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Hydrogen storage and structure variation in Mg/Pd multi-layer film

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ABSTRACT

The hydrogen storage properties of the as-deposited Mg/Pd multi-layer films by magnetron sputtering have been studied in this work. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis revealed that the Mg/Pd multi-layer film was composed of fine-crystalline Pd layers and columnar crystalline Mg layers. The cycle hydrogenation and dehydrogenation of the film were performed at different temperatures (305 K, 373 K and 323 K). The film absorbed and desorbed about 2.6 wt.% hydrogen at a low temperature of 373 K, which is close to the theoretical hydrogen absorption value of 2.8 wt.% for Mg_6Pd. When lowering to 323 K, the film can still absorb–desorb about 2.5 wt.% of hydrogen. During hydrogenation–dehydrogenation, Mg_6Pd formed first, followed by MgH_2 and Mg_5Pd_2. After desorption there were only Mg_6Pd and Mg_5Pd_2 phases identified in the film, showing complete dehydrogenation of the thin film at 323 K. It is believed that additional interfacial free energy in the thin film and the catalytic effect of Pd, can be accounted for the low temperature hydrogen absorption–desorption cycles.

1. Introduction

Mg based hydrides have attracted great attention as a potential candidate for applications in energy storage systems because of their high theoretical hydrogen storage capacity (7.6 wt.% for MgH_2). However, the hydrogen absorption and desorption of the conventional Mg based alloys occur at high temperature (in thermodynamic equilibrium a plateau pressure of 1 bar for bulk Mg to form MgH_2 requires 300 °C [1]) and the kinetics is usually sluggish. A lot of efforts have been devoted to overcome the barriers for the use of Mg alloys in hydrogen storage. It has been found that by reducing the particle size to nanoscale [2–4], adding catalysts [5–8] and fabricating thin films [9–15], the kinetic properties of Mg based hydride can be remarkably improved and the absorbing or desorbing temperature substantially reduced. For instances, MgH_2 with nanosize of around 5 nm can remarkably desorb hydrogen at 85 °C [3]. An addition of 3d-transition metals as catalysts to MgH_2 can drastically improve the kinetics two times and decrease the desorption temperature of Mg hydride by 145 °C [5]. Alloying Mg with 3d-transition metals can tailor the hydrogen reaction enthalpy and accordingly reduce the operating temperatures during desorption [6]. Decreasing the particle size of Mg to ~300 nm and doping with 5 wt.% TiF_3, 4.2 wt.% hydrogen can be absorbed within 1 min under ~20 bar at room temperature [7].

To explore the way of improving the performance of Mg based hydride and to reveal the related mechanism, Mg based thin films have been used as a model system [4,12,13,15]. In particular, Mg/Pd double-layer film has been investigated and Pd has been shown to be a good catalyst for the dissociation of hydrogen molecules and recombination of hydrogen atoms into molecules [12]. However, the actual mechanism of catalysis of Pd in film system is still unclear. Higuchi et al. [9] found that the hydrogen absorption–desorption temperature of Pd/Mg/Pd sandwich structured film was 373 K, which was attributed to the “cooperative effect” caused by the elastic interaction within the interfacial region. When compared to trilayer thin films, the efficiency of Pd as a catalyst in ultra-thin Mg nanoblades with a sandwich structure is more significant on reducing the desorption temperature. This cannot be explained by the conventionally proposed mechanism on grain size and strain only [12]. Our group [10] had prepared MgNi/Pd multi-layer films with MgNi and Pd layers with only tens of nanometers in thickness by magnetron sputtering deposition. The multi-layer films were found to absorb and desorb hydrogen at room temperature. However, there was a large hysteresis in the hydrogenation and dehydrogenation cycles.

The stability of the film structure is important for maintaining the optimum hydrogen storage performance. For instances, when the top Pd layer degraded during the cycling, the maximum hydrogen absorption content reduced [11] and the hydrogen desorption kinetics worsen [12]. It was also found that alloying

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occurs at the interfaces of Mg and Pd layer or Mg layer and Si substrate [11]. Reddy et al. [14] reported that in Mg/Pd double-layer films, Mg_6Pd and Mg_5Pd_2 formed along the grain boundaries of Mg films during annealing in vacuum, but not during hydrogenation. However, the influence of the microstructure variation on the hydrogen storage of Mg–Pd thin films has not been reported. Little work has been devoted to the study of interfacial reactions in Mg/Pd (or other component) multi-layer films and the structure stability were not well understood. The purpose of the present work is to clarify the microstructure variation of Mg/Pd multi-layer film in aging and hydrogenation/dehydrogenation cycling, and to reveal the influence of microstructure variation on hydrogen absorption–desorption performance. For this purpose, the phase transition and the hydrogen absorption–desorption in Mg/Pd multi-layer films during hydrogenation–dehydrogenation cycles at different temperatures have been studied in detail using XRD, SEM, TEM and pressure–composition–isotherm (PCI) instrument.

2. Experimental

2.1. Film preparation

Mg/Pd multi-layer films were prepared on (1 0 0) Si wafer substrate by magnetron sputtering. The Si wafer was ultrasonically cleaned successively in acetone for 20 min in ethanol for another 20 min and then dried naturally within a dish prior to be put into the work chamber. Two targets were used with one being Mg and another being Pd. The purity of the Mg and Pd targets was 3 N and 4 N, respectively. Magnetron sputtering systems with a direct current (dc) for Pd and a radio frequency (rf) for Mg were adopted to prepare the Mg/Pd multi-layer films. The working pressure of Ar in the chamber was maintained at 1 Pa. The applied power for depositing Mg and Pd was 110 W and 65 W, respectively. The multi-layer films have a total of 33 layers, with Mg layers and Pd layers deposited in turns. The top and the bottom layers were both Pd layers. The thickness of each layer was controlled by fixing the sputtering time. After taken out from the sputtering chamber the film was put in a glove box under Ar atmosphere immediately.

2.2. Structural and microstructural characterizations

Mg/Pd multi-layer films were characterized by XRD using a Philips X-ray diffractometer with Cu Kα radiation. The morphology and composition of the films were analyzed by LEO 1530 VP SEM equipped with an energy dispersive spectrometer (EDS) of INCA 300. Cross-sectional TEM was carried out to study the microstructure using a Philps CM200 microscope. The TEM samples were prepared using FEI xT Nova Nanolab 200 Dual-Beam FIB.

2.3. PCI measurements

To measure the hydrogen absorption and desorption at different temperatures the film was peeled off from the Si substrate for PCI measurement using an advanced materials corporation (AMC) gas reaction controller. The average weight of the samples was ~220 mg. The samples were activated twice 473 K under 30 bar hydrogen pressure for a total of 4 h before cyclic tests. The first cycle was performed at room temperature, followed by the cycle at 373 K and 323 K.

3. Results and discussion

3.1. Structural characterization of as-deposited Mg/Pd multi-layer film

Fig. 1(a) shows the X-ray diffraction pattern of the as-deposited Mg/Pd multi-layer film. It can be seen that (0 0 1) was the preferred orientation of Mg, as-expected for this kind of deposited films. As all peaks of Pd appeared clearly in the XRD pattern, there was no preferential orientation in Pd layers during film growth. No peak corresponding to any intermetallic compounds was detected for the as-deposited Mg/Pd film, indicating that there was no reaction between Mg and Pd during deposition.

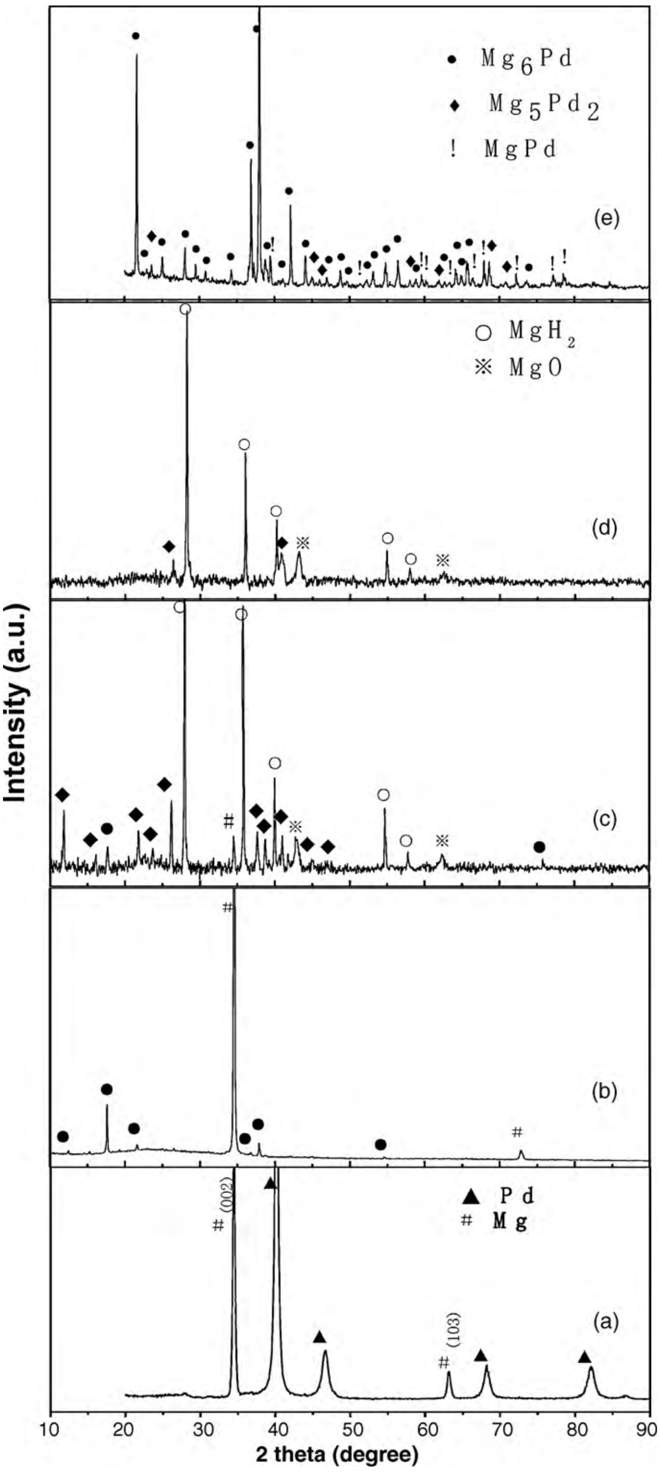

Fig. 1. XRD patterns of the Mg/Pd multi-layer film: (a) as-deposited; (b) activated at 473 K for 2 h under hydrogen pressure of 30 bar; (c) absorbed hydrogen at 373 K for 30 min; (d) absorbed hydrogen at 373 K for 60 min; (e) desorbed hydrogen after three cycles.

Fig. 2(a) is a cross-sectional TEM bright field image of the as-deposited film. It shows that Mg layer and Pd layer are about 470 nm and 80 nm in thickness, respectively. The columnar Mg crystals along the film growing direction can be observed, and their (0 0 1) planes parallel to the surface of substrate as indicated by XRD results in Fig. 1(a). This is also the case in other Mg based films [13,15]. The concentration of Mg and Pd in the film is 70.3 at.% and 29.7 at.%, respectively, as determined by EDS. It can also be noted that the distinct interfaces between Mg layers and Pd layers, with no intermixing along the interface region. This observation is in accord with the result of the XRD analysis that no intermetallic compounds were found during deposition. This is as expected as the deposition

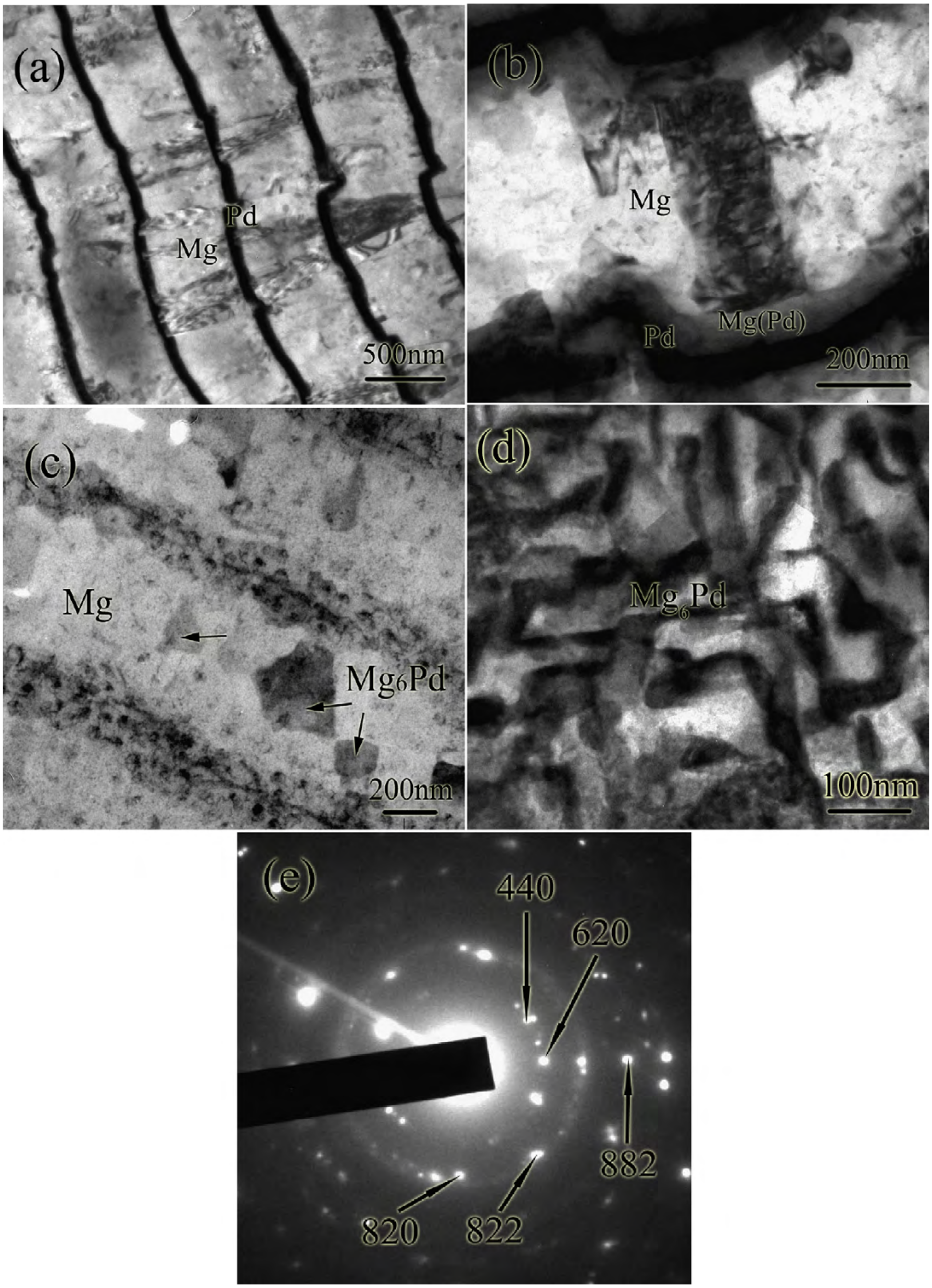

Fig. 2. Bright field TEM images of Mg/Pd multi-layer film: (a) as-deposited; (b) stored a few weeks later; (c) activated at 473 K for 2 h under hydrogen pressure of 30 bar; (d) after desorption of three absorption–desorption cycles;(e) selected area electron diffraction pattern of the film after three absorption–desorption cycles.

was carried out at low temperature where interdiffusions of Mg and Pd were quite slow.

3.2. Hydrogen absorption–desorption cycling properties

The PCI curves measured sequentially at room temperature, 373 K and 323 K are shown in Fig. 3. The PCI curves show that the film can absorb about 2.4 wt.%, 2.6 wt.% and 2.5 wt.% of hydrogen at room temperature, 373 K and 323 K, respectively. The maximum hydrogen absorption capacity does not change appreciably with increasing the temperature, and the hydrogen storage capacity was quite constant during cycling. For dehydrogenation at room temperature, there was about 0.7 wt.% hydrogen retained in the film. However, the film can desorb hydrogen completely even at a very low temperature of 323 K. It means that the multi-layer films can absorb and desorb hydrogen at such a low temperature. No obvious pressure plateau in the PCI curves was observed during the absorption processes, which is similar to previous reports on Mg thin films [10]. Absorption and desorption hydrogen pressure plateaus shortening or even disappearing were also found in nanostructure

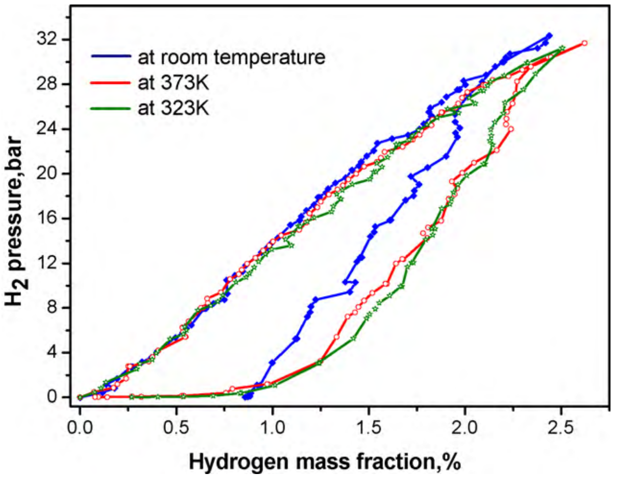

Fig. 3. PCI curves of the Mg/Pd multi-layer film performed at different temperatures of room temperature, 373 K and 323 K, respectively.

powder of $Ml_{0.7}Mg_{0.3}Ni_{3.2}$ prepared by ball milling just for 3 h [16]. One important reason is the strain created upon milling.

3.3. *Structural variation of the film during cycling*

Fig. 1(b) is the XRD pattern of the film activated at 473 K for 2 h under a hydrogen pressure of 30 bar. It shows that the film still maintained the preferred orientation along (0 0 2) of Mg layer, however, the peaks of Mg_6Pd appeared. This is in contrast with the work by Reddy et al. [14] which reported no significant intermixing or formation of an intermetallic in films annealed in hydrogen atmosphere. According to their work, the formation of Mg_6Pd only appeared in vacuum. Fig. 1(c) and (d) are the XRD patterns of the film after hydrogenation at 373 K for 30 min and 60 min, respectively. It can be found that the phases included Mg_6Pd, MgH_2, Mg_5Pd_2 and MgO in Fig. 1(c), and MgH_2, Mg_5Pd_2 and MgO in Fig. 1(d) after prolong hydrogenation. The formation MgO in the pattern in Fig. 1(c) and (d) can be attributed to the reaction of the film when exposure to air when taking out from reaction chamber. The XRD pattern of the film after dehydrogenation of the third cycle at 323 K is shown in Fig. 1(e). Most of the diffraction peaks were identified as Mg_6Pd, but with the disappearance of MgH_2 peak. Comparing with Fig. 1(a) and (b), it is clear that the film changed obviously after activation. It is interesting to note that although the hydrogenation caused more structure change for the sample activated at 473 K, it still maintained the preferential orientation of Mg. On the contrary, the phase structure of the film has completely changed after hydrogenation at only 373 K.

The above results can further be proven by TEM observation as shown in Fig. 2. Fig. 2(b) shows the film after storing in air at room temperature for four weeks. While the film still possessed the layer structure, there were inter-layers on both sides of each Pd layer. These inter-layers were not observed with freshly prepared thin film in Fig. 2(a). It clearly shows that reaction between Mg and Pd already took place along their interface boundary during the storage. This observation suggests that the structure of Mg/Pd multi-layer film was quite unstable as the film was kept at such a low temperature. Fig. 2(c) shows the morphology of the thin film activated at 473 K for 2 h. The original Pd layer has changed its morphology as some densely gathered phase were newly formed on this layer which, was identified as Mg_6Pd according to XRD analysis given in Fig. 1(b). This phase also appeared inside the Mg layers. The above results prove that the reaction has taken place in the entire film, where there were both Pd and Mg diffusions into their adjacent layers. Fig. 2(d) is the bright field TEM image of the Mg/Pd multi-layer film after three absorption–desorption cycles at room temperature, 373 K and then 323 K. It can be seen that the original layer structure of Mg/Pd multi-layer film, as well as the columnar structure within each Mg layer, disappeared totally. The selected area electron diffraction (SAD) pattern (Fig. 2(e)) reveals diffraction rings indexed to Mg_6Pd, further confirming the change of the original multi-layer structure after hydrogenation–dehydrogenation cycles.

All above results indicate that Mg reacted with Pd easily and the multi-layer structure was destroyed by activation and hydrogen absorption/desorption cycle, even at quite low temperatures. Similar results have been obtained for Mg/Pd bilayer film, where the original texture was lost during hydrogen absorption–desorption [11,14,17,18], although detailed investigation was not available in these works. And the alloying between Mg and Pd in the Mg/Pd film is mentioned [11,14,17], but there is no detail report of alloying process. The nature of multi-layer structure of the thin films in this work facilitates the interfacial reactions. The extra interfacial energy stored along the interface reduced the energy barrier for formation of new phases, making the multi-layered films highly unstable during hydrogenation–dehydrogenation, even at much low temperature than the peritectic reaction at 973 K. By calculation using the model of our work [19], the interface free energy of as-deposited Mg–Pd multi-layer film was about −2.34 kJ/mol. The interface free energy would play a role in reduce the enthalpy of formation. To reduce Mg particle size in Pd/Mg/Pd film to 50 nm, the enthalpy of formation of MgH_2 was found only to be −68 kJ/mol H_2 [4].

It is now possible to consider the phase transitions occurred in Mg/Pd multi-layer film according to above experiment results: Mg_6Pd phase forms first, which then reacts with hydrogen disproportionally, and at the same time. The remaining Mg in the film is also hydrogenated. Thus, the reaction process is expressed as follows:

$$\mathrm{Mg} + \mathrm{Pd} \rightarrow \mathrm{Mg_6Pd} + \mathrm{Mg(rich)} + \mathrm{H_2} \leftrightarrow \mathrm{Mg_5Pd_2} + \mathrm{MgH_2}$$

With respect to Mg_6Pd phase, it decomposes into Mg_5Pd_2 and Mg hydride upon hydrogenation, which is a reversible disproportion hydrogenation as proposed [20]. Our PCI results show that the hydrogen storage capacity at 373 K is about 2.6 wt.%, which is a little lower than the theoretical value of 2.8 wt.% for Mg_6Pd and the reason will be addressed below. There is no peak of MgH_2 appearing in the XRD pattern (Fig. 1(e)) after hydrogen desorption, which indicates that MgH_2 dissociated to Mg and H_2, and then formed Mg_6Pd intermetallic compound with Pd. As we know that the atomic composition of Mg and Pd is about 70:30 within the film, assuming stoichiometry of Mg_6Pd is largely maintained, there should be some Pd remaining even though all the Mg reacts with Pd to form Mg_6Pd. Thus Pd can catalyze hydrogenation–dehydrogenation contributed to hydrogen absorption–desorption even lowering to room temperature. The existence of extra Pd is also a reason for that the hydrogen storage capacity in this film is a little lower than the theoretical value.

4. Conclusions

Mg/Pd multi-layer films, with Mg and Pd layer thickness 470 nm and 80 nm thick, respectively, were prepared by magnetron sputtering. The microstructure and hydrogenation properties of these composite films were characterized in this work. The film can absorb and desorb hydrogen at room temperature and it can reversibly absorb/desorb about 2.5 wt.% of hydrogen at a temperature as low as 323 K. Hydrogen storage properties of the multi-layer Mg/Pd film were found to be quite stable even though their microstructure changed during activation and absorption–desorption cycles. Because of the high interfacial energy, Mg_6Pd phase was formed along the interface between Mg and Pd when the film was kept even at room temperature. The multi-layer structure was destroyed even after the film undergone hydrogenation at 373 K for 1 h, Mg and Pd reacted and formed Mg_6Pd and Mg_5Pd_2 phase in dehydrogenation and hydrogenation, respectively. The high interfacial free energy stored in multi-layer film was responsible for the high structure instability of the film.

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