Solidification Microstructure, Thermal Properties and Hardness of Magnesium Alloy 20 mass% Gd Added AZ91D*1

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The solidification microstructure, the thermal property, and the hardness were investigated on AZ91D magnesium alloy and on AZ91D magnesium alloy with 20 mass% gadolinium addition. AZ91D and AZ91D + 20 mass% Gd were solidified by the furnace cooling technique starting from 700 °C in an Ar flow atmosphere. The microstructure of AZ91D was composed of main αMg grains and web-like grain boundary phases of eutectic αMg + Mg17Al12, while that of AZ91D + 20 mass% Gd changes into an αMg matrix with dispersed Al2Gd particles. SEM-EDS analyses showed that the Al content in an αMg matrix of this alloy was very low compared to AZ91D, because Al is consumed in the Al2Gd particles. Differential thermal analysis and quenching experiments were performed in order to clarify this microstructure formation. The thermal conductivity of this alloy, as measured by the laser-flash method, was 129.2 W/mK at room temperature. This alloy exhibited a substantial variance from that of AZ91D at 45.1 W/mK. A higher Vickers hardness HV was yielded compared to AZ91D at HV = 96.6 was yielded compared to AZ91D at HV = 63.7. These properties were well correlated with the results of microstructure and quantitative analysis. [doi:10.2320/matertrans.F-M2009802]

Keywords: AZ91D, magnesium alloy, gadolinium, microstructure, solidification

1. Introduction

AZ91D is a magnesium alloy that is widely used in die-casting and sand-casting processes. Since this alloy shows a good balance of castability and mechanical properties, it is often used for structural components in vehicles, airplanes, mobile computers, digital video recorders, and sports products. Industrial demand for this alloy is increasing rapidly because usage of lightweight materials can reduce the energy consumption of various products. The regulated composition of cast metal AZ91D is 8.5–9.5%Al, 0.45–0.9%Zn, <0.05%Si, 0.17–0.4%Mn, <0.004%Fe, <0.025%Cu, and <0.001%Ni balanced with Mg in mass.1) The addition of aluminum strengthens Mg alloys and enhances the fluidity of the melt, and precipitated Mg17Al12 at the grain boundary promotes corrosion resistance.2) Figure 1(a) shows the Mg-Al binary phase diagram schematically.3) On the Mg side, the eutectic reaction, $L = \alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$, is observed at 437 °C (Here, (Mg) denotes αMg.) Figure 1(a) also shows that, with the increase in Al content to 12.9 mass%, the liquidus temperature of αMg decreases and the solidification range increases. Depending on the amount added, this element significantly reduces thermal conductivity.4) The addition of a small amount of zinc also improves the mechanical properties and castability, but the addition of an excessive amount of zinc causes the formation of micro- and macro-cracks during casting.5) In addition, the low boiling point of zinc promotes the formation of pores. A small amount of silicon improves the castability, and precipitated Mg2Si at the grain boundary improves the creep resistance characteristics. A small amount of manganese improves corrosion resistance,6) whereas iron, nickel, copper, and chromium are known to degrade corrosion resistance.

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The solidification microstructure of AZ91D alloy has been widely reported5,6) and is composed of primary αMg grains and web-like grain boundaries, where eutectic αMg + Mg17Al12 is residual. Trace elements of zinc and other impurities are not found and do not form the third phase in the microstructure, indicating that these impurities are dissolved.

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Fig. 1 Schematic phase diagrams of (a) Mg-Al5) and (b) Mg-Gd binary system.6) $T_1$ and $T_5$ of Mg-9mass% Al are shown in (a).
in grains. The liquidus and solidus temperatures of AZ91D are $T_L = 598^\circ C$ and $T_S = 470^\circ C$, respectively, and, between these temperatures, primary and main $\alpha$Mg grains begin to nucleate and grow. The final solidification occurs at 420°C, as the eutectic reaction takes place at the grain boundary. Figure 1(a) indicates that the $T_L$ and $T_S$ of Mg-9 mass%Al binary alloy are approximately 600°C and 500°C, respectively. Thus, small amounts of impurities in AZ91D reduce $T_L$ and $T_S$ by a few degrees Celsius and approximately 30°C, respectively. Grain size generally depends on the cooling rate. This results in the die-cast microstructure being much finer than that obtained under sand-casting, even though the microstructures are composed of the same phases. Advantages of AZ91D over other Mg-based alloys include the fact that it contains a large amount of Al, and both $T_L$ and the casting temperature are low, which is advantageous for extending the life of mold dies. However, its disadvantages include low thermal and electrical conductivities, low ductility, and low impact resistance.

Alloying is a conventional but effective technique used to improve microstructure and material properties. The addition of secondary elements yields the effects of solid-solutioning, grain refinement, precipitation, and grain boundary control for metallic materials. The addition of rare-earth (RE) elements to Mg alloys increases mechanical strength and fluidity, and also enhances thermal stability and corrosion resistance by the precipitation of hard and thermally stable intermetallics. Figure 1(b) shows the Mg-Gd binary phase diagram, where eutectic reaction, $L = \text{Mg} + \text{Mg}_5\text{Gd}$, is found at 548°C on the Mg side. The maximum solid solubility of 23.5 mass% Gd (4.5 mol%) is found at 548°C, and because the solubility is sufficiently large compared to the maximum solubility of Al of 12.9 mass% (Fig. 1(a)), it is expected that Gd-added Mg alloys will enhance the mechanical properties by solid-solutioning. Moreover, since the Gd solubility limit in $\alpha$Mg decreases from 23.5 mass% Gd at the eutectic temperature to 3.8 mass% Gd at 200°C and since the gradient of the solvus line of $\alpha$Mg/$\alpha$Mg + $\gamma$MgGd is quite small, precipitation control by subsequent ageing treatment is effective and can improve hardness.

Since the solidification behavior of AZ91D is similar to that of Mg-9 mass% Al, the Mg-Al-Gd ternary phase diagram can be used to predict the solidification behavior of Gd-added AZ91D alloy. Figure 2(a) shows the liquidus surface of the Mg-Al-Gd ternary equilibrium phase diagram, showing that the primary phase field of $\alpha$Mg is located near the Mg corner. The primary phase field of $\alpha$Mg is broad and is extended to that of $\alpha$Mg. $\gamma$MgGd is a line compound with a cubic structure of Mg$_2$Cu$_2$-type and a congruent melting temperature of 1525°C. Assuming that Gd is added to Mg-9 mass% Al alloy, the composition of (Mg-9 mass% Al) + x mass% Gd is then located along the broken line in Fig. 2(a). The primary phase is $\alpha$Mg when $x$ is below approximately 2, but changes to $\gamma$MgGd as $x$ increases. Figure 2(b) shows an isothermal section at 400°C of this ternary diagram. In the vicinity of the Mg corner, there is region of $\alpha$Mg solid solution, and regions of $\alpha$Mg + $\gamma$MgGd, $\alpha$Mg + $\gamma$MgGd, $\alpha$Mg + $\gamma$MgGd, $\alpha$Mg + $\gamma$MgGd, and $\alpha$Mg + $\gamma$MgGd are connected to the region of $\alpha$Mg solid solution. The composition around (Mg-9 mass% Al) + 20 mass% Gd, denoted by a solid square in this figure, is located inside the $\alpha$Mg + $\gamma$MgGd two-phase region, where microstructure with no third phase may be obtained. Assuming equilibrium solidification of (Mg-9 mass% Al) + 20 mass% Gd and $\gamma$MgGd, the arrows A1 and A2 in Fig. 2(a) shows its solidification route. A1 is directed along the extrapolation of the dotted line between (Mg-9 mass% Al) + 20 mass% Gd and $\gamma$MgGd, and represents the primary $\gamma$MgGd crystallization. A2 corresponds to eutectic solidification of $\alpha$Mg + $\gamma$MgGd. Since A2 locates near the Mg-Gd binary side, Gd partitions principally into the solidified $\alpha$Mg, but Al does not. Consequently, the solidified alloy is expected to improve the thermal conductivity. Recalling that the solidification occurs on the Mg-Al side in Mg-9 mass% Al alloy, a completely different solidification route and microstructure can be obtained by the addition of a large amount of Gd.

Based on these considerations, it is thought that the mechanical and thermal properties of AZ91D can be improved by the addition of 20 mass% Gd, while fluidity is not degraded because its melt contains a large amount of fluidity effective Al and Gd, an RE element. The objective of the present study is to examine the solidification micro-
structure of AZ91D + 20 mass% Gd alloy (Mg-7.9 mol% Al-3.8 mol% Gd-0.3 mol% Zn) and to clarify its formation behavior during solidification. The thermal properties and hardness of the obtained solidification microstructure were also investigated, along with those of AZ91D solidified under the same conditions.

2. Experimental

Alloyed samples were prepared by the conventional solidification technique. The nominal composition of the samples is AZ91D + 20 mass% Gd and AZ91D. The melt was created in the desired composition by mixing the appropriate amount of 1–5 mm AZ91D chips and Gd blocks that were 10 mm in size. Approximately 30 g of this mixture was placed into a graphite crucible with an inner diameter of 16 mm and a height of 150 mm and then heated to melting in an Ar gas atmosphere within a box-type vacuum furnace (SMA-20S, Shimadzu Co., internal volume of 460 × 500 × 435 mm³). Evacuation by rotary pump and Ar gas introduction was performed three times before heating to ensure gas replacement, after which Ar flow was maintained at 1 L/min during heating and cooling. The mixture was held at a temperature of 700°C for 1 h and then furnace-cooled to room temperature, which took 3–5 hours. Rod-shaped samples of φ16 mm × 80 mm were formed by mechanical breakage of the alumina crucible.

Small pieces cut from the rods were polished, and microstructure observation was performed by optical microscopy and EDS quantitative analysis. A diffractometer (XRD, JDX-3530, JEOL) was used, and the diffraction patterns of the samples were measured from their surfaces. The thermal properties were measured by the laser flash method20) (TC-7000, Ulvac Co.). The thermal diffusivity (α) and specific heat capacity (Cp) of disk-shaped samples 10 mm in diameter and 1 mm in thickness were analyzed at room temperature. The half time method was used for the thermal diffusivity measurements, and sapphire was used as the standard sample for the absorbed heat measurement. The thermal conductivity (κ) was calculated using the following equation: κ = ρ × Cp × α, where the mean values of three measurements were obtained. Micro-Vickers hardness was measured (Akashi HV-114) on the polished surfaces of the samples. The mean values of 20 measurements were obtained under the condition of a 0.1 kgf load with a duration of 15 sec.

3. Results and Discussion

Figure 3 shows the optical microstructure of samples (a) AZ91D + 20 mass% Gd and (b) AZ91D. In Fig. 3(a), αMg is the matrix phase, and globular Al2Gd particles are dispersed within it. These particles were 10 μm in size and were approximately uniformly distributed. No grain boundary phase was observed. In Fig. 3(b), a typical microstructure of AZ91D was observed. αMg grains are surrounded by a web-like grain boundary of αMg + Mg17Al12 eutectic. These figures showed a drastic change in the solidification microstructure of AZ91D by the addition of 20 mass% Gd. Figure 4 shows XRD patterns of AZ91D + 20 mass% Gd and AZ91D. In Fig. 4(a) of the AZ91D + 20 mass% Gd alloy, diffraction patterns of αMg and Al2Gd...
were detected. In Fig. 4(b), $\alpha$Mg and $\alpha$Mg$_{17}$Al$_{12}$ phases of the AZ91D alloy were detected, revealing good correspondence to the differences in the microstructure.

Figure 5(a) shows an SEM composition image of AZ91D + 20 mass% Gd, and the concentration distributions by the EDS line analyses along horizontal line AA are shown for (b) Mg, (c) Al, (d) Zn, and (e) Gd. Figure 6(a) shows the SEM composition image of AZ91D, and the concentration distributions along horizontal line BB are shown for (b) Mg, (c) Al, and (d) Zn. In Fig. 5(a), the matrix is shown in gray, and blocky particles are shown in white. These correspond to $\alpha$Mg and $\alpha$Al$_2$Gd, respectively. In Fig. 6(a), AZ91D contains $\alpha$Mg grains, shown in gray, along with $\alpha$Mg$_{17}$Al$_{12}$, shown in white. From Figs. 5(b) through 5(e), each element had a flat distribution in the $\alpha$Mg matrix, but Mg was depressed and Al and Gd were concentrated at particles. The compositions of these regions were approximately consistent with that of $\alpha$Al$_2$Gd (Al : Gd = 25.5 : 74.5 in mass%). The figures also show that most of the Al and Gd concentrated in the $\alpha$Al$_2$Gd and not distributed in the $\alpha$Mg matrix. Figures 6(b) through 6(e) show that Mg was reduced and Al was concentrated at the grain boundary, but 5–10% of the Al was distributed in $\alpha$Mg grains. The Al concen-
The Al concentration distribution of AZ91D + 20 mass% Gd shown in Fig. 5(c) and that of AZ91D shown in Fig. 6(c) are presented together in Fig. 7, which shows that the Al concentration in Mg grains largely decreased in AZ91D + 20 mass% Gd, as compared to AZ91D. This occurs because the solidification route has progressed along arrows A1 and A2 in Fig. 2(a).

Figures 8 and 9 show the DTA heating and cooling curves of AZ91D + 20 mass% Gd and AZ91D, respectively. Figure 8(a) shows that the endothermic peak started at ~590°C and ended at 674°C upon heating. Since the melt started to oxidize almost simultaneously upon its formation, heat release occurred and the DTA curve moved upwards slightly at ~590°C. This leads to difficulty in drawing
tangents. The second peak was located at 784°C, which is assumed to be the $T_{L}$ of AZ91D + 20 mass% Gd. In Fig. 8(b), $T_{cr} = 730$°C. Thus, undercooling for crystallization, $\Delta T_{cr} = T_{L} - T_{cr} = 54$°C, appeared in this measurement. The second and largest exothermic peak began at 636°C. This peak converged with the base line at 463°C, and no other peak was found below this temperature. Figure 9(a) shows that the first endothermic peak on heating appears at 428°C, which corresponds to the decomposition of eutectic $\alpha$Mg. This peak ended at 479°C, which agrees with the results of the preliminary measurement ($T_{L} = 599$°C) and the value of 598°C reported in Ref. 2) within the measurement errors. Figure 9(b) shows that the first exothermic peak appears at $T_{cr} = 580$°C. Thus, $\Delta T_{cr} = T_{L} - T_{cr} = 20$°C. The peak ended at 479°C, which was assumed to be the solidus temperature. The second and smaller peak is located at 430°C, which corresponds to the eutectic reaction. The DTA behavior of AZ91D changed remarkably due to the addition of 20 mass% Gd, which is related to the microstructure in the next section.

The solidification behavior of AZ91 + 20 mass% Gd and AZ91D was examined by quenching experiments, and the results are shown in Figs. 10 and 11. In AZ91 + 20 mass% Gd, Figs. 10(a) $T_{WQ} = 700$°C and 10(b) $T_{WQ} = 650$°C showed that the quenched microstructure contained dispersed Al$_2$Gd particles in very fine dendrites, which are considered to have been the melt prior to quenching. This indicates that the exothermic peak at 730°C is induced by the crystallization of Al$_2$Gd, and primary phase is not $\alpha$Mg but Al$_2$Gd in this alloy. In Fig. 10(c), for $T_{WQ} = 620$°C, large $\alpha$Mg dendrites appeared, causing the exothermic peak at 636°C, as shown in Fig. 8(b). $\alpha$Mg grain growth continues until $T_{WQ} = 490$°C, as shown in Fig. 10(d). At this temperature, however, a small amount of liquid remains at the grain boundary, as indicated by the arrow in the figure. Further cooling to room temperature yielded the microstructure, as shown in Fig. 3(a).

In Fig. 11(a), for $T_{WQ} = 600$°C, the quenched microstructure was that of the melt of AZ91D. In Fig. 11(b), for $T_{WQ} = 560$°C, an $\alpha$Mg dendrite was observed, showing that the exothermic peak starting at $T_{cr} = 580$°C in Fig. 9(b) was caused by crystallization of the $\alpha$Mg dendrites. The $\alpha$Mg grains grow as the temperature decreases. As shown in Figs. 11(c), for $T_{WQ} = 550$°C, and 11(d), for $T_{WQ} = 440$°C, the volume fraction of $\alpha$Mg grains increased as the grain shape became globular, and almost the entire volume was filled at this temperature. At the exothermic peak at 430°C shown in Fig. 9(b), eutectic reaction of $\alpha$Mg + Mg$_{17}$Al$_{12}$ occurs, and the resulting microstructure forms, as shown in Fig. 3(b).

The thermal properties of these samples are shown in Table 1. The density ($\rho$), thermal diffusivity ($\alpha$), specific heat capacity ($C_p$), and calculated thermal conductivity ($k$) are listed. The table shows that the densities of AZ91D + 20 mass% Gd and AZ91D were 1.55 g/cm$^3$ and 1.65 g/cm$^3$, respectively. These were small compared to the value in the literature for AZ91D of 1.81 g/cm$^3$.\(^2\) The values of $C_p$ were 0.91 J/gK for AZ91 + 20 mass% Gd and 0.90 J/gK for AZ91D. These were also small compared to the value of 1.02 J/gK reported in the literature.\(^2\) This is attributed to the

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Table 1 Thermal and mechanical properties of samples.

<table>
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<th>Samples</th>
<th>Diameter, (mm)</th>
<th>Thickness, (mm)</th>
<th>Weight, mg</th>
<th>Density, ($\rho$), (g/cm$^3$)</th>
<th>Thermal diffusivity ($\alpha$), (cm$^2$/s)</th>
<th>Specific heat capacity ($C_p$), J/gK</th>
<th>Thermal conductivity ($k$), W/mK</th>
<th>Vickers hardness, Hv</th>
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<td>10</td>
<td>0.985</td>
<td>120.2</td>
<td>1.55</td>
<td>0.92</td>
<td>0.90</td>
<td>129.2</td>
<td>96.6</td>
</tr>
<tr>
<td>AZ91D</td>
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<td>0.995</td>
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<td>1.65</td>
<td>0.30</td>
<td>0.91</td>
<td>45.1</td>
<td>63.7</td>
</tr>
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</table>
numeros pores in the microstructure. As shown in Fig. 12, a number of pores were observed in the solidified microstructure, particularly at the grain boundaries. Gas bubbles tended to remain in the liquid upon melting. That results from the process used to mix the AZ91D chips and the 10 mm Gd blocks. The filling effect of the melt by its own weight was small, whereas the light weight of the sample, approximately 30 g, caused pore formation. However, a and k increased remarkably by the addition of 20 mass% Gd, where $\kappa = 45.1 \text{ W/mK}$ for AZ91D and $\kappa = 129.2 \text{ W/mK}$ for AZ91D + 20 mass% Gd. From the microstructure and SEM-EDS analyses, Al$_2$Gd particles were revealed to consume Al, thus reducing the Al content in $\alpha$Mg grains, as shown in Figs. 5 through 7. Al significantly reduces the $\kappa$ of magnesium.\(^5\) This is interpreted as being the result of lattice distortion of $\alpha$Mg crystals due to solid-solutioning, and, as a result, the mean free path of free electrons, which are heat carriers of solid metals, decreases. The reduction in Al content in the $\alpha$Mg grains should have substantially increased $\alpha$ and $\kappa$. The microstructure also showed that secondary phases, such as eutectic reaction products, were not observed at the grain boundary. This should have enhanced grain connectivity and heat conductance between $\alpha$Mg grains. The Vickers hardness is also listed in Table 1, where $H_v = 96.6$ for AZ91 + 20 mass% Gd and $H_v = 63.7$ for AZ91D. As shown in Fig. 13, the Vickers hardness was measured as $H_v = 513$–626 for three points on coarse Al$_2$Gd particles that were locally residual in the microstructure. Based on these results, the number of hard Al$_2$Gd particles dispersed in the microstructure was found to increase the mean hardness of the alloy.

4. Summary

In order to investigate the solidification microstructure and the material properties of AZ91D magnesium alloy and AZ91D with 20 mass% Gd addition, these materials were prepared by use of the furnace cooling technique. From microstructure observation by optical microscopy and SEM-EDS and from differential thermal analysis, quenching experiments, and measurements of the thermal properties and hardness, the following results were obtained.

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REFERENCES