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Hydrogen storage properties of Mg/Cu and Mg/Pd laminate composites and metallographic structure

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Abstract

The Mg-based laminate composites, Mg/Cu and Mg/Pd, were prepared by repetitive-rolling, which is considered to suit for mass production. Mg/Cu laminate composites (Mg/Cu = 2) absorb and desorb hydrogen reversibly at 473 K, and the laminate composites have a better reaction kinetics than melting-casting alloys. TEM observations revealed that the as-rolled Mg-based laminate composite had the sub-micrometer-ordered layered structure with dense dislocations and vacancies. After initial activation and dehydrogenation process, the samples have kept the sub-micrometer-ordered laminate structure with dense dislocations and vacancies. The nano-structure of Mg-based laminate composites leads to lower hydrogen desorption temperature and better kinetics, which would contribute to achieve high capacity hydrogen storage materials. In Mg/Pd laminate composites (Mg/Pd = 6), Mg_6Pd is formed during initial activation process. This Mg_6Pd also can store hydrogen reversibly through the disproportionation and recombination process.

Keywords: Hydrogen storage material; Magnesium; Laminate composite

1. Introduction

From the viewpoint of hydrogen storage system, Mg is a promising material as hydrogen storage media because it can absorb a large amount of hydrogen up to 7.6 mass%, as MgH_2 [1]. However, the hydrogen absorption/desorption kinetics is too low for practical use and needs high temperature such as 573 K. A reduction of the grain size into nanocrystalline dimensions can significantly improve the reaction kinetics and diffusion properties in MgH_2 [2–4]. In addition, the MgH_2 with amount of 3d-transition metals lead to even better performance and lower hydrogen desorption temperature than magnesium [5–7].

Various Mg-based alloys and Mg-based intermetallic compounds have been investigated to improve hydrogen desorption temperature [8,9]. Mg_2Ni intermetallic compound is well known to form Mg_2NiH_4 hydride with high reaction rate, with hydrogen storage, which has hydrogen storage capacity of 3.6 mass% [9]. However, it is difficult to cast Mg-containing alloys accurately with desirable composition by conventional melt-cast methods because of a high vapor pressure of Mg, etc., and single phase Mg-containing compounds can not be obtained just by casting, due to the phase separation during solidification in many systems.

Accordingly, various methods, such as mechanical alloying [10], vapor phase process [11], and combustion synthesis [12], have been applied for investigation on Mg-based alloys. However, the alloys synthesized through these methods do not usually show original properties on hydrogenation and dehydrogenation because oxygen element contained in starting materials influences characteristics of the alloys.

Recently, Ueda et al. have started the investigation on synthesis and hydrogen storage properties of Mg-based laminate composites prepared by repetitive-rolling [13]. The Mg/Ni laminate composites with (Mg/Ni) = 2, where (Mg/Ni) means the ratio of number of Mg to Ni, were shown to change by heat treatment after rolling form the composite of Mg and Ni to the

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single phase Mg_2Ni, and the specimens were hydrogenated to Mg_2NiH_4 completely. In this paper, the Mg-based laminate composites of Mg/Cu and Mg/Pd will be reported to show reversible hydrogen reaction. The reaction mechanism of the Mg/Cu laminate composites with hydrogen will be discussed in relation to nano-structure and disproportionation. The nano-structure leads to lower hydrogen desorption temperature and better kinetics, which would contribute to achieve high capacity hydrogen storage materials. In Mg/Pd composite, Mg_6Pd is formed during initial activation process. This Mg_6Pd also can store hydrogen reversibly through the disproportionation and recombination process.

2. Experimental

Commercial Cu, Pd sheet (99.99% purity, 10 μm in thickness) and Mg sheet (prepared in our laboratory 99.9% purity, rolled to 40 μm in thickness) was used as starting materials. The foils were cut into 20 mm width and 30 mm length. They were stacked in alternating layers of magnesium and another metal, of which thickness ratio was determined to obtain the intended composition of the super-laminates. The stack was sandwiched by metal plate (e.g. SUS316L) and cold-rolled through two carbide rolls. During this process, the layers were joined by solid-phase diffusion between layers. When the length of the stack plate got doubled, it was cut and stacked again. These procedures were repeated 20 times to obtain the intended number of layers and stack thickness.

Investigation of as-rolled sample and heat-treated specimens were carried out on scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDX). The identification of the crystal structure of samples were examined by powder X-ray diffractometer (RINT2000, Rigaku Co., Ltd.) with Cu-Kα radiation at room temperature.

The 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. Then hydrogen was gradually introduced into the vessel up to 3.3 MPa and vessel was heated up to 573 K. After the pressure decreases by activation, the vessel was evacuated at 573 K in order to get a hydrogen pressure zero points and experiments were carried out after setting temperature of vessel. Each equilibrium pressure at the respective hydrogen contents was determined at least 7.2 ks after adding or removing the hydrogen. The dehydrogenation kinetics properties were examined by a thermogravimetry (TG)-differential thermal analysis (DTA) (Mettler Toledo TGA/SDTA851^e). In the thermal analysis measurement, helium gas was adopted, as a carrier gas, and the heating rate were 5, 10, 15, and 20 K/min.

The nano-structure of Mg-based laminate composites was studied by transmission electron microscope (TEM). TEM specimens were prepared by conventional mechanical grinding followed by dimpling and ion thinning. TEM specimens were observed using JEOL JEM-3000F equipped with scanning transmission electron microscope (STEM) system.

3. Results and discussion

3.1. Mg/Cu laminate composites

Fig. 1 shows the PC-isotherms of Mg/Cu laminate composites (Mg/Cu = 2) at 573 and 473 K. The maximum hydrogen contents of this specimen were 1 H/M, where H/M means the atomic ratio of hydrogen to metal. We observed Mg_2Cu phases are formed at the interface by interdiffusion between Mg and Cu layers in hydrogenation process, and then Mg_2Cu decomposes to MgH_2 and $MgCu_2$ by disproportionation using by in situ XRD measurement [14]. From those results, reaction equation is expressed as follows

$$2Mg_2Cu + 3H_2 \leftrightarrow 3MgH_2 + MgCu \qquad (1)$$

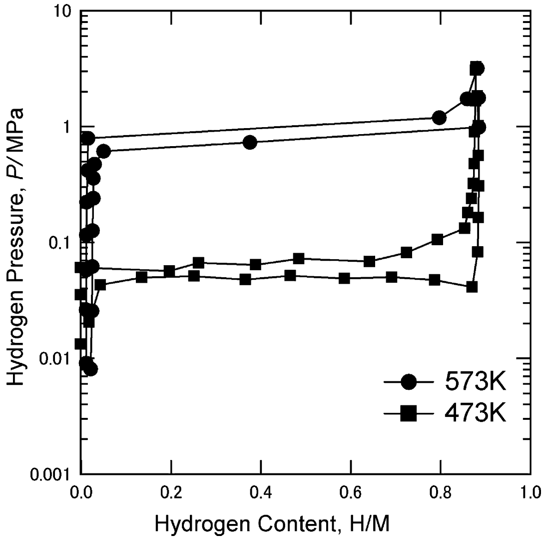

Fig. 1. Pressure-composition isotherms of hydrogenation and dehydrogenation for Mg/Cu laminate composites (Mg/Cu = 2) at 573 and 473 K.

This equation is the same as the result of Mg_2Cu prepared by conventional melt-cast process. In our study, the dissociation pressure at 473 K is 0.05 MPa. Reilly et al. obtained the thermodynamic parameter, $\Delta H = -72.8$ kJ/mol H_2 and $\Delta S = -142.3$ J/K mol H_2, from PC-isotherm of Mg_2Cu alloy prepared by melting [8]. The dissociation pressure, calculated from these thermodynamic parameters, at 473 K is 0.025 MPa, and the value is a similar to the pressure we measured.

Thermogravimetry (TG) profiles of the specimen hydrogenated at 573 K and 3.3 MPa hydrogen pressure are shown in Fig. 2. In the laminate composites hydride, the dehydrogenation reaction starts around ~660 K. In the conventional Mg_2Cu

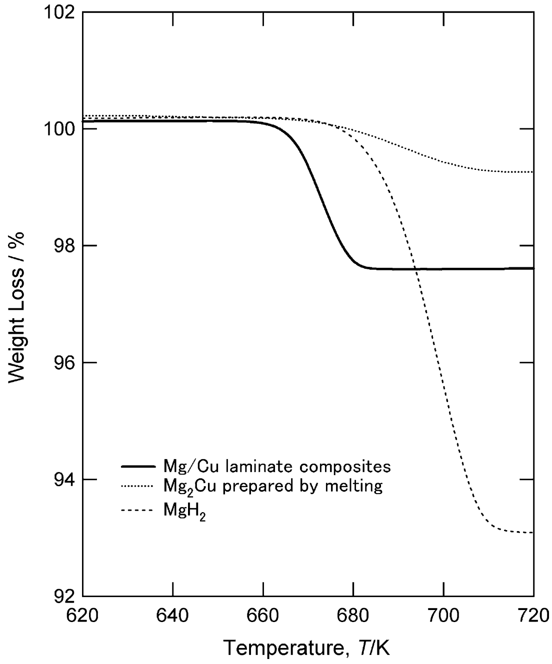

Fig. 2. Thermogravimetric (TG) profiles of Mg/Cu laminate composites (Mg/Cu = 2) and Mg_2Cu alloy. The heating ratio was 10 K/min.

alloy, the dehydrogenation reaction starts ∼670 K and onset temperature of dehydrogenation of casting sample is higher about 10 K compared with those of the laminate composites. Also, the weight-loss and slope of TG profile of laminate composites is larger than those of conventional Mg_2Cu alloy. The TG profiles are affected by the hydrogenation/dehydrogenation reaction kinetics properties.

Hydrogen contents as a function of reaction time at 573 K are shown in Fig. 3. Initial activated Mg_2Cu alloy prepared by melting started to absorb immediately, but the reaction was slow. On the other hand, initial activated Mg/Cu laminate composites started to absorb hydrogen immediately and the reaction was very fast as compared with Mg_2Cu alloy. From those results, we consider that the laminate composites have a better reaction kinetics than melting-casting alloys. Generally, the metallographic properties such as crystalline size, defects and dislocation, have influence on hydrogenation/dehydrogenation temperature and hydrogen diffusion. Thus, we examined using by TEM the micro/nano-structure of laminate composites.

Fig. 4 shows annular dark field (ADF-)STEM, high angle annular dark field (ADF-)STEM and TEM images of the as-rolled Mg/Cu laminate composites together with TEM image of Mg_2Cu alloy prepared by melting and casting. In HAADF-STEM images, heavier elements appear as brighter contrast. Therefore, we consider bright contrast in (b) as Cu and Mg_2Cu. (EDS was used for elemental analysis at the same time.) The interesting points of Mg/Cu laminate composites are summarized as follows: (1) the as-rolled Mg/Cu laminate composites have the sub-micronmeter-ordered laminate layered structure composed of Mg and Cu. (2) The Mg and Cu layers have dense lattice defects. On the other hand, the as melting and casting Mg_2Cu particle is composed a single crystalline grain, has sparse

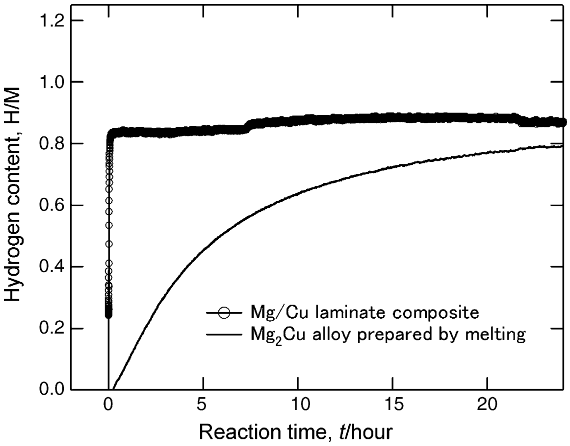

Fig. 3. Hydrogen content values as a function of reaction time at 573 K in Mg/Cu laminate composites and Mg_2Cu alloy prepared by melting.

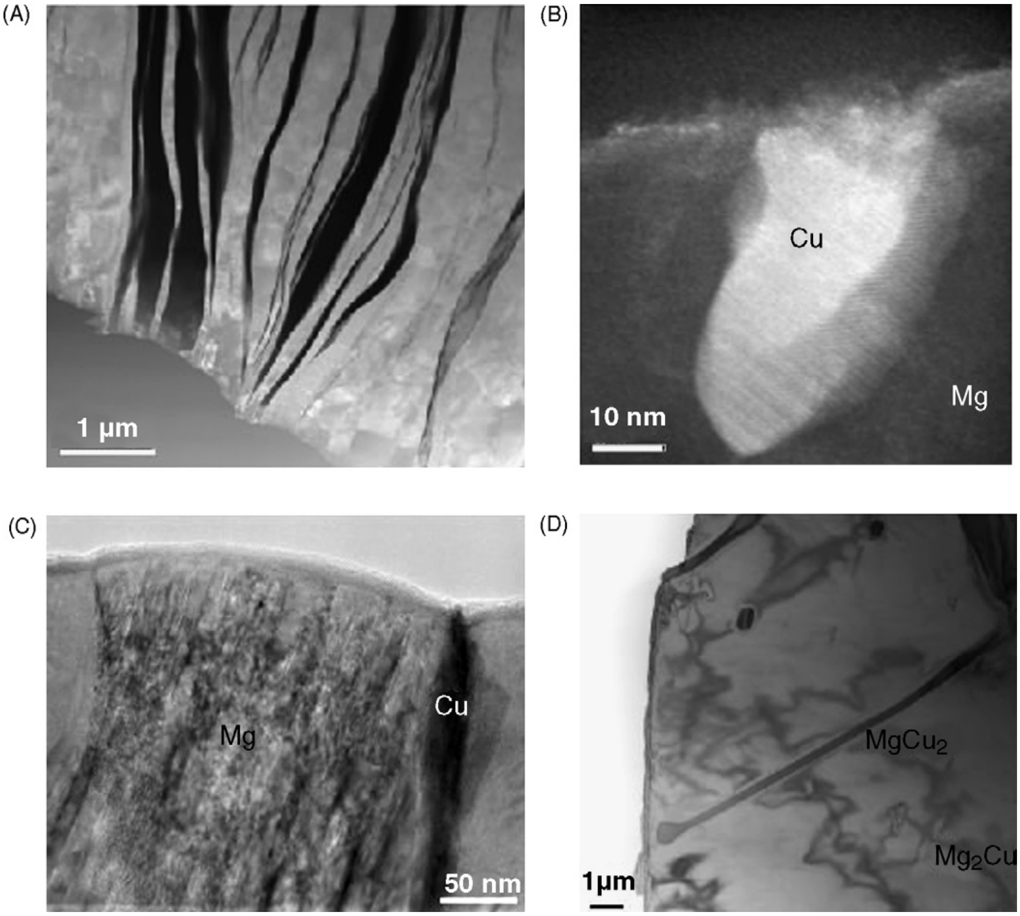

Fig. 4. Transmission electron microscopy (TEM) images of as-rolled Mg/Cu laminated composites, (a) ADF-STEM image, (b) HAADF-STEM image of near boundary, (c) high resolution TEM image, and together with (d) TEM image of Mg_2Cu alloy prepared by melting.

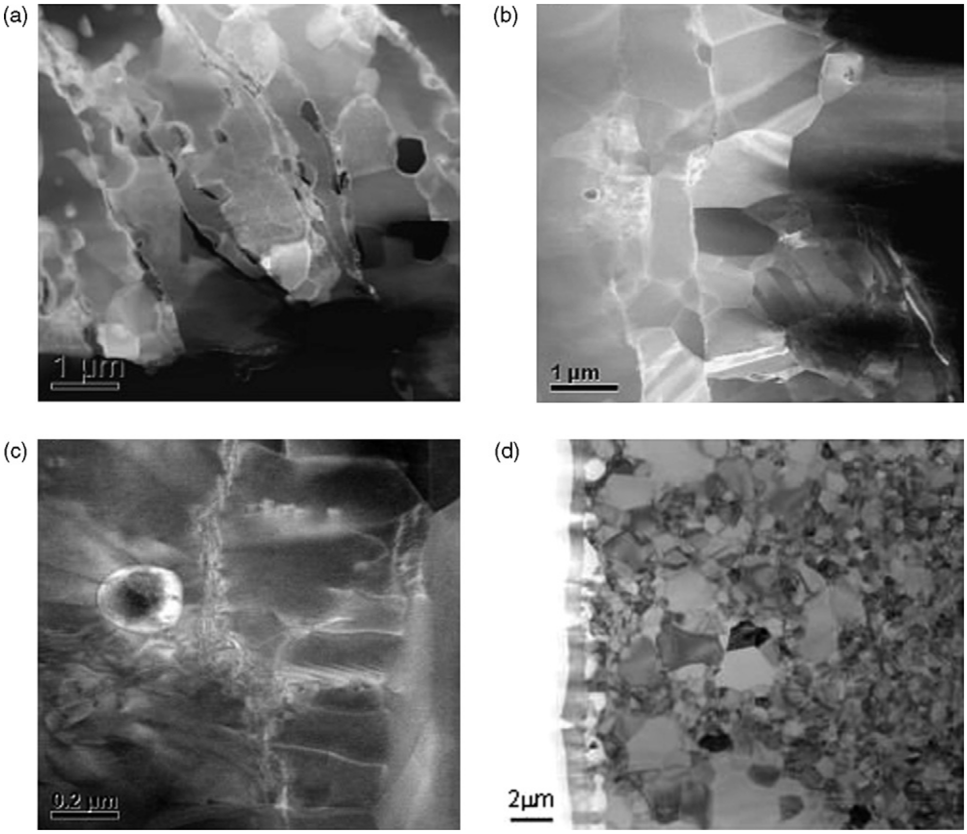

Fig. 5. Transmission electron microscopy (TEM) images of Mg/Cu laminated composites after initial activation, (a) ADF-STEM image, (b) ADF-STEM image of near boundary, (c) ADF-STEM image in high power, and together with (d) ADF-STEM image of Mg_2Cu alloy after initial activation.

lattice defect and its surface is coated by oxides. The TEM observation of Mg_2Cu particle does not show a unique metallurgical structure.

Fig. 5 shows that TEM images of the Mg/Cu laminate composites after initial activation with TEM image of the Mg_2Cu prepared by melting and casting after initial activation. The interesting points of Mg/Cu laminate composites are summarized as follows: (1) the Mg/Cu laminate composites after initial activation have kept the sub-micrometer-ordered laminate structure composed of Mg_2Cu. The Mg_2Cu grain size is kept sub-micrometer order. (2) The Mg/Cu laminate composites after initial activation have uniformly distributed pores with a sub-micrometer diameter. The porous layer structure is formed. (3) The crystalline grains of Mg_2Cu, that constituted the laminate structure, have dense lattice defects. On the other hand, the observations on Mg_2Cu alloy after activation are summarized as follows: (1) The Mg_2Cu particle is polycrystalline materials. This crystalline size varies from 1 μm order to sub-micrometer order. (2) The lattice defect and strain are introduced during the initial activation. The crystalline grain located the center of particle has a dense dislocation. (3) There is a crack in the oxides of particle surface. The pores distribute along the boundary between oxides and Mg_2Cu.

From TEM observation, the difference between nano-structure of laminate composites and conventional Mg_2Cu alloy is obvious. In laminate composites, the compressive forces and tensile forces that are generated by the rolling media could be responsible for the formation of this metallographic structure such as malutilayer and nano-grain [15]. Also, local stress and strain are introduced in the matrix, near grain boundary and interface of nano-composites, due to deformation and defects introduced during repetitive-rolling. The difference between nano-structure of laminate composites and conventional Mg_2Cu alloy has a great influence on hydrogenation/dehydrogenation reaction kinetics. It is considered that this structure, that has sub-micrometer-ordered laminate structure with dense dislocation and vacancies, enhances the diffusion of hydrogen as well as the chemical mobility of Cu and Mg in the laminate composites. These results show that the nano-structure of Mg-based laminate composites such as dislocations and stacking faults, preferred-orientation of Mg and twining, leads to lower hydrogen desorption temperature and better kinetics, which would contribute to achieve high capacity hydrogen storage materials.

3.2. Mg/Pd laminate composites

Pd actively reacts with hydrogen even after it is placed in air because of good catalytic activity of surface and diffusion property [16]. Therefore, adding Pd to Mg is expected to improve the activation properties and kinetics for hydrogen reaction. The Mg/Pd laminate composites (Mg/Pd = 6) were prepared, of which composition is identical with Mg_6Pd, that is the Mg-richest binary intermetallic compound with Pd. Fig. 6 shows

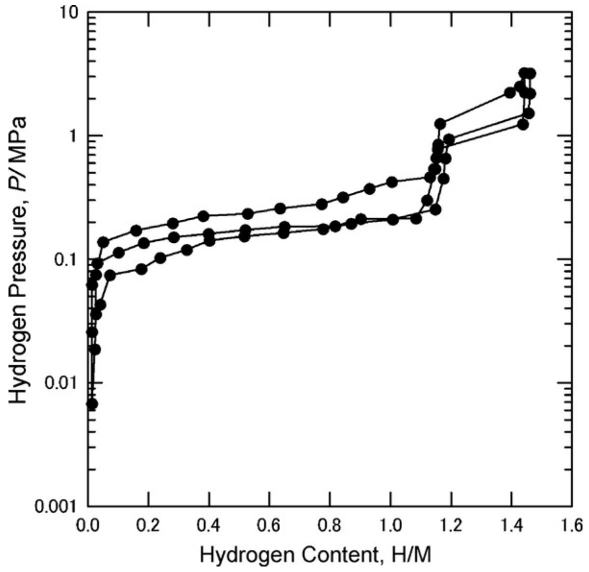

Fig. 6. Pressure-composition isotherms of hydrogenation and dehydrogenation for Mg/Pd laminate composites (Mg/Pd = 6) at 573 K.

the PC-isotherms of this specimen at 573 K. The PC-isotherms showed multi-plateaus and the maximum hydrogen content were 1.47 H/M.

Fig. 7 shows the XRD profiles of Mg/Pd laminate composites after initial activation process and after hydrogen absorption process at 3.3 MPa at 573 K. The profile of the Mg/Pd laminate composites after initial activation process consists of only Mg_6Pd phase with the detection ability of our XRD instrument. On the other hand, the profile of hydrogenated Mg/Pd laminate composites indicated the existence of MgH_2 phase and CsCl-type MgPd phase.

Judging from those results, the Mg/Pd laminate composites were considered to react with hydrogen accompanying the disproportionation and recombination of Mg and Pd, as well as Mg/Cu laminates composites. The reaction equation is expressed as follows:

$$Mg_6Pd + 5H_2 \leftrightarrow MgPd + 5MgH_2 \qquad (2)$$

From this equation, the maximum hydrogen contents are 1.428 H/M, and this value is about the same value obtained from PC-isotherms. Also, the plateau of the specimen Mg/Pd = 6 is splited into two, 0.2 and 2 MPa at 573 K. In the lower plateau pressure region, an intermediate product is formed during Mg_6Pd react with hydrogen. But, we do not have information concerned with this product at this time. In the higher plateau pressure region, an intermediate product decomposed to MgH_2 and MgPd. This complicated reactions occurred reversibly at 573 K (Fig. 6), in spite of disproportionation and recombination of Mg and Pd. It is speculated that the nano-structure introduced to the laminate composites improves the kinetics of the reaction. Detail study on the process of hydrogenation/dehydrogenation of Mg/Pd laminate composites is under way. It was considered that this reaction was enhanced by the nano-structure introduced to the Mg/Pd laminate composites.

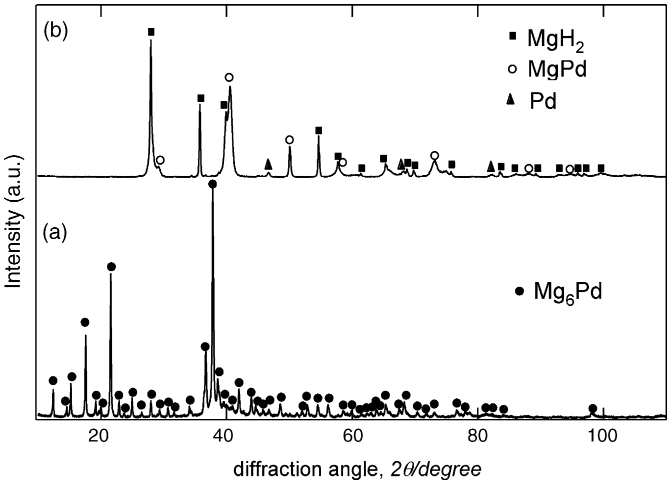

Fig. 7. The X-ray diffraction profiles of (a) Mg/Pd laminate composites (Mg/Pd = 6) after activation process with (b) Mg/Pd laminate composites (Mg/Pd = 6) after hydrogenation at 573 K and 3.3 MPa hydrogen pressure.

4. Conclusion

It is interesting to apply for repetitive-rolling method to Mg-based hydrogen storage materials. The Mg-based laminate composites have a large hydrogen capacity as well as good kinetics and reversibility for hydrogen reaction. The following conclusions are deduced from the present study.

(1) Mg/Cu laminate composites have a good kinetics compared with conventional Mg_2Cu alloy and they can reversibly absorb and desorb hydrogen at 473 K.
(2) TEM observations revealed that as-rolled Mg/Cu laminate composites and hydrogenated ones have a sub-micrometer-ordered laminate structure. Also, defects such as dislocations and stacking faults, preferred-orientation of Mg and twining were observed in the specimen by TEM observations. This special structure leads to increase the hydrogen and metallic atoms diffusion in laminate composites.
(3) In Mg/Pd laminate composites, MgH_2 is formed when the Mg/Pd laminate composites absorbed hydrogen. As they desorbed hydrogen, MgH_2 dissociated Mg, which, at least partly, formed intermetallic compounds with Pd.

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