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# Magnesium-Based Materials for Hydrogen Storage: Microstructural Properties

*Ryota Kondo and Takeshita T. Hiroyuki*

## Abstract

Magnesium (Mg) is hydrogenated as core-shell-type hydride. Therefore, increase of absorption capacity to the theoretical hydrogen capacity is still one of the most important issues for the hydrogen storage materials. In this study, the procedure of the core-shell structure as well as effect of Al concentration in Mg on the growth MgH<sub>2</sub> in Mg were investigated. MgH<sub>2</sub> was formed on the surface as well as inside of unreacted Mg core. The inside MgH<sub>2</sub> was formed in a granular form on Mg grain boundary and its size increased by applying plastic deformation. Thickness of the surface MgH<sub>2</sub> and size of the internal MgH<sub>2</sub> increased with an increase in hydrogenation time until the hydride surface was completely covered with MgH<sub>2</sub>. However, the growth of the surface and internal MgH<sub>2</sub> came to a halt after the surface was covered with MgH<sub>2</sub>. From these results, supplying H from metal side was dominantly contributed for growth of the surface and internal MgH<sub>2</sub> because diffusion rate of H in Mg was much higher than that in MgH<sub>2</sub>. In addition, the growth of internal MgH<sub>2</sub> as well as control of surface MgH<sub>2</sub> can contribute to the promotion of the complete hydrogenation of Mg-based hydrogen storage materials.

**Keywords:** magnesium, hydride, internal, three-dimension, surface, microstructure, distribution, grain boundary

## 1. Introduction

Magnesium (Mg) can store 7.6 mass% of hydrogen after formation of magnesium hydride (MgH<sub>2</sub>), which has attractive features for hydrogen storage material such as low cost, abundant resource and light weight [1]. However, dehydrogenation temperature is very high (560 K at 0.1 MPaH<sub>2</sub>) because MgH<sub>2</sub> is thermodynamically stable ( $\Delta_r H = -72.8 \pm 4.2 \text{ kJ mol}^{-1}$ ,  $\Delta_r S = -142 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ ) [2]. In addition, their hydrogenation/dehydrogenation kinetics is also lower, then the conditions of hydrogenation and dehydrogenation are severe and core-shell-type hydride is formed. In order to obtain MgH<sub>2</sub> completely from Mg and effectiveness of hydrogenation/dehydrogenation process, it is necessary to finely pulverize, severe plastic deformation, heat treatment for a long time, and addition of catalyst [3–10].

Mg is a metal and when it reacts with H<sub>2</sub>, MgH<sub>2</sub> forms an ionic bond and a weak covalent bond between Mg-H and the valence number of the ion is indicated as Mg<sup>1.91+</sup> and H<sup>0.26-</sup> [11]. The diffusion coefficient of H in MgH<sub>2</sub> is several order of magnitude lower when compared to that in Mg:  $D_{\text{H}}^{\text{Mg}} = 7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$

(300 K) in Mg and  $D_H^{\text{MgH}_2} = 1.1 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$  (305 K) in  $\text{MgH}_2$  [12, 13]. Based on these characteristics, powder Mg forms core-shell-type structure hydride,  $\text{MgH}_2$  as a shell and unreacted Mg remains in the core [14, 15] making progress of completely hydrogenation difficult. On the other hand, the hydrogen partial pressure has a great influence on the progress of the hydrogenation. When the hydrogen partial pressure is high, since  $\text{MgH}_2$  quickly covers the Mg powder surface, hydrogenation halts and the amount of hydride concentration decreases markedly, whereas when the hydrogen partial pressure is low, the time until  $\text{MgH}_2$  covers the Mg surface extends, then the hydride concentration increases [16]. Therefore, to accomplish the efficient hydrogenation, the process of hydrogenation should be revealed.

As a result of investigation aiming at efficient hydrogenation, some curious microstructural characteristics were obtained, that is shell of  $\text{MgH}_2$  and core Mg in addition to  $\text{MgH}_2$  in the core Mg. In the following,  $\text{MgH}_2$  on the surface layer named as  $\text{MgH}_2(\text{sur})$  and that in Mg core named as  $\text{MgH}_2(\text{int})$ .  $\text{MgH}_2(\text{int})$  formed in the Mg core is distinguished from  $\text{MgH}_2(\text{sur})$ . The particle size of  $\text{MgH}_2(\text{int})$  in  $\text{Mg}^{-6}$  mass%, Al-1 mass%, Zn alloy was larger than that in pure Mg. This result shows the grain size of  $\text{MgH}_2(\text{int})$  would be in correlation with Al concentration. Therefore, in this study, the influence of Al concentration in Mg on formation of  $\text{MgH}_2(\text{int})$  is clarified. To reveal the mechanism of  $\text{MgH}_2(\text{int})$  formation, coarse-type Mg-based hydrogen storage materials will be developed. Bulky hydrogen storage materials are attractive for handling, safety, and applying large module.

## 2. Materials and methods

Pure Mg manufactured by Rare Metallic Co., Ltd. and Mg- (3, 6, 9) mass%, Al-1 mass%, Zn alloy (hereinafter referred to as AZ31, AZ61, AZ91) manufactured by Sankyo Aluminum Co., Ltd. were used as samples. **Table 1** shows the composition of the samples.

As pretreatment, these samples were cut into prismatic shapes (8 mm in width, 5 mm in length, 3 mm in thickness) and then annealed, evacuated to  $2 \times 10^{-4}$  Pa in a stainless steel container, and replacing it with Ar gas (nominal purity 99.9999 vol%) was repeated several times and then heated under an Ar atmosphere of 3 kPa at a temperature of 723 K and a treatment time for 32.4 ks. For AZ61, annealed material (annealed) and 10% cold-rolled sample (cold-rolled) were subjected to hydrogenation (129.6 ks), respectively. An observation of the cross-sectional structure was carried out using an optical microscope (OM). Mg alloys are known to produce  $\text{MgH}_2$  at low temperature by applying severe plastic deformation [17]. **Table 2** shows the crystal grain sizes of annealed Mg and AZ31, AZ61, and AZ91 alloys.

Material	Composition (mass%)							
	Al	Zn	Mn	Si	Fe	Cu	Ni	Ca
Mg	0.0013	0.0024	0.012	0.022	0.0016	0.0031	0.0003	0.01
AZ31	2.80	0.80	0.32	0.022	0.003	0.003	<0.002	
AZ61	6.26	0.63	0.26	0.015	0.005	0.001	0.0007	
AZ91	8.70	0.82	0.22	0.007	0.005	<0.002	0.002	

**Table 1.**  
Composition of Mg and AZ31, AZ61, AZ91 alloys.

Material	Grain size, $d/\mu\text{m}$ (standard deviation)
Mg	250 (70)
AZ31	34 (3.4)
AZ61	36 (4.8)
AZ91	40 (3.5)

**Table 2.**  
*Grain size of annealed Mg and AZ31, AZ61, and AZ91 alloys.*

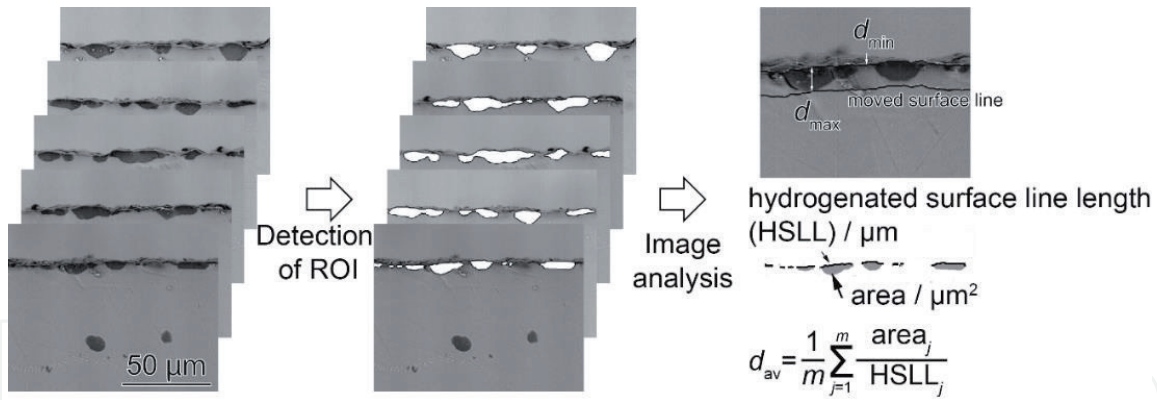
For hydrogenation of Mg alloys, these samples after annealing was dry-polished with SiC abrasive paper (# 320) in Ar gas circulation-type glove box (dew point  $-55$  to  $-70^\circ\text{C}$ , oxygen concentration 1 ppm or less), dry polished and immediately sealed in a stainless steel reaction vessel with a gasket made of stainless steel with Ag plating. In this reaction vessel, a sheath-type thermocouple was installed inside the container and the temperature in the vicinity of the samples was set. In order to generate  $\text{MgH}_2$ , hydrogenation was carried out at a hydrogen pressure of 3.61 MPa and a temperature of 673 K using a Siebert's type apparatus, and the nominal purity of the hydrogen gas used was 99.99999 vol%. The time was maintained in the range of 0–259.2 ks, and it is shown in parentheses here after.

The X-ray diffraction (XRD) instrument was used for the identification of  $\text{MgH}_2(\text{sur})$ . X-ray source of  $\text{CuK}\alpha$  with the tube voltage of 40 kV and the tube current of 15 mA was used. Microstructure of  $\text{MgH}_2$  was judged with presence or absence of charge up by using of scanning electron microscope (SEM). Crystal structure of  $\text{MgH}_2(\text{int})$  was investigated using an electron beam backscatter diffraction (EBSD) analyzer.

Samples for microstructural observation and analysis were cut at a position of 4 mm which is half in the width direction and roughly polished using SiC polishing paper (# 320  $\rightarrow$  # 800  $\rightarrow$  # 1000) followed by an  $\text{Al}_2\text{O}_3$  suspension (0.05  $\mu\text{m}$ ) or  $\text{SiO}_2$  suspension (0.04  $\mu\text{m}$ ). Dehydrated methanol was used as the extension liquid. The sample after polishing was promptly washed with an ultrasonic washing machine in dehydrated methanol. After washing, the sample was dried using pure nitrogen gas (99.99%).

Three-dimensional analysis of  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$  was carried out based on data constructed by a continuous serial sectional method, and an optical microscope (OM) was used for microstructural observation. Information at the position and observation depth was obtained by driving a pyramidal indentation into the sample using a Vickers hardness instrument. ImageJ was used for geometrical analysis and the construction of the three-dimension image [18, 19].

**Figure 1** described quantitative analysis method for obtaining information on the thickness of the  $\text{MgH}_2(\text{sur})$  layer. In the analysis, five or more images are selected and the  $\text{MgH}_2$  was observed as a dark area. The mean thickness ( $d_{\text{av}}$ ) of  $\text{MgH}_2(\text{sur})$  was calculated by dividing the area of each observed  $\text{MgH}_2(\text{sur})$  by the length of  $\text{MgH}_2(\text{sur})$  on the surface. Next, the shape of the surface is extracted. The surface line was translated in the direction of the inside. The maximum thickness of  $\text{MgH}_2(\text{sur})$  was evaluated as the translated length at point of the surface line parted from  $\text{MgH}_2(\text{sur})$  particle. The minimum thickness ( $d_{\text{min}}$ ) was evaluated at the first point of intersection between the shape line and Mg. The average particle size of  $\text{MgH}_2(\text{int})$  is calculated by calculating the area of  $\text{MgH}_2(\text{int})$ , and the value of the diameter calculated when assuming  $\text{MgH}_2(\text{int})$  as a spherical calculation on average.

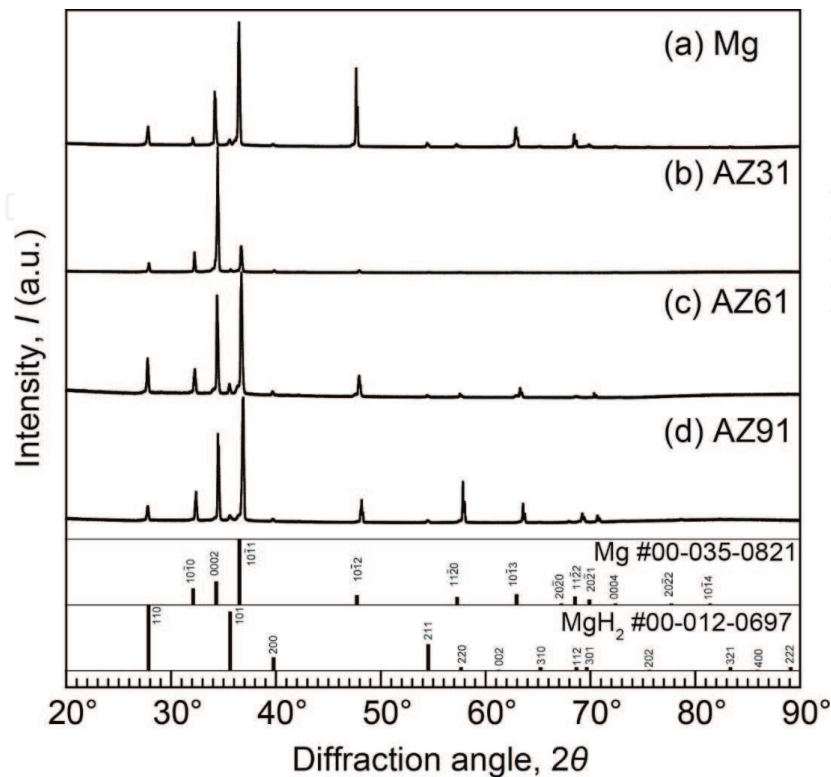


**Figure 1.** Method of quantitative analysis for average ( $d_{av}$ ), maximum ( $d_{max}$ ) and minimum ( $d_{min}$ ) thickness values of  $MgH_2(sur)$  from SEM-BSE images.

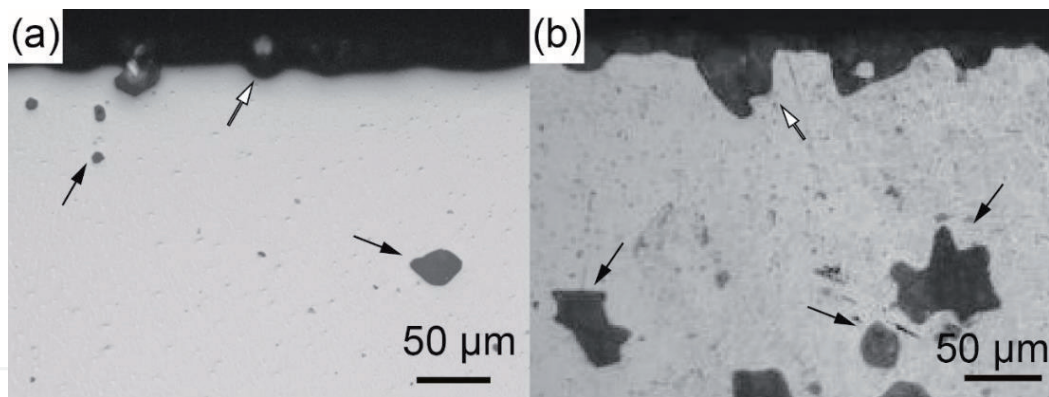
### 3. Results

**Figure 2** shows the XRD pattern of hydrogenated Mg, AZ31, AZ61, AZ91 alloys for 1.8 ks. In all the samples, formation of  $MgH_2$  was observed. These samples were not polished, therefore the information from XRD was mainly from  $MgH_2(sur)$ . The peaks from Mg were shifted to higher angle side with Al concentration due to substitutional solid solution formation. On the other hand, in the peak pattern of  $MgH_2$ , obvious peak shifts were not observed with increase of Al concentration.

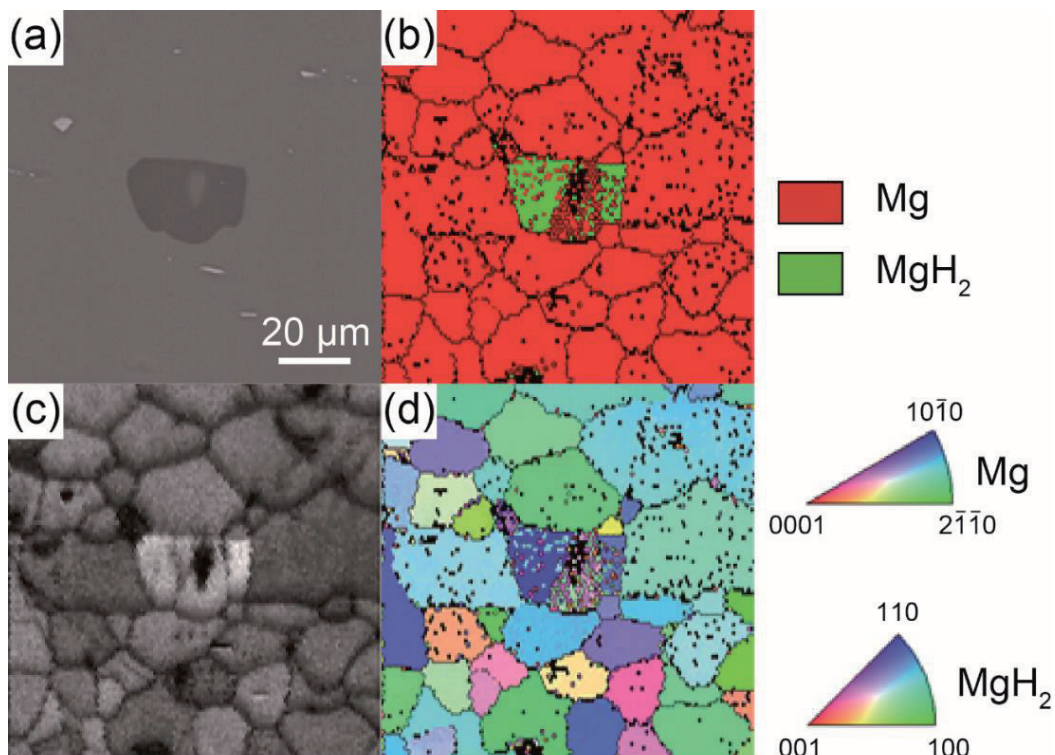
**Figure 3** shows cross-sectional OM images of annealed and cold rolled AZ61 alloy. The annealed and cold rolled AZ61 exhibited both  $MgH_2(sur)$  (white arrow) and  $MgH_2(int)$  (black arrow). There were no difference on  $MgH_2(sur)$  between annealed and cold rolled AZ61 alloy as  $d_{av}$  was  $9 \mu m$  ( $d_{max}$ :  $22 \mu m$ ,  $d_{min}$ :  $2 \mu m$ ) in annealed and  $d_{av}$  was  $8 \mu m$  ( $d_{max}$ :  $22 \mu m$ ,  $d_{min}$ :  $2 \mu m$ ) in cold rolled condition. However, particle size of  $MgH_2(int)$  was larger in cold rolled condition than in



**Figure 2.** XRD profiles of hydrogenated Mg, AZ31, AZ61 and AZ91 alloys at 673 K in 3.61 MPa  $H_2$  for 1.8 ks.



**Figure 3.** Cross-sectional optical micrographs of hydrogenated AZ61 in 3.61 MPa  $H_2$  at 673 K for 129.6 ks (a) annealed and (b) cold-rolled samples. Open and solid arrows point out  $MgH_2(sur)$  and  $MgH_2(int)$ , respectively.

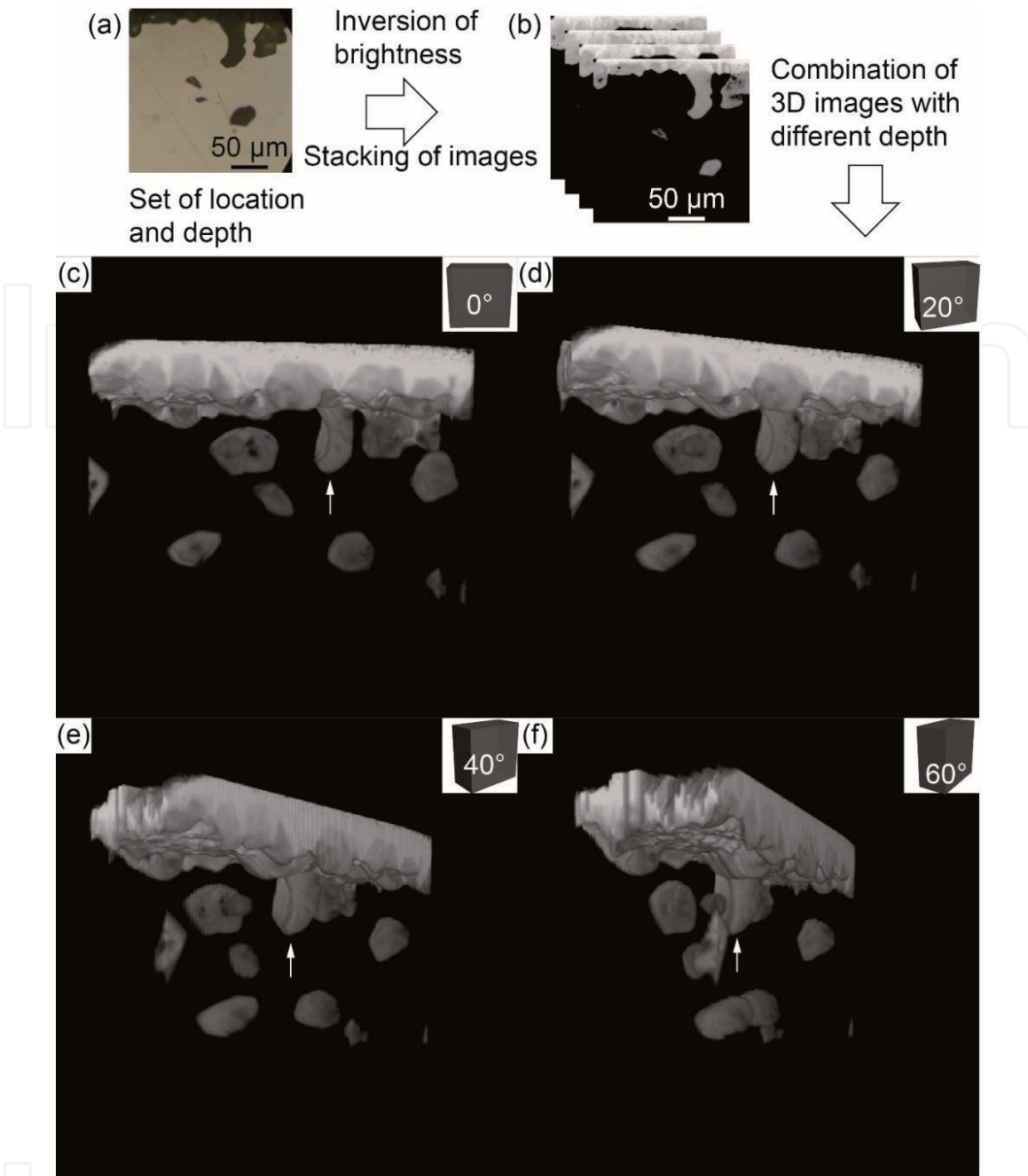


**Figure 4.** SEM-EBSD analyzed images of AZ31 hydrogenated at 673 K in 3.61 MPa  $H_2$  for 64.8 ks. (a) SEM-BSE image, (b) phase map, (c) IQ map, and (d) IPF.

annealed condition as mean diameter was 15  $\mu m$  (maximum: 38  $\mu m$ , minimum: 3  $\mu m$ ) in annealed condition and mean diameter was 53  $\mu m$  (maximum: 125  $\mu m$ , minimum: 14  $\mu m$ ) in cold rolled condition.

**Figure 4** shows the SEM image and results of EBSD analysis of hydrogenated AZ31. **Figure 4** (a) shows the backscattered electron image (BSE), (b) shows the phase map in the same area with (a), (c) is image quality (IQ) map, and (d) is an inverse pole figure (IPF). In phase map (b), Mg was shown in red and  $MgH_2$  was shown in green color. Comparing (a) and (b), dark area in BSE (a) corresponds to  $MgH_2$  area in phase map (b). As focused on IQ map (c), image quality of  $MgH_2$  area was lower than that of Mg area. The decrease of quality at  $MgH_2$  was due to high volume change between Mg to  $MgH_2$  about 32% as the result of residual strain and/or nonconducting material;  $MgH_2$  tends to charge up.

The  $MgH_2(int)$  observed in **Figures 3** and **4** was surrounded with metallic Mg, and the  $MgH_2(int)$  has not interface with hydrogen gas at glance. Therefore,



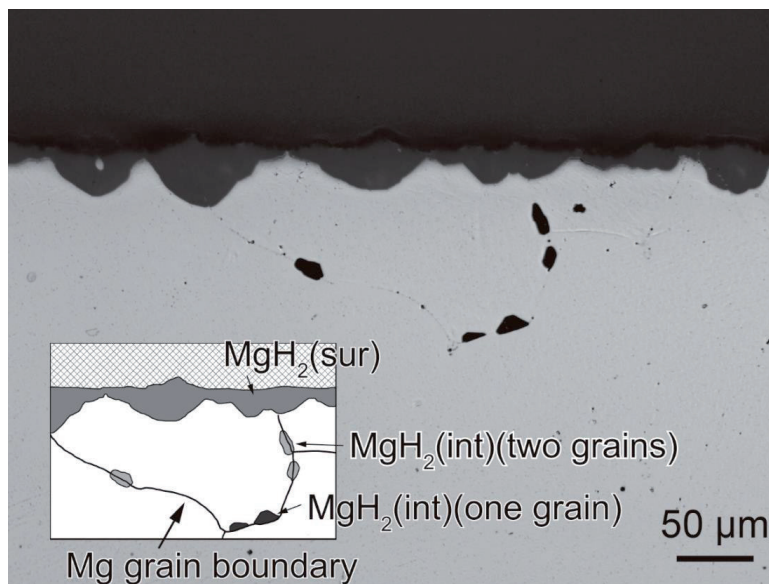
**Figure 5.** Three-dimensional microscopic images obtained from optical micrographs of cold rolled and hydrogenated AZ61 for 129.6 ks (a) a sample of optical micrograph, (b) samples of inverted black and white micrographs, and three-dimensional images (c) 0°, (d) 20°, (e) 40°, and (f) 60°.

three-dimensional analysis was conducted at the area shown in **Figure 5**. **Figure 5** taken from cold rolled and hydrogenated AZ61 sample show (a) part of OM micrograph, (b)  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$  extracted as ROI area contrast inverted, and construction of three-dimensional image rotated from 0 to 60° ((c) 0°, (d) 20°, (e) 40°, and (f) 60°). From **Figure 5c–f**, the  $\text{MgH}_2(\text{int})$  was not in contact with hydrogen gas and  $\text{MgH}_2(\text{sur})$ .

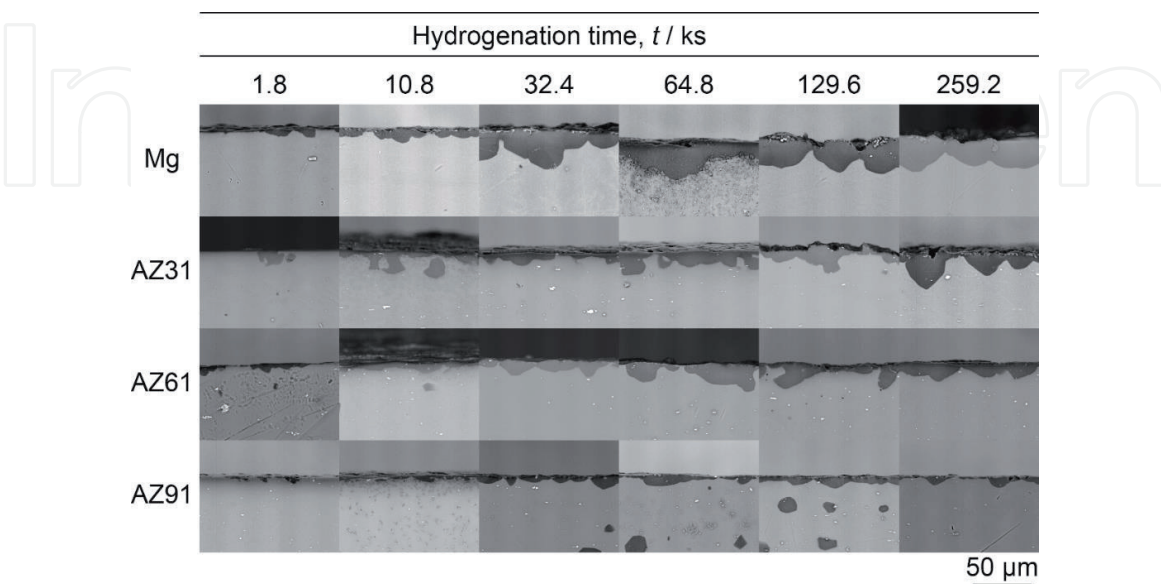
Focusing on  $\text{MgH}_2(\text{sur})$ , homogeneous hydride layer does not growth from surface and structure with variations in thickness was spread out in a planar manner with respect to the surface. The white arrow point of  $\text{MgH}_2(\text{sur})$  was grown abnormally like as heteroepitaxially, however size of the part of  $\text{MgH}_2(\text{sur})$  was same size with surrounding  $\text{MgH}_2(\text{int})$ , since the part of  $\text{MgH}_2(\text{sur})$  would be formed by collision between  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$  at near surface.

**Figure 6** shows an OM micrograph of hydrogenated Mg and a schematic image. Focusing on  $\text{MgH}_2(\text{int})$ , the shape of  $\text{MgH}_2(\text{int})$  was granular and precipitated on the Mg grain boundary. In addition, two types of  $\text{MgH}_2(\text{int})$  were observed as growth to two adjacent Mg grains (at pointed two grains) and on only one side of Mg grain. They were indicated in the inset image.

**Figure 7** shows the SEM-BSE images of the  $\text{MgH}_2(\text{sur})$  of hydrogenated Mg, AZ31, AZ61, and AZ91 alloys for 1.8–259.2 ks. Focusing on images of hydrogenated in relatively short time, for example at 1.8 ks,  $\text{MgH}_2(\text{sur})$  formed with granular and dotted and that was not formed uniformly like a layer at the time when the entire surface was not covered with hydride. With increase of hydrogenation time, the granular hydride,  $\text{MgH}_2(\text{sur})$ , grew in the direction parallel to the surface and formed a rough layer. For images of samples exposed to relatively long hydrogenation time, the thickness of  $\text{MgH}_2(\text{sur})$  decreased with an increase in Al concentration. **Figure 8** shows the thickness of  $\text{MgH}_2(\text{sur})$  of Mg, AZ31, AZ61, and AZ91

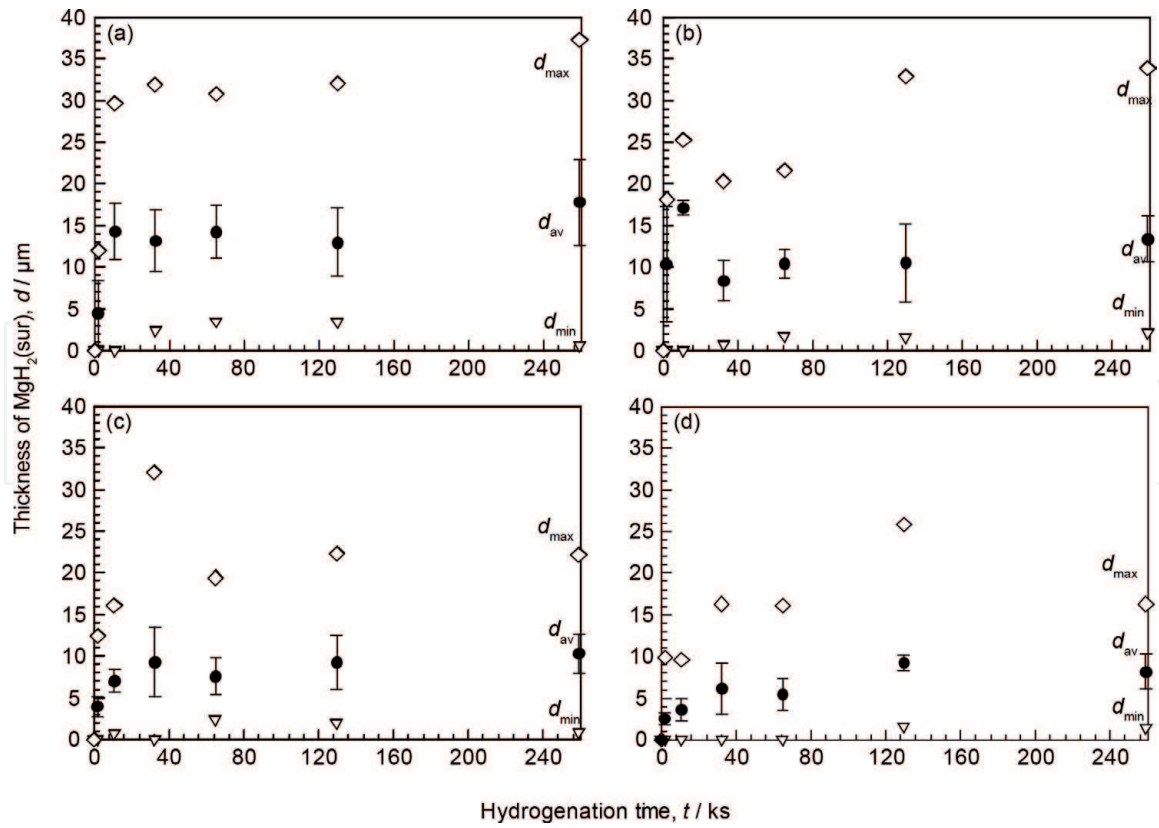


**Figure 6.**  
 SEM-BSE image of Mg hydrogenated at 673 K in 3.61 MPa  $\text{H}_2$  for 129.6 ks.

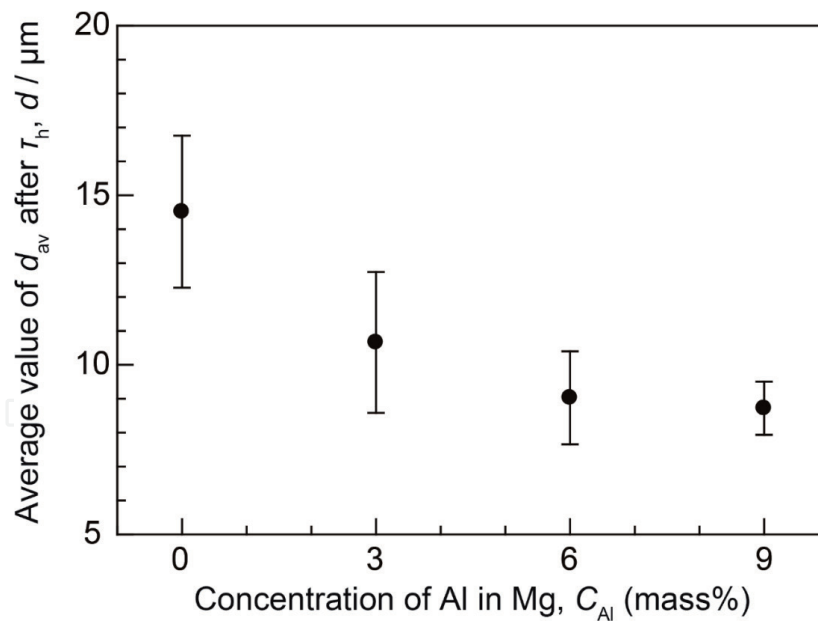


**Figure 7.**  
 SEM-BSE images at  $\text{MgH}_2(\text{sur})$  of Mg, AZ31, AZ61 and AZ91 after hydrogenation at 673 K in 3.61 MPa  $\text{H}_2$  for 0–259.2 ks.



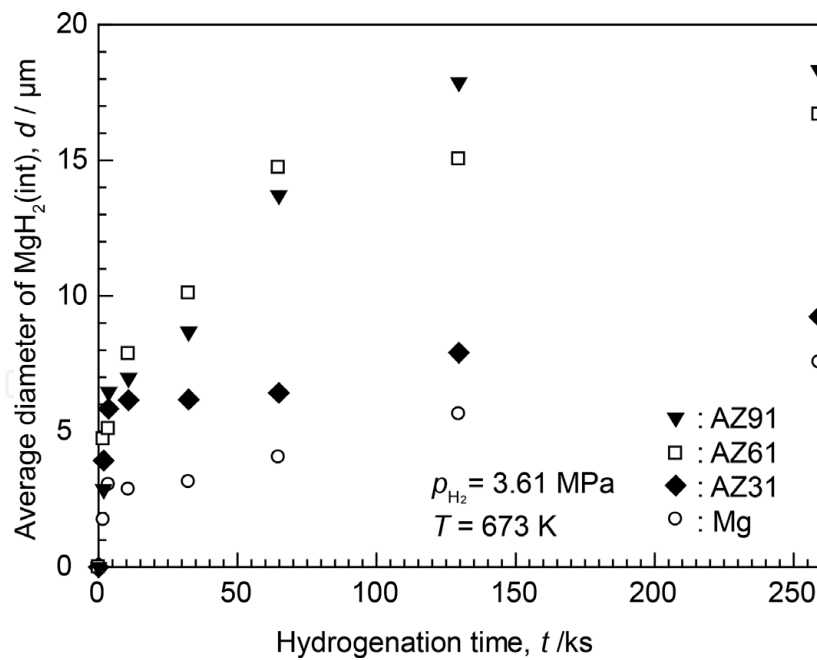


**Figure 8.** Relation between thickness of  $MgH_2(sur)$  and hydrogenation time of (a) Mg, (b) AZ31, (c) AZ61, and (d) AZ91.



**Figure 9.** Relation between average value of  $d_{av}$  and concentration of Al in Mg after  $\tau_h$ .

alloys with hydrogenation time. The white rhombi and the reverse triangles are shown as  $d_{max}$  and  $d_{min}$ , respectively. The black circles are shown as  $d_{av}$  and the vertical lines are expressed as standard deviation. Focusing on  $d_{min}$ ,  $d_{min} = 0$  means that the surface was not completely covered with  $MgH_2(sur)$ . Therefore, paying attention to the value of  $d_{min}$ , it is possible to estimate the time when entire surface is covered with  $MgH_2(sur)$ , and the time describes as time of halt ( $\tau_h$ ).  $\tau_h$  was 32.4 ks for Mg and AZ31, 64.8 ks for AZ61, 129.6 ks for AZ91, and  $\tau_h$  increased with increasing Al concentration. Next, looking at  $d_{av}$ , it was found that  $d_{av}$  grew greatly



**Figure 10.**  
 Relation between average diameter of  $\text{MgH}_2(\text{int})$  and hydrogenation time of Mg, AZ31, AZ61 and AZ91.

with increasing hydrogenation time before  $\tau_h$ , whereas the growth rate drastically decreased after the time of  $\tau_h$ . These results indicate that the growth of  $\text{MgH}_2(\text{sur})$  halted when sample surface was covered with  $\text{MgH}_2(\text{sur})$ .

To reveal the influence of Al concentration on thickness of  $\text{MgH}_2(\text{sur})$ , the relationship between average of  $d_{\text{av}}$  after  $\tau_h$  and Al concentration is shown in **Figure 9**. As shown in **Figure 9**, it was found that the thickness of  $\text{MgH}_2(\text{sur})$  decreased with the increase of Al concentration, and the decrease ratio is remarkable from 0 to 3 mass% Al than from 6 to 9 mass% Al.

Changes in the growth rate of  $\text{MgH}_2(\text{int})$  are described as follows. **Figure 10** shows the average particle size of  $\text{MgH}_2(\text{int})$  of Mg, AZ31, AZ61, and AZ91 alloys with hydrogenation time. As with the changes of  $\text{MgH}_2(\text{sur})$ , the growth rate of  $\text{MgH}_2(\text{int})$  was high over short time and low on longer hydrogenation time side. The time of infection point was almost correlated with  $\tau_h$  as 3.6 ks for Mg and AZ31, 64.8 ks for AZ61, 129.6 ks for AZ91. **Figure 10** shows the relationship between the average particle size of  $\text{MgH}_2(\text{int})$  after  $\tau_h$  and Al concentration. The average particle size of  $\text{MgH}_2(\text{int})$  increased with increase of Al concentration, contrary to the change of thickness of  $\text{MgH}_2(\text{sur})$ .

## 4. Discussion

### 4.1 Formation of $\text{MgH}_2$ in Mg core

After hydrogenating Mg and AZ alloys, two types of  $\text{MgH}_2$  were formed: on the surface,  $\text{MgH}_2(\text{sur})$  and in the unreacted Mg core,  $\text{MgH}_2(\text{int})$ .  $\text{MgH}_2(\text{int})$  formed only along Mg grain boundary, and did not form in Mg crystal grain. It is known that the diffusion of H atoms in Mg made the grain boundary a preferential route [20]. Therefore, the reason why  $\text{MgH}_2(\text{int})$  preferentially formed on grain boundary would be one factor of the fast diffusion of H atoms at Mg grain boundary. In addition,  $\text{MgH}_2$  preferentially formed with existence of defect as nanocrystalline Mg showed fast hydrogenation and dehydrogenation [3]. This observation also supports the reason why  $\text{MgH}_2(\text{int})$  formed on Mg grain boundary.

As shown in **Figure 6**,  $\text{MgH}_2(\text{int})$  grew for adjacent Mg crystal grain or only on one crystal grain. In addition, some Mg grain boundaries did not form  $\text{MgH}_2(\text{int})$ . Some orientation relationship between Mg and  $\text{MgH}_2$  was reported as  $(0001)_{\text{Mg}}// (001)_{\text{MgH}_2}$ ,  $[-1-120]_{\text{Mg}}//[001]_{\text{MgH}_2}$  [21] and  $(-2110)_{\text{Mg}}// (12-1)_{\text{MgH}_2}$ ,  $[0001]_{\text{Mg}}//[101]_{\text{MgH}_2}$  [22]. Because interface energy between new phase and mother phase was low in orientation relationship, solid-solid transformation easily proceeded in orientation relationship with a small lattice mismatch. On the other hand, hydrogenation rate of Mg increased with formation of (0002) crystal texture [23, 24]. From above results, nucleation and growth of  $\text{MgH}_2(\text{int})$  would also depend on adjacent Mg crystal orientation. However, influence of Mg crystal texture for  $\text{MgH}_2$  formation had other formation of MgO factor [24], and particle shape of  $\text{MgH}_2(\text{int})$  was ellipsoidal. Therefore, consideration with complex effects for formation of  $\text{MgH}_2(\text{int})$  should be needed such as orientation relationship, precipitates on Mg grain boundary, interface energy with adjacent Mg grains, and flux of H atom and so on.

#### 4.2 Relationships between particle size of $\text{MgH}_2(\text{int})$ and Al concentration

Before  $\tau_h$ ,  $\text{MgH}_2(\text{sur})$  formed in granular form and spread and the growth rate of average thickness was larger than that after  $\tau_h$ . After  $\tau_h$ , the growth of  $\text{MgH}_2(\text{sur})$  apparently halted. These growth rate change was same in  $\text{MgH}_2(\text{int})$ . These results be attributed to extremely low diffusion rate of H in  $\text{MgH}_2$  when compared to that in Mg [12, 13]. When the whole surface was covered with  $\text{MgH}_2(\text{sur})$ , the supply rate of H to unreacted internal metallic Mg or AZ significantly decreased, halting the growth of  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$ .

Some studies have reported that the amount of  $\text{MgH}_2$  formed depends on Gibbs free energy ( $\Delta_r G$ ) of  $\text{MgH}_2$  from Mg and  $\text{H}_2$  gas [16, 25, 26]. The microstructure of  $\text{MgH}_2(\text{sur})$  at initial state was formed as granular and scattered. Concerning this result, the nucleation rate of  $\text{MgH}_2(\text{sur})$  was low and the nucleation rate would depend on absolute value of  $\Delta_r G$ . Applying low value of  $\Delta_r G$ , growth of  $\text{MgH}_2(\text{int})$  proceeded because nucleation rate of  $\text{MgH}_2(\text{sur})$  was low and  $\tau_h$  is shift to longer time. However, when high value of  $\Delta_r G$  was applied, the nucleation rate of  $\text{MgH}_2(\text{sur})$  increased and immediately the surface covered with thin  $\text{MgH}_2(\text{sur})$  rapidly and the particle size of  $\text{MgH}_2(\text{int})$  was explained to be small size.

The average particle size of  $\text{MgH}_2(\text{int})$  increased with increasing Al concentration. As shown in **Figure 10**, the growth rate of  $\text{MgH}_2(\text{int})$  decreased when the surface was covered with  $\text{MgH}_2(\text{sur})$ . The thickness of  $\text{MgH}_2(\text{sur})$  decreased with increasing Al concentration. From these results, the reasons why the particle size of  $\text{MgH}_2(\text{int})$  decreased with increasing Al concentration would be shifting of long time  $\tau_h$  and small diffusion distance of H in  $\text{MgH}_2$  at high Al content. Therefore, the amount of supplying H increased and large size of  $\text{MgH}_2(\text{int})$  formed with increasing Al concentration.

## 5. Conclusion

In this study, focusing on the formation of  $\text{MgH}_2$  in the Mg core, the effects of Al concentration in Mg for microstructure of hydrogenated Mg and Mg-Al-Zn alloys were investigated.  $\text{MgH}_2(\text{int})$  formed at Mg grain boundary and the growth rate of  $\text{MgH}_2(\text{int})$  was investigated including plastic deformed condition. From three-dimensional analysis, it was found that the  $\text{MgH}_2(\text{int})$  was surrounded by metallic Mg or Mg-Al-Zn alloys and they had not interfaced with  $\text{H}_2$  gas and  $\text{MgH}_2$  on the surface area (sur). The time when the surface covered with  $\text{MgH}_2(\text{sur})$  was described as time of halt,  $\tau_h$ . Comparing growth rate of  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$

before and after  $\tau_h$ , the growth rate of both  $\text{MgH}_2$  were higher before  $\tau_h$  than after  $\tau_h$ . The growth of  $\text{MgH}_2(\text{sur})$  and  $\text{MgH}_2(\text{int})$  were observed to stop after  $\tau_h$  because H supply route change from in Mg to  $\text{MgH}_2$ . After  $\tau_h$ , the thickness of  $\text{MgH}_2(\text{sur})$  decreased and particle size of  $\text{MgH}_2(\text{int})$  increased with increasing Al concentration. This result could be explained by increase of supplied H amount to  $\text{MgH}_2(\text{int})$  due to the shifting  $\tau_h$  to longer time and small diffusion distance of  $\text{MgH}_2(\text{sur})$  which had low value of diffusion coefficient.

Findings from this research point out in following:

- Hydrogenated Mg plate formed  $\text{MgH}_2$  on surface(sur) and in internal area(int).
- The thickness of  $\text{MgH}_2(\text{sur})$  decreased with increase of Al concentrations in Mg.
- The particle size of  $\text{MgH}_2(\text{int})$  increased with increase of Al concentrations in Mg.

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