Neutron Diffraction on LPSO Structure in Mg–Zn–Y Alloys

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Crystal structure, phase fraction and texture of long period stacking ordered structure (LPSO) phase in ternary Mg–Zn–Y alloys have been investigated by analysis on time-of-flight (TOF) neutron diffraction profiles using the Rietveld method. It has been shown that the LPSO phase in the alloys is 18R-type structure of space group $P3_212$ with $a = 1.1182(0)$ nm and $c = 4.7032(5)$ nm. The LPSO phase shows very strong $[10\bar{1}0]$ texture parallel to the growth direction in a directionally-solidified crystal alloy. [doi:10.2320/matertrans.MI201215]

(Received December 25, 2012; Accepted March 12, 2013; Published April 26, 2013)

Keywords: long period stacking ordered structure, magnesium alloy, neutron diffraction, crystal structure

1. Introduction

Recently, ternary Mg–Zn–Y alloys with the microstructure consisting of α -Mg and long period stacking ordered structure (LPSO) phases, which exhibit excellent mechanical properties have attracted great attention.^{1–3)} The mechanical properties of these magnesium alloys have been widely studied, and the results reported that the LPSO phase plays an important role in the deformation process. Hence, to clarify the crystal structure of LPSO phase is the key point to understand the strengthening mechanisms of these alloys. A lot of effort has been devoted to study the crystal structure of the LPSO phase by high-resolution transmission electron microscopy (HRTEM), atomic-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS), etc. Some significant crystal structure models have been built.^{4–6)} Neutron diffraction acts as a powerful tool which can provide the average crystal information in bulk volumes up to several cubic centimeters, however, it has not been employed to study the LPSO structure until now. In this study, the crystal information such as crystal structure of LPSO phase, phase fraction, and texture in ternary Mg–Zn–Y alloys was investigated by time-of-flight (TOF) neutron diffraction technique.

2. Experimental Procedure

The chemical composition and manufacturing method of four specimens studied in this work are listed in Table 1.

The neutron diffraction experiments were performed by the engineering neutron diffractometer, TAKUMI at Japan Proton Accelerator Research Complex (J-PARC). The geometrical arrangement of TAKUMI is shown in Fig. 1, where the cylindrical specimen is set up on a sample table horizontally with its axial direction at +45 degree to the incident neutron beam, and two detector banks are used to collect the diffracted neutron patterns at +90 and –90 degrees relative to the incident beam, respectively. That is, the +90 bank collects the diffraction profiles corresponding

Table 1 Chemical composition and manufacturing method of alloys studied.

Specimen No.	Chemical composition (at%)	Manufacturing method
S0	Mg ₈₅ Zn ₆ Y ₉	(1)
S1	Mg ₉₇ Zn ₁ Y ₂	(2)
S2	Mg ₈₅ Zn ₆ Y ₉	(2)
S3	Mg ₈₉ Zn ₄ Y ₇	(2) + (3)

(1) Directionally-solidified crystal produced by the Bridgman technique.⁷⁾

(2) High frequency induction heating in an argon atmosphere.⁸⁾

(3) Extrusion: Extrusion ratio of 10, extrusion temperature of 723 K.

to the axial direction ($Q//$), while –90 bank to the radial direction ($Q\perp$) of the specimen. Details of the diffraction instrument are similar to that published elsewhere.⁹⁾ Here, the d -range covered by TAKUMI was 0.06–0.33 nm.

3. Results and Discussions

Figure 2 shows the measured and fitted neutron diffraction patterns in the radial direction of specimen S2 and the calculation on profile of 18R LPSO phase by using the crystal structure model of $P3_212$, which was reported in Ref. 6). Z-Rietveld code¹⁰⁾ was employed for Rietveld refinement. Most peaks were fitted very well except two peaks at 0.247 and 0.236 nm (Fig. 2(b)). However, these two peaks were absent in the diffraction profile of specimen S0, which was produced by the Bridgman technique (see Fig. 3(a)). The $(01\bar{1}1)$ reflection in α -Mg phase with the d -spacing of 0.245 nm has the highest diffraction intensity. Hence, the unfitted peak at 0.247 nm could be the $(01\bar{1}1)$ reflection of α -Mg, while the d -spacing expanded from 0.245 to 0.247 nm due to the solution of Zn and Y in the material. In previous reports,^{5,11,12)} a 14H-type LPSO phase could be formed after heat treatment in the temperature range 623–773 K in Mg–Zn–Y alloys. The peak at 0.236 nm should be the $(\bar{2}4\bar{2}8)$ reflection of 14H-LPSO phase, which is the second strongest diffraction peak in d -range measured in this study, assuming the crystal structure model in Ref. 6). It indicates that a third phase of a small amount consisting of the 14H-type LPSO phase already exists in the as-cast Mg–Zn–Y alloys. Hence, a modified refinement was performed in company with the 18R-type

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Fig. 1 (a) Photograph of the specimen in the measured place and (b) diffraction geometry of TAKUMI diffractometer.

LPSO, 14H-type LPSO and α -Mg phase, and R factor was 9.4% after fitting. The lattice parameters of 18R-type LPSO obtained from the Rietveld refinement are: $a = 1.1182(0)$ nm and $c = 4.7032(5)$ nm.

Figure 3 shows the diffraction profiles of specimen S0, S1, S3 with different Zn and Y addition. The solid arrows show the reflections of LPSO phase and the hollow arrows stand for α -Mg. The phase fraction of LPSO phase was calculated by employing the Rietveld refinement. There is no α -Mg and 14H-type LPSO phase in specimen S0 ($\text{Mg}_{85}\text{Zn}_6\text{Y}_9$) because of the absence of their diffraction peaks, with 100% 18R-LPSO phase contained in this specimen. In specimen S3 $\text{Mg}_{89}\text{Zn}_4\text{Y}_7$ and S1 $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$, there are 78.2 and 19.7% 18R-LPSO phase, respectively. It is similar to the results from microstructure observation.^{11,13} The LPSO phase fraction increased with the increase of Zn and Y content.

Figures 4(a) and 4(b) show the neutron diffraction patterns along axial and radial directions of specimen S0 at 2 mm position from the rod bottom (see Fig. 5(a)). Figure 4(c) plots the simulation results of the 18R-LPSO structure, $P3_212$ reported in Ref. 6). By comparing on the measured diffraction patterns with the simulated one, the peak positions are in good agreement with each other. Only a strong (6060) peak appears along axial direction while very weak (6060) and (60618) peaks in radial direction, which indicates very strong $[10\bar{1}0]$ texture parallel to growth direction in the LPSO phase.

In order to clarify the texture distribution along the growth direction, a square neutron beam with size of $2\text{ mm} \times 2\text{ mm}$

Fig. 2 (a) Measured (circles) and calculated (continuous line) profiles of 18R-LPSO phase in the crystal structure $P3_212$. Tick marks indicate the positions of allowed reflections. The difference curve (Iobs.–Ical.) is shown at the bottom. (b) Details in region from 0.23 to 0.26 nm where two unfitted peaks coming from 14H LPSO and α -Mg phase, respectively.

Fig. 3 Neutron diffraction profiles of specimen (a) S0 $\text{Mg}_{85}\text{Zn}_6\text{Y}_9$, (b) S3 $\text{Mg}_{89}\text{Zn}_4\text{Y}_7$ and (c) S1 $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$. The peak positions of 18R-LPSO phase are marked by solid arrows and the hollow arrows are for α -Mg phase.

was employed to measure the diffraction profile evolution along the axial direction of specimen S0 with a measurement interval of 3.5 mm (Fig. 5(a)). The structure started to grow from the tapered end. As shown in Figs. 4(a) and 4(b), the diffraction intensity of the peaks in axial and radial direction in the d-region marked by dashed box in the Fig. 4(b) are quite different, which was selected to evaluate changes of texture. Figure 5(b) shows the change of diffraction profiles in radial direction of specimen at different position along

Fig. 4 Neutron diffraction profiles in (a) axial and (b) radial direction of S0 $\text{Mg}_{85}\text{Zn}_6\text{Y}_9$ alloy compared with (c) a simulation result of 18R-LPSO structure.

growth direction. The intensity of peak $(60\bar{6}0)$ decreases with increasing distance to the tapered end of specimen in the range of 0–38.5 mm, while no obvious change was observed in the neighboring peak $(4\bar{2}23)$. The intensity of peak $(60\bar{6}0)$ becomes very weak from 42 mm. It indicates that the texture along the growth direction is inhomogeneous, a strong $[10\bar{1}0]$ texture parallel to growth direction appeared after specimen growth of approximate 42 mm from the taper end.

4. Conclusion

The crystal information of the Mg–Zn–Y alloys was investigated by TOF neutron diffraction, the obtained results are summarized as follows,

(1) The crystal structure of 18R-LPSO, $P3_212$, $a = 1.1182(0)$ nm and $c = 4.7032(5)$ nm, is in good agreement with the measured neutron diffraction profiles of LPSO phase in Mg–Zn–Y alloys.

(2) The $\text{Mg}_{85}\text{Zn}_6\text{Y}_9$ specimen produced by high frequency induction heating method in an argon atmosphere consists of 18R-LPSO, a small amount of 14H-LPSO and α -Mg phases.

(3) The LPSO phase volume fraction increased with increasing of Zn and Y content.

(4) In directionally-solidified $\text{Mg}_{85}\text{Zn}_6\text{Y}_9$, strong $[10\bar{1}0]$ texture parallel to the growth direction in the LPSO phase appeared after growth of approximate 42 mm from the head.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (Project: “Materials Science on Synchronized LPSO Structure —The Evolution of the Material Science for Innovative Development of the Next-Generation Lightweight Structure Materials—”) from the Ministry of Education, Culture, Sports, Science and Tech-

Fig. 5 (a) The measured S0 specimen of directionally-solidified crystal $\text{Mg}_{85}\text{Zn}_6\text{Y}_9$. (b) Changes of neutron diffraction profiles of 18R-LPSO $(60\bar{6}0)$ along the growth direction of specimen S0.

nology of Japan. The authors thank Kawamura laboratory and Hagihara laboratory for providing the specimens.

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