

Experimental study of phases I and H in selected (56-60)Zn-(29-35)Mg-(8-13)Y alloys after long-term annealing at 400°C

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Abstract. Five (56-60)Zn-(29-35)Mg-(8-13)Y alloys (metal compositions are given in at.%) were investigated after annealing at 400°C for 150h. In the investigation, the scanning electron microscopy equipped with energy dispersive X-ray spectroscopy and the X-ray diffraction were used. The alloys were selected with the intention to collect experimental data about the (I+H) phase equilibrium at 400°C and to show trends applicable in a refinement of the related isothermal section of the Zn-Mg-Y phase diagram. As a result, a specific isothermal section at 400°C of Zn-Mg-Y phase diagram is presented, showing present experimental results and related thermodynamic and experimental data available in literature.

1. Introduction

Even though Zn-Mg-Y alloys have been studied sporadically since nineties [1-8], the findings do not facilitate any exhaustive description of this system. For instance, Tsai et al. [1] described a stable icosahedral quasicrystalline phase (I-phase) in the $\text{Zn}_{60}\text{Mg}_{30}\text{Y}_{10}$ alloy, earlier reported by Luo et al. [3]. Langsdorf et al. [6] showed that this phase solidifies through a peritectic reaction and coexists with brittle intermetallic compounds in the Zn-rich Zn-Mg-Y alloys with the Y contents higher than 4 at.%. Besides the I-phase (symmetry $\text{Fm}\bar{3}\bar{5}$ [1,7]), other binary or ternary phases can also appear in the Zn-Mg-Y system. For instance, the hexagonal H-phase MgZn_3Y ($\text{P6}_3/\text{mmc}$ [9,10]), the cubic W-phase $\text{Mg}_3\text{Zn}_2\text{Y}_3$ ($\text{Fm}\bar{3}\text{m}$), the hexagonal Z-phase Mg_{12}ZnY ($\text{P6}_3/\text{mmc}$ [1,11]), or the orthorhombic Mg_7Zn_3 (Immm [7,12]). Based on experimental results, Tsai et al. [1] proposed partial isothermal sections of the Zn-Mg-Y phase diagram at temperatures 427°C, 500°C and 600°C, containing homogeneity ranges of ternary phases Z, W, H and I. The calculated isothermal sections of this diagram at 600 °C, 500 °C and 400 °C were reported by Grobner et al. [7].

A lack of experimental and calculated data related to the (I+H) area evoked the current study. Five Zn-Mg-Y alloys compositionally close to the (I+H) area were investigated experimentally at 400 °C to collect data applicable in a refinement of the related isothermal section.



2. Experimental procedure

The investigated alloys, $\text{Zn}_{56.7}\text{Mg}_{34.3}\text{Y}_9$, $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$, $\text{Zn}_{57.2}\text{Mg}_{29.9}\text{Y}_{12.9}$, $\text{Zn}_{56.8}\text{Mg}_{32.2}\text{Y}_{11}$, and $\text{Zn}_{59.6}\text{Mg}_{31.6}\text{Y}_{8.8}$, were prepared of pure metals in induction furnace under argon atmosphere. After casting, the samples were annealed at 400°C for 150 h and rapidly cooled in water to preserve their high-temperature microstructures. Particular microstructure constituents were observed and their metal compositions were determined by a JEOL JSM-7600F scanning electron microscope equipped with an Oxford Instruments X-max50 EDX spectrometer. An X-ray Panalytical Empyrean PIXCel 3D diffractometer with Bragg–Brentano geometry was used for phase identification. The characteristic $\text{CoK}\alpha_{1,2}$ radiation was generated at 40 kV and 40 mA. Measurements were done in the angular range 20° to 80°, with a step size of 0.0131° and the counting time 98 seconds per step.

3. Results

The microstructure constituents observed in the investigated alloys are listed in Table 1 by metal compositions and volume fractions. All of them were identified to be single-phase constituents comprising either I- or H-phases. In Figure 1 the microstructure of the $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$ alloy is recorded, being characteristic for all the alloys. Similarly, the characteristic XRD pattern of double-phase microstructures (see Table 1) correspond to the $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$ alloy (Figure 2). Besides the single-phase $\text{Zn}_{56.7}\text{Mg}_{34.3}\text{Y}_9$ alloy, the I-phase was found to dominate over the H-phase in all the alloys (Table 1).

Table 1. Metal compositions and other measured values of investigated alloys

alloy	colour of microstructure constituent	phase	atomic content in %			volume fraction in %
			Zn	Mg	Y	
$\text{Zn}_{56.7}\text{Mg}_{34.3}\text{Y}_9$	dark-grey	I	56.7 ± 0.1	34.3 ± 0.2	9.0 ± 0.2	100
$\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$	dark-grey	I	54.7 ± 0.4	35.3 ± 0.2	10.0 ± 0.2	80
	light-grey	H	65.3 ± 0.2	16.3 ± 0.2	18.4 ± 0.3	20
$\text{Zn}_{57.2}\text{Mg}_{29.9}\text{Y}_{12.9}$	dark-grey	I	53.8 ± 0.3	35.9 ± 0.2	10.3 ± 0.1	65
	light-grey	H	64.3 ± 0.2	17.4 ± 0.1	18.3 ± 0.3	35
$\text{Zn}_{56.8}\text{Mg}_{32.2}\text{Y}_{11}$	dark-grey	I	55.6 ± 0.4	34.7 ± 0.2	9.7 ± 0.2	95
	light-grey	H	62.5 ± 0.2	19.7 ± 0.4	17.8 ± 0.3	15
$\text{Zn}_{59.6}\text{Mg}_{31.6}\text{Y}_{8.8}$	dark-grey	I	59.5 ± 0.1	31.8 ± 0.2	8.7 ± 0.1	99
	light-grey	H	65.3 ± 0.4	16.4 ± 0.4	18.3 ± 0.3	1

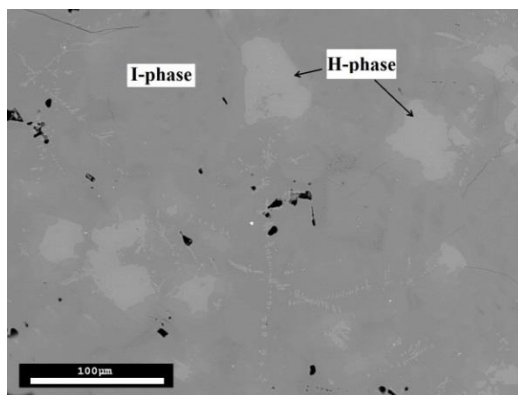


Figure 1. BEI/SEM image of microstructure of $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$ alloy after annealing at 400°C for 150 h. Dark- and light-grey areas correspond to I- and H-phases, respectively. Black areas are pores.

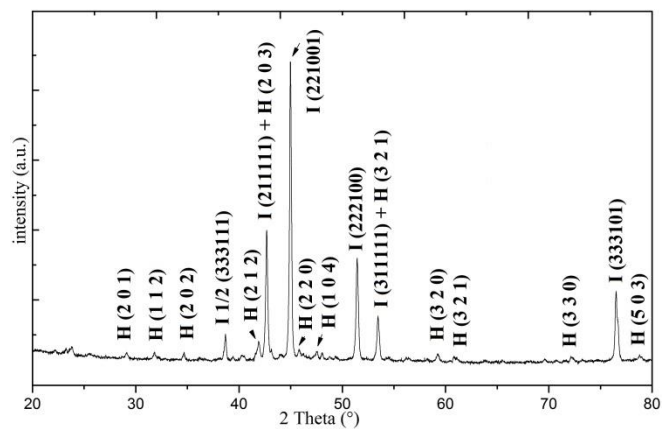


Figure 2. XRD pattern of $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$ alloy after annealing at 400°C for 150 h. Corresponding phase and diffracting plane are assigned to each peak.

4. Discussion

The experimental data obtained at 400°C for phases I and H in this work were compared with those published in literature for compositionally comparable alloys annealed at the same temperature [7,8]. All the relevant data are illustrated in Figure 3 in the form of a specific isothermal section at 400°C of the Zn-Mg-Y phase diagram. The most complex experimental data for the Zn-Mg-Y system were presented by Tsai et al. [1]. Since part of them was obtained at 427°C, that is temperature slightly higher than 400°C, a mathematical extrapolation was used to estimate presumed shapes of I and H areas at 400°C. In this procedure, data from the isothermal sections at 500 °C and 427°C [1] were taken into account. For convenience, the linear regression was used based on the following function [13]:

$$y(x^*) = y_{k+1} + \frac{x^* - x_{k+1}}{x_k - x_{k+1}}(y_k - y_{k+1}), \quad (1)$$

where x_k and x_{k+1} represent independent variables of x (temperature in this work), and y_k and y_{k+1} stand for dependent variables of y (concentration). The symbol x^* corresponds to the temperature to extrapolate. The obtained extrapolated areas for both the phases [1] were inserted into the specific isothermal section at 400°C, together with the thermodynamically predicted data [7], and present and earlier published experimental data [8], Figure 3.

An approximate homogeneity range of the H-phase was determined as (62-66)Zn-(16-20)Mg-(17-19)Y according to the data summarised in Table 1. The present experimental points are arranged in line, but they are localised at a higher Y level (about 18 at.%, Table 1) and in evidently shorter ranges of Zn and Mg contents (both about 5 at.%), as it was reported by Grobner et al. [7]. Similarly, the extrapolated homogeneity range of the H-phase ([1], Figure 3) enables variabilities in Zn and Mg contents inside ranges both of about 6 at.%. If compared to the present experimental data with the extrapolated data [1], the H-area proposed in the present work is shifted to higher Mg and Y contents, and to lower Zn contents. The shifts are not dramatic and could be caused by annealing conditions. For instance, the annealing time plays in this matter an important role, because shorter times lead to an insufficient homogenization and longer times can evoke evaporation of light elements from annealed samples. In the present work, the optimal duration of annealing was determined experimentally as 150 h. Annealing times used in the work [1] were not specified.

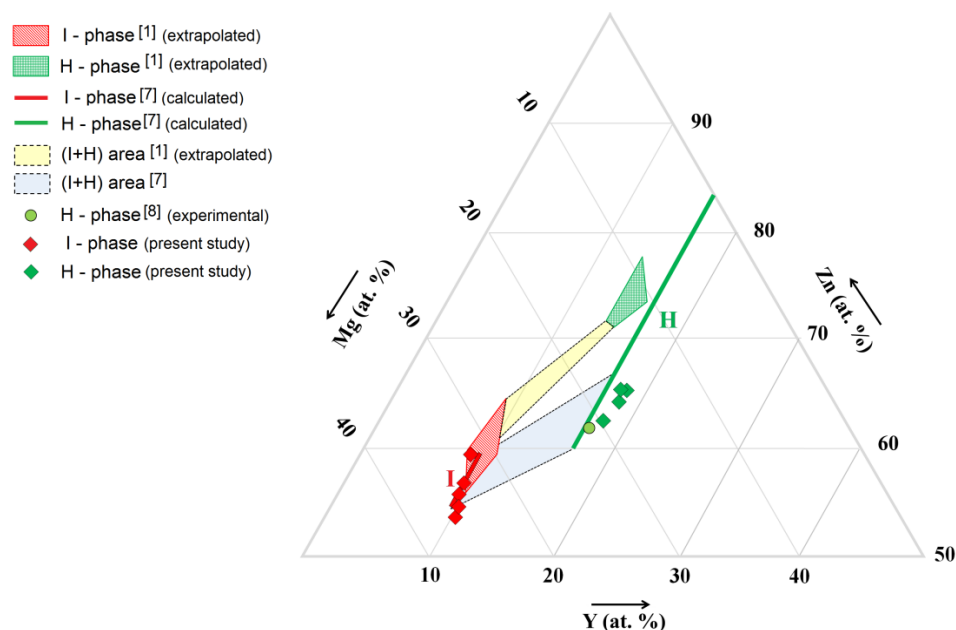


Figure 3. Specific isothermal section at 400°C of Zn-Mg-Y phase diagram to compare present experimental results with those available in literature (see legend for more detail description).

According to the present experimental results, an approximate homogeneity range of the I-phase was determined as (53-60)Zn-(31-36)Mg-(8-11)Y (Table 1). Positions of the I-area specified by extrapolated [1], predicted [7], and present experimental data correlate with each other very well (Figure 3). The former position is shifted only slightly to higher Zn and lower Mg contents. The results obtained in this work confirmed the earlier published finding about the compositionally limited I-area [1,7].

The thermodynamically predicted and the extrapolated (I+H) areas have no common point in the specified isothermal section (Figure 3). The experimental results both obtained in the present work and presented by Hamaya et al. [8] correlate better with the (I+H) position predicted thermodynamically by Grobner et al. [7].

5. Conclusions

The results obtained in the investigation of alloys $\text{Zn}_{56.7}\text{Mg}_{34.3}\text{Y}_9$, $\text{Zn}_{57.9}\text{Mg}_{29.8}\text{Y}_{12.3}$, $\text{Zn}_{57.2}\text{Mg}_{29.9}\text{Y}_{12.9}$, $\text{Zn}_{56.8}\text{Mg}_{32.2}\text{Y}_{11}$, $\text{Zn}_{59.6}\text{Mg}_{31.6}\text{Y}_{8.8}$ after annealing at 400°C for 150 h can be summarised as follows:

- The I-phase identified in all the investigated alloys was found to fall within the (53-60)Zn-(31-36)Mg-(8-11)Y area. This finding correlates with the data available in literature very well and confirms the suggestion about the compositionally limited I-area.
- The H-phase was found in double-phase microstructures only, coexisting with the I-phase. Its metal composition ranges within the (62-66)Zn-(16-20)Mg-(17-19)Y area.
- A specific isothermal section at 400°C of Zn-Mg-Y phase diagram is presented, showing both the present experimental results and the related results available in literature. It follows from the section that the (I+H) area determined experimentally in this work correlates with that predicted thermodynamically by Grobner et al. very well.

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