Formation of LPSO Phases in As-Cast Mg–Al–Zn–Gd Quaternary Alloys^{*1}

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Mg alloys with a long-period stacking-order (LPSO) phase are categorized into two types. Those in which the LPSO phase forms in as-cast state are referred to as Type I, while those in which the LPSO phase does not appear until a heat treatment is performed are categorized as Type II. However, the reason that gives rise to these two types of alloy is still not well understood. In the present study, in an attempt to clarify this issue, three different Mg₈₅(Al,Zn)₆Gd₉ quaternary alloys were prepared. The α -Mg, Al₂Gd, Mg₃Gd and LPSO phases were identified in the as-cast quaternary alloys by microstructural observations, composition analysis and crystal structure analysis using electron probe microanalysis and X-ray diffraction. The results indicated that all the quaternary alloys could be categorized as Type I, even though ternary Mg₈₅Al₆Gd₉ and Mg₈₅Zn₆Gd₉ alloys were Type II. The crystal structure of the LPSO phase in the as-cast alloys is considered to be 18R with dilute solute elements, and the fraction of this phase increases with increasing Zn content. The presence of this phase is thought to be the cause of destabilization of the primary Al₂Gd phase. It is thus concluded that the relative stability of phases in the vicinity of the LPSO phase is crucial in determining the type of Mg alloy formed. [doi:10.2320/matertrans.MT-MM2019008]

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1. Introduction

Due to their low density (about 25% of that of Fe and 66% of that of Al), Mg alloys are being actively investigated as structural materials for automotive and aviation applications. In 2001, Kawamura *et al.* developed a Mg–1Zn–2Y (at%) alloy with a very high strength of 610 MPa and 5% tensile elongation using a special fabrication process.¹⁾ These characteristics were attributed to the coexistence of a long-period stacking-order (LPSO) phase and an α -Mg phase.²⁾ Consequently, Mg alloys containing a LPSO phase have attracted a large amount of attention in recent years.^{3–8)}

The LPSO phase has a unique crystal structure consisting of stacked HCP Mg layers interspersed with stacked FCC layers containing isolated L1₂-type clusters composed of transition metal (TM) and rare-earth (RE) elements in a ratio of 3:4.⁹⁾ The number of HCP-Mg layers varies from 0 to 4, and the corresponding polymorphic crystal structures are referred to as 12R, 10H, 18R, 14H and 24R, respectively.

There are two different types of LPSO phase. The Type I phase in the Mg–Zn–Y and Mg–Zn–Dy systems forms during casting, whereas the Type II phase in the Mg–Zn–Tb system does not appear in the as-cast state, but forms during heat treatment.¹⁰⁾ The type of LPSO phase that is formed is thought to be related to its stability relative to other phases in the alloy. To fully control the microstructure, the additive elements used and the type of LPSO phases present are essential factors.

In ternary Mg–Al–Gd alloys, a Type II 18R-LPSO phase appears during heat treatment, while the primary phases are α -Mg and Al₂Gd. A 14H-LPSO phase has been reported in as-cast Mg_{96.5}Zn₁Gd_{2.5} alloy.¹¹⁾ However, Yamasaki *et al.*

and Miyakawa *et al.* found no LPSO phases in as-cast ternary Mg–Zn–Gd alloys,^{6,12,13)} but reported the formation of a 14H-LPSO phase during heat treatment. Therefore, both ends of the series of Mg–Al–Zn–Gd quaternary alloys, i.e., Mg₈₅Al₆Gd₉ and Mg₈₅Zn₆Gd₉, are Type II LPSO phases.

Based on the structure of the L1₂ clusters composed of TM and RE elements formed in the LPSO phase, it is expected that Al and Zn occupy the same sites. However, there is no information available for LPSO phases composed of Mg, Al, Zn and Gd. Miura *et al.* performed an experimental study on the substitutional behavior of RE elements in Mg–Zn–RE (RE = Y, Dy, Gd, Ho, Ce) systems, and found that it is strongly affected by interaction between RE elements, i.e., no interaction between RE elements seems to be a criterion for full substitution. In the binary Al–Zn system, the solubility of Zn in FCC-Al is high, and no intermetallic compound is formed.¹⁴⁾ This strongly suggests a weak interaction between Al and Zn, and the stability of the quaternary Mg–(Al,Zn)–Gd LPSO phases is considered to be similar to that of the ternary Mg–Al–Gd and Mg–Zn–Gd LPSO phases. On the other hand, the primary phases in the ternary Mg–Al–Gd alloy are different from those in the Mg–Zn–Gd alloy, which implies that the stability of the primary phases may depend on the alloy composition. In the present study, Mg–Al–Zn–Gd quaternary alloys are employed to investigate the solidification process and the type of LPSO phases formed. The quaternary Mg–(Al,Zn)–Gd LPSO phases are also investigated to determine the main factors responsible for their formation.

2. Experimental Procedure

The alloy composition was Mg₈₅(Al,Zn)₆Gd₉ with an Al/Zn ratio of 2.0, 1.0 or 0.5. Alloy ingots with a weight of about 30 g were prepared from high-purity raw materials (99.95% Mg, 99.99% Al, 99.5% Zn and 99.9% Gd) in high-purity graphite crucibles. The crucibles were placed in an

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Ar-filled induction heater, and the contents were cast in a mild steel mold. A part of each ingot was subsequently encapsulated in a glass tube filled with Ar gas and isothermally heat-treated at 450°C for 1000 h, followed by water quenching. As-cast and heat-treated samples were cut into small pieces and polished. The microstructure was investigated by scanning electron microscopy (SEM) in conjunction with electron probe microanalysis (EPMA; JXA-8230, JEOL, Tokyo) with an accelerating voltage of 15 kV. The probe current was 5×10^{-10} A for SEM observations and 3×10^{-8} A for wavelength dispersive X-ray spectroscopy (WDS). X-ray diffraction (XRD; SmartLab, Rigaku, Tokyo) analysis using a copper target with an X-ray tube voltage of 40 kV and a tube current of 35 mA was also conducted to identify the LPSO phases.

3. Results and Discussion

3.1 As-cast alloys

Figure 1 shows backscattered electron images of the as-cast alloys $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$, hereafter denoted 4Al2Zn, 3Al3Zn and 2Al4Zn alloys, respectively. Each image contains black, white, lamellar and plate-like regions. No significant differences are observed among the alloys, although the amount of plate-like regions increases with increasing Zn content. Figure 2 shows the results of a WDS analysis of 300 randomly selected points (white circles) together with gray circles indicating the results of point analyses on the black, white, lamellar and plate-like regions in each alloy on the Mg–(Al,Zn)–Gd ternary section of the quaternary system. The broken line representing a (Al+Zn):Gd ratio of 3:4 indicates the stoichiometric ratio of TM to RE for LPSO phase polymorphs.

The average chemical compositions (at%) of the black, white, lamellar and plate-like regions in the as-cast alloys are shown in Table 1. It should be noted that the results for the lamellar region represent weighted average chemical compositions of the two-phase lamellar microstructure because the lamellar region has a fine microstructure that is beyond the spatial resolution of SEM-WDS. For all the alloys, the black regions contain mostly Mg, while the Mg content in the lamellar regions is about 87%, and the Al:Gd ratio in the white regions is about 1:2. This suggests that the black and white regions are the α -Mg and Al_2Gd phases, respectively. The average chemical compositions of the plate-like structures fall on the broken line, suggesting the LPSO phase. It is noteworthy that the average chemical compositions of the lamellar regions in all the alloys are similar and almost no Al is soluble.

Figure 3 shows the results of XRD analyses ($2\theta = 10\text{--}90^\circ$) of the as-cast alloys. Peaks associated with Mg, Al_2Gd and Mg_3Gd are seen to be present. Therefore, the fine lamellar region is considered to be composed of Mg_5Gd (white) and Mg (black).

Figure 4 shows XRD patterns in the range $2\theta = 4\text{--}10^\circ$ to identify the polymorphic LPSO phases. The peak angles for (000n) reflections for each LPSO structure calculated based on the lattice constant c for pure Mg are tabulated in Table 2 (n for 10H, 18R, 14H, 24R is 2, 3, 2 and 3, respectively). The

Fig. 1 Backscattered electron images of as-cast (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys. Each image contains black, white, lamellar and plate-like regions.

18R structure is confirmed to be present in the as-cast 2Al4Zn alloy. On the other hand, none of the low-angle peaks listed in Table 2 are present for the 4Al2Zn or 3Al3Zn alloy, in spite of the existence of similar plate-like structures to those in the 2Al4Zn alloy. The amount of plate-like structures in the 4Al2Zn and 3Al3Zn alloys is apparently much smaller than that in the 2Al4Zn alloy, leading to an absence of low-angle XRD peaks. However, these quaternary alloys containing both Al and Zn should be classified as Type I. Egusa *et al.* reported that the stoichiometric composition of the 18R LPSO phase is $\text{Mg}_{80.6}\text{TM}_{8.3}\text{RE}_{11.1}$,⁹⁾ while the chemical composition of the LPSO phases evaluated in the present study is about $\text{Mg}_{90}\text{TM}_4\text{RE}_6$, as shown in Table 1. This discrepancy in chemical composition remains to be clarified in the future.

3.2 Heat-treated alloys

Figure 5 shows backscattered electron images of the heat-

Fig. 2 Analyzed chemical compositions of as-cast (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys. Chemical compositions for plate-like regions are located in the vicinity of a line with a $(\text{Al}+\text{Zn})\text{:Gd}$ ratio of 3:4.

treated 4Al2Zn, 3Al3Zn and 2Al4Zn alloys. Each image contains black, white, light gray and dark gray regions. The boundaries between the light gray and dark gray regions are unclear, and the amount of light gray regions decreases with increasing Zn content. Figure 6 shows the results of a WDS analysis of 300 randomly selected points (white circles) together with gray circles indicating the results of point analyses on the black, white, light gray and dark gray regions in each alloy on the Mg–(Al,Zn)–Gd ternary section of the quaternary system. The broken line indicates a $(\text{Al}+\text{Zn})\text{:Gd}$ chemical composition ratio of 3:4. By averaging the 300

Table 1 Average chemical compositions (at%) of the black, white, lamellar and plate-like regions in as-cast (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys. The results for the lamellar regions represent average chemical compositions of the lamellar microstructures.

(a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	98.2	0.0	0.2	1.6
White region	9.9	53.9	2.3	33.9
Lamellar region	87.8	0.4	3.3	8.5
Plate-like region	90.6	1.2	2.3	5.9
(b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	97.7	0.0	0.3	2.0
White region	9.6	52.9	3.3	34.2
Lamellar region	87.1	0.5	3.5	8.9
Plate-like region	92.4	0.7	2.0	4.9
(c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	97.5	0.0	0.3	2.2
White region	13.8	46.4	5.6	34.2
Lamellar region	86.3	0.4	3.6	9.8
Plate-like region	90.2	1.1	2.7	6.0

Fig. 3 X-ray diffraction patterns (10–90°) for as-cast (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys.

randomly selected points, the chemical compositions for the 4Al2Zn, 3Al3Zn and 2Al4Zn alloys are estimated to be $\text{Mg}_{86.4}\text{Al}_{3.6}\text{Zn}_{2.1}\text{Gd}_{7.9}$, $\text{Mg}_{85.5}\text{Al}_{3.0}\text{Zn}_{3.0}\text{Gd}_{8.5}$ and

Fig. 4 X-ray diffraction patterns (4–10°) for as-cast (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys.

Table 2 XRD peak positions (000n) for each LPSO structure calculated based on the lattice constant for pure Mg. The value of n for 10H, 18R, 14H and 24R is 2, 3, 2 and 3, respectively.

LPSO structure	2θ[deg]
10H	6.78
18R	5.66
14H	4.84
24R	4.24

$\text{Mg}_{85.7}\text{Al}_{2.0}\text{Zn}_{4.0}\text{Gd}_{8.3}$, respectively. The nominal and estimated chemical compositions of the alloys are also indicated in Figs. 2 and 6. The average chemical compositions of the black, white, light gray and dark gray regions in the heat-treated alloys are shown in Table 3. For all the alloys, the black regions contain mostly Mg, and the Al:Gd ratios in the white regions are about 1:2. Therefore, it is concluded that the black and white regions are the α -Mg and Al_2Gd phases, respectively. The light gray and dark gray regions are considered to be LPSO phases because their chemical compositions are located in the vicinity of the broken lines. Hereafter, the dark gray and light gray regions are denoted as LPSO ① and LPSO ②, respectively. It is also noteworthy that the lamellar regions found in the as-cast alloys are not present.

Fig. 5 Backscattered electron images of (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys after isothermal heat treatment at 450°C for 1000 h. Each image contains black, white, light gray, and dark gray regions.

Figure 7 shows XRD patterns in the range $2\theta = 4\text{--}10^\circ$ for each heat-treated alloy. As is clear from Table 2, both the 14H ($2\theta = 4.8^\circ$) and 18R ($\theta = 5.6^\circ$) structures are present in each alloy, whereas the 14H structure is not found in the as-cast alloys. The peak intensity for the 14H structure becomes much larger than that for the 18R structure with increasing Zn content. As shown in Fig. 5, the volume fraction of LPSO ① also increases with increasing Zn content. Therefore, it is concluded that LPSO ① and LPSO ② represent the 14H and 18R LPSO phases, respectively. The peaks at around 9.2° correspond to two-dimensional ordering of L1_2 clusters.¹⁵⁾ The Mg-TM-RE ratios for LPSO ① in each alloy are summarized in Table 4 together with the stoichiometric ratios for the 14H and 18R LPSO phases. It is confirmed that the Mg-TM-RE ratio in LPSO ① for all the alloys is close to that for the 14H LPSO phase, suggesting that LPSO ① is an LPSO phase polymorph with a 14H structure.

Fig. 6 Analyzed chemical compositions of (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys after isothermal heat treatment at 450°C for 1000 h. Chemical compositions for LPSO ① and LPSO ② phases are located in the vicinity of the line with a (Al+Zn):Gd ratio of 3:4.

3.3 Factors determining the formation of Type I and Type II alloys

Although the ternary $\text{Mg}_{85}\text{Al}_6\text{Gd}_9$ and $\text{Mg}_{85}\text{Zn}_6\text{Gd}_9$ alloys are Type II,^{13,16)} the quaternary $\text{Mg}_{85}\text{Al}_{4-x}\text{Zn}_{2+x}\text{Gd}_9$ alloys are found to be Type I, for which an LPSO phase appears in the as-cast state. This is attributed to the higher stability of the LPSO phase compared to other competing phases. The Al/Zn ratios for the phases in the heat-treated alloys and

Table 3 Average chemical compositions (at%) of the black, white, light gray, gray and dark gray regions in (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys after isothermal heat treatment at 450°C for 1000 h.

(a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	99.1	0.0	0.1	0.8
White region	11.4	52.7	2.6	33.3
Dark gray region (LPSO ①)	83.5	4.3	2.7	9.5
Light gray region (LPSO ②)	82.8	4.5	2.8	9.9
(b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	99.1	0.0	0.1	0.8
White region	15.3	47.8	4.5	32.4
Dark gray region (LPSO ①)	83.7	3.7	3.2	9.4
Light gray region (LPSO ②)	82.5	4.0	3.4	10.1
(c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$	Mg	Al	Zn	Gd
Black region	98.9	0.0	0.2	0.9
White region	12.0	47.9	6.0	34.1
Dark gray region (LPSO ①)	84.1	2.4	4.3	9.2
Light gray region (LPSO ②)	82.3	3.2	4.3	10.2

Fig. 7 X-ray patterns for (a) $\text{Mg}_{85}\text{Al}_4\text{Zn}_2\text{Gd}_9$, (b) $\text{Mg}_{85}\text{Al}_3\text{Zn}_3\text{Gd}_9$ and (c) $\text{Mg}_{85}\text{Al}_2\text{Zn}_4\text{Gd}_9$ alloys after isothermal heat treatment at 450°C for 1000 h.

Table 4 Mg–TM–RE ratio (at%) for each alloy after isothermal heat treatment at 450°C for 1000 h together with the ideal stoichiometric composition of the 14H and 18R LPSO phases.³⁾

Element	Mg	TM (Al+Zn)	RE(Gd)
Mg ₈₅ Al ₄ Zn ₂ Gd ₉	83.5	7.0	9.5
Mg ₈₅ Al ₃ Zn ₃ Gd ₉	83.7	6.9	9.4
Mg ₈₅ Al ₂ Zn ₄ Gd ₉	84.1	6.8	9.2
Ideal stoichiometry ³⁾	Mg	TM(Zn)	RE(Y)
14H LPSO	83.3	7.1	9.5
18R LPSO	80.6	8.3	11.1

Table 5 Comparison of Al/Zn ratio for different alloy compositions and phases after isothermal heat treatment at 450°C for 1000 h.

Actual composition (at%)	Al / Zn ratio				
	Alloy composition	14H LPSO	18R LPSO	Al ₂ Gd	α -Mg
Mg _{87.3} Al _{3.6} Zn _{2.0} Gd _{7.4}	1.7	1.6	1.6	20.3	0.13
Mg _{85.5} Al _{3.0} Zn _{3.0} Gd _{8.5}	1.0	1.1	1.2	10.7	0.03
Mg _{85.7} Al _{2.0} Zn _{4.0} Gd _{8.3}	0.5	0.6	0.7	7.9	0.02

those based on the actual alloy compositions are summarized in Table 5. Figure 8 shows the Al/Zn ratio for each phase as a function of that based on the alloy composition. It is noteworthy that the relationship is almost linear for the LPSO phases, but not for the α -Mg and Al₂Gd phases. This implies that Al and Zn atoms can easily substitute for each other at the same sites in L₁ clusters in the LPSO phase, whereas this is difficult in the α -Mg and Al₂Gd phases. As seen in Figs. 1, 4, 5 and 7, the fraction of the LPSO phase increases with increasing Zn content. This is attributed to destabilization of the Al₂Gd phase in Zn-rich alloys relative to the LPSO phase because of the difficulty of Zn substitution for Al. In Zn-rich alloys, Al₂Gd is considered to be no longer one of the primary phases that suppress the formation of the LPSO phase during solidification in Mg–Al–Gd alloys. Similarly, the Mg₃Gd phase present in the lamellar regions only in the as-cast state is thought to have almost no Al solubility and to become less stable with increasing Al content. This implies that the addition of Al to Mg–Zn–Gd alloys results in the relative stabilization of the LPSO phase. Therefore, a transition from Type II to Type I is expected because the Mg₃Gd is considered to be no longer one of the primary phases that suppress the formation of the LPSO phase during solidification in Mg–Zn–Gd alloys. It can therefore be concluded that the relative destabilization of competing phases may be the main factor determining the type of LPSO-containing Mg alloy formed.

4. Concluding Remarks

Mg–Al–Zn–Gd quaternary alloys were investigated to clarify the type (Type I or Type II) of LPSO phase formed and to discover what factors determine the LPSO phase. The main conclusions of the present study are as follows.

Fig. 8 Relationship between Al/Zn ratio for actual alloy composition and that for each phase in the alloys after isothermal heat treatment at 450°C for 1000 h. (b) is a magnified version of (a).

- (1) Addition of Zn to a Type II ternary Mg–Al–Gd alloy or addition of Al to a Type II ternary Mg–Zn–Gd alloy results in a Type I quaternary Mg–Al–Zn–Gd alloy.
- (2) The chemical composition of the 18R LPSO phases in the as-cast quaternary alloys is about Mg₉₀TM₄RE₆, in which the Mg content is much larger than the stoichiometric value.
- (3) The 14H LPSO phase is considered to be an equilibrium phase at 450°C for the quaternary alloys employed in the present study.
- (4) Al and Zn atoms easily substitute for each other in the LPSO phase, whereas this is difficult in the α -Mg, Al₂Gd and Mg₃Gd phases, suggesting relative destabilization of these phases by the additional elements (Al or Zn).
- (5) The relative stability of the LPSO phase against competing phases such as Al₂Gd and Mg₃Gd may be the main factor determining the type of LPSO-containing Mg alloy formed.

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