# Interfacial Alloy Hydride Destabilization in Mg/Pd Thin Films

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# Interfacial Alloy Hydride Destabilization in Mg/Pd Thin Films

C.-J. Chung, Sang-Chul Lee, James R. Groves, Edwin N. Brower, Robert Sinclair, and Bruce M. Clemens
*Department of Materials Science and Engineering,*
*Stanford University, Stanford, California 94305, USA*

Recently, a remarkable increase in the equilibrium hydrogen pressure has been reported for magnesium thin films capped with a palladium layer. We show here that this increase is due to intermixing of magnesium and palladium at the interface region, as opposed to a strain effect associated with the mechanical constraint of the overlayer or substrate impeding the volume expansion of magnesium during hydrogenation, as previously claimed. Transmission electron microscopy and depth profiling x-ray photoemission spectroscopy are used to directly measure interfacial intermixing between Mg and Pd, and we find that the extent of intermixing and the equilibrium hydrogen pressure both increase with annealing. We present a simple thermodynamic model to assess the effect of alloying on equilibrium pressure, and find that the observed equilibrium pressure increase is consistent with the observed thickness of the intermixed region, which is of the order of a few nm. We also directly measure the stress during hydrogenation and show that the observed values correspond to a negligible increase in equilibrium pressure.

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Modifying reaction thermodynamics and equilibrium conditions in solid state reactions is fundamentally interesting and practically important. In particular, the relative influence of chemical energies and mechanical strain is of interest, where large strains can cause changes in chemical reactions[1–4]. The ability to tune reaction thermodynamics for hydrogen storage materials could create a larger suite of candidate materials that can meet the myriad materials requirements. Magnesium hydride is an attractive hydrogen storage candidate due to its high reversible hydrogen mass capacity of 7.6 wt%. However, slow kinetics and low equilibrium hydrogen pressures at room temperature remain difficulties in practical applications. Baldi et al. have observed a significant increase in equilibrium hydrogen pressure of about 200 times the bulk Mg value for Mg thin films capped with Pd[5–9]. This significant increase is attributed to the elastic strain energy associated with the 32% volume increase during hydrogenation. They assert that the Pd cap has a clamping effect, constraining the volume expansion in the in-plane direction. The resulting strain increases the energy of the $MgH_2$ hydride, pushing the hydride reaction:

$$\mathrm{Mg} + \mathrm{H_2} \leftrightarrow \mathrm{MgH_2} \tag{1}$$

to the left, and increasing the equilibrium hydrogen pressure.

However, analysis of the effect of strain energy on the equilibrium pressure shows that strain energy is insufficient to produce the remarkable equilibrium pressure increase. Including strain energy into the equilibrium condition for equation 1 gives the equilibrium pressure:

$$P^{(\mathrm{eq})}\left(E_{\mathrm{el}}\right) = P^{(\mathrm{eq})}\left(0\right) e^{E_{\mathrm{el}}/RT}, \tag{2}$$

where $P^{(eq)}(0)$ is the equilibrium hydrogen pressure for the strain-free state, $R$ is the ideal gas constant, and $T$ is the temperature. The observed increase of a factor of 200 at a temperature of 333 K would result from a strain energy of 14.7 kJ/mol. Assuming linear elasticity and using elastic constants for Mg, this corresponds to a linear strain of 13%, while even a modest increase in equilibrium pressure of a factor of 10 implies an elastic strain of 8%. These are roughly an order of magnitude larger than typical thin film strains and two orders of magnitude larger than typical bulk strains[10]. In short, it is not physically reasonable that strains this large exist in the $MgH_2$.

Furthermore, x-ray measurements and in-situ stress measurements give no indication of large stresses. Using a thin film curvature apparatus described elsewhere[11] , we measured stress during hydrogenation in a variety of Pd-capped Mg films, which were grown in an UHV sputter deposition apparatus[12]. Figure 1 a shows the force per width ($F/w$) behavior during hydrogenation at 1 Atm $H_2$ and dehydrogenation in vacuum of a Pd/Mg/Pd layered film (each layer 20 nm thick). Attributing the relatively rapid ($\sim$ 1 min) change in $F/w$ during hydrogenation to elastic strain in the $MgH_2$ layer gives a stress of about 700 MPa and an elastic strain of $\epsilon \approx 1\%$, which is far smaller than that associated with an appreciable increase in equilibrium pressure. However the rapid response makes it much more likely that this $F/w$ behavior is associated with volume changes associated with hydrogen uptake in the Pd layers, which occurs much more rapidly than formation of $MgH_2$. For example, the time required to react 20 nm Mg takes about 1 hour at 5.5 bar hydrogen pressure and 393 K[13]. Also, we observe a time scale of few hours for hydride reaction of multilayer samples in this study. Moreover, there is no further change in stress after this initial transient, indicating that there is no stress signature in the appropriate time scale for formation of $MgH_2$. X-ray diffraction (figure 1 b) also shows that the $MgH_2$ lattice parameter in similar hydrogenated films is the same as the bulk value, while that of Pd reflects a tensile stress, consistent with the residual $F/w$ of the in-situ measurement. So both x-ray and substrate curvature apparatus indicate that the $MgH_2$ is formed with near zero stress. This suggests that the volume change associated with forming the hydride phase is accommodated by a stress-free vertical expansion of the new phase. This is also born out by neutron diffraction measurements which show a $\sim 30\%$ thickness increase in Mg layers that have been hydrogenated and dehydrogenated[14]. Thus it is unlikely that the proposed strain energy mechanism is responsible for the observed increase in equilibrium hydrogen pressure for Pd-capped Mg thin films.

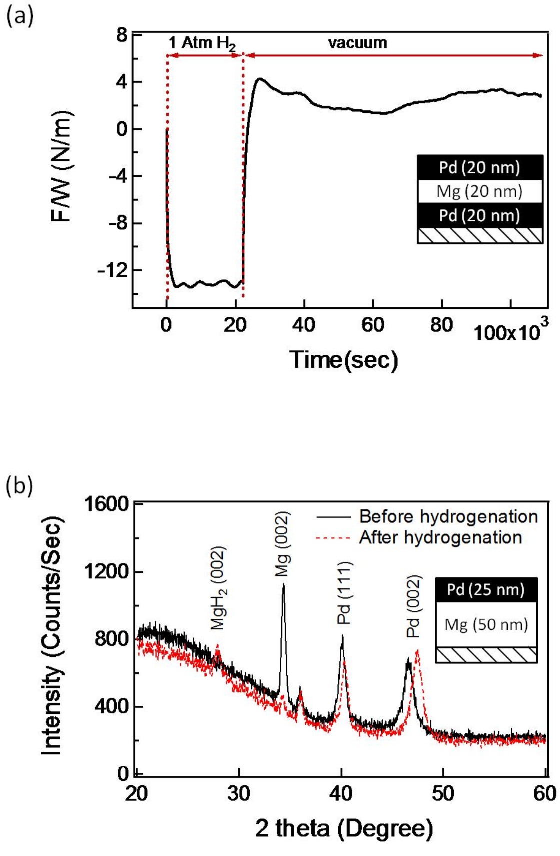

FIG. 1. a) Force per width during hydrogenation at 1 atm $H_2$ and dehydrogenation in vacuum of a Pd/Mg/Pd layered thin film. b) Symmetric reflection x-ray diffraction results for a Pd-capped, 50 nm thick Mg film, before and after hydrogenation at $T = 363$ K under 1.6 atm $H_2$ gas.

A more likely source of this enhanced equilibrium pressure is the chemical energy associated with the Mg-Pd bonds in the layered film, consistent with previous results that show that MgPd alloys and compounds have a larger equilibrium hydrogen pressure than Mg[15]. This equilibrium pressure increase is an example of a destabilization of the hydride as discussed by Vajo[16]. The hydrogenation reaction for a MgPd alloy can be represented by:

$$\left(\frac{1}{1-x}\right) \mathrm{Mg}_{1-x}\mathrm{Pd}_x + \mathrm{H}_2 \leftrightarrow \mathrm{MgH}_2 + \left(\frac{x}{1-x}\right) \mathrm{Pd} \quad (3)$$

The strong Md-Pd bonds lower the enthalpy of the left side of this reaction, with the result that the net enthalpy reduction is smaller for pure Mg hydrogenation, from -76 kJ/mol to around -56 kJ/mol depending on the MgPd phase being reacted[17].

Figure 2 shows the pressure-transmission-isotherm, extracted from in-situ measurement of optical transmission of 700 nm visible light during a continuous increase in $H_2$ gas pressure for a Pd-capped, 20 nm thick Mg films. Shown are results for films with 10 nm Ti and 10 nm Pd underlayers, as well as the result from the film with the Pd underlayer after an anneal at 373 K for 1 hour. The equilibrium pressure of all three samples is greatly enhanced over that of pure Mg, which is expected to be from 0.0003 torr to 0.0009 torr depending on the reference[18, 19]. The equilibrium hydrogen pressure of the Pd/Mg/Pd increases from 4.5 torr to 21 torr as a result of the anneal. This significant increase in the equilibrium hydrogen pressure from annealing is consistent with the observed increase in alloying as discussed below. The Ti/Mg/Pd sample has the lowest equilibrium pressure, reflecting the absence of intermixing with Pd at the bottom interface that occurs in the Pd/Mg/Pd sample.

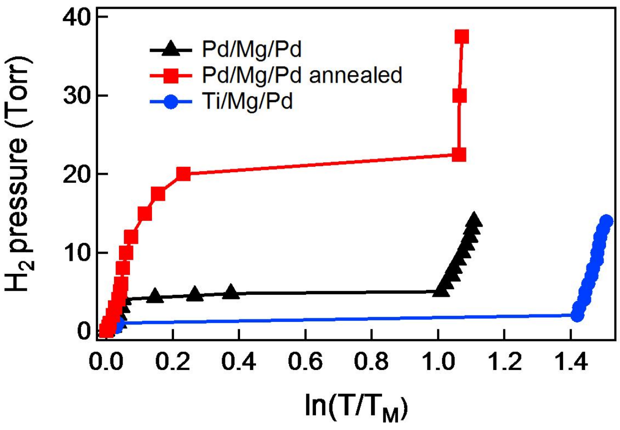

FIG. 2. Pressure-transmission-isotherm (PTI) curves of Mg-based thin film samples: as-deposited Pd/Mg/Pd, annealed Pd/Mg/Pd, and Ti/Mg/Pd

Figure 3 summarizes the high resolution transmission electron microscopy (HRTEM) observations of intermixing layer between the magnesium and palladium layer. These images allow identification of an intermixed region with lattice spacing intermediate between that of Pd and Mg. The thickness of intermixing layer before annealing is approximately 5 nm while that of annealed sample is around 10 nm (Fig. 4c, 4d). The interface between Ti and Mg shows no intermixed region, consistent with the immiscibility between the Mg and Ti.

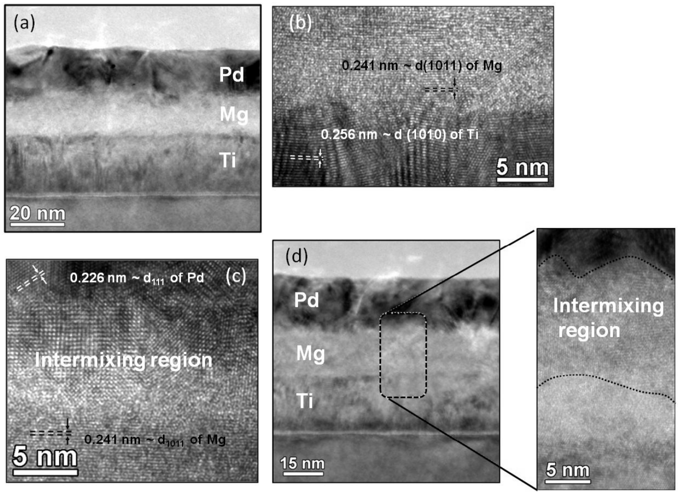

FIG. 3. (a) Cross-section TEM image of Ti/Mg/Pd multilayer samples. (b) HRTEM image of the Ti/Mg interface in (a). (c) HRTEM image of the Mg/Pd interface in(a). (d) Cross-section TEM image and HRTEM of annealed Ti/Mg/Pd sample. The dashed area highlights the intermixing region.

X-ray photoemission spectroscopy provides further evidence of intermixing between Mg and Pd, where the binding energy of palladium is observed to be a function of position in the Pd layer, as presented in Figure 4. The depth profiles shows that the binding energy of Pd $3d_{5/2}$ peaks at top of the palladium layer are different from those at the intermixed region, which implies the change of chemical states is due to alloying of palladium with magnesium.

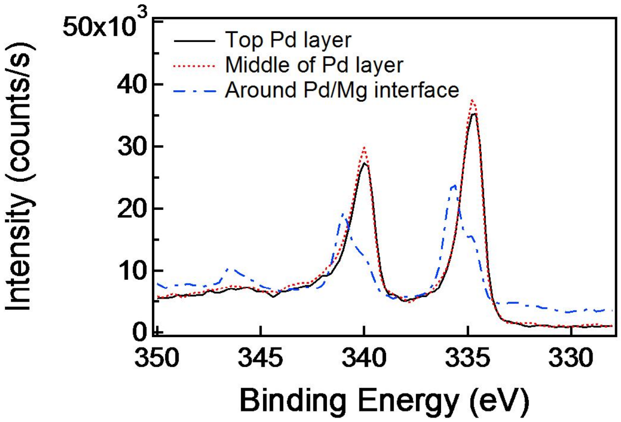

FIG. 4. Pd 3d XPS signals at different position in the palladium layer of the Ti/Mg/Pd multilayer.

As mentioned above, the observed intermixing increases the equilibrium hydrogen pressure due to the chemical energy associated with Mg-Pd bonds in the intermixed region at the Mg/Pd interface. This is an interfacial version of hydride destabilization, whereby the thermodynamics of the hydride forming reaction is modified by a second reaction that competes with hydrogen for the hydride forming constituents[20]. Here the hydride is destabilized by interface alloying between Mg and Pd, since formation of the hydride involves competition for the Mg between Pd and H. We imagine that hydrogenation of a Pd-capped thin Mg film occurs via the reaction in equation 3, where $x$ is now the *local* concentration of Pd in the Mg layer. The formation enthalpy of the $Mg_{1-x}Pd_x$ alloy drives the reaction to the left, destabilizing the hydride and increasing the equilibrium pressure. The large mixing enthalpy between Mg and Pd is reflected in the large number of MgPd compounds in the binary phase diagram. Here, for simplicity, we ignore compound formation and use a regular solution model to estimate the mixing enthalpy of the $Mg_{1-x}Pd_x$ alloy, where:

$$\Delta H_{\text{mix}} = H_{\text{PdMg}} x(1-x)$$

We use the method of Miedema [21] to estimate the regular solution bond parameter $H_{\text{PdMg}} \approx -160$ kJ/mol, and we assume a composition profile given by:

$$x = \frac{1}{2}\left[1 + \text{erf}(z/\sigma)\right]$$

where $z$ is the position measured from the nominal Pd/Mg interface, and $\sigma$ is the width of the intermixed region. The enthalpy associated with this intermixing can be found by integrating over the composition profile:

$$\langle \Delta H \rangle = \frac{1}{h_{\text{Mg}}} \int_{-h_{\text{Mg}}}^{h_{\text{Pd}}} \Delta H_{\text{mix}}(x(z))\, dz$$

Thus a thinner Mg layer will have a larger intermixing enthalpy, since the intermixed region is a larger fraction of the total Mg layer. The equilibrium hydrogen pressure is then given by equation 4[22]:

$$P^{(\text{eq})}(\langle \Delta H \rangle) = P^{(\text{eq})}\ e^{-\langle \Delta H \rangle / RT} \qquad (4)$$

This is shown plotted as a function of the reciprocal of the magnesium film thickness $h_{\text{Mg}}$ in figure 5, where a fit has been done to match our model with the the equilibrium hydrogen pressure from films with different thickness of Mg on a 10 nm Ti base layer and a 20 nm Pd cap, as well as the data from Baldi et al. from similar films. In both cases the intermixed region thickness $\sigma$ and the bulk equilibrium pressure were used as fitting parameters. The interface width extracted from these fits is 1.5 nm and 1.9 nm for our data and the data of Baldi et al respectively. Thus a relatively small amount of interfacial intermixing can have a large effect in the equilibrium pressure. This reflects the large negative enthalpy of mixing between the two constituents. Forming the hydride requires breaking relatively strong Mg-Pd bonds, and thus the hydride is destabilized, resulting in an increase in equilibrium hydrogen pressure. Taken on a per area basis, this intermixing gives an effective interface energy of $\sim$ 6 to 8 J/m$^2$, which is much larger than that associated with interfacial disorder or dipole formation[23]. Thus, this chemical energy associated with nanometer-scale intermixing dominates.

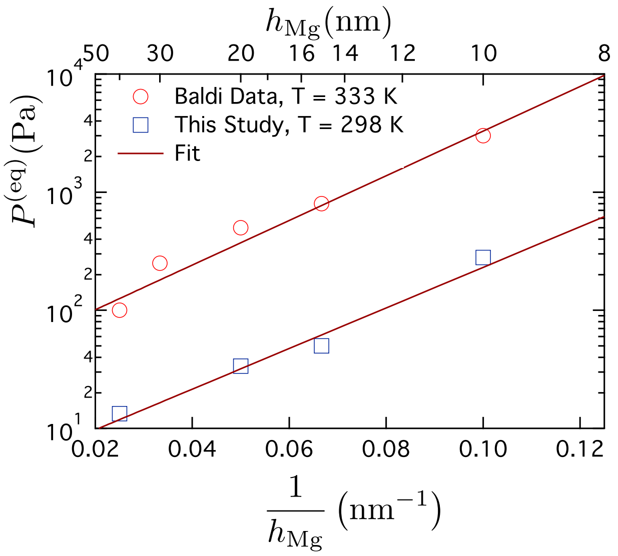

FIG. 5. Mg layer thickness dependence of the equilibrium hydrogen pressure from equation 4 fit to the data using the interface width $\sigma$ and bulk equilibrium pressure as fitting parameters. The data of Baldi et al.[5] is also shown fitted to the same expression. The interface widths extracted from these fits is 1.5 nm and 1.9 nm respectively for our data and the data of Baldi et al.

In summary we show by numerical estimates and physical measurement that strain is not responsible for the observed increase in equilibrium pressure in Pd capped nanometer-scale Mg thin films. We propose a new mechanism - an interfacial version of hydride destabilization, where the enthalpy of the hydride forming reaction is altered by the necessity to break strong Pd-Mg bonds. We observe significant intermixing between Mg and Pd in these material and show that the degree of intermixing increases with annealing, as does the equilibrium hydrogen pressure. Our simple intermixing enthalpy model gives good agreement with the observed Mg layer thickness dependence of the equilibrium pressure, with an intermixed region of order 2 nm.

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[22] This ignores the mixing entropy, which is small compared to the mixing enthalpy in this case.

[23] Assuming a typical interface dipole energy of order 0.5 eV and a typical interfacial atomic density gives an interface energy of order 1 J/m$^2$. Typical interfacial disorder energies are a fraction of that.