



Letter

A catalytic effect on hydrogen absorption kinetics in Pd/Ti/Mg/Ti multilayer thin films



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ABSTRACT

In this work, we have investigated the microstructural and hydrogen storage properties of a 60 layer film of Pd(40 nm)/Ti(*x* nm)/Mg(360 nm)/Ti(*x* nm) (*x* = 10, 20, 30, 40, and 50) using an ultra-high vacuum DC magnetron sputtering system. The highest hydrogen absorption capacity of the Pd/Ti/Mg/Ti film was 4.46 wt% for *x* = 50. The hydrogen absorption rate accelerated remarkably with increased thickness of the Ti layer, from 209 min for *x* = 10 to 39 min for *x* = 40 – overall, an increase by a factor of ~5. These results demonstrate that the Ti layer in the Pd/Ti/Mg/Ti films serves as a blocking layer preventing the formation of Mg Pd intermetallic phases and provides additional diffusion paths for hydrogen atoms, which leads to enhanced hydrogen storage properties.

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1. Introduction

Among a number of alternative energy sources that includes sunlight, battery, and fuel cells, hydrogen is one of the most interesting source for future clean energy systems. Magnesium is considered a promising candidate material for a hydrogen storage system because of its low cost, accessibility, and relatively high reversible hydrogen storage capacity (7.6 wt% as MgH₂). Nevertheless, Mg based materials have critical drawbacks such as high dehydrogenation reaction temperature (>350 °C), high thermodynamic stability ($\Delta H = -75$ kJ/mol), and slow Mg H₂ reaction kinetics [1]. A number of approaches to improve the reaction kinetics of Mg through modification of hydrogenation temperatures have been studied, including bulk powder ball milling [2,3] and the use of additives [4,5], catalysts [6–9], and thin films [10–27]. In particular, in Mg based thin films with transition metal catalysts have been demonstrated to be an effective way to enhance the performance of magnesium hydrides. For example, studies on Mg/Pd films showed that Pd not only prevents the oxidation of Mg but also acts as a catalyst [10–16]. However, poor hydrogenation kinetics was observed since binary intermetallic Mg Pd alloys were formed at 373 K [12,15]. Recently, Mg based bilayer films such as MgAl [21], MgNi [22], MgTi [24,25], MgV [26], and MgCr [26] were shown to have enhanced H₂ absorption behavior, which leads to rapid kinetics at low temperatures. Mg based multilayer films

including MgAlTi [28] and MgFeTi [29] were also reported to have superior absorption/desorption hydrogen kinetics at relatively reduced temperatures.

Herein, we report the catalytic effect on the microstructure and hydrogen absorption kinetics of Pd/Ti/Mg/Ti multilayer films at various film thicknesses of the Ti interlayers, which are well controlled from 10 to 50 nm. Based on our previous study [27], the insertion of Ti interlayers between Mg and Pd prevents interdiffusion at the Mg/Pd interface and improves the absorption behavior of Mg during hydrogenation. The kinetics and capacity of Pd/Ti/Mg/Ti multilayer films, determined under a hydrogen pressure of 30 bar at 150 °C, were significantly enhanced as the thickness of the Ti interlayers increased.

2. Experiment

Sixty multilayers of Pd(40 nm)/Ti(*x* nm)/Mg(360 nm)/Ti(*x* nm) films (*x* = 10, 20, 30, 40, and 50) were deposited on a glass substrate (25 × 75 mm) and then coated with a Pd (40 nm) layer on the top Ti surface via ultra-high vacuum DC magnetron sputtering in Ar atmosphere. The deposition process was carried out below 5.0×10^{-3} Torr for Mg and 2.5×10^{-3} Torr for both Pd and Ti in Ar at a flow rate of 34 sccm and base pressure of 4×10^{-8} Torr. Typical deposition rates of multilayer films at room temperature were ~12.9 Å/s for Mg at 50 W, ~1.7 Å/s for Ti at 50 W, and ~4 Å/s for Pd at 20 W. The purity of the Mg, Ti, and Pd targets was 4 N. The deposited films were easily peeled from the glass substrates.

Microstructural characteristics were determined by X ray diffraction (XRD, Ultima IV/ME 200DX, Rigaku) and cross sectional transmission electron microscopy (TEM, JEOL JEM ARM 200F) with energy dispersive X ray (EDX, X Max Oxford). Prior to cross sectional TEM observation, the samples were cut perpendicular to the surface using a focused ion beam system (FIB, JEOL JIB 4601F). Hydrogen uptake was measured using a magnetic suspension microbalance (Rubotherm, Isosorp) via a

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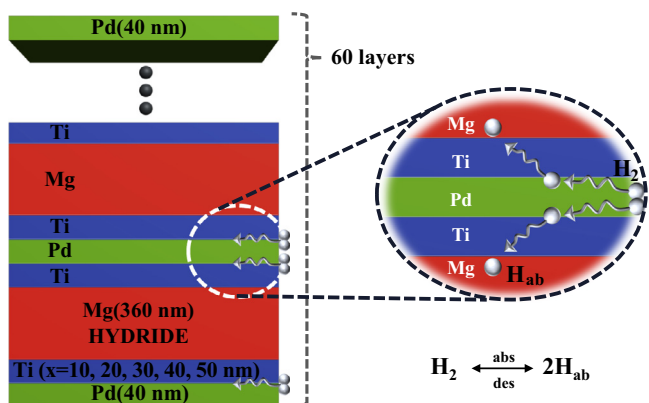


Fig. 1. Schematic diagram of the 60 layer film of Pd/Ti/Mg/Ti with varying Ti film thickness.

gravimetric method performed under a hydrogen pressure of 30 bar at 150 °C. The amount of sample used for the measurements was about 0.1–0.2 g. All sorption isotherms were obtained using ultrahigh purity gases (H_2 : 99.999%; He : 99.99%). Further experimental details can be found in our previous work [27].

3. Results and discussion

Fig. 1 displays a schematic diagram of the hydrogenation kinetics in the 60 layer film of Pd/Ti/Mg/Ti with varying Ti film thickness. H_2 molecules adsorb at both Ti and Pd catalyst surfaces, dissociate into hydrogen atoms, diffuse into the Ti/Pd catalyst subsurface layer, and cross the Ti/Pd catalyst/Mg H_2 boundary.

Subsequently, molecular hydrogen is absorbed inside the host metal lattice while two H atoms recombine to form a H_2 molecule in the desorption process. The Ti interlayers not only prevent intermixing of Mg and Pd [23,27], but also function as effective catalysts for hydrogen dissociation and recombination. In addition, the optimal Ti film thickness plays an important role in enhancing catalytic activity and hydrogenation kinetics.

Fig. 2 shows the XRD patterns of the Pd(40 nm)/Ti(x nm)/Mg(360 nm)/Ti(x nm) films with $x = 10, 20, 30,$ and 40 (a) before hydrogenation and (b) after dehydrogenation under a 30 bar hydrogen atmosphere at 150 °C. Fig. 2(a) indicates that Mg (JCPDS: #35-0821) and Ti (JCPDS: #44-1294) formed hexagonal phases while Pd (JCPDS: #46-1043) formed a cubic phase. The diffraction peaks for Mg show that the preferred growth orientations of the film are the (002) and (004) planes, while the overlapping sharp peaks correspond to the Pd (111) and Ti (101) planes. The diffraction intensity of the Ti film increased with increasing thickness. All Pd/Ti/Mg/Ti multilayer films showed no reaction, such as Mg_xPd_y intermetallic compound formation, after dehydrogenation, as shown in Fig. 2(b). Based on our previous work, the Ti layer plays a role as an inter-diffusion barrier between the Mg and the Pd layers in their hydride state [27]. The XRD data reveal that Ti interlayers in the Pd/Ti/Mg/Ti multilayer films, with thickness ranging from 10 to 40 nm, effectively prevented inter diffusion of Mg Pd alloys.

To assess the catalytic effect in the 60 layer film of Pd/Ti/Mg/Ti with varying Ti film thickness (10–50 nm), hydrogenation properties were measured under a hydrogen pressure of 30 bar at 150 °C, as shown in Fig. 3. Hydrogen absorption capacities for the Pd(40 nm)/Ti(x nm)/Mg(360 nm)/Ti(x nm) films were 3.54, 4.44, 4.08, 4.35, and 4.46 wt% for $x = 10, 20, 30, 40,$ and 50 , respectively

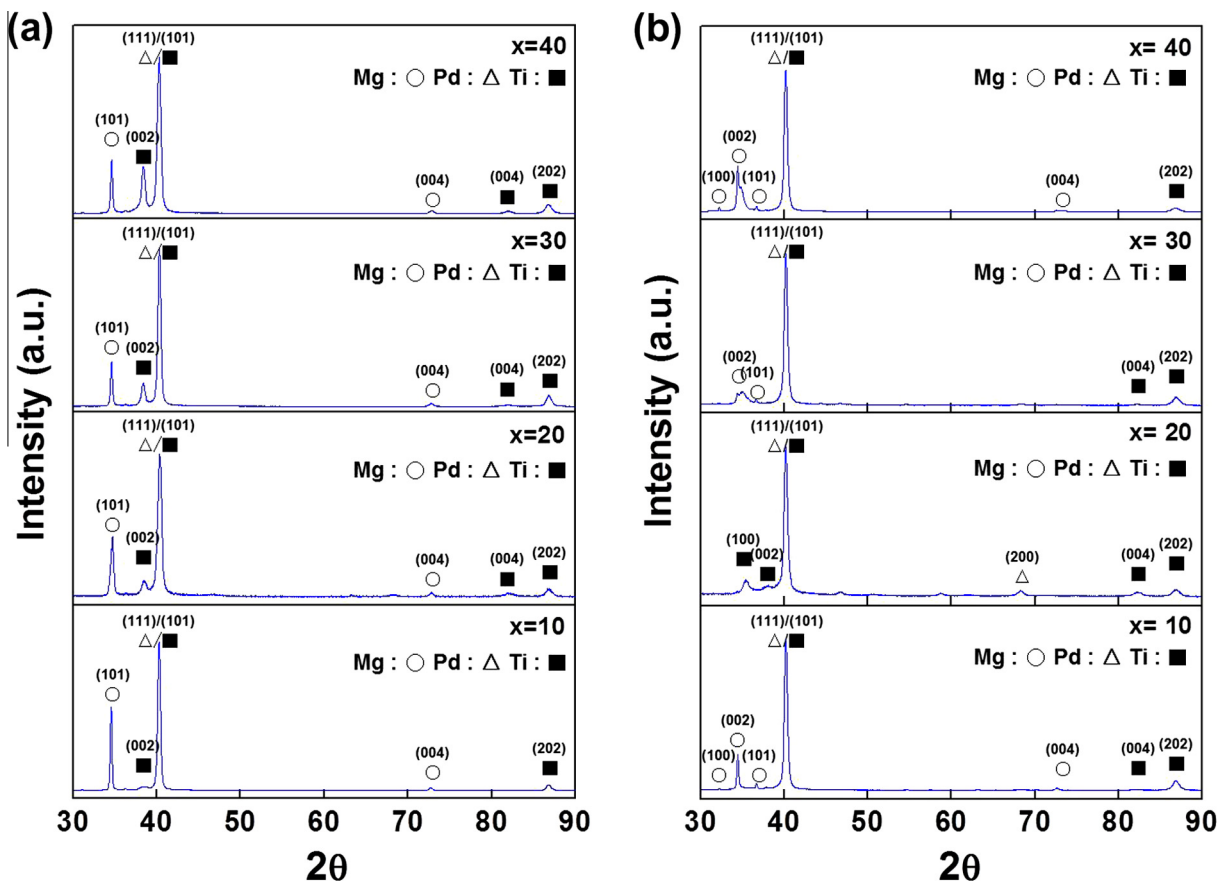


Fig. 2. XRD patterns of Pd(40 nm)/Ti(x nm)/Mg(360 nm)/Ti(x nm) multilayer films with $x = 10, 20, 30,$ and 40 (a) before hydrogenation and (b) after dehydrogenation under 30 bar of hydrogen/vacuum at 150 °C.

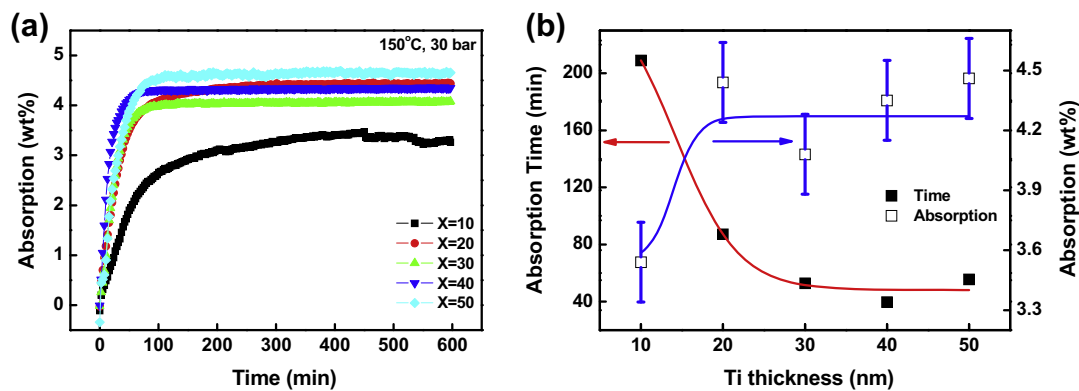


Fig. 3. (a) Hydrogen absorption capacity of Pd(40 nm)/Ti(x nm)/Mg(360 nm)/Ti(x nm) multilayer films with $x = 10, 20, 30, 40,$ and 50 and (b) saturation time vs. Ti thickness under a hydrogen pressure of 30 bar at 150 °C.

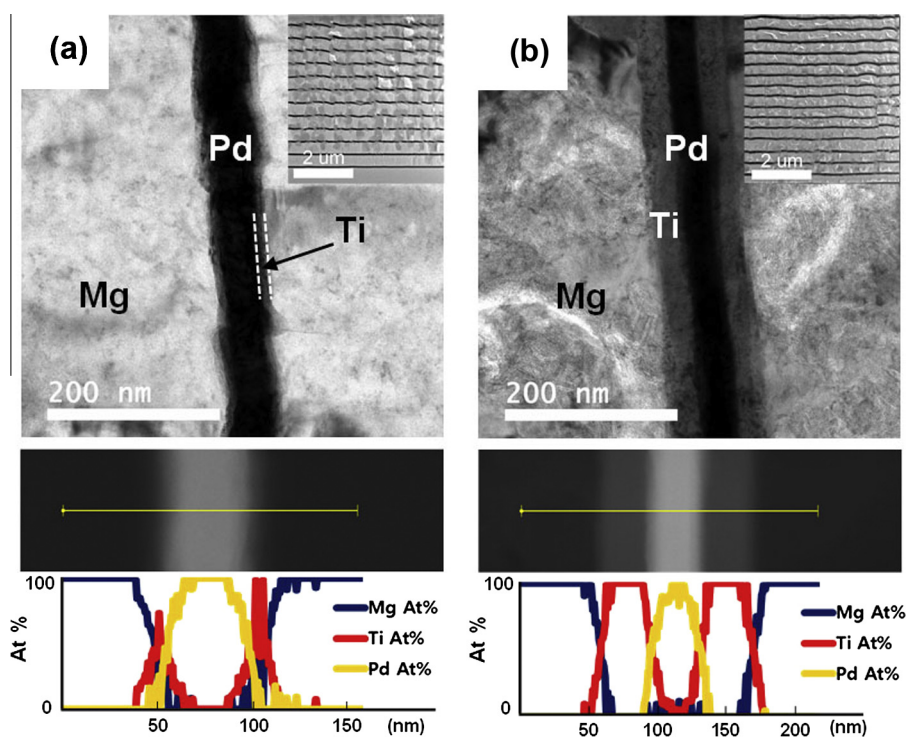


Fig. 4. Cross sectional TEM images of (a) Pd(40 nm)/Ti(10 nm)/Mg(360 nm)/Ti(10 nm) and (b) Pd(40 nm)/Ti(40 nm)/Mg(360 nm)/Ti(40 nm) multilayer films after hydrogenation/dehydrogenation under 30 bar of hydrogen/vacuum at 150 °C.

(Fig. 3(a)). The hydrogen absorption rate for $x = 10$ was much slower than that for $x = 20, 30, 40,$ and 50 in the Pd/Ti/Mg/Ti multilayer films. The absorption amount of hydrogen almost saturated at absorption time of 39–56 min in the thickness range 30–50 nm. Fig. 3(b) shows an overview of the data from Fig. 3(a), where it is clear that the hydrogen absorption rate increased with increasing Ti film thickness, from 209 min for $x = 10$ to 87 min for $x = 20$, to 52 min for $x = 30$, to 39 min for $x = 40$, and finally, to 56 min for $x = 50$. The hydrogen absorption capacity appeared to reach full saturation when the Ti film thickness was from 20 to 50 nm, indicating that the apparent optimal Ti thickness in the Pd/Ti/Mg/Ti films is ~ 50 nm. The optimal Ti film thickness of ~ 50 nm is attributed to a catalytic effect resulting in superior hydrogenation kinetics and stable saturation during the hydrogenation process, as well as prevention of Mg Pd alloy formation. The catalytic effect can be explained by the extra interfacial energy in the Pd/Ti/Mg/Ti films, which likely decreases the energy barrier required for

the formation of MgH_2 at the interface [24], and the increase in the Ti film thickness, which causes a relatively large amount of hydrogen atoms to diffuse into the Ti/Pd surface layers owing to additional diffusion paths during hydrogenation. However, if the thickness of the Ti layer further increases, an overall hydrogen absorption capacity will be decreased due to a low hydrogen storage capacity of the Ti layer and the hydrogenation rate will also be increased since the Ti hydride is more stable than the Mg hydride.

More detailed cross sectional TEM analysis was carried out for the $x = 10$ and $x = 40$ films after a hydrogenation/dehydrogenation cycle as shown in Fig. 4(a) and (b), respectively. The thicknesses of the Pd and Ti films in the $x = 10$ film were ~ 40 and ~ 10 nm, respectively. Well-deposited multilayer films were observed with slightly wavy lines due to volume expansion. In an EDX line scan profile (inset in Fig. 4(a)), the signals of Mg, Pd, and Ti were observed with no intermixing after one cycle. The EDX scan profile in Fig. 4(b) shows solid and clear layers (inset) with no obvious intermixing.

The EDX data for both films are in good agreement with the XRD data shown above, indicating that the Ti interlayer, whose thickness influences the catalytic effect, can play a role as an effective barrier layer in the Pd/Ti/Mg/Ti multilayer films.

4. Conclusions

60 layer films of Pd(40 nm)/Ti(x nm)/Mg(360 nm)/Ti(x nm) ($x = 10, 20, 30, 40,$ and 50) were prepared by an ultra-high vacuum DC magnetron sputtering system. The hydrogen absorption capacities of the Pd/Ti/Mg/Ti films were 3.54, 4.44, 4.08, 4.35, and 4.46 wt% for $x = 10, 20, 30, 40,$ and 50 , respectively. Hydrogen absorption increased and reached full saturation as the thickness of the Ti layer increased. XRD and TEM analyses confirmed the absence of Mg Pd intermetallic phases in the Pd/Ti/Mg/Ti film after a hydrogenation/dehydrogenation cycle, indicating that the Ti interlayer between the Mg and Pd layers can prevent the formation of this phase during hydrogenation. We conclude that the hydrogen storage capacity and kinetics can be considerably enhanced and stable saturation during hydrogenation can be reached by insertion of a Ti layer with an optimal thickness of ~ 40 nm between Mg and Pd. This can be attributed to the increased number of diffusion paths for hydrogen atoms.

Acknowledgements

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