Experimental details:

Deposition of the samples used for NR, XRD and hydrogen sorption measurements was done by rf (Ta) and dc (Mg, Cr, V) magnetron sputtering. Sputtering was performed in sputter-up configuration with continuous substrate rotation. The Ar pressure during sputtering was 4 mTorr and the base pressure was better than $5*10^{-8}$ Torr. Mg was deposited at 100 W power (~2.5 Å/s) and the powers for the Cr and V target were adjusted for stoichiometry. The NR and XRD samples were deposited on Si covered by its native oxide. The hydrogen sorption sample was deposited on a 4 inch Si wafer coated with a layer of photoresist. Subsequent dissolution of the photoresist in acetone resulted in a free-standing 1.5 μm film that was used for hydrogen sorption measurements.

Neutron Reflectometry was performed on the D3A instrument at the NRU reactor in Chalk River Laboratories, Chalk River ON, Canada. Deuterium absorption was performed in-situ using an aluminum sample cell and high purity deuterium (99.999%). Pressure accuracy was +/- 0.25 mbar. The (initial) applied deuterium pressure was 10 mbar for Mg-10%Cr-10%V and 50 mbar for pure Mg as absorption was observed to be extremely slow at lower pressures (see Fig. S5). The reflectivity curves were measured at grazing incidence in specular geometry as a function of the incident angle θ. The neutron wavelength that was used was 2.37 Å using a focusing pyrolytic graphite monochromator.

Hydrogen sorption cycling was performed in a Sieverts type apparatus (HyEnergy PCT-Pro2000) at 200^{o}C. The hydrogen pressure was set to 3 bar for absorption (reservoir volume 11.9 ml, absorption finishing at ~1.5 bar) and primary vacuum for desorption (reservoir volume 1025 ml, desorption finishing at ~25 mbar). Ab-and desorption steps were terminated when the average rate fell below 0.005 wt.%/min for a period of 4 minutes. Samples used for XRD and AFM were hydrogenated in a high-pressure differential scanning calorimeter (TA instruments, Q20) under a pressure of 5 psi (~350 mbar).

X-Ray Diffraction was performed on a Bruker AXS diffractometer (Bruker Discover 8) using Cu-K_{α} radiation ($\lambda = 1.5406$ Å). The diffractometer uses a HiStar general area 2-dimensional detection system (GADDs) with a sample-detector distance of 15 cm.

Atomic Force Microscopy (AFM) was performed using a multimode AFM (Veeco Instruments Inc.) operating in tapping mode, equipped with an E-type piezo element. ACTA probes (AppNano) having a nominal radius of 6 nm and resonant frequency of 300 kHz were used.

Table S1: Model parameters for Mg layer

Mg_as deposited			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Pd	55.11	3.978E-6	9.14
CrV	55.03	1.331E-6	3.99
Mg	555.67	2.183E-6	10.86
Ta	94.32	3.421E-6	0.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 1.95E-2			
Mg_1hour at 50 mbar			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Catalyst	121.93	2.607E-6	25.00
Mg_D-rich	120.32	6.485E-6	25.00
Mg_D-poor	452.04	2.029E-6	90.04
Ta	94.31	4.26E-6	0.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 7.32E-2			
Mg_10hours at 50 mbar			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Catalyst	125.63	2.782E-6	32.95
Mg_D-rich	168.93	5.708E-6	32.97
Mg_D-poor	462.81	3.937E-6	78.66
Ta	87.39	4.983E-6	9.56
bulk	N/A	2.073E-6	5.00
Chi^2 = 2.26E-2			
Mg_20hours at 50 mbar			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Catalyst	125.68	2.801E-6	32.19
Mg_D-rich	297.19	5.901E-6	32.97
Mg_D-poor	346.11	3.964E-6	101.63
Ta	83.31	5.053E-6	13.15
bulk	N/A	2.073E-6	5.00
Chi^2 = 1.79E-2			

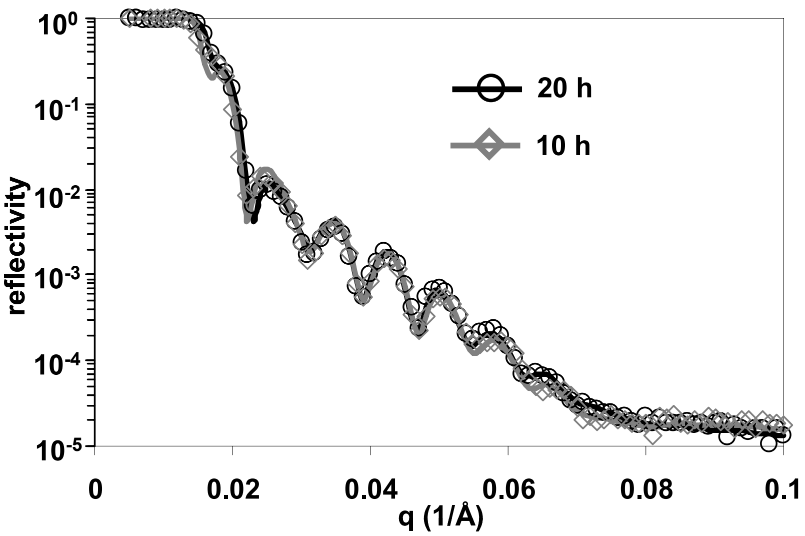

Fig. S1: Reflectivity curve and fit of Mg layer after 10h and 20h at 50 mbar deuterium pressure

Data after 10h and data 0.05 < q < 0.1 were not shown in the main body of the paper. As can be seen in Fig. S1, the fit (solid line) is still excellent up to q = 0.1. There is very little change in the reflectivity curve over this 10 h period, once more underlining the blocking effect of the MgD_2 layer underneath the CrV layer.

Table S2: Model parameters for Mg-10%Cr-10%V layer

As-deposited Mg-10%Cr-10%V			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Pd	57.42	4.08E-6	4.00
CrV	52.19	1.322E-6	10.00
Mg-10%Cr-10%V	553.62	2.25E-6	5.78
Ta	93.25	3.65E-6	5.834
bulk	N/A	2.073E-6	5.00
Chi^2 = 5.5E-2			
Mg-10%Cr-10%V after 10 minutes at 10 mbar			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Pd	57.40	4.00E-6	5.00
CrV	56.18	2.221E-6	5.00
Mg-10%Cr-10%V	554.00	3.045E-6	5.00
Ta	92.04	5.529E-6	5.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 2.27E-2			
Mg-10%Cr-10%V after 20 minutes at 10 mbar			
	Thickness (Å)	SLD (Å^{-2})	Roughness (Å)
Pd	58.40	3.839E-6	5.00
CrV	55.50	2.592E-6	5.00
Mg-10%Cr-10%V	551.96	3.936E-6	5.00
Ta	95.36	5.639E-6	5.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 2.77E-2			

Table S2 (continued)

Mg-10%Cr-10%V after 30 minutes at 10 mbar

	Thickness (Å)	SLD ($Å^{-2}$)	Roughness (Å)
Pd	51.00	3.80E-6	10.00
CrV	60.50	1.901E-6	10.00
Mg-10%Cr-10%V_top	427.03	5.602E-6	10.00
Mg-10%Cr-10%V_bottom	283.18	4.270E-6	264.85
Ta	92.65	5.467E-6	5.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 7.14E-2			

Mg-10%Cr-10%V after 6.5 h at 10 mbar (saturated)

	Thickness (Å)	SLD ($Å^{-2}$)	Roughness (Å)
Pd	51.34	3.668E-6	8.45
CrV	60.40	1.879E-6	6.83
Mg-10%Cr-10%V	718.33	5.585E-6	7.99
Ta	98.57	5.005E-6	0.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 1.33E-2			

Mg-10%Cr-10%V at 1 bar

	Thickness (Å)	SLD ($Å^{-2}$)	Roughness (Å)
Pd	51.34	4.948E-6	7.17
CrV	61.00	2.267E-6	10.74
Mg-10%Cr-10%V	717.80	5.598E-6	6.85
Ta	100.79	5.48E-6	0.00
bulk	N/A	2.073E-6	5.00
Chi^2 = 2.25E-2			

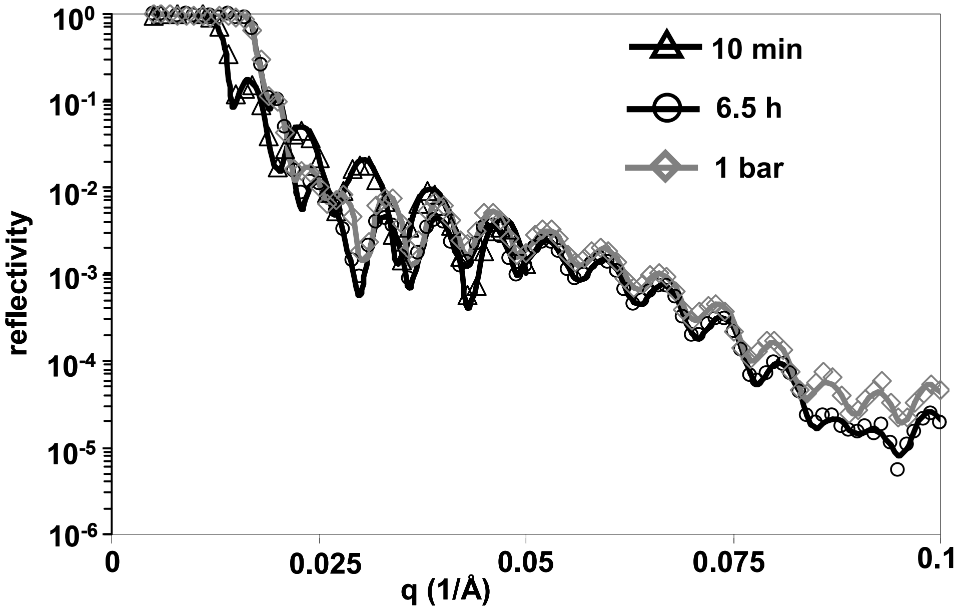

Fig. S2: Reflectivity curves and fits for Mg-10%Cr-10%V after 10 minutes and 6.5h at 10 mbar and at 1 bar pressure.

These data in Fig. S2 were not shown in the main body of the paper. From the corresponding SLD profiles in the bottom panel of Fig. 3 it could be seen that the main effect of increasing the pressure from 10 mbar to 1 bar is an increase in the SLD/deuterium content of the Pd and CrV layers. The only change observed in the reflectivity curves is a small increase in intensity in the region $0.085 < q < 0.1$.

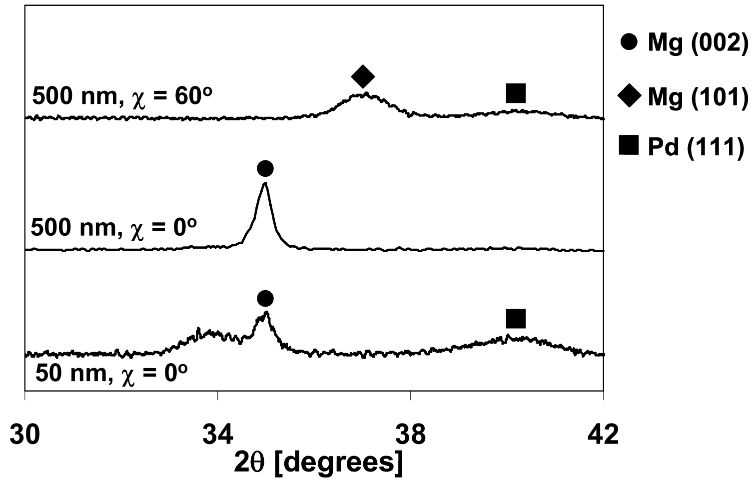

Fig. S3: XRD patterns at $\chi = 0$ for a 50 and 500 nm and $\chi = 60^\circ$ for a 500 nm Mg-10%Cr-10%V film. At $\chi = 60^\circ$ the (101) reflection is visible and allows for calculation of the a-axis as well.

Note that for measuring the (101) reflection, a 10x thicker film was used than for the NR measurements in order to get sufficient signal. However, it is obvious from Fig. S3 that the (002) reflections are at identical angles for the 50 and 500 nm thick layers, so it is safe to assume the NR sample is identical.

From the Scherrer equation

$$D = \frac{\lambda}{B\cos\theta}$$

where D is the crystallite size and B is the integral breadth of the peak in radians[i], a crystallite size of 246 Å was calculated from the (002) reflection in the lower pattern in Fig. S3. The grain size of MgH_2 after hydrogenation was calculated in the same way from the integral breadth of the MgH_2 (110) reflection.

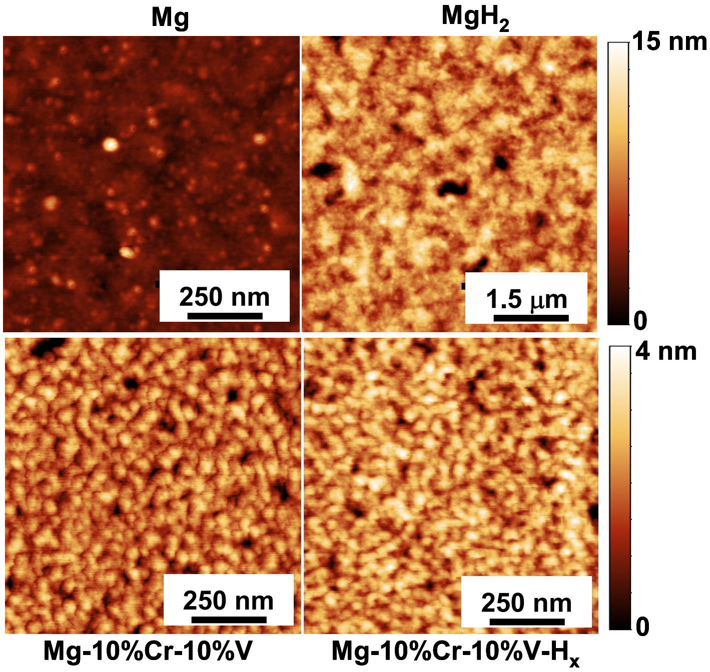

Fig. S4: AFM micrographs of Mg (top) and Mg-10%Cr-10%V (bottom) in as-deposited (left) and hydrogenated state (right).

From the AFM micrographs, it is obvious that there is a big difference between the Mg and Mg-10%Cr-10%V layer, especially in the hydrogenated state. Note that the brightness-scale spans 15 nm for the Mg layer and only 4 nm for Mg-10%Cr-10%V. Obviously, the alloy film is much smoother than the pure Mg film, especially after hydrogenation. Note that the scale bar for the hydrided Mg layer is 6x larger for the hydrided Mg film, showing that the surface features have very large lateral dimensions as well. The R_q values determined with AFM are 9.2, 21.4, 5.8 and 6.1 Å for as-deposited Mg, hydrided Mg, as-deposited Mg-10%Cr-10%V and hydrided Mg-10%Cr-10%V, respectively.

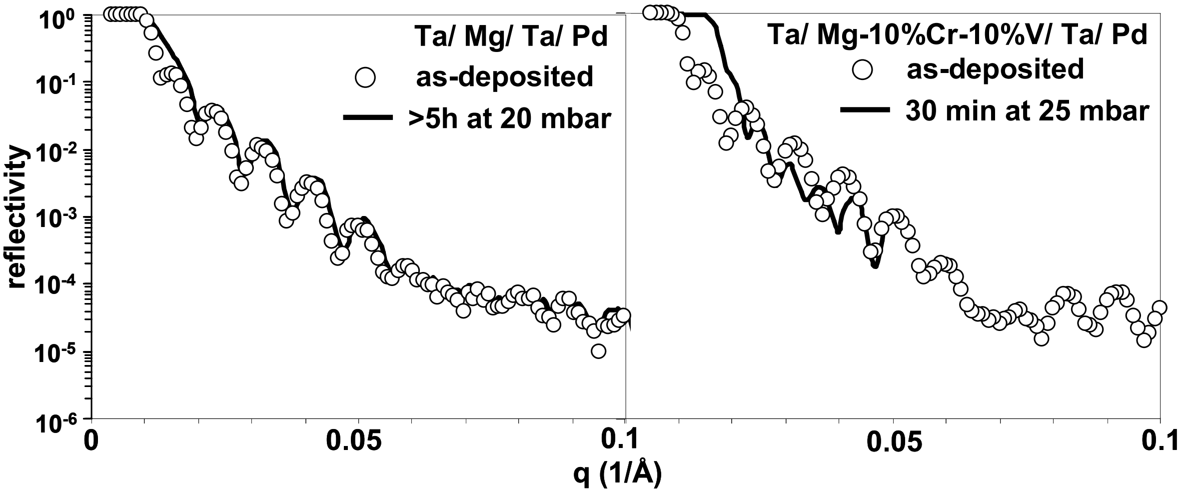

Fig. S5: Reflectivity curves for Mg with Ta/Pd bilayer catalyst (left) in as-deposited state and after more than 5 h of exposure to 20 mbar deuterium and of Ta/Pd capped Mg-10%Cr-10%V (right) in as-deposited state and after 30 minutes exposure to 25 mbar deuterium.

As Fig. S5 shows, the reflectivity curve of a pure Mg layer hardly changes when exposed to a deuterium pressure of only 20 mbar. Even after more than 5 h, there is only a minor change around the critical edge. The layer does not expand significantly during this period as the distance between oscillation maxima, which is inversely proportional to the layer thickness[ii], does not change. This particular sample had a Ta/Pd bilayer catalyst as opposed to the CrV/Pd bilayer presented in the paper. To rule out a decisive influence of the catalyst bilayer, an alloyed film with the same Ta/Pd bilayer catalyst was measured under virtually identical conditions. As shown on the right-hand side of Fig. S5, deuteration is equally fast for this film compared to the sample capped with CrV/Pd at 10 mbar. After only 30 minutes, the critical edge has shifted from q = 0.009 to 0.015 and the periodicity of the oscillations has clearly decreased, indicating significant expansion of the film. These results show that nucleation of MgD_2 in a pure Mg layer is indeed intrinsically more difficult compared to an alloyed film.

References

[i] M. Birkholz, *Thin film analysis by X-Ray scattering*, chapter 3, p110, Wiley-VCH Weinheim 2006
[ii] X.L. Zhou and S.H. Chen, *Phys. Rep.*, 1995, **257**, 223