. On the other hand, the maximum Mn content in the commercial AZ91 alloy is ca. 0.3%. However, the crystal grain size is 150–200 μm, and it is significantly greater than that of the high-purity alloy containing Mn. We are currently investigating the reason for this phenomenon.

Table 4  Al and Mn contents in samples top, kept for 21.6 ks at given temperature (mass%).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mg-5.7%Al</th>
<th>Mg-8.7%Al</th>
<th>Mg-11.7%Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Mn</td>
<td>Al</td>
</tr>
<tr>
<td>933 K</td>
<td>5.16</td>
<td>0.73</td>
<td>8.21</td>
</tr>
<tr>
<td>998 K</td>
<td>5.25</td>
<td>1.05</td>
<td>8.23</td>
</tr>
<tr>
<td>1073 K</td>
<td>5.30</td>
<td>1.46</td>
<td>8.46</td>
</tr>
</tbody>
</table>

Fig. 6  Results of EPMA line analysis of Al and Mn elements on the line AB across the particles observed sample bottom at 1073 K.

Fig. 7  Al content dependence of Mn solubility at given temperature.

Fig. 8  Influence of Mn content on the grain size of Mg-9%Al alloy.

Fig. 9  Superheating effect of Mn bearing Mg-9%Al alloys.

4. Conclusion

In order to clarify the effect of Mn on the cast grain size of Mg-Al alloys, the solubility of Mn in molten Mg-Al alloys
was investigated. The effects of Mn on the grain size of the Mg-Al alloys and the superheating treatment were also examined. The main conclusions are summarized as follows.

1) If X (X: 6%–11%) denotes the Al content of the Mg-Al alloys, then the Mn solubility Y can be expressed by the following empirical formulas:

\[
Y = 1.79 - 6.22 \times 10^{-2}X \quad (1073 \text{ K})
\]
\[
Y = 1.28 - 4.41 \times 10^{-2}X \quad (998 \text{ K})
\]
\[
Y = 0.90 - 3.35 \times 10^{-2}X \quad (933 \text{ K})
\]

2) High-purity Mg-9.0%Al alloy consists of fine grains with a size of ca. 40μm. The crystal grain size increases with the Mn content.

3) Crystal grains whose size increases due to the addition of Mn can be converted into fine grains (structure of the high-purity alloy) by superheating.

4) No correlation is observed between the crystal grain size of the Mg-9.0%Al alloy, effect of the superheating treatment, and Mn solubility.

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Fig. 10 Effect of Mn content on grain size, and solubility of Mn in Mg-9%Al alloy.