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 α Mg grains and web-like grain boundary phases of eutectic α Mg + $\text{Mg}_{17}\text{Al}_{12}$, while that of AZ91D + 20 mass% Gd changes into an α Mg matrix with dispersed Al_2Gd particles. SEM-EDS analyses showed that the Al content in an α Mg matrix of this alloy was very low compared to AZ91D, because Al is consumed in the Al_2Gd 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 $H_V = 96.6$ was yielded compared to AZ91D at $H_V = 63.7$. These properties were well correlated with the results of microstructure and quantitative analysis. [doi:10.2320/matertrans.F-M2009802]

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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 $\text{Mg}_{17}\text{Al}_{12}$ 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 α Mg). Figure 1(a) also shows that, with the increase in Al content to 12.9 mass%, the liquidus temperature of α Mg 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.²⁾ In addition, the low boiling point of zinc promotes the formation of pores. A small amount of silicon improves the castability, and precipitated Mg_2Si at the grain boundary improves the creep resistance characteristics. A small amount of manganese improves corrosion resistance,²⁾ whereas iron, nickel, copper, and chromium are known to degrade corrosion resistance.

Fig. 1 Schematic phase diagrams of (a) Mg-Al³⁾ and (b) Mg-Gd binary system.⁹⁾ T_L and T_S of Mg-9 mass% Al are shown in (a).

The solidification microstructure of AZ91D alloy has been widely reported^{5,6)} and is composed of primary α Mg grains and web-like grain boundaries, where eutectic α Mg + $\text{Mg}_{17}\text{Al}_{12}$ 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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in grains. The liquidus and solidus temperatures of AZ91D are $T_L = 598^\circ\text{C}$ and $T_S = 470^\circ\text{C}$, respectively, and, between these temperatures, primary and main αMg 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 strength⁷⁾ and fluidity,⁸⁾ 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.⁹⁾ 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 αMg 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 $\alpha\text{Mg}/\alpha\text{Mg} + \text{Mg}_5\text{Gd}$ is quite small, precipitation control by subsequent ageing treatment is effective and can improve hardness.^{10–14)}

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,^{15,16)} showing that the primary phase field of αMg is located near the Mg corner. The primary phase field of Al_2Gd is broad and is extended to that of αMg . Al_2Gd is a line compound with a cubic structure of MgCu_2 -type and a congruent melting temperature of 1525°C .^{17,18)} 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 αMg when x is below approximately 2, but changes to Al_2Gd as x increases. Figure 2(b) shows an isothermal section at 400°C of this ternary diagram.¹⁹⁾ In the vicinity of the Mg corner, there is region of αMg solid solution, and regions of $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$, $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12} + \text{Al}_2\text{Gd}$, $\alpha\text{Mg} + \text{Al}_2\text{Gd}$, $\alpha\text{Mg} + \text{Al}_2\text{Gd} + \text{Mg}_5\text{Gd}$, and $\alpha\text{Mg} + \text{Mg}_5\text{Gd}$ are connected to the region of αMg solid solution. The composition

Fig. 2 Schematic phase diagrams of (a) the liquidus surface¹⁵⁾ and (b) the isothermal section at 400°C ¹⁹⁾ of Mg-Al-Gd ternary system. The solid square indicates (Mg-9 mass% Al) + 20 mass% Gd.

around (Mg-9 mass% Al) + 20 mass% Gd, denoted by a solid square in this figure, is located inside the $\alpha\text{Mg} + \text{Al}_2\text{Gd}$ two-phase region, where microstructure with no third phase may be obtained. Assuming equilibrium solidification of (Mg-9 mass% Al) + 20 mass% Gd, 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 Al_2Gd , and represents the primary Al_2Gd crystallization. A2 corresponds to eutectic solidification of $\alpha\text{Mg} + \text{Al}_2\text{Gd}$. Since A2 locates near the Mg-Gd binary side, Gd partitions principally into the solidified αMg , 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 an alumina (SSA-S) 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 $460 \times 500 \times 435 \text{ mm}^3$). 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 $\phi 16 \text{ mm} \times 80 \text{ mm}$ 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 was done by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, JEOL JSM-7400F, acceleration voltage of 15 kV). Lines of Mg K α , Al K α , Zn K α , and Gd L α were taken, where ZAF calibration was performed automatically for EDS quantitative analyses. Phase identification was performed by X-ray diffraction analysis with a Cu target (XRD, JDX-3530, JEOL). The measurements were performed by the $\theta/2\theta$ method, and detected phases were identified by the JCPDS database.

Differential thermal analysis (DTA, Shimadzu DTG-60H) was performed in order to determine the melting, crystallization, and eutectic temperatures of each alloy. Using alumina crucibles, 30–40 mg of each sample was supplied. The heating and cooling rates of AZ91D were 5°C/min in the range of 300–700°C in flowing Ar at 200 cc/min. Since the reaction temperature of AZ91D + 20 mass% Gd was high compared to AZ91D and liquid evaporation was problematic in preliminary studies, heating and cooling rates of 20°C/min and a range of 300–800°C were chosen for this alloy. The melting temperature (T_L) was determined at the cross-points of extrapolated tangents of the end of the endothermic peak in heating curves. The crystallization temperature (T_{cr}) was determined from the cooling curve defined at the cross-points of extrapolated tangents of the first exothermic peak. Generally, the reaction temperature of DTA depends on the heating and cooling rates, and the lower rate can detect a value closer to the equilibrium reaction temperature. In preliminary studies on AZ91D, $T_L = 599^\circ\text{C}$ and $T_{cr} = 581^\circ\text{C}$ were obtained upon heating and cooling at 5°C/min. $T_L = 612^\circ\text{C}$ and $T_{cr} = 587^\circ\text{C}$ were obtained upon heating and

cooling at 20°C/min. These results revealed that T_L had good correspondence with the value (598°C) reported in the literature²⁾ at 5°C/min, and differences of 13°C in T_L and 6°C in T_{cr} at 20°C/min were observed. However, for the above-mentioned reasons, the values obtained at heating and cooling rates of 20°C/min were taken as the reaction temperatures for AZ91D + 20 mass% Gd. Thus, for AZ91D + 20 mass% Gd, as in the preliminary measurements, it is necessary to take into account the difference due to the heating and cooling rates.

Water-quenching experiments were conducted in order to investigate the solidification behavior of the alloy samples. Samples were prepared from alloy blocks of 0.2 g to 0.9 g in mass. These were heated to 700°C and maintained at that temperature for 15 min. Then, each block was cooled at 5°C/min in the same furnace. This cooling rate was chosen because it is similar to that used for the sand-casting of Mg alloys. In order to preserve the solidified morphology, the alloy blocks were quenched during cooling by dropping them into a water bath. Since the difference in the exothermic peak temperatures of the DTA cooling curve due to different cooling rates was relatively small in the preliminary experiments, the water-quench temperature (T_{WQ}) was selected based on four conditions above and below these temperatures. These samples were also subjected to microstructure observation.

Thermal properties were measured by the laser flash method²⁰⁾ (TC-7000, Ulvac Co.). The thermal diffusivity (α) and specific heat capacity (C_p) 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, where glassy carbon was attached as the light recipient plate. The density (ρ) of the samples was measured from their volumes and weights. No calibration was conducted for the volume fraction or the weight of pores in samples. The thermal conductivity (κ) was calculated using the following equation: $\kappa = \rho \times C_p \times \alpha$, 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 Al_2Gd 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 $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$ 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 Al_2Gd

Fig. 3 Optical photomicrographs of solidification microstructure of (a) AZ91D + 20 mass% Gd and (b) AZ91D.

Fig. 4 XRD patterns of (a) AZ91D + 20 mass% Gd and (b) AZ91D.

were detected. In Fig. 4(b), α Mg and $Mg_{17}Al_{12}$ 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

Fig. 5 (a) SEM composition image of AZ91D + 20 mass% Gd, and results of EDS line analysis of (b) Mg, (c) Al, (d) Zn, and (e) Gd along horizontal line AA.

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 α Mg and Al_2Gd , respectively. In Fig. 6(a), AZ91D contains α Mg grains, shown in gray, along with $Mg_{17}Al_{12}$, shown in white. From Figs. 5(b) through 5(e), each element had a flat distribution in the α 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 Al_2Gd (Al : Gd = 25.5 : 74.5 in mass%). The figures also show that most of the Al and Gd concentrated in the Al_2Gd and not distributed in the α 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 α Mg grains. The Al concen-

Fig. 6 (a) SEM compositional image of AZ91D, and results of EDS line analysis along horizontal line BB, (b) Mg, (c) Al, and (d) Zn.

Fig. 7 Al concentration distribution along horizontal lines AA in Fig. 5(a) and BB in Fig. 6(a).

tration 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 α Mg grains largely decreased in AZ91D + 20 mass% Gd, as compared to AZ91D. This occurs because the solidification route has progressed along arrows A_1 and A_2 in Fig. 2(a).

Fig. 8 (a) DTA heating and (b) cooling curves of AZ91D + 20 mass% Gd. The downward arrows indicate the water-quench temperature (T_{wQ}) in Fig. 10.

Fig. 9 (a) DTA heating and (b) cooling curves of AZ91D. The downward arrows indicate the water-quench temperature (T_{wQ}) in Fig. 11.

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 $\sim 590^\circ\text{C}$ 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 $\sim 590^\circ\text{C}$. This leads to difficulty in drawing

Fig. 10 Quenching temperature dependence of the optical photomicrographs of microstructure of AZ91D + 20 mass% Gd. Water quenching was performed during cooling at 5°C/min from 700°C, at (a) $T_{WQ} = 700^\circ\text{C}$, (b) $T_{WQ} = 650^\circ\text{C}$, (c) $T_{WQ} = 620^\circ\text{C}$, and (d) $T_{WQ} = 490^\circ\text{C}$.

Fig. 11 Quenching temperature dependence of the optical photomicrographs of microstructure of AZ91D. Water quenching was performed during cooling at 5°C/min from 700°C, at (a) $T_{WQ} = 600^\circ\text{C}$, (b) $T_{WQ} = 560^\circ\text{C}$, (c) $T_{WQ} = 500^\circ\text{C}$, and (d) $T_{WQ} = 440^\circ\text{C}$.

Table 1 Thermal and mechanical properties of samples.

Samples	Diameter, (mm)	Thickness, (mm)	Weight, mg	Density, (ρ), (g/cm ³)	Thermal diffusivity (α), cm ² /s	Specific heat capacity (C_p), J/gK	Thermal conductivity (κ), W/mK	Vickers hardness, Hv
AZ91D + 20%Gd	10	0.985	120.2	1.55	0.92	0.90	129.2	96.6
AZ91D	10	0.995	128.8	1.65	0.30	0.91	45.1	63.7

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), $T_{cr} = 730^\circ\text{C}$. Thus, undercooling for crystallization, $\Delta T_{cr} = T_L - T_{cr} = 54^\circ\text{C}$, 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 phase. In the figure, T_L was found to be 600°C, which agreed well with the results of the preliminary measurement ($T_L = 599^\circ\text{C}$) 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 $T_{cr} = 580^\circ\text{C}$. Thus, $\Delta T_{cr} = T_L - T_{cr} = 20^\circ\text{C}$. 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) $T_{WQ} = 700^\circ\text{C}$ and 10(b) $T_{WQ} = 650^\circ\text{C}$ showed that the quenched microstructure contained dispersed Al_2Gd 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_2Gd , and primary phase is not αMg but Al_2Gd in this alloy. In Fig. 10(c), for $T_{WQ} = 620^\circ\text{C}$, large αMg

dendrites appeared, causing the exothermic peak at 636°C, as shown in Fig. 8(b). αMg grain growth continues until $T_{WQ} = 490^\circ\text{C}$, 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 $T_{WQ} = 600^\circ\text{C}$, the quenched microstructure was that of the melt of AZ91D. In Fig. 11(b), for $T_{WQ} = 560^\circ\text{C}$, an αMg dendrite was observed, showing that the exothermic peak starting at $T_{cr} = 580^\circ\text{C}$ in Fig. 9(b) was caused by crystallization of the αMg dendrites. The αMg grains grow as the temperature decreases. As shown in Figs. 11(c), for $T_{WQ} = 500^\circ\text{C}$, and 11(d), for $T_{WQ} = 440^\circ\text{C}$, the volume fraction of αMg 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 $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$ 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 (ρ), thermal diffusivity (α), specific heat capacity (C_p), and calculated thermal conductivity (κ) are listed. The table shows that the densities of AZ91D + 20 mass% Gd and AZ91D were 1.55 g/cm³ and 1.65 g/cm³, respectively. These were small compared to the value in the literature for AZ91D of 1.81 g/cm³.²⁾ 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

Fig. 12 Optical photomicrograph of solidification microstructure of AZ91D, showing pores at the grain boundary.

Fig. 13 Optical photomicrograph of micro-Vickers indentation on Al_2Gd particle.

numerous 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, α and κ 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_2Gd particles were revealed to consume Al, thus reducing the Al content in αMg grains, as shown in Figs. 5 through 7. Al significantly reduces the κ of magnesium.⁴⁾ This is interpreted as being the result of lattice distortion of αMg 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 αMg grains should have substantially increased α and κ . 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 αMg 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 $H_V = 513\text{--}626$ for three points on coarse Al_2Gd particles that were locally residual in the microstructure. Based on these results, the number of hard Al_2Gd 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.

- (1) In the microstructure of AZ91D + 20 mass% Gd, globular Al_2Gd particles were dispersed within the αMg matrix, and no grain boundary phases were observed. This differs from the microstructure of AZ91D, where eutectic $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$ surround Mg grains in a web-like manner.
- (2) SEM-EDS analyses revealed that the Al concentration in the αMg grains of AZ91D + 20 mass% Gd alloy decreased remarkably compared to that of AZ91D.
- (3) Differential thermal analyses revealed that the melting temperature increased from 600 to 784°C by 20 mass% Gd addition, and the crystallization temperature increased from 580 to 730°C.
- (4) Quenching experiments were carried out in order to clarify the solidification behavior of AZ91D. In AZ91D + 20 mass% Gd, the primary Al_2Gd particles were found at 700°C, and αMg equi-axed dendrites began to solidify at 636°C. In AZ91D, the primary αMg began to solidify at 580°C and $\alpha\text{Mg} + \text{Mg}_{17}\text{Al}_{12}$ eutectic precipitates from the remaining liquid at approximately 430°C.
- (5) Measurements of the material properties of these samples revealed that the thermal conductivity increased from 45.1 W/mK to 129.2 W/mK and the Vickers hardness H_V increased from 63.7 to 96.6 by the addition of 20 mass% Gd. The increment of the thermal conductivity was explained by the decrease in the Al concentration in the αMg grains in the microstructure and the diminishment of the grain boundary phases, and the increment in hardness was explained by the dispersion of Al_2Gd particles of high hardness.

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