

Thermodynamically Destabilized Hydride Formation in "Bulk" Mg - AlTi Multilayers for Hydrogen Storage

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Supporting information

Experimental details:

Mg-AlTi and Mg-Ti multilayer thin films of 0.5 μm total thickness with various thicknesses of Mg and AlTi or Ti layers were prepared using dc magnetron sputtering (Orion 5, AJA International) on silicon wafers coated with a layer of photoresist to enable lift-off of the entire film from the substrate by post-deposition immersion in acetone. The base pressure in the deposition chamber was 5×10^{-8} Torr or lower. Sputtering was performed at an Ar pressure (5N purity) of 4 mTorr in sputter-up configuration with continuous substrate rotation. AlTi layers were prepared through co-sputtering of Al and Ti in 1:1 atomic ratio at a combined sputter rate of $\sim 0.5 \text{ \AA/s}$. The Ti and AlTi interlayers are fixed at 2 nm thickness unless indicated otherwise. Depending on the layer thickness, the sputter rate of Mg was adjusted so that deposition of even the thinnest layers took a minimum of 10 seconds, i.e. a rate between 0.5 and a maximum of $\sim 2 \text{ \AA/s}$. Samples are denoted as X/Y in which X is the thickness of magnesium and Y is the thickness of the interlayers (AlTi or Ti) in nm. All multilayer stacks are terminated with a 7 nm Pd/Ti or Pd/AlTi bilayer on both sides to protect samples from oxidation and catalyze hydrogen dissociation and to prevent interdiffusion of Mg and Pd.

A Sieverts type apparatus (HyEnergy LLC. PCTPro 2000) was used to measure capacity and thermodynamic properties of the specimens. The sample mass varied between 5 and 10 mg. A small 4 ml reservoir was used to set up the equilibrium pressure for both absorption and desorption processes. PCT measurements were run at 473 K.

The microstructure of as-prepared and cycled samples was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD was performed on a Bruker AXS diffractometer (Discover 8) equipped with a HiStar general area 2-D detector operating with Cu- K_{α} radiation. TEM sample preparation was performed using focused ion beam (FIB) lift-out on a Zeiss NV vision 400 Focused Ion Beam-equipped scanning electron microscope. TEM analysis was performed on a JEOL 2010 and JEOL 2200FS operating at 200 kV and was also used to verify the layer thicknesses.

Full derivation of equation (3)

Considering the formation of MgH_2 , the hydriding reaction is the following



The Gibbs free energy change associated with this reaction at a given temperature and hydrogen pressure is related to the standard free energy of formation ΔG^0 and the equilibrium constant K .

$$\Delta G = \Delta G^0 + RT \ln K = \Delta G^0 - RT \ln(p_{H_2}) \quad (s2)$$

And because $\Delta G = 0$ in equilibrium:

$$\Delta G_{bulk}^0 = -RT \ln K = RT \ln p_{bulk} \quad (s3)$$

where “ p_{bulk} ” denotes the equilibrium plateau pressure of bulk Mg, as opposed to nano-Mg. Upon formation of the hydride as a new phase, the original interface between Mg and AlTi is annihilated and a new interface between MgH_2 and the interlayer is formed. The change in the interfacial energy associated with transformation of an Mg layer to an MgH_2 layer can be written as:

$$\Delta E_{int} = \sum_i \{A\gamma\}_{MgH_2|TiAl} - \{A\gamma\}_{Mg|TiAl} \quad (s4)$$

where A is the interfacial area per mole Mg, and γ is the energy per unit area of the interface. The term ΔE_{int} has to be added to the bulk Gibbs free energy change to obtain:

$$\Delta G_{nano}^0 = RT \ln p_{nano} = \Delta G_{bulk}^0 + A\Delta\gamma \quad (s5)$$

Assuming a uniform thickness of Mg across each layer, the interface area per mole of thin film is equal to the molar volume V of magnesium divided by its thickness d , V/d , and since each Mg layer is sandwiched between two layers, there are two interfaces contributing to the total energy of the system. Thus:

$$A = \frac{2V}{d}. \quad (s6)$$

Combining equations (s3)-(s6) we obtain the following expression for the plateau pressure of a thin Mg film of thickness d , p_d :

$$\ln\left(\frac{p_d}{p_{bulk}}\right) = \frac{2V}{RTd}\Delta\gamma \text{ or } \ln(p_d) = \ln(p_{bulk}) + \frac{2V\Delta\gamma}{RT} \frac{1}{d} \quad (s7)$$

Results

Fig. S1 shows the X-ray diffraction patterns of the as deposited Mg/AlTi and Mg/Ti multilayers with different combinations of nominal layer thicknesses. From the spacing of the satellite peaks, the bilayer thickness Λ can be calculated according to (see ref. 23):

$$\frac{1}{\Lambda} = \frac{1}{d_1} - \frac{1}{d_2} \quad (s8)$$

where d_1 and d_2 are the d-spacings calculated from Bragg's law for adjacent satellite peaks. The bilayer thickness calculated in this manner is 45 Å, which is close to the nominal thickness of 40 Å. The central peak for the Mg/Ti 2/2 multilayer is located at $36.6^\circ 2\theta$ which corresponds to the average (002) spacing in the multilayer stack. For the 5/2 multilayer, the satellite peak spacing

gives a bilayer thickness of 72 Å, which is also close to nominal. Both the Mg (002) and Pd (111) reflections are also visible for this sample. For the Mg/AlTi stacks, the Mg has strong (002) texture for the 10/2 multilayer. For the 2/2 material, some small satellite peaks are also evident and the bilayer thickness derived from their spacing is 46 Å.

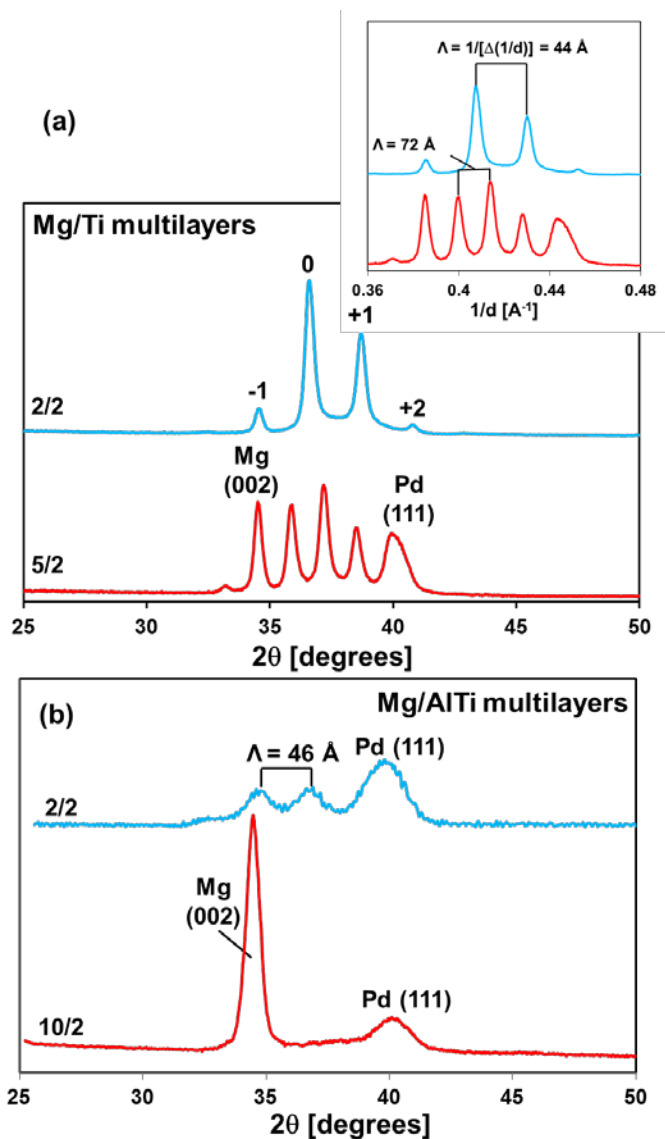


Fig. S1: XRD patterns of (a) Mg/Ti multilayers and (b) Mg/AlTi multilayers. For Mg layers < 10 nm, satellite peaks are clearly visible and the inset illustrates how the bilayer thickness can be estimated from their spacing.

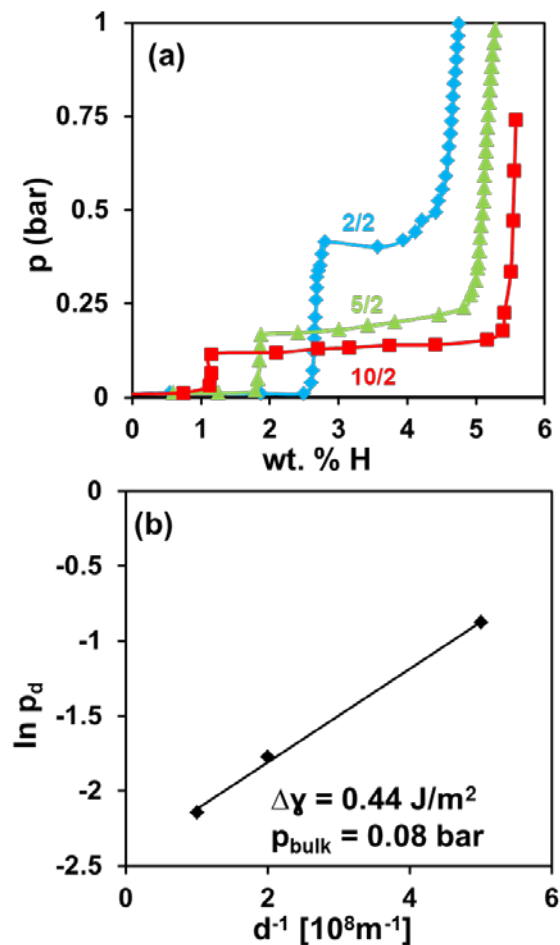


Fig. S2: Absorption pressure–composition isotherms of Mg-Ti samples of three different Mg thicknesses (d) with constant Ti thickness of 2 nm at 473 K (a) and the corresponding $\ln(p_d)$ as a function of $1/d$ (b).

To investigate the effect of the interlayer structure (metallic versus hydride) on the interfacial energy and the amount of hydride destabilization, we also examined multilayers of Mg/Ti with Mg thicknesses of 2, 5 and 10 nm and Ti thickness of 2 nm. As noted before, due to the very high stability of titanium hydride ($\Delta H_f = -140 \text{ kJ/mol H}_2^{16}$), its formation occurs prior to MgH_2 at very low pressures. Therefore, the original interface is Mg/TiH_2 and the new interface forming during hydrogenation will be $\text{MgH}_2/\text{TiH}_2$. PCT results for Mg/Ti multilayers of different Mg thicknesses are shown in Fig. S2a. The first plateau belongs to TiH_2 formation which is wider for thinner Mg layers as the mass ratio of Mg:Ti decreases. As was found for Mg/AlTi in Fig. 2, the

plateau pressure, p_d , is higher for thinner Mg layers as the influence of the interfacial energy becomes larger. These results are summarized in Fig. S2b where the linear relationship between $\ln(p_d)$ and $1/d$ is shown using equation s7. Extrapolation predicts a p_{bulk} of 80 mbar which is basically identical to the value obtained from the Mg/AlTi isotherms. $\Delta\gamma$ is calculated as 0.44 J.m⁻²; identical to the result by Mooij *et al.* based on optical measurements and using the same thermodynamic model equations³⁰.

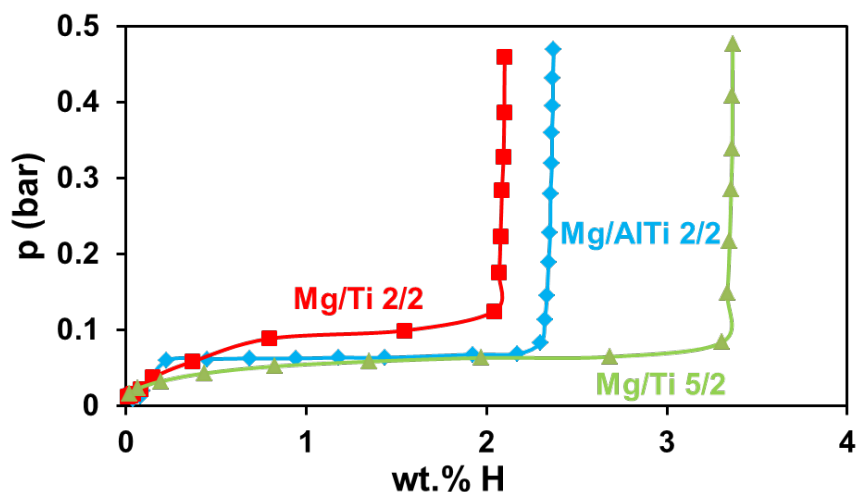


Fig. S3: Desorption isotherm of Mg/AlTi (2/2) and Mg/Ti (2/2) at 473 K

We also recorded desorption pressure composition isotherms of the Mg/Ti 5/2 and 2/2 and Mg/AlTi 2/2 multilayers and the results are shown in Fig. S3. The Mg/Ti 5/2 and Mg/AlTi 2/2 multilayers did not show any change in the desorption plateau pressure compared to bulk Mg. For the 2/2 multilayer of Mg/Ti, the desorption pressure in the middle of the plateau is approximately 100 mbar which is a factor two higher than what is commonly found at 473K.

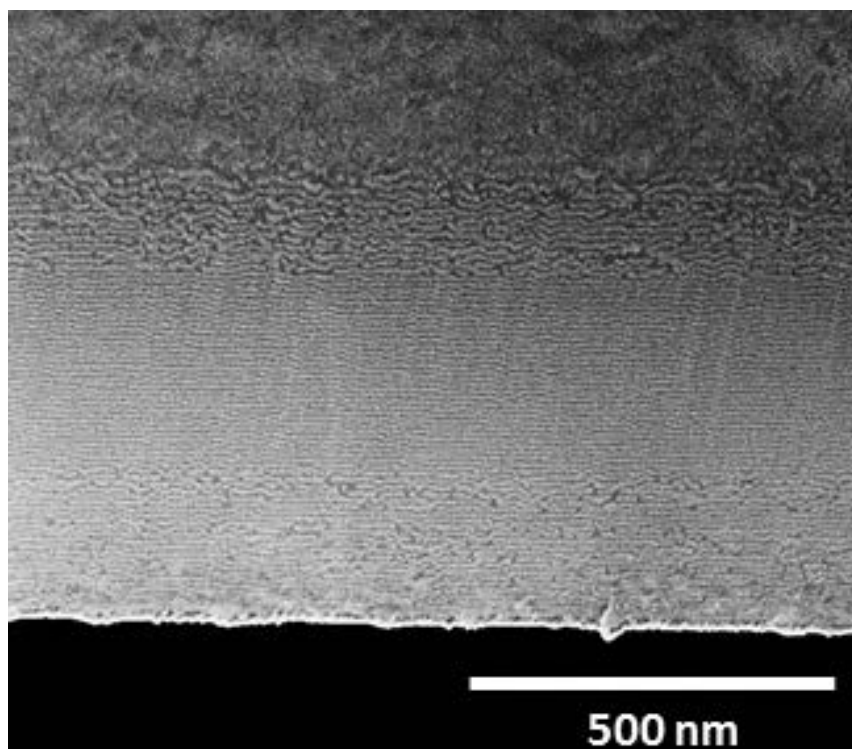


Fig. S4: An SEM image of a FIB cross-section of the 2/2 Mg/AlTi sample after partial absorption, showing disintegration of the interfaces in top and bottom.

After partial absorption of a Mg/AlTi 2/2 multilayer, we see a very big difference between the central, unreacted part of the stack and the hydrogenated parts at the top and bottom. The interfaces are heavily deformed and the layers are starting to break up in the reacted parts of the material.

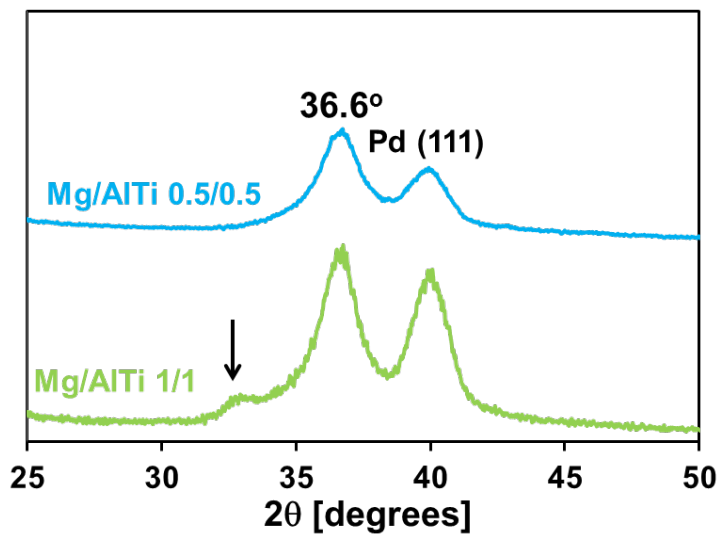


Fig. S5: XRD patterns of Mg/AlTi 1/1 and 0.5/0.5 multilayers. The arrow indicates a satellite peak in the pattern of the 1/1 multilayer.