

Hydrogen Storage Properties and Corresponding Phase Transformations of Mg/Pd Laminate Composites Prepared by a Repetitive-Rolling Method

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Mg/Pd laminate composites (Mg/Pd = 6) prepared by a repetitive-rolling method can reversibly absorb and desorb a large amount of hydrogen, up to 1.47 H/M (4 mass%) at 573 K. Pressure-composition isotherms of the Mg/Pd laminate composites show two plateaux, $P_L = 0.2$ MPa and $P_H = 2$ MPa, during hydrogen absorption and desorption. To clarify the correlation between hydrogen storage properties and phase transformations, we investigated structural changes of the Mg₆Pd intermetallic compound with in-situ XRD. The low-pressure plateau P_L corresponds to the decomposition of Mg₆Pd into Mg₅Pd₂ and MgH₂, and the high-pressure plateau P_H to the decomposition of Mg₅Pd₂ into MgPd and MgH₂. In subsequent dehydrogenation processes, part of the MgH₂ reformed Mg, and the Mg and MgPd form Mg₅Pd₂ at the high-pressure plateau P_H and then the remaining MgH₂ reformed Mg, and the Mg and Mg₅Pd₂ form Mg₆Pd at the low-pressure plateau P_L . According to this mechanism, the Mg₆Pd can absorb and desorb hydrogen through reversibly disproportionation and recombination processes.
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1. Introduction

From the viewpoint of hydrogen storage systems, Mg¹⁾ and Mg-based alloys^{2,3)} are promising materials for hydrogen storage media because they can absorb a large amount of hydrogen as, for example, MgH₂ and Mg₂NiH₄. However, the hydrogen absorption/desorption kinetics are too slow for practical use and needs high temperatures such as 573 K. To improve the reaction kinetics and diffusion properties, a reduction of the grain size and the addition of various catalysis have been investigated.⁴⁻⁹⁾

In addition, various methods, such as mechanical alloying, vapor phase processing, and combustion synthesis, have been used in investigations of Mg-based alloys. However, the alloys synthesized through these methods do not usually exhibit original properties on hydrogenation and dehydrogenation because the oxygen element contained in the starting materials influences the characteristics of the alloys. Laminate composites have been attracting attention since Ueda *et al.* reported that Mg/Cu laminate composites showed reversible hydrogenation and dehydrogenation at 473 K, a lower reaction temperature than those of conventional Mg-based materials.¹⁰⁾

Pd reacts rapidly with hydrogen, even after it is placed in air, because its surface and diffusion properties produce high catalytic activity.¹¹⁾ Tsukahara *et al.* reported Mg/Pd laminate composites can reversibly absorb and desorb a large amount of hydrogen.¹²⁾ The hydrogen storage properties of Mg₆Pd have been investigated by Kume and Weiss¹³⁾ and Dufour and Huot.¹⁴⁾ Kume concluded that Mg₆Pd decomposed to MgH₂ and Mg₅Pd₂ through a disproportionation reaction. Dufour *et al.* proposed a two-step hydrogenation process, involving first the decomposition of Mg₆Pd into Mg_{78.5}Pd_{21.5} and MgH₂, and then a further decomposition of Mg_{78.5}Pd_{21.5} into Mg₅Pd₂ and MgH₂. In the dehydrogenation process, the recombination process is a one-

step reaction, Mg₆Pd is formed from Mg₅Pd₂ and MgH₂. In these two studies, the reaction mechanism was derived from the results of ex-situ XRD measurements.

In this study, we investigated the structural changes of the Mg-based laminate composites of Mg/Pd with (Mg/Pd) = 6, where (Mg/Pd) means the ratio of the numbers of Mg to Pd atoms, to clarify the correlation between hydrogen storage properties and phase transformations. From analysis of the in-situ X-ray diffraction profiles, we here report that Mg₆Pd is formed during the initial activation process, and this Mg₆Pd can also reversibly store hydrogen through disproportionation and recombination processes.

2. Experimental

Commercial Pd sheet (99.99% purity, 10 μm in thickness) and Mg sheet (prepared in our laboratory 99.9% purity, rolled to 94 μm in thickness) were used as starting materials. The foils were cut into pieces of 20 mm width and 30 mm length. They were stacked in alternating layers of magnesium and the other metal. The Mg/Pd laminate composites were prepared by a repetitive-rolling method using a conventional two-high roll mill as described previously.¹⁵⁾

The identification of the crystal structure of the as-rolled samples and hydride samples were examined by powder X-ray diffractometer (RINT2000, Rigaku Co., Ltd.) with Cu-Kα radiation at room temperature.

The pressure-composition (PC) isotherms were measured with a Sieverts' apparatus. The samples were put into a vessel, and then evacuated at room temperature using a rotary vacuum pump. The samples were then heated to a 573 K, and hydrogen was gradually introduced into the vessel up to a pressure of 3.3 MPa. After the pressure decreased by activation, the vessel was evacuated at 573 K in order to obtain the hydrogen pressure zero points. Further experiments were carried out after the vessel had equilibrated at a

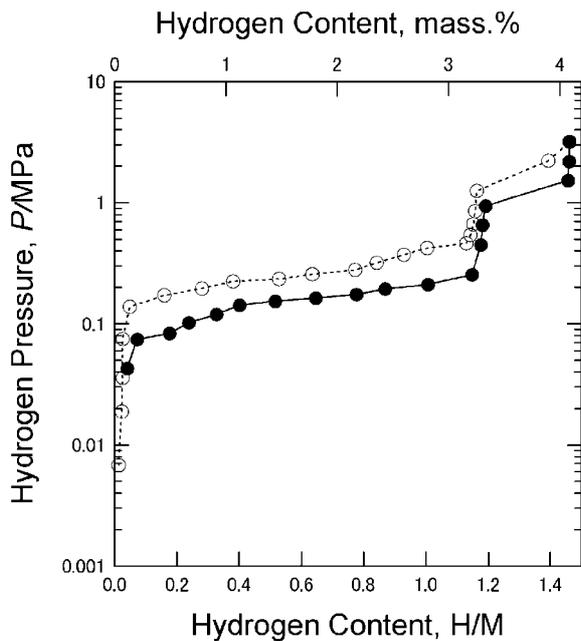


Fig. 1 Pressure-composition isotherms for hydrogen absorption (empty symbols) and desorption (filled symbols) for Mg/Pd laminate composites (Mg/Pd = 6) at 573 K.

desired temperature. Each equilibrium pressure at the respective hydrogen content was determined at least 2 hours after adding or removing the hydrogen.

Phase transformations of the Mg/Pd laminate composites during hydrogen absorption and desorption were analyzed by in-situ XRD measurements. In-situ measurements were made using a special cell, which can control the temperature and pressure up to 5 MPa at 573 K. The specimen, cut into a piece of 10 mm × 20 mm in size, was set on a sample cell. The measurement conditions were 40 kV and 200 mA with Cu-K α radiation with data taken over the range of diffraction angles between 2θ (degrees) = 20–90. Before the in-situ XRD measurements, the specimen was evacuated by use of a rotary pump connected in series with a liquid nitrogen trap. The hydrogen gas was purified with a liquid nitrogen trap to remove trace amounts of water and other impurity gases. For initial activation, the temperature of the sample cell was increased from room temperature to 573 K at a heating rate of 20 K/min. When the cell's temperature reached 573 K, hydrogen gas was gradually introduced into the system up to a pressure of 4.8 MPa. After the pressure decreased due to activation, the vessel was evacuated at 573 K. The in-situ XRD measurements were carried out after the temperature and hydrogen pressure of the sample cell had equilibrated.

3. Results and Discussions

The Mg/Pd laminate composites (Mg/Pd = 6) prepared by the repetitive-rolling method had a composition identical to Mg₆Pd, the most Mg-rich binary intermetallic compound in the Mg-Pd system.^{16,17} Figure 1 shows the PC-isotherms of this specimen at 573 K. They show two plateaux, $P_L = 0.2$ MPa and $P_H = 2$ MPa, and the maximum hydrogen content was 1.47 H/M (4 mass%).

The crystal structures of the Mg/Pd laminate composites

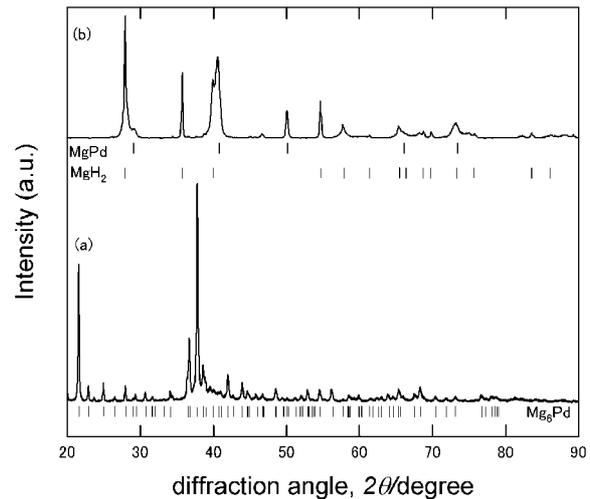
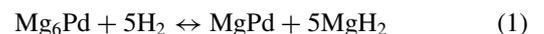


Fig. 2 Ex-situ X-ray diffraction profiles of Mg/Pd laminate composites (Mg/Pd = 6) (a) after the activation process (b) after hydrogenation at 573 K and 3.3 MPa hydrogen pressure.

after the initial activation process and after hydrogen absorption were investigated using ex-situ XRD. The crystal structures in hydride state were analyzed by hydriding a specimen under 3.3 MPa hydrogen pressure at 573 K and then quenching it at room temperature while being kept under that hydrogen pressure. The XRD profile of the Mg/Pd laminate composites after the initial activation process shown in Fig. 2(a) consists of only the Mg₆Pd intermetallic compound phase within the detection ability of our XRD instrument. On the other hand, the profile of the hydrogenated composites shown in Fig. 2(b) indicated the existence of the MgH₂ phase and the CsCl-type MgPd intermetallic compound phase. No other phase was observed in the hydrogenated sample.

Judging from those results, the reactions between Mg/Pd laminate composites and hydrogen involve the disproportionation and recombination of Mg and Pd, according to the scheme



From this equation, the maximum hydrogen content is 1.428 H/M, a value that is about the same as that obtained from PC-isotherms.

Figure 3 shows the in-situ XRD profiles of composites in various conditions: (a) at room temperature under a vacuum; (b) at 573 K under 3.3 MPa hydrogen pressure for hydrogen absorption; and (c) at 573 K after evacuation for hydrogen desorption. In the XRD profiles, some minor peaks corresponding to Be, BeO and Mo (coming from the sample holder) were observed. We assume that these minor phases are not involved in the reactions.

The initial XRD profile of the specimen (Fig. 3(a)) indicated the presence of solely Mg and Pd; no other phase was observed in the sample within the detection ability of the XRD. The highest intensity peak of the Mg phase of the specimen was the (002) reflection. Usually, the highest intensity XRD peak of Mg is the (101) reflection. Therefore, the metallographic structure of the specimen has a preferred orientation.

Figure 3(b) shows the XRD profile of the Mg/Pd laminate

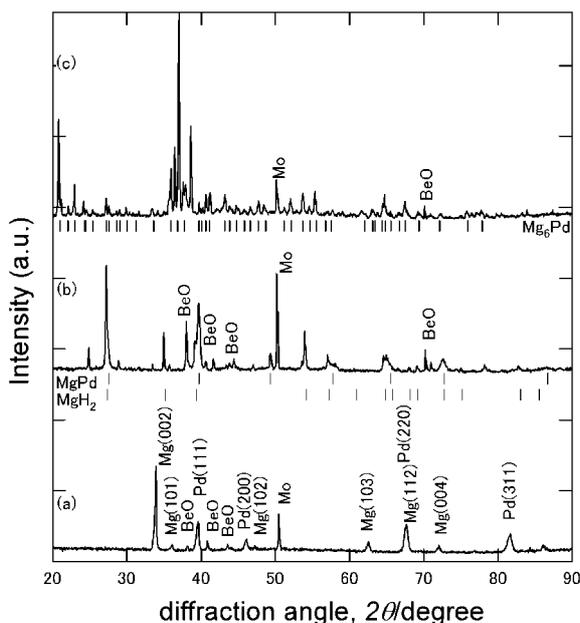


Fig. 3 In-situ XRD profiles of Mg/Pd laminate composites during the initial activation treatment: (a) at room temperature under a vacuum, (b) hydrogenation process at 573 K under 3.3 MPa hydrogen pressure, and (c) in dehydrogenation process at 573 K in vacuum.

composites were kept at 3.3 MPa hydrogen pressure at 573 K for 24 hours. The diffraction peaks associated with Mg and Pd disappeared, and peaks from new phases were observed. The set of new peaks agreed well with those corresponding to MgPd and MgH₂. Hence, new phases form due to reaction with hydrogen.

After that, the sample cell was to induce hydrogen desorption. Figure 3(c) shows the in-situ XRD profile of the specimen after reaction time of 24 hours in vacuum at 573 K. The diffraction peaks of MgPd and MgH₂ weakened and the diffraction peaks of Mg₆Pd were observed, while peaks corresponding to pure Mg phase did not appear in this XRD profile. Therefore, Mg₆Pd intermetallic compound formed from MgH₂ and MgPd during the hydrogen desorption process at 573 K.

Next, we paid attention to the details of the hydrogen absorption/desorption process at 573 K in the Mg/Pd laminate composites-H system. The pressure of the hydrogen gas was increased in steps from 0.1 MPa to 4.8 MPa. XRD measurements at these respective hydrogen pressures were performed at least 2 hours after adding or removing the hydrogen. Figure 4 shows the XRD profiles of the specimen under vacuum, 0.1, 1 and 4 MPa hydrogen pressures. The XRD profile of the specimen under 0.1 MPa pressure was unchanged from that of the specimen under vacuum. We did not observe a solid solution phase, such as Mg₆PdH_x, in this study. Under a 1 MPa hydrogen pressure, the diffraction peaks associated with Mg₅Pd₂ and MgH₂ were observed, while those associated with Mg₆Pd disappeared. At a pressure of 4 MPa, the diffraction peaks associated with Mg₅Pd₂ disappeared and those of associated with MgH₂ became strong compared with those at 1 MPa. This high pressure also resulted in the appearance, diffraction peaks from MgPd.

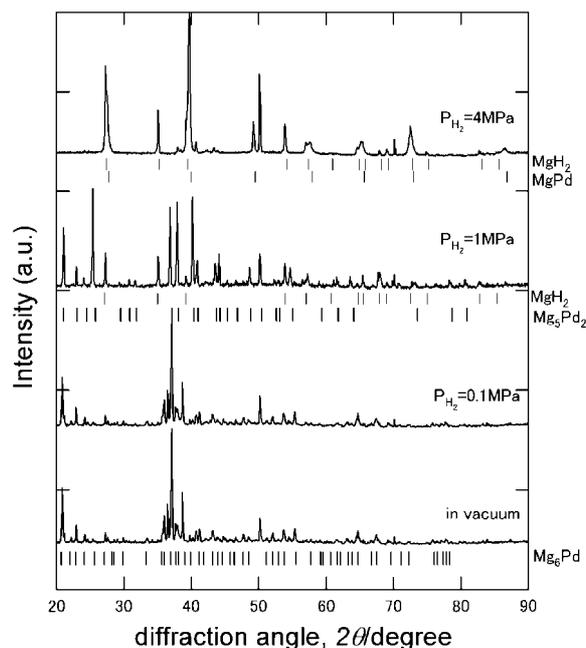


Fig. 4 In-situ XRD profiles of Mg/Pd laminate composites during the hydrogenation process at 573 K under various hydrogen pressures.

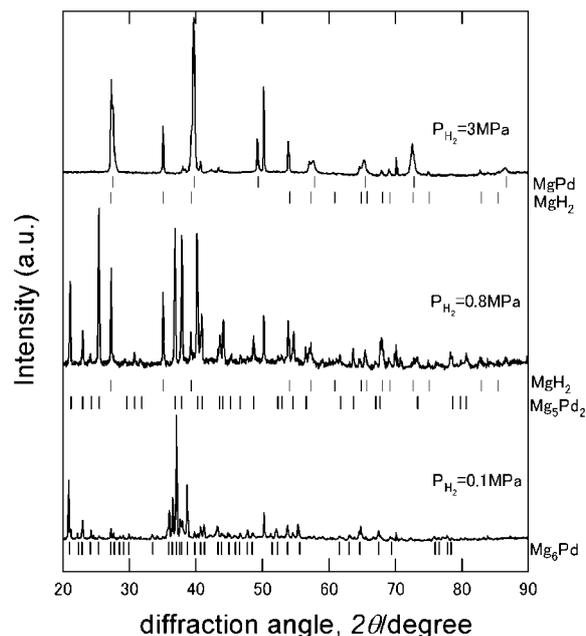


Fig. 5 In-situ XRD profiles of Mg/Pd laminate composites during the dehydrogenation process at 573 K under various hydrogen pressures, and in vacuum.

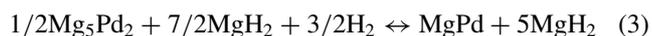
Figure 5 shows the XRD profiles of the specimen under 3, 0.8, and 0.1 MPa hydrogen pressure during the hydrogen desorption process. The diffraction peaks of MgPd disappeared and those of MgH₂ became weak, while the diffraction peaks of Mg₅Pd₂ appeared at 0.8 MPa. From 0.8 MPa down to 0.1 MPa, the diffraction peaks from MgH₂ and Mg₅Pd₂ disappeared, while the peaks associated with Mg₆Pd were present at the lowest pressure.

Take into account the absorption/desorption processes seen in the PC-isotherms in Fig. 1, the in-situ XRD results

clarify the correlation between hydrogen storage properties and phase transformation. The plateau is split into two, 0.2 MPa and 2 MPa at 573 K. In the low-pressure plateau region, the Mg₆Pd intermetallic compound decomposed to Mg₅Pd₂ and MgH₂.



The amount of hydrogen absorbed during this process, 1 H/M, corresponds to the large low-pressure plateau seen in the PC-isotherms. In the small high-pressure plateau region, Mg₅Pd₂ decomposed to MgH₂ and MgPd.



The combination of reaction equations (2) and (3), equates to the total reaction expressed in reaction equation (1), and agree with the PC-isotherms of Fig. 1.

In our previous study, we have shown that the micro/nano-structure is introduced to the laminate composites by the repetitive rolling.¹⁸⁾ This unique structure improves the diffusion rate of the metallic elements and hydrogen, and increases the kinetics of hydrogen absorption/desorption.¹⁹⁾ Therefore, Mg₆Pd can absorb and desorb hydrogen reversibly at 573 K, in spite of the complex multistage disproportionation and recombination reactions of Mg and Pd that occur. A detailed study of the micro/nano-structure of Mg/Pd laminate composites is underway.

4. Conclusion

Phase transformations occurring in Mg/Pd (Mg/Pd = 6) laminate composites during hydrogen absorption and desorption were investigated by means of in-situ XRD measurements. During the initial activation process, Mg₆Pd intermetallic compound is formed. In the hydrogen absorption process, the Mg₆Pd intermetallic compound decomposed to MgH₂ and MgPd via Mg₅Pd₂ and MgH₂ by a disproportionation reaction. During hydrogen desorption, the Mg₆Pd intermetallic compound formed from MgH₂ and MgPd via Mg₅Pd₂ and MgH₂ by recombination. These phase transformations correspond to the two plateaux observed in PC-isotherms. According to this mechanism, Mg₆Pd can absorb and desorb hydrogen through reversible multistage disproportionation and recombination processes.

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