

# Hydrogen absorption in Mg–Y–Zn ternary compounds

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## Abstract

The ternary magnesium alloys  $Mg_{12}YZn$  and  $Mg_3Y_2Zn_3$  have been investigated from a hydrogen absorption point of view. The crystal structure, morphology and hydrogen absorption properties were investigated using X-ray diffraction, scanning electron microscopy, and differential thermal analysis. Hydrogenations were performed at temperatures between 25–400 °C and hydrogen pressures ranging from 70 kPa to 1 MPa. Both  $Mg_{12}YZn$  and  $Mg_3Y_2Zn_3$  decompose into  $MgH_2$ ,  $MgZn_2$  and  $YH_3$  at pressures above 1 MPa and 400 °C.

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## 1. Introduction

Alloying magnesium with other elements has shown to facilitate the diffusion of hydrogen through magnesium [1–5]. Chacon et al. have shown that the diffusion of hydrogen through the hydride layer increases with the amount of yttrium for solid solutions of yttrium in magnesium thin films, in the range from 0 to 17 atomic percents yttrium in the film [6]. The absorption of hydrogen in bulk  $Mg_{24}Y_5$  leads to a decomposition into  $YH_3$  and  $MgH_2$  while forming hydride nanostructures [7]. Alloying magnesium with yttrium and zinc might improve the hydrogen absorption properties of magnesium. Two intermediate phases,  $Mg_{12}YZn$  and  $Mg_3Y_2Zn_3$ , have previously been reported [8]. For cubic  $Mg_3Y_2Zn_3$  there are four different crystal structures considered and  $AlMnCu_2$  is the suggested type structure, although no full profile refinement has been performed. The present investigation considers new possible hydrogen absorbers in the Mg–Y–Zn system [8–11].

## 2. Experimental details

Two compositions in the Mg–Y–Zn system have been studied,  $Mg_{12}YZn$  and  $Mg_3Y_2Zn_3$ . The mother compounds were prepared by heating appropriate amounts of the elements (Mg 99.95%, Y 99.9% and Zn 99.999%) at 1000 °C for 30 min. The synthesis was performed under argon inside a sealed tantalum tube. The furnace used was a high frequency induction furnace [12].

X-Ray diffraction (XRD) measurements were performed using a Guinier–Hägg powder diffraction camera with  $CuK\alpha_1$  radiation and Si ( $a=5.43088$  Å,  $T=20$  °C) [13] as internal calibration standard. Diffraction intensities were measured with a linear position sensitive detector (PSD) on a STOE & CIE GmbH STADI transmission X-ray powder diffractometer. The crystal structure of  $Mg_3Y_2Zn_3$  was refined using the Rietveld method [14].

SEM images were recorded using a LEO 1550, scanning electron microscope. Elemental analysis was made using a LEO 440 scanning electron microscope with an EDAX EDS spectrometer. All samples were ground and placed on a carbon film. Quantitative analysis was performed using the ZAF correction method.

DTA/TG measurements were performed using a NETZSCH, STA 409 PC thermal analysis instrument. The samples were measured under flowing argon atmosphere. The measurements were made with increasing temperature from 25 to 500 °C, using a heating rate of 20 °C/min.

Hydrogen loading was performed in a high-pressure furnace that can have hydrogen pressures up to 6.7 MPa. All syntheses were performed without any exposure to air.

## 3. Results and discussion

At both mother compositions  $Mg_3Y_2Zn_3$  is the dominating phase, suggesting that this phase is the most stable ternary phase in the Mg-rich corner of the ternary phase diagram.

### 3.1. $Mg_{12}YZn$

All samples were multiphase containing  $Mg_{12}YZn$ , Mg and  $Mg_3Y_2Zn_3$ , as seen in Fig. 1. At temperatures above 300 °C,  $Mg_{12}YZn$  decomposes into Mg and  $Mg_3Y_2Zn_3$ .

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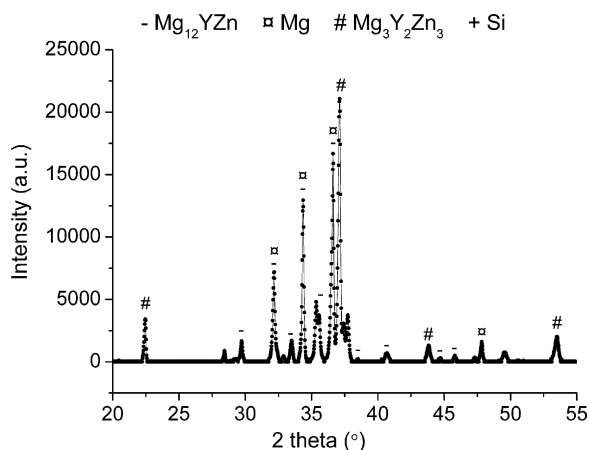


Fig. 1.  $Mg_{12}YZn$ . Above  $300^\circ C$  the compound decomposes completely to  $Mg_3Y_2Zn_3$  and Mg. Simulated from a Guinier–Hägg powder diffraction camera film.

### 3.2. $Mg_3Y_2Zn_3$

#### 3.2.1. Crystal structure determination

All  $Mg_3Y_2Zn_3$  samples contained small amounts of an unidentified phase. Results from XRD are illustrated in Fig. 2. Crystal structure refinements were made by the Rietveld method using the program FULLPROF [15]. The peak shape was described by the pseudo-Voigt function and the background was modeled by interpolation between fixed points. Eleven parameters were varied. Profile parameters:  $2\theta$  zero point (1); scale factor (1); profile shape parameter (1); half-width parameters (3); asymmetry parameters (2). Structural parameters: atomic occupations (1); lattice parameter (1); overall temperature factor (1).  $R_{Bragg}$  and  $R_{Profile}$  values are 4.23 and 5.91 %, respectively; see Table 1 for details. Refinements of the occupancies showed that the 4a position is filled with Y and the 4b position with Mg. The 8c position has a mixed occupation of Mg and Zn. It was thus confirmed that  $Mg_3Y_2Zn_3$  crystallizes in the ordered AlMnCu<sub>2</sub>-type structure, *Fm*-3*m* (225). However, after heat treatment at  $300^\circ C$  for four weeks new Bragg peaks appear and a phase transition seems to occur, which indicates that the AlMnCu<sub>2</sub>-type is a high temperature phase.

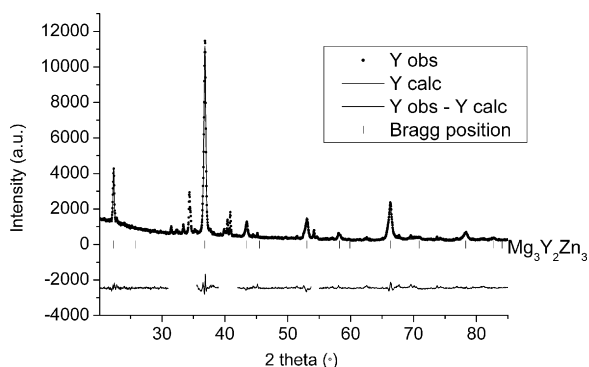


Fig. 2.  $Mg_3Y_2Zn_3$ . AlMnCu<sub>2</sub>-type structure, refined with the Rietveld method. Unidentified diffraction peaks were excluded in the structure refinement.

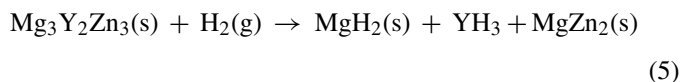
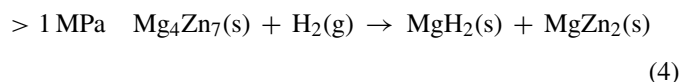
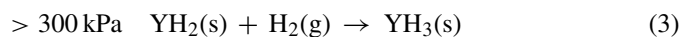
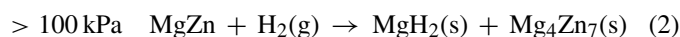
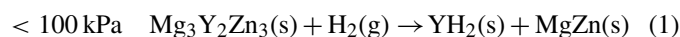
Table 1  
Final structural parameters

Atom	Wyckoff site	x	y	z	Occupancy
Y	4a	0	0	0	1
Mg1	4b	0.5	0.5	0.5	1
Mg2	8c	0.25	0.25	0.25	23.5(3)%
Zn	8c	0.25	0.25	0.25	76.5(3)%
$B_{overall}$ ( $\text{\AA}^2$ )	1.912(8)				
$R_{Bragg} = 4.23\%$	$R_{Profile} = 5.91\%$				

Estimated standard deviations in parentheses. Space group *Fm*-3*m*, unit cell parameter  $a = 6.9116(6) \text{\AA}$

#### 3.2.2. Hydrogen loading and unloading

During hydrogenation  $Mg_3Y_2Zn_3$  decomposes into  $YH_2$  and  $MgZn$  at hydrogen pressures below 100 kPa and  $400^\circ C$ , see reactions (1–5). Above 100 kPa magnesium starts to absorb hydrogen, which leads to the formation of  $Mg_4Zn_7$  and  $MgH_2$ . At pressures above 1 MPa  $Mg_4Zn_7$  decomposes into  $MgH_2$  and  $MgZn_2$ , as shown in Fig. 3. No solid solution of hydrogen in  $Mg_3Y_2Zn_3$  was observed.



The  $[YH_2]/[YH_3]$ -ratio is strongly dependent on the hydrogenation pressure. Below 300 kPa  $YH_2$  is the dominant phase.

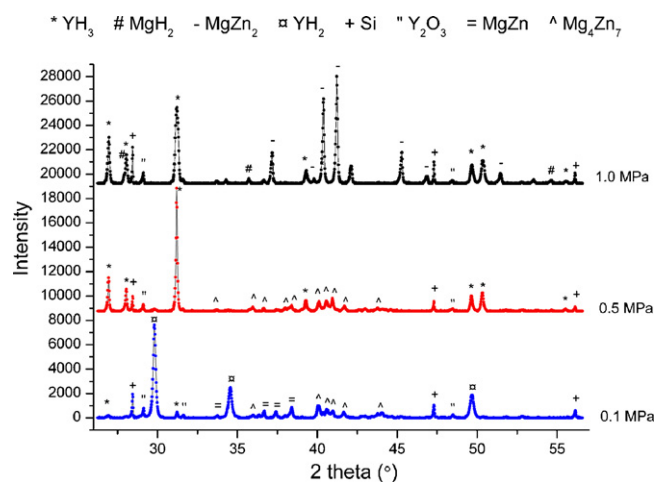


Fig. 3. Hydrogen loading at different pressures. Different stages of decomposition as the hydrogen pressure increases. From 0.1 to 0.5 MPa,  $YH_2$  transforms into  $YH_3$ , and from 0.5 to 1.0 MPa,  $Mg_4Zn_7$  transforms into  $MgH_2$  and  $MgZn_2$ . Simulated from a Guinier–Hägg powder diffraction camera film.

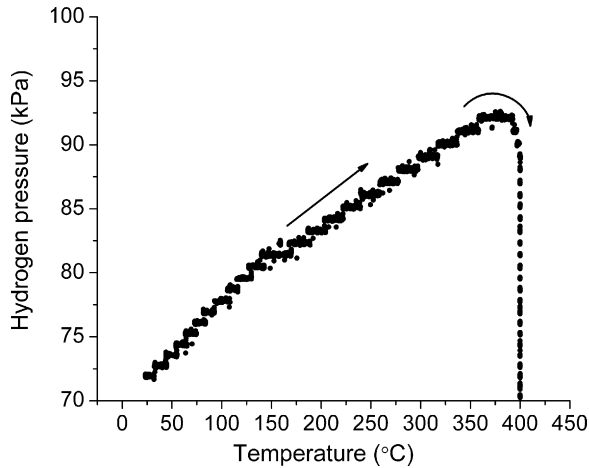


Fig. 4. Hydrogen pressure as a function of the applied temperature, inside a closed system. No hydrogen absorption below 400 °C is detected.

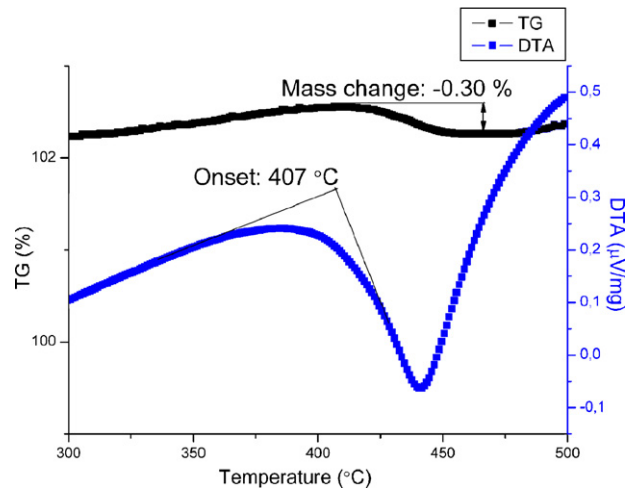


Fig. 5. DTA measurement of the fully hydrogenated sample. An endothermic peak at 406.9 °C, together with a decrease in mass indicates the desorption of hydrogen as structural changes take place, see reaction (6).

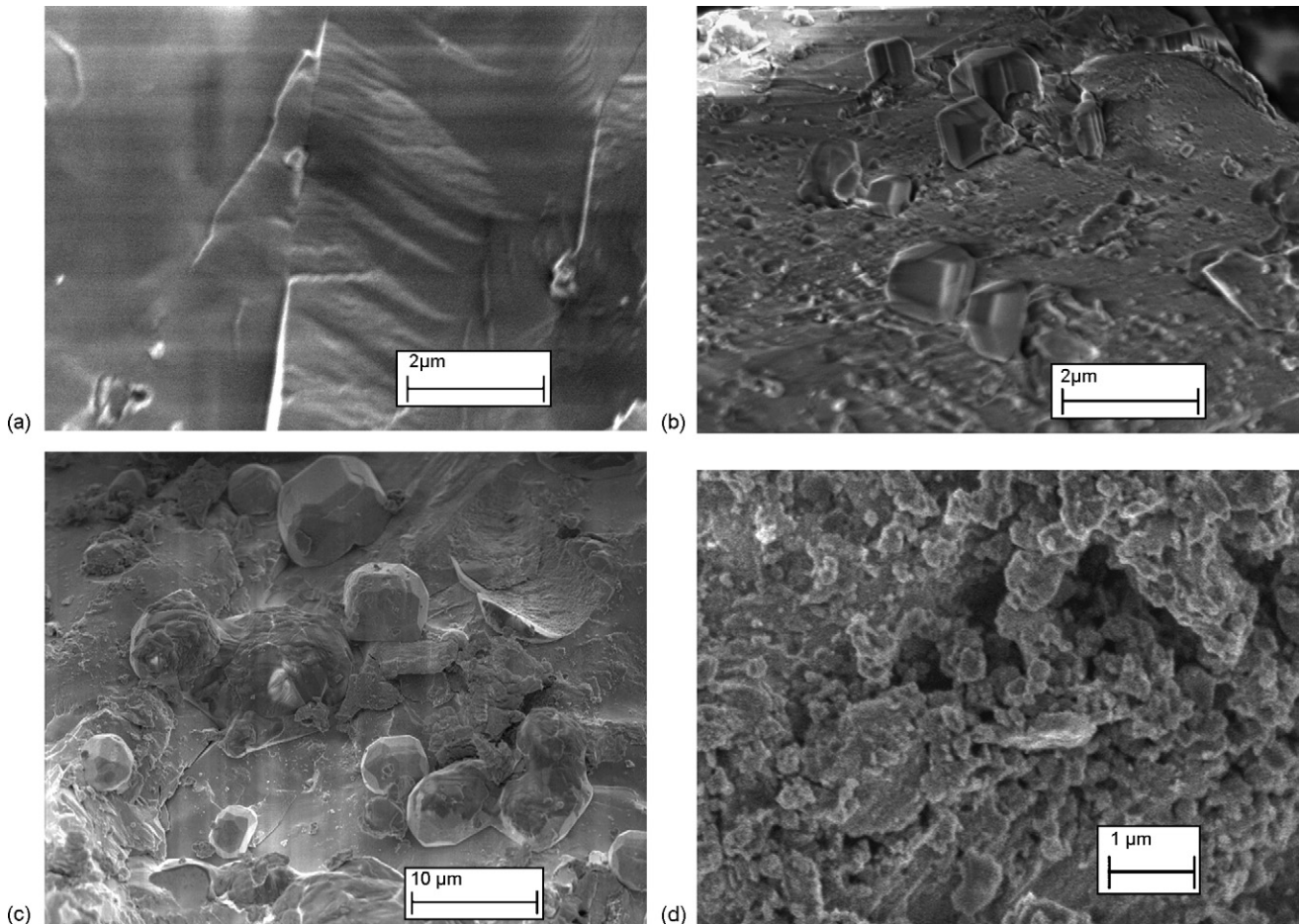


Fig. 6. SEM images of  $\text{Mg}_3\text{Y}_2\text{Zn}_3$  before and after hydrogenation. Figure (a) shows the mother compound with a flat crystalline surface. (b) Shows  $\text{Mg}_3\text{Y}_2\text{Zn}_3$  hydrogenated at 400 °C and 1 MPa, cycled two times for 10 h. Small polyhedral grains of  $\text{MgZn}_2$  start to grow on the surface of the mother compound, 0.5–1  $\mu\text{m}$  in diameter. (c) Is the sample cycled 10 times for 10 h. The polyhedral grains have grown significantly during cycling, up to 10  $\mu\text{m}$  in diameter. (d) Is the fine surface below the polyhedral grains. It is very porous and is constituted mainly of nanosized grains of  $\text{YH}_3$ .

To determine the hydrogen absorption temperature of the compound the hydrogen pressure was recorded as a function of the furnace temperature, Fig. 4 shows the P-T-scan during loading. There is no absorption of hydrogen below 400 °C, which is 100 °C higher than for Mg<sub>24</sub>Y<sub>5</sub> [7]. The measurements were performed in a closed system with a constant heating rate of 50 °C per hour.

The desorption properties were obtained from differential thermal analysis, in the temperature range 25–500 °C. DTA/TG measurements show a big endothermal peak together with a decrease in mass at 407 °C, Fig. 5. XRD analysis of the desorbed sample indicates formation of Mg<sub>3</sub>YZn<sub>6</sub>, see reaction (6).



### 3.2.3. Microstructure

The mother compounds and hydrogenated samples were analyzed with SEM to investigate the surface morphology. The mother compounds have a flat crystalline surface, as seen in Fig. 6(a). During hydrogenation, polyhedral grains of MgZn<sub>2</sub> form on the sample surface. After two 10 h cycles at 400 °C and 1 MPa hydrogen these polyhedral grains are about 0.5–1 μm in diameter, and after ten 10 h cycles they are approximately 10 μm in diameter. The fine structure of the surface below is very porous. It is formed by a large number of small grains, about 100 nm in size, formed mainly by YH<sub>3</sub>, as seen in Fig. 6(d).

## 4. Summary

Mg<sub>12</sub>YZn and Mg<sub>3</sub>Y<sub>2</sub>Zn<sub>3</sub> have been synthesized and hydrogenated. Mg<sub>3</sub>Y<sub>2</sub>Zn<sub>3</sub> has been confirmed to crystallize in the

AlMnCu<sub>2</sub>-type structure. It has been shown that Mg<sub>3</sub>Y<sub>2</sub>Zn<sub>3</sub> absorbs hydrogen while decomposing into MgH<sub>2</sub>, YH<sub>3</sub> and MgZn<sub>2</sub> at 400 °C and P(H<sub>2</sub>) above 1 MPa. During hydrogenation polyhedral MgZn<sub>2</sub> grains are formed on the surface of the mother compound. During desorption of hydrogen there is formation of Mg<sub>3</sub>YZn<sub>6</sub>. No hydrogen absorption or desorption is observed below 400 °C.

## Acknowledgements

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