Materials Science and Technology (MS&T) 2013
October 27-31, 2013, Montreal, Quebec, Canada

Applied Neutron Scattering in Engineering and Materials Science Research

INTERDIFFUSION OF FE AND MG LAYERS DURING ANNEALING AND DEUTERIUM ABSORPTION

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Keywords:
Hydrogen storage, magnesium, neutron reflectometry, thin films

Abstract

We compared the interdiffusion of a Ta/Mg/Fe/Ta/Pd thin film system after deuterium absorption and desorption at 250ºC with an annealing of the film structure to 250ºC. The combined x-ray and neutron reflectometry study shows that the layers start to interdiffuse at 250ºC with the film structure still clearly visible. In contrast, after deuterium absorption and desorption the changes of the film structure are more severe. We observe an intermixing of the Mg/Fe/Ta/Pd layers with only the bottom Ta layer staying intact.

Introduction

MgH_2 is a very attractive hydrogen storage material because it possesses a high gravimetric storage density of 7.6 wt.% and is relatively cheap. However, the temperatures needed to overcome the slow kinetics are too high for most practical applications. Therefore, a lot of experimental work has been done to improve the sorption kinetics and lower the temperatures needed for absorption and desorption. Most approaches consisted of using high energy ball milling [1] to reduce the grain sizes and adding metals or metal oxides as catalysts [2]. Especially bcc metals [3] and combinations thereof like Fe-Ti [4], Cr-V [5], and Fe-Cr [6] showed very fast sorption kinetics when alloyed with Mg.

In the last years research on thin films has attracted a lot of attention. Using thin films as model systems makes it possible to discriminate between the catalytic surface effect of a cap layer on top of a Mg film and the catalytic bulk effect of alloying the Mg film with other elements. These thin film systems have the big advantage that they can be fabricated in a controlled and reproducible way so that e.g. a Mg film can be completely covered with a surface catalyst layer.

A 5 nm thick Pd cap layer has turned out to be sufficient to avoid oxidation of the hydrogen storage film underneath and to dissociate the hydrogen molecules. As a consequence, thin films

do not need to be activated at high temperature and they always show much better sorption behaviour than the corresponding bulk material. Thin films absorb hydrogen fast even at room temperature and hydrogen pressures below 1 bar [7]. Interestingly, a Ta/Pd bilayer turned out to even improve the absorption and desorption kinetics [8] compared to a single Pd layer [9].

As the structural properties (like e.g. interdiffusion and alloy formation) can change the properties of a hydrogen storage material drastically, we applied X-Ray Reflectometry (XRR) and Neutron Reflectometry (NR) in the present work to study the structural properties of a 55 nm thick Mg film sandwiched between a Ta and Fe layer and capped by a Ta/Pd bilayer during annealing and deuterium absorption, respectively.

Experimental

The thin films were prepared by co-sputtering onto a Si(100) wafer in a confocal sputtering chamber (Orion 5 instrument from AJA International) operating at an Ar (purity 99.999 %) pressure of 5×10^{-3} mbar which had been previously evacuated to a pressure less than 3×10^{-8} mbar. First a 10 nm Ta buffer layer was deposited onto the wafer, followed by a 55 nm Mg, 12.5 nm Fe, 5 nm Ta, and 5 nm Pd layer.

The neutron reflectometry experiments were performed on the D3 reflectometer at the neutron research reactor NRU in Chalk River using a focusing pyrolytic graphite (PG) monochromator at a neutron wavelength of $\lambda = 0.237$ nm. More technical details can be found elsewhere [10].
In a NR experiment the neutron beam hits the surface of a sample at the scattering angle θ and is specularly reflected off the sample at the same angle, which is typically in the range between 0 and 2º. The interfaces of the samples are arranged perpendicular to the scattering vector

$$|\vec{q}| = \left|\overrightarrow{k_r} - \overrightarrow{k_\iota}\right| = \frac{4\pi}{\lambda}\sin\theta$$

with $\overrightarrow{k_r}$ and $\overrightarrow{k_\iota}$ being the reflected and incoming neutron wave vector. At grazing incidence the interaction of the neutron with the sample can be described with a neutron index of refraction analogous to optical reflectivity. The neutron index of refraction depends on the strength of the interaction of neutrons with a specific isotope in the film and can be represented by

$$n = \sqrt{1 - \frac{\lambda^2}{\pi} N_j b_j}$$

where N_j and b_j are the nuclear scattering length of the elements/isotopes in layer j. The product $N_j b_j$ is called scattering length density (SLD). We used the software PARRATT32, which is based on the Parratt recursion algorithm [11], to fit our NR data by varying the SLD, layer thickness, and interface roughness of each individual layer j.

In our NR experiments we used deuterium because of its large coherent scattering length, which leads to a large increase in the SLD of the absorbing layer, thus leading to a change in the index

of refraction and finally in the measured reflectivity curve. Total reflection of neutrons occurs up to a critical scattering vector q_c :

$$q_c = 4\sqrt{\pi\, Nb}$$

The SLD of Mg film is larger than the SLD of the Si substrate. Therefore, the increase of q_c is a good measure of the average deuterium content absorbed by the film.

The x-ray reflectometry (XRR) measurements were performed with an ULTIMA III x-ray system from Rigaku. The system is equipped with the so-called Cross Beam Optics providing a parallel beam. The used wavelength is λ = 0.15419 nm corresponding to the Cu K_α radiation, whereas the K_β radiation was absorbed by a Ni filter.

Results

The neutron reflectometry data of the as-prepared (blue circles) and annealed (red circles) thin film structure 10 nm Ta / 55 nm Mg / 12.5 nm Fe / 5 nm Ta / 5 nm Pd is shown in Fig. 1. The fits (solid lines) are based on the SLD profiles shown in Fig. 2. The different layers of the thin film structure are clearly visible which proves the high quality of the film. The Pd and top Ta layer cannot be distinguished because the SLDs of these materials are very close: 4.0 and 3.8x10^{-6} $Å^{-2}$, respectively.

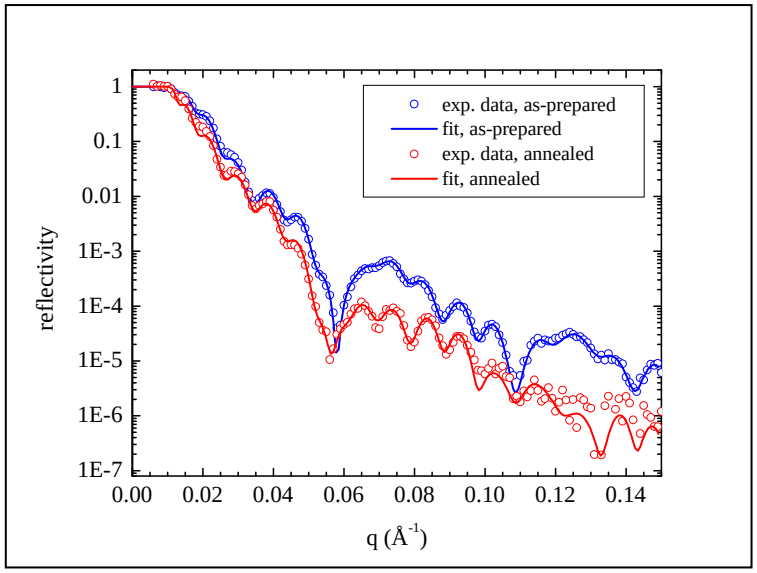

Figure 1. Neutron reflectivity curves for the as-prepared sample (blue circles) and the sample annealed for 6 hours at 250º C (red circles) along with the fits (solid lines).

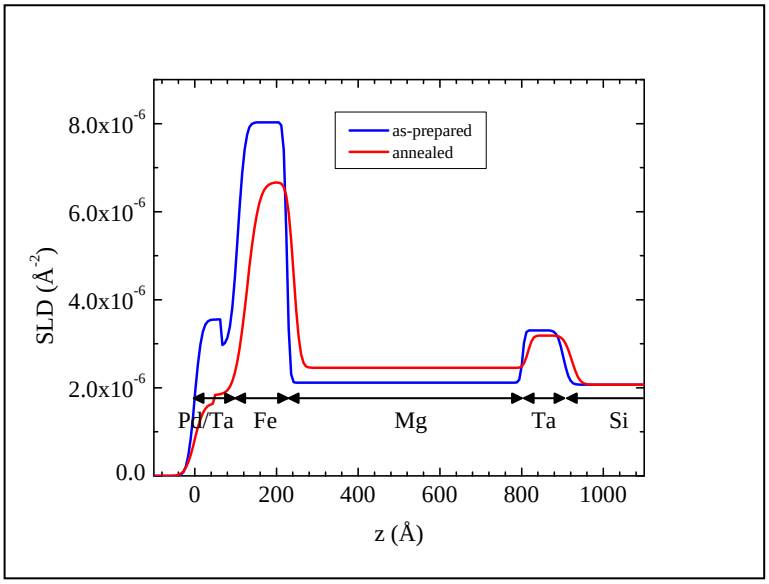

Figure 2. SLD-profiles corresponding to the fits displayed in Fig. 1. The blue line represents the as-prepared sample, the red line the sample after 6 hours annealing at 250º C.

The film structure changes after annealing for 6 hours at 250ºC, as can be inferred immediately from the NR curve shown in Fig. 1. The SLD profile for the fit shows that the SLD for the Ta, Pd, and Fe layer changes, i.e. there is noticeable interdiffusion at 250ºC.
When exposing the sample at RT to 1 bar of D_2 the reflectivity curve changes dramatically as can be seen in Fig. 3 (red circles). The increase of q_c is due to the uptake of D_2 which has a large positive scattering length. From the SLD profile corresponding to the fit shown in Fig. 3 (red line) we can conclude that the whole Mg layer has absorbed deuterium because the SLD increased from 2.1×10^{-6} Å^{-2} to 5.7×10^{-6} Å^{-2}. The quantity of the absorbed D_2 can then be calculated from the SLD and expansion of the Mg layer [12]. We calculate a D/M ratio of 1.9 for our Mg film, i.e. 95% of the Mg reacts to MgD_2.

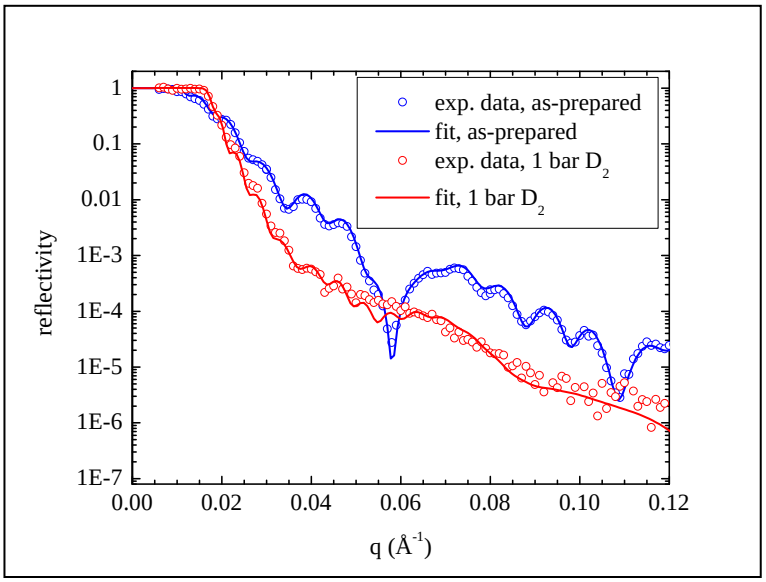

Figure 3. Neutron reflectivity curves for the as-prepared sample (blue circles) and the sample absorbed in 1 bar deuterium (red circles) along with the fits (solid lines).

In this study we did not investigate the kinetics of the absorption process. To make sure that we are in equilibrium we kept measuring the NR curve until it did not change anymore. To measure the reflectivity curve shown in Fig. 3 took about 4 hours. The low-q region of the first NR curve is identical to the following measurements, i.e. after about 4 hours we reach the state of equilibrium.

After evacuating the sample space and raising the temperature to 250° C, q_c decreases again back to the value of the as-prepared sample (see Fig. 5 – red circles). This is a clear indication of a full desorption. However, the sample structure has changed so much that it was impossible to obtain a reasonable fit.
We also performed XRR on our samples – shown in Fig. 6. The SLD profiles inferred from the XRR curves are similar to the SLD profiles from NR experiments. It also was impossible to obtain a reasonable fit for the XRR curve of the desorbed sample. The clearly visible fringes are due to the bottom Ta layer which stays intact in contrast to the other layers which have intermixed in a way that it is impossible to find a reasonable model for.

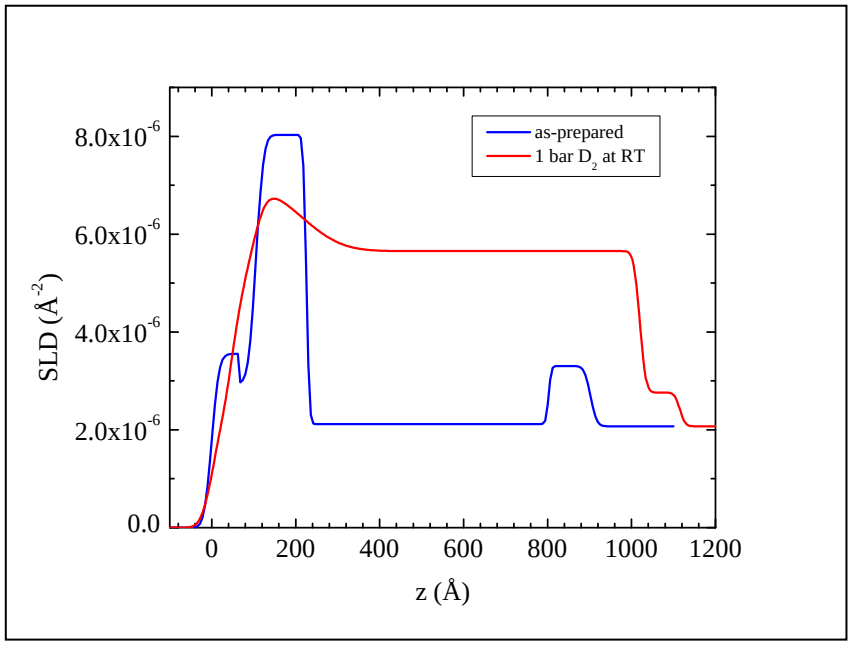

Figure 4. SLD-profiles corresponding to the fits displayed in Fig. 3. The blue line represents the as-prepared sample, the red line after absorption at RT in 1 bar D_2.

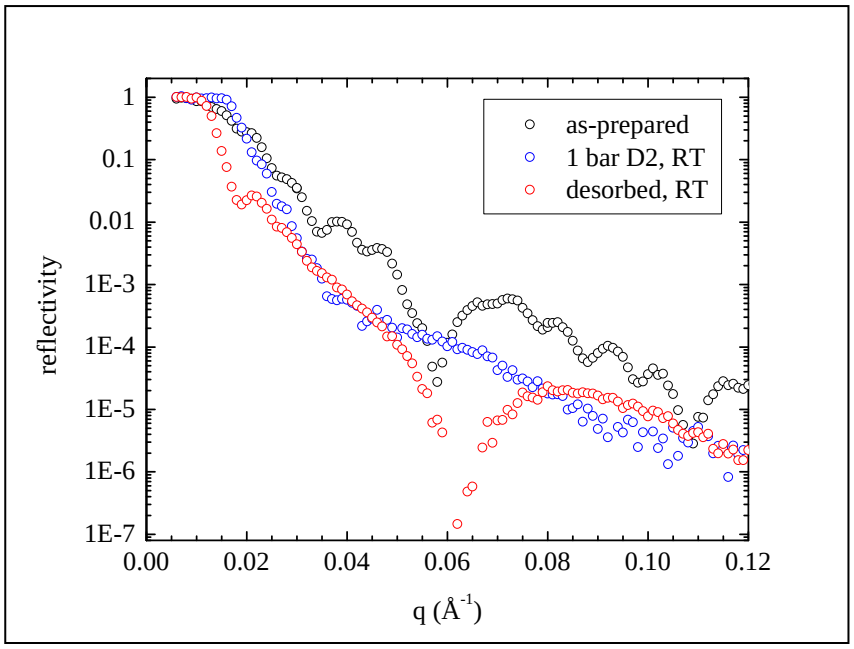

Figure 5. Neutron reflectivity curves for the as-prepared sample (black circles), the sample absorbed in 1 bar deuterium (blue circles), and the desorbed sample (red circles) along with the fits (solid lines).

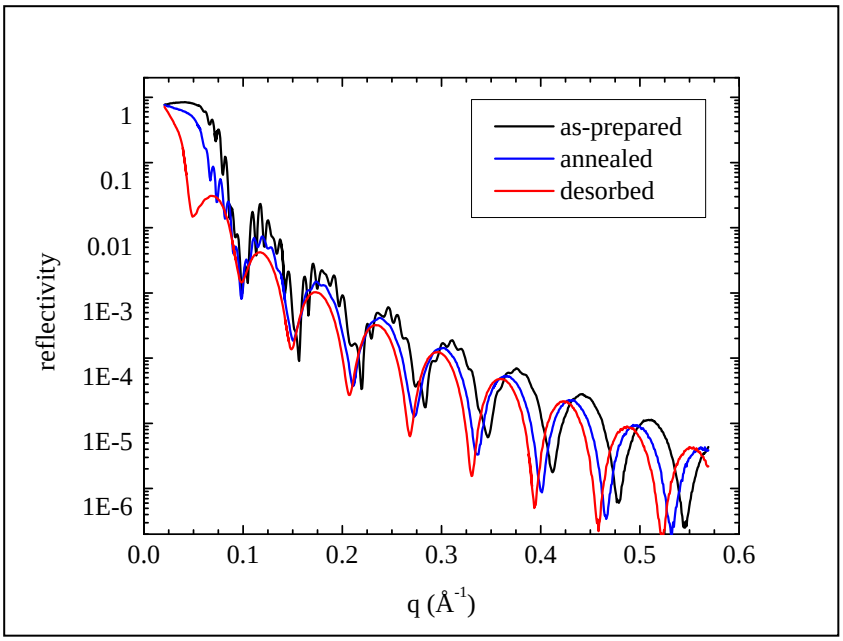

Figure 6. X-ray reflectivity curves for the as-prepared sample (black line), the annealed sample (blue line) and the desorbed sample (red line).

Conclusions

The NR and XRR data clearly show that the as-prepared Ta/Mg/Fe/Ta/Pd sample has a well-defined layered structure. After annealing for 6 hours at 250º C the Pd, Ta, and Fe layer show a noticeable interdiffusion, however, the Fe, Mg, and bottom Ta layer are still recognizable as can be seen in Fig. 2.
The Mg layer absorbs deuterium at RT in a 1 bar D_2 atmosphere very well, i.e. with a D/M ratio of 1.9 achieving almost full absorption. This is the same behaviour as observed in previous experiments on thin Mg layers [4-9] which did not have this extra Fe layer between the Mg layer and the Pd/Ta catalyst bilayer. After the desorption at 250º C the layer structure has changed completely with an intermixing of the Mg/Fe/Ta/Pd layers. The only layer that stays intact is the bottom Ta layer.

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