Experimental Study on Phase Equilibria in the Vicinity of X, W and H Phases in the Mg–Zn–Y Ternary System

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Three Mg–Zn–Y ternary alloys in the vicinity of X, W and H phases were prepared and were isothermally heat treated at 833, 793, 723 and 673 K to attain thermodynamic equilibrium. The microstructure was observed using electron probe microanalysis and transmission electron microscopy, and the chemical compositions of the equilibrium phases were analyzed using wavelength dispersive X-ray spectroscopy. The crystal structure of the W and H phases were analyzed using X-ray diffraction, electron back scattering diffraction and electron diffraction pattern obtained by transmission electron microscopy. The Mg–Zn–Y ternary phase diagrams of the isothermal section were also calculated using the Thermo-Calc to compare with the experimental results. The X phase was found to be solidified in high-Mg alloys not in a manner of eutectic reaction as reported previously but in a manner of peritectic reaction. The W phase has a Heusler (L21) type crystal structure with a stoichiometric composition of Mg2ZnY, and fine mesh texture composed of α (Mg) and W phases was occasionally observed in non-equilibrium solidified parts, implying that the transient W phase has potential to be utilized as an additional strengthening phase. The equilibrium chemical composition of the H phase with a hexagonal crystal structure (P6/mmc) was found to be different from that of the previous reports.

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1. Introduction

Mg alloys, as the lightest practical metallic materials, have been applied in various fields to reduce the weight of products.1) In recent years, attention has been concentrated on the Mg–Zn–Y ternary alloy due to its remarkably high yield strength of 610 MPa, ductility and adequate strength at elevated temperatures of the Mg97Zn1Y2 (at%) alloy compared with conventional Mg alloys.2–4) Although the strengthening mechanism of Mg–Zn–Y alloys is still under investigation, it is considered to be mainly due to grain size refinement in Mg solid solution (α phase) and kinking strengthening by an intermediate phase (X phase; Mg12Zn3Y1)3–5) which has distinctive long-period stacking ordered (LPSO) structures that vary with alloy composition or heat treatment.5) On the other hand, an intermetallic compound (W phase; Mg2Zn1Y2) has also received attention in recent years as a new strengthening phase in Mg–Zn–Y ternary alloys in addition to the α and X phases.7,8) Authors have reported that the X phase is not solidified in a manner of eutectic reaction as reported previously,9) but in a manner of peritectic reaction. Moreover, the W phase is transiently formed from the liquid phase in high temperatures, and is disappeared after the subsequent isothermal heat treatment. This implies that the W phase has potential to be utilized as an additional transient strengthening phase in high-Mg alloys. Therefore, it is important to control the amount of W phase for alloy design and microstructural control in the Mg–Zn–Y ternary system.

The establishment of a phase diagram is crucial for efficient alloy development and optimization of manufacturing processes. However, only a few attempts have so far been made at establishing the Mg–Zn–Y ternary phase diagram.10–15) Thus the phase diagram still requires clarification, especially in the vicinity of not only the X phase but also the W and H (Mg70Zn15Y15) phases, which affect phase equilibria including the α and X phases. Authors have recently reported that the W phase has a Heusler (L21) type crystal structure with a stoichiometric composition of Mg2ZnY1, and that only Mg and Zn in the W phase may be substituted for each other.16) However, the equilibrium H phase could not be identified only by the chemical composition because the reported chemical compositions of the H, I (Mg30Zn60Y10) and Z (Mg28Zn65Y7) phases are very close to each other.13) Shown in Fig. 1 are the previously reported chemical compositions of the H phase13–15,17) together with the calculated phase diagram of the isothermal section at 773 K in the Mg–Zn–Y ternary system using Thermo-Calc.18) Although the reported value by Deng et al.17) is at a different temperature from the other three reported values, there is considerable discrepancy among them. Therefore, further investigation is necessary to establish phase equilibria including the X, W and H phases, for control of the microstructure.

In the present study, three Mg–Zn–Y ternary alloys including at least one of the X, W and H phases were prepared and were isothermally heat treated at various temperatures to reach thermodynamic equilibrium. After isothermal heat treatment, the microstructure and chemical compositions of the equilibrium phases of the alloys were investigated in order to establish phase equilibria in the vicinity of the X, W and H phases. Particular focus was placed on the equilibrium chemical compositions and the crystal structure of the H phase.

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2. Experimental Procedure

Master ingots of three Mg–Zn–Y ternary alloys were prepared from high-purity raw materials and a raw alloy: 99.95% Mg bar, 99.5% Zn sheet and small pieces of 99.9% Y and a Mg–30 mass% Y alloy. These metals were melted in a 30.5-mm-diameter graphite crucible using a high-frequency induction furnace under a high-purity argon atmosphere, and were then cast into a steel mold and furnace cooled for approximately 2 h. The weight of each master ingot was ca. 100 g. Nominal chemical compositions of the alloys were approximately 2 h. The weight of each master ingot was were then cast into a steel mold and furnace cooled for

30.5-mm-diameter graphite crucible using a high-frequency induction furnace under a high-purity argon atmosphere, and were then cast into a steel mold and furnace cooled for approximately 2 h. The weight of each master ingot was ca. 100 g. Nominal chemical compositions of the alloys were Mg97.0Zn1.3Y1.7, Mg53.0Zn36.0Y11.0 and Mg25.0Zn58.0Y17.0 (at%). The chemical compositions of the alloys were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES). Samples for isothermal heat treatment were cut into 20-mm-long × 4 square mm pieces and were encapsulated in lidded 6-mm-diameter graphite crucibles to avoid the reaction between molten Mg and water during water-quenching. The samples were then encapsulated again in quartz tubes with high-purity argon gas and were isothermally heat treated at 833, 793, 723 and 673 K for 2–2273 h to reach thermodynamic equilibrium. The isothermal heat treatment conditions for each alloy are tabulated in Table 1.

After isothermal heat treatment, the samples were quenched in water. The microstructure of each sample was observed using an electron probe microanalyzer (EPMA; JEOL JXA-8200) and transmission electron microscope (TEM; JEOL JEM-2000FX), and the chemical compositions of the equilibrium phases were analyzed using wavelength dispersive X-ray spectroscopy (WDS). In addition, the crystal structure of the W and H phases were analyzed using X-ray diffractometer (XRD; Rigaku SmartLab), electron back-scattering diffraction (EBSD) installed in field emission scanning electron microscope (FE-SEM; JEOL JSM-6500F) and electron diffraction pattern obtained by TEM. Finally, the phase equilibria and the equilibrium chemical compositions of the H phase for each sample are summarized.

The Mg–Zn–Y ternary phase diagram of the isothermal section at 723 K was also calculated using the Thermo-Calc software package with an CALPHAD thermodynamic database, which has been under development by the present authors, and were compared with the experimental results in the present study.

3. Results and Discussions

The analyzed chemical compositions of nominal Mg97.0–Zn1.3–Y1.7, Mg53.0–Zn36.0–Y11.0 and Mg25.0–Zn58.0–Y17.0 alloys were Mg97.2Zn1.3Y1.5, Mg50.7Zn37.4Y11.9 and Mg21.8Zn59.4–Y18.8 (at%), respectively, which were adopted to distinguish the alloys.

Figure 2 shows backscattered electron images (BEIs) and analyzed chemical compositions of the black and gray regions for the Mg97.2Zn1.3Y1.5 alloy after the isothermal heat treatment at 833 K. Figure 3 shows the chemical compositions of black and gray regions for each alloy after isothermal heat treatment at 833 K.

Fig. 1 (a) The calculated phase diagram of the isothermal section at 773 K using Thermo-Calc and (b) previously reported chemical compositions of the Mg–Zn–Y ternary phase diagram of the isothermal section at 773 K was also calculated using the Thermo-Calc software package with an CALPHAD thermodynamic database, which has been under development by the present authors, and were compared with the experimental results in the present study.

![Phase Diagram](image)

**Table 1** Isothermal heat treatment conditions for each alloy.

<table>
<thead>
<tr>
<th>Analyzed chemical composition (at%)</th>
<th>Holding time, t/h</th>
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<tbody>
<tr>
<td>Mg97.2Zn1.3Y1.5</td>
<td>833 K  793 K  723 K  673 K</td>
</tr>
<tr>
<td>Mg50.7Zn37.4Y11.9</td>
<td>2.0  72 — —</td>
</tr>
<tr>
<td>Mg21.8Zn59.4Y18.8</td>
<td>24  300  2273  2000</td>
</tr>
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Fig. 2 BEIs and analyzed chemical compositions of the black and gray regions for the Mg97.2Zn1.3Y1.5 alloy after the isothermal heat treatment at 833 K.
schematically illustrated in Fig. 3. The $\alpha$ phase was seemingly solidified as a primary phase from the liquid (Fig. 3(a)). During the subsequent quenching, the $X$ phase appeared at the surface of the $\alpha$ phase and presented oriented crystal growth in a manner of peritectic reaction,\(^9\) and thus surface asperity of the $\alpha$ phase was formed (Fig. 3(b)). Finally, the $\alpha$-$W$ eutectic lamellar structure was produced from the remaining concentrated liquid (Fig. 3(c)). Figure 4 represents a TEM bright field image (BFI) for mesh texture obtained in the present study. The chemical compositions of the black and white parts were analyzed using energy dispersive X-ray spectroscopy (EDS) and are also indicated in Fig. 4. The results represent that black and white parts are considered to be the $\alpha$ and $W$ phases, respectively. As was indicated in our previous study,\(^9\) the $W$ phase in the Mg$_{97.2}$Zn$_{1.3}$Y$_{1.5}$ alloy was completely disappeared after the isothermal heat treatment at 793 K. It implies that the $W$ phase is considered to be in equilibrium with the $\alpha$ and $X$ phases only in high temperatures, and the transient $W$ phase has potential to be utilized as an additional strengthening phase in this alloy.

Shown in Fig. 5 is a BEI for the Mg$_{50.7}$Zn$_{37.4}$Y$_{11.9}$ alloy after the isothermal heat treatment at 723 K. The microstructure is composed of black, dark gray and light gray regions. The chemical compositions of these three regions were analyzed using WDS and are also represented in Fig. 5. As a result of analyzed chemical compositions, the black region is considered to be the $\alpha$ phase, while dark gray and light gray regions are not identified because their chemical compositions were not analyzed.
compositions are rather similar to each other, and are not the same as the reported values. The subsequent analysis of a crystal structure using EBSD was thus conducted. Figure 6 represents a BEI and an inverse pole figure (IPF) map for a bcc crystal structure of this sample. The dark gray regions in Fig. 5 such as inside rectangle in Fig. 6 were painted in IPF map, indicating that it was identified as a bcc-based phase, while the light gray regions in Fig. 5 such as inside ellipsoid in Fig. 6 were not. Therefore, it could be concluded that the dark gray region was the $W$ phase, which has a bcc-based Heusler ($L_21$) type crystal structure with a stoichiometric composition of $\text{Mg}_1\text{Zn}_2\text{Y}_1$. Shown in Fig. 7 are the experimental electron diffraction pattern from the light gray region obtained by TEM and the calculated one for the same incident direction using CrystalMaker software package with literature data by Deng et al. They are in fairly good agreement, and thus it seems reasonable to conclude that the light gray region is the $H$ phase, which has the same hexagonal crystal structure as the previous report (P6$_3$/mmc). However, as shown in Figs. 1 and 5, the chemical composition of the $H$ phase in the present study is different from the reported value by Deng et al.

Figure 8 represents a BEI for the $\text{Mg}_{21.8}\text{Zn}_{59.4}\text{Y}_{18.8}$ alloy after the isothermal heat treatment at 723 K. The microstructure is composed of dark gray and light gray regions, which show relatively complicated shapes with a size almost comparable to the probe diameter of the EPMA. Therefore, chemical compositions from many (170) points were randomly selected and analyzed using WDS as shown in Fig. 9 to determine the tie-line between the two equilibrium phases. Almost all the data are on a line with a deviation of about 1 at%, which might be in the allowable limit of the accuracy of the analysis by WDS. Finally, the chemical composition at each end of the line was adopted as the equilibrium one of each phase, and is represented in the figure. The calculated phase diagram of the isothermal section at 723 K using Thermo-Calc is also represented in Fig. 9. Although the chemical compositions of the $H$ phase are slightly different between the experimental value and calculated one, the experimentally determined two equilibrium phases are considered to be the $W$ and $H$ phases from their chemical compositions. Shown in Fig. 10 are the X-ray diffraction patterns for the $\text{Mg}_{50.3}\text{Zn}_{37.4}\text{Y}_{11.9}$ and $\text{Mg}_{21.8}\text{Zn}_{59.4}\text{Y}_{18.8}$ alloys after the isothermal heat treatment at 723 K. The spectra for the $\alpha$, $W$ and $H$ phases and the $W$ and $H$ phases were clearly observed in the $\text{Mg}_{50.3}\text{Zn}_{37.4}\text{Y}_{11.9}$ and $\text{Mg}_{21.8}\text{Zn}_{59.4}\text{Y}_{18.8}$ alloys, respectively. Considering resultant analyzed chemical compositions in Fig. 5, it could be concluded that the dark gray and light gray regions in Fig. 8 were the $W$ and $H$ phases, respectively.
Equilibrium phases for each alloy were determined in a similar manner and are summarized in Table 2. The $H$ phase appeared as an equilibrium phase after isothermal heat treatment in the $\text{Mg}_{50.7}\text{Zn}_{37.4}\text{Y}_{11.9}$ and $\text{Mg}_{21.8}\text{Zn}_{59.4}\text{Y}_{18.8}$ alloys, and the analyzed equilibrium chemical compositions are represented in Fig. 11 with the previously reported ones.\textsuperscript{13–15,17} It was clarified that the equilibrium chemical composition of the $H$ phase in the same alloy was almost constant regardless of temperature, and that only the Mg and Zn contents in the $H$ phase varied a little with alloy composition, while the Y content was almost constant. This indicates that only Mg and Zn can substitute with each other in the $H$ phase. Li et al. reported that the $H$ phase had a ternary solubility of Mg in the $\text{YZn}_5$ phase by substitution of Zn.\textsuperscript{19} The results in the present study agree rather well with their report in terms of the Y content in the $H$ phase. The $H$ phase is different from that of the previous reports, especially for the Mg content, as shown in Fig. 11. As far as the present results, the equilibrium Y and Mg contents in the $H$ phase are approximately 16 and 22–26 at%, respectively.

The calculated phase diagram of the isothermal section at 723 K in the Mg–Zn–Y ternary system using Thermo-Calc is also represented in Fig. 11. As a result of the calculation, the $\text{Mg}_{50.7}\text{Zn}_{37.4}\text{Y}_{11.9}$ alloy was evaluated to be in the ternary phase equilibria of $\alpha$, $W$ and $I$ phases at 723 K, which is different from the experimental results in the present study. This alloy should be in the ternary phase equilibria of $\alpha$, $W$ and $H$ phases at 723 K.
and H phases at 723 K as described above. Therefore, the CALPHAD thermodynamic database should be modified, especially in the vicinity of the H phase as indicated by the dotted line in Fig. 11. The authors have been assessing it based on the experimental results obtained in the present study. The newly assessed database and the calculated phase diagrams in the Mg–Zn–Y ternary system using Thermo-Calc, which could be quite helpful for alloy design and microstructural control including the X, W and H phases will be represented in our next paper.

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REFERENCES