Chapter

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 MgH2 in Mg were investigated. MgH2 was formed on the surface as well as inside of unreacted Mg core. The inside MgH2 was formed in a granular form on Mg grain boundary and its size increased by applying plastic deformation. Thickness of the surface MgH2 and size of the internal MgH2 increased with an increase in hydrogenation time until the hydride surface was completely covered with MgH2. However, the growth of the surface and internal MgH2 came to a halt after the surface was covered with MgH2. From these results, supplying H from metal side was dominantly contributed for growth of the surface and internal MgH2 because diffusion rate of H in Mg was much higher than that in MgH2. In addition, the growth of internal MgH2 as well as control of surface MgH2 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 (MgH2), 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 MPaH2) because MgH2 is thermodynamically stable (\(\Delta H = -72.8 \pm 4.2\) kJ mol\(^{-1}\), \(\Delta S = -142 \pm 3\) J K\(^{-1}\) 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 MgH2 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\(_2\), MgH\(_2\) forms an ionic bond and a weak covalent bond between Mg-H and the valence number of the ion is indicated as Mg\(^{1.91+}\) and H\(^{0.26-}\) [11]. The diffusion coefficient of H in MgH\(_2\) is several order of magnitude lower when compared to that in Mg: \(D_{H}^{Mg} = 7 \times 10^{-11}\) m\(^2\) s\(^{-1}\)
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(300 K) in Mg and $D_{H}^{MgH_2} = 1.1 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ (305 K) in MgH$_2$ [12, 13]. Based on these characteristics, powder Mg forms core-shell-type structure hydride, 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 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 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 MgH$_2$ and core Mg in addition to MgH$_2$ in the core Mg. In the following, MgH$_2$ on the surface layer named as MgH$_2$(sur) and that in Mg core named as MgH$_2$(int). MgH$_2$(int) formed in the Mg core is distinguished from MgH$_2$(sur). The particle size of MgH$_2$(int) in Mg$^{-6}$ mass%, Al-1 mass%, Zn alloy was larger than that in pure Mg. This result shows the grain size of MgH$_2$(int) would be in correlation with Al concentration. Therefore, in this study, the influence of Al concentration in Mg on formation of MgH$_2$(int) is clarified. To reveal the mechanism of MgH$_2$(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 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%) |
|----------|---------------------|
| Mg       | Al 0.0013  Zn 0.0024  Mn 0.012  Si 0.022  Fe 0.0016  Cu 0.0031  Ni 0.0003  Ca 0.01 |
| AZ31     | Al 2.80  Zn 0.80  Mn 0.32  Si 0.022  Fe 0.003  Cu 0.003  Ni <0.002 |
| AZ61     | Al 6.26  Zn 0.63  Mn 0.26  Si 0.015  Fe 0.005  Cu 0.001  Ni 0.0007 |
| AZ91     | Al 8.70  Zn 0.82  Mn 0.22  Si 0.007  Fe 0.005  Cu <0.002  Ni 0.002 |

Table 1. Composition of Mg and AZ31, AZ61, 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°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 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 hereafter.

The X-ray diffraction (XRD) instrument was used for the identification of MgH$_2$(sur). X-ray source of CuK$\alpha$ with the tube voltage of 40 kV and the tube current of 15 mA was used. Microstructure of MgH$_2$ was judged with presence or absence of charge up by using of scanning electron microscope (SEM). Crystal structure of MgH$_2$(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 → # 800 → # 1000) followed by an Al$_2$O$_3$ suspension (0.05 μm) or SiO$_2$ suspension (0.04 μm). 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 MgH$_2$(sur) and MgH$_2$(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 MgH$_2$(sur) layer. In the analysis, five or more images are selected and the MgH$_2$ was observed as a dark area. The mean thickness ($d_{av}$) of MgH$_2$(sur) was calculated by dividing the area of each observed MgH$_2$(sur) by the length of MgH$_2$(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 MgH$_2$(sur) was evaluated as the translated length at point of the surface line parted from MgH$_2$(sur) particle. The minimum thickness ($d_{min}$) was evaluated at the first point of intersection between the shape line and Mg. The average particle size of MgH$_2$(int) is calculated by calculating the area of MgH$_2$(int), and the value of the diameter calculated when assuming MgH$_2$(int) as a spherical calculation on average.
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 μm ($d_{max}$: 22 μm, $d_{min}$: 2 μm) in annealed and $d_{av}$ was 8 μm ($d_{max}$: 22 μm, $d_{min}$: 2 μm) in cold rolled condition. However, particle size of MgH$_2$(int) was lager in cold rolled condition than in...
annealed condition as mean diameter was 15 μm (maximum: 38 μm, minimum: 3 μm) in annealed condition and mean diameter was 53 μm (maximum: 125 μm, minimum: 14 μm) 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 MgH2 was shown in green color. Comparing (a) and (b), dark area in BSE (a) corresponds to MgH2 area in phase map (b). As focused on IQ map (c), image quality of MgH2 area was lower than that of Mg area. The decrease of quality at MgH2 was due to high volume change between Mg to MgH2 about 32% as the result of residual strain and/or nonconducting material; MgH2 tends to charge up.

The MgH2(int) observed in Figures 3 and 4 was surrounded with metallic Mg, and the MgH2(int) has not interface with hydrogen gas at glance. Therefore,
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) MgH$_2$(sur) and MgH$_2$(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 MgH$_2$(int) was not in contact with hydrogen gas and MgH$_2$(sur).

Focusing on MgH$_2$(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 MgH$_2$(sur) was grown abnormally like as heteroepitaxially, however size of the part of MgH$_2$(sur) was same size with surrounding MgH$_2$(int), since the part of MgH$_2$(sur) would be formed by collision between MgH$_2$(sur) and MgH$_2$(int) at near surface.
Figure 6 shows an OM micrograph of hydrogenated Mg and a schematic image. Focusing on MgH$_2$(int), the shape of MgH$_2$(int) was granular and precipitated on the Mg grain boundary. In addition, two types of MgH$_2$(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 MgH$_2$(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, MgH$_2$(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, MgH$_2$(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 MgH$_2$(sur) decreased with an increase in Al concentration. Figure 8 shows the thickness of MgH$_2$(sur) of Mg, AZ31, AZ61, and AZ91.
alloys with hydrogenation time. The white rhombi and the reverse triangles are shown as $d_{\text{max}}$ and $d_{\text{min}}$, respectively. The black circles are shown as $d_{\text{av}}$ and the vertical lines are expressed as standard deviation. Focusing on $d_{\text{min}}, d_{\text{min}} = 0$ means that the surface was not completely covered with MgH$_2$(sur). Therefore, paying attention to the value of $d_{\text{min}},$ 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 $d_{\text{av}},$ it was found that $d_{\text{av}}$ grew greatly.

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 $d_{\text{av}}$ and concentration of Al in Mg after $\tau_h$. 
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 MgH$_2$(sur) halted when sample surface was covered with MgH$_2$(sur).

To reveal the influence of Al concentration on thickness of MgH$_2$(sur), the relationship between average of $d_{av}$ after $\tau_h$ and Al concentration is shown in Figure 9. As shown in Figure 9, it was found that the thickness of MgH$_2$(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 MgH$_2$(int) are described as follows. Figure 10 shows the average particle size of MgH$_2$(int) of Mg, AZ31, AZ61, and AZ91 alloys with hydrogenation time. As with the changes of MgH$_2$(sur), the growth rate of MgH$_2$(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 MgH$_2$(int) after $\tau_h$ and Al concentration. The average particle size of MgH$_2$(int) increased with increase of Al concentration, contrary to the change of thickness of MgH$_2$(sur).

### 4. Discussion

#### 4.1 Formation of MgH$_2$ in Mg core

After hydrogenating Mg and AZ alloys, two types of MgH$_2$ were formed: on the surface, MgH$_2$(sur) and in the unreacted Mg core, MgH$_2$(int). MgH$_2$(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 MgH$_2$(int) preferentially formed on grain boundary would be one factor of the fast diffusion of H atoms at Mg grain boundary. In addition, MgH$_2$ preferentially formed with existence of defect as nanocrystallize Mg showed fast hydrogenation and dehydrogenation [3]. This observation also supports the reason why MgH$_2$(int) formed on Mg grain boundary.
As shown in Figure 6, MgH₂(int) grew for adjacent Mg crystal grain or only on one crystal grain. In addition, some Mg grain boundaries did not form MgH₂(int). Some orientation relationship between Mg and MgH₂ 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]\(\text{Mg}\)/[010]\(\text{MgH}_2\) [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]. Form above results, nucleation and growth of MgH₂(int) would also depend on adjacent Mg crystal orientation. However, influence of Mg crystal texture for MgH₂ formation had other formation of MgO factor [24], and particle shape of MgH₂(int) was ellipsoidal. Therefore, consideration with complex effects for formation of MgH₂(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 MgH₂(int) and Al concentration

Before \(\tau_h\), MgH₂(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 MgH₂(sur) apparently halted. These growth rate change was same in MgH₂(int). These results be attributed to extremely low diffusion rate of H in MgH₂ when compared to that in Mg [12, 13]. When the whole surface was covered with MgH₂(sur), the supply rate of H to unreacted internal metallic Mg or AZ significantly decreased, halting the growth of MgH₂(sur) and MgH₂(int).

Some studies have reported that the amount of MgH₂ formed depends on Gibbs free energy (\(\Delta_rG\)) of MgH₂ from Mg and H₂ gas [16, 25, 26]. The microstructure of MgH₂(sur) at initial state was formed as granular and scattered. Concerning this result, the nucleation rate of MgH₂(sur) was low and the nucleation rate would depend on absolute value of \(\Delta_rG\). Applying low value of \(\Delta_rG\), growth of MgH₂(int) proceeded because nucleation rate of MgH₂(sur) was low and \(\tau_h\) is shift to longer time. However, when high value of \(\Delta_rG\) was applied, the nucleation rate of MgH₂(sur) increased and immediately the surface covered with thin MgH₂(sur) rapidly and the particle size of MgH₂(int) was explained to be small size.

The average particle size of MgH₂(int) increased with increasing Al concentration. As shown in Figure 10, the growth rate of MgH₂(int) decreased when the surface was covered with MgH₂(sur). The thickness of MgH₂(sur) decreased with increasing Al concentration. From these results, the reasons why the particle size of MgH₂(int) decreased with increasing Al concentration would be shifting of long time \(\tau_n\) and small diffusion distance of H in MgH₂ at high Al content. Therefore, the amount of supplying H increased and large size of MgH₂(int) formed with increasing Al concentration.

### 5. Conclusion

In this study, focusing on the formation of MgH₂ in the Mg core, the effects of Al concentration in Mg for microstructure of hydrogenated Mg and Mg-Al-Zn alloys were investigated. MgH₂(int) formed at Mg grain boundary and the growth rate of MgH₂(int) was investigated including plastic deformed condition. From three-dimensional analysis, it was found that the MgH₂(int) was surrounded by metallic Mg or Mg-Al-Zn alloys and they had not interfaced with H₂ gas and MgH₂ on the surface area(sur). The time when the surface covered with MgH₂(sur) was described as time of halt, \(\tau_h\). Comparing growth rate of MgH₂(sur) and MgH₂(int)
before and after $\tau_h$, the growth rate of both MgH$_2$ were higher before $\tau_h$ than after $\tau_h$. The growth of MgH$_2$(sur) and MgH$_2$(int) were observed to stop after $\tau_h$ because H supply route change from in Mg to MgH$_2$. After $\tau_h$, the thickness of MgH$_2$(sur) decreased and particle size of MgH$_2$(int) increased with increasing Al concentration. This result could be explained by increase of supplied H amount to MgH$_2$(int) due to the shifting $\tau_h$ to longer time and small diffusion distance of MgH$_2$(sur) which had low value of diffusion coefficient.

Findings from this research point out in following:

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

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Author details

Ryota Kondo* and Takeshita T. Hiroyuki
Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University Suita, Osaka, Japan

*Address all correspondence to: rkondo@kansai-u.ac.jp

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