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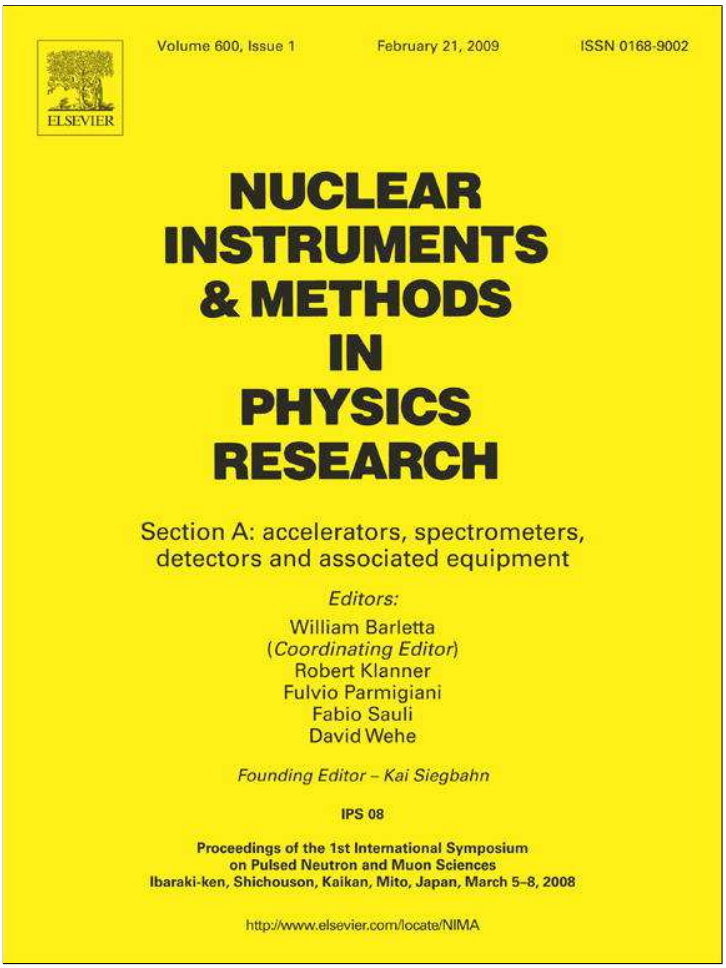
**Publisher's version / Version de l'éditeur:**
https://doi.org/10.1016/j.nima.2008.11.113
*Nuclear Instruments and Methods in Physics Research A, 600, pp. 301-304, 2009-02-01*



Nuclear Instruments and Methods in Physics Research A 600 (2009) 301–304

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

# Structural changes of thin MgAl films during hydrogen desorption

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ARTICLE INFO

Available online 6 December 2008

*Keywords:*
Neutron reflectometry
Thin films
Hydrogen storage
Hydrogen absorption

ABSTRACT

We used neutron reflectometry (NR) to study the structural changes of thin Pd-capped $Mg_{0.7}Al_{0.3}$ and $Mg_{0.6}Al_{0.4}$ alloy films after hydrogen absorption and during hydrogen desorption. NR enabled us to determine the hydrogen content and hydrogen distribution in these thin MgAl alloy films along with the structural changes associated with the desorption process. The thin films expand by about 20% during the hydrogen absorption and the hydrogen is stored only in the MgAl layer with no hydrogen content in the Pd layer. The $Mg_{0.7}Al_{0.3}$ films are fully desorbed at 448 K, whereas for the $Mg_{0.6}Al_{0.4}$ films a temperature of 473 K is needed to fully desorb the hydrogen. Our NR measurements show that the higher annealing temperature needed to desorb the hydrogen from the $Mg_{0.6}Al_{0.4}$ films led to an interdiffusion of the Pd layer into the MgAl layer. This Pd interdiffusion was also observed in a $Mg_{0.7}Al_{0.3}$ film after a 9 h annealing at 473 K. So, the Pd interdiffusion into a MgAl film that has been charged with hydrogen is a common feature of the $Pd/Mg_{0.7}Al_{0.3}$ and $Pd/Mg_{0.6}Al_{0.4}$ alloy system. In contrast, for the as-prepared hydrogen-free $Pd/Mg_{0.7}Al_{0.3}$ film the Pd layer stays intact and only a small interdiffusion zone occurs at the Pd/MgAl interface.



## 1. Introduction

There are 3 main parameters for hydrogen storage materials: hydrogen storage capacity, absorption/desorption temperature, and recyclability. In the past the focus in hydrogen research was mainly on optimizing the storage capacity and the desorption temperature. For $MgH_2$ holding an appreciable amount of 7.6 wt% hydrogen [1,2], the problem of its unacceptable high charging and discharging temperature has to be solved. Appreciable hydrogenation of untreated Mg occurs near 673 K, which is of too high temperature for most applications. The only meaningful way to circumvent the impossibly high sorption temperature of Mg is to reduce the magnitude of the heat of the hydride formation. Mostly, approaches to lower the hydrogen absorption consist of creating nanocrystalline hydrides using high-energy ball milling and the use of catalysts or additives [3–7]. The nanocrystalline $MgH_2$ shows improved kinetics with a desorption temperature that is about 100 K less compared to that of the untreated conventional powder. Recently, co-sputtering of Mg and Al has been used to destabilize the Mg matrix and create nanocrystalline or amorphous thin films [8,9]. Recent neutron reflectometry (NR) experiments on thin MgAl films [10] confirmed that $Mg_{0.7}Al_{0.3}$ is the optimum composition to maximize the stored hydrogen content (4.1 wt%) and minimize the desorption temperature (448 K). The NR measurements [10] showed that the $Mg_{0.6}Al_{0.4}$ films are desorbed at slightly higher temperatures (473 K). Along with the hydrogen desorption, an interdiffusion of the Pd into the MgAl film was observed, which destroys the film structure and makes it impossible to recycle the film. As structural changes during absorption/desorption cycles are important for the recyclability of hydrogen storage materials we performed a systematic study of this interdiffusion process before and after hydrogen absorption.

## 2. Experimental

The films were co-sputtered onto a Si (1 0 0) substrate with a native oxide layer of about 1 nm thickness. The Mg sputter rate was held constant at 0.4 nm/s, the sputter rate of Al was adjusted to the different compositions, and the Pd was sputtered at a rate of 0.1 nm/s. We used Ar gas of purity 99.999% at a pressure of $5.3 \times 10^{-3}$ mbar with a maximum base pressure of $2.7 \times 10^{-7}$ mbar. The MgAl films had a thickness of about 52 nm and were covered with a 10 nm-thick Pd layer in order to facilitate the hydrogen uptake [11]. The films were adsorbed with hydrogen in a dedicated high-pressure furnace at 430 K for 20 h at 6.8 MPa.

The neutron reflectometry experiments were performed on the newly commissioned D3 reflectometer at the neutron research reactor NRU, Chalk River. We used a focusing pyrolytic graphite (PG) monochromator at a neutron wavelength of $\lambda$=0.237 nm along with a PG filter [12] to reduce the higher order contamina-

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doi:10.1016/j.nima.2008.11.113

tion ($\lambda/2$ and $\lambda/3$). Desorption was done at 1 bar Ar atmosphere in a sample cell [13] equipped with a heater to reach sample temperatures up to 673 K.

For reflectometry, the interfaces of the films are arranged perpendicular to the scattering vector $q=k_f-k_i$ with $k_i$ and $k_f$ as the incoming and outgoing neutron wave vector with $k=2\pi/\lambda$. Thus, the interaction with the film is reduced to a one-dimensional problem. For grazing incidences, the reflectivity can be described with an optical potential $V_j$, known as Fermi's pseudopotential [14]

$$V_j = 2\pi\hbar/mN_jb_j \quad (1)$$

where $m$ is the neutron mass, $N_j$ the number density, $b_j$ the coherent nuclear scattering length, and the product $N_jb_j$ the scattering length density (SLD) in layer $j$. The SLD depends on the elements and their isotopes in the sample [15,16]. From Eq. (1), the neutron refractive index and the Fresnel reflectivity arising at interfaces of the media with different refractive indices can be calculated based on the Parratt recursion algorithm [17]. A layer model is fitted to the measured data by varying the SLD, the layer thickness and the interface roughness of each individual layer $j$.

## 3. Experimental results

Fig. 1 displays the experimental data of a $Mg_{0.6}Al_{0.4}H_y$ film: (a) after hydrogen absorption ($y$=0.85), measured at 295 K, (b) after partial hydrogen desorption ($y$=0.65), measured at 448 K for 12 h, and (c) after annealing at 473 K for 24 h ($y$=0), measured at 295 K. The fits, displayed as solid lines were calculated using the software Parratt32 [18]. As can be seen, the reflectivity curve contains a series of maxima and minima, the so-called Kiessig fringes [19]. In general, the observation of oscillations in the reflectivity curve corresponds to a characteristic thickness in the specimen. The oscillations seen in Fig. 1 are due to the total film thickness of the sample, i.e. the Pd plus the MgAl layer.

The changes in the film structure can be best visualized by plotting the SLD profile, i.e. the SLD along the surface normal $z$ of the film. The SLD profiles corresponding to the fits are shown as insets in Fig. 1. The model for the film structure consisted of a Si substrate with a $SiO_2$ layer, a MgAl layer, and a Pd layer, as displayed in Fig. 1a and b. In addition, an interface and surface roughness was taken into account. From the SLD profile, you can conclude a Pd layer thickness of 12 nm and a MgAl layer thickness of 60 nm. This corresponds to a 20% increase of both Pd and MgAl layer thickness compared to that of the unsorbed film [10]. The SLD of the MgAl layer after absorption is $6.5\times10^{-7}$ Å$^{-2}$, which corresponds to $y$=0.85 or 3.1 wt% stored hydrogen. The amount of hydrogen absorbed into the MgAl layer can be determined from the decrease from $2.3\times10^{-6}$ Å$^{-2}$, the SLD of the unsorbed film (see Fig. 3a for a NR curve of an unsorbed film). The decrease in SLD is due to the large negative scattering length $b_H$=−3.739 fm of the hydrogen [15,16]. Furthermore, from SLD profiles before and after hydrogen absorption we were able to conclude that no hydrogen is stored in the Pd cap layer [10]. This has also been observed in Pd cap Fe/Nb multilayers [20].

A partial desorption occurs at 448 K as can be concluded from the fact that the SLD of the MgAl film slightly increases as displayed in Fig. 1b. In order to fit the data at 448 and 473 K properly, we had to describe the SLD profile of the sample with a 7 box model. In this model the sample was divided up into seven independent layers and for each box the SLD, thickness, and interface roughness were varied to optimize the fit. The $Mg_{0.6}Al_{0.4}H_y$ film desorbs the hydrogen fully only at 473 K. However, the desorption is accompanied by a destruction of the Pd cap layer due to an interdiffusion of the Pd into the MgAl film.

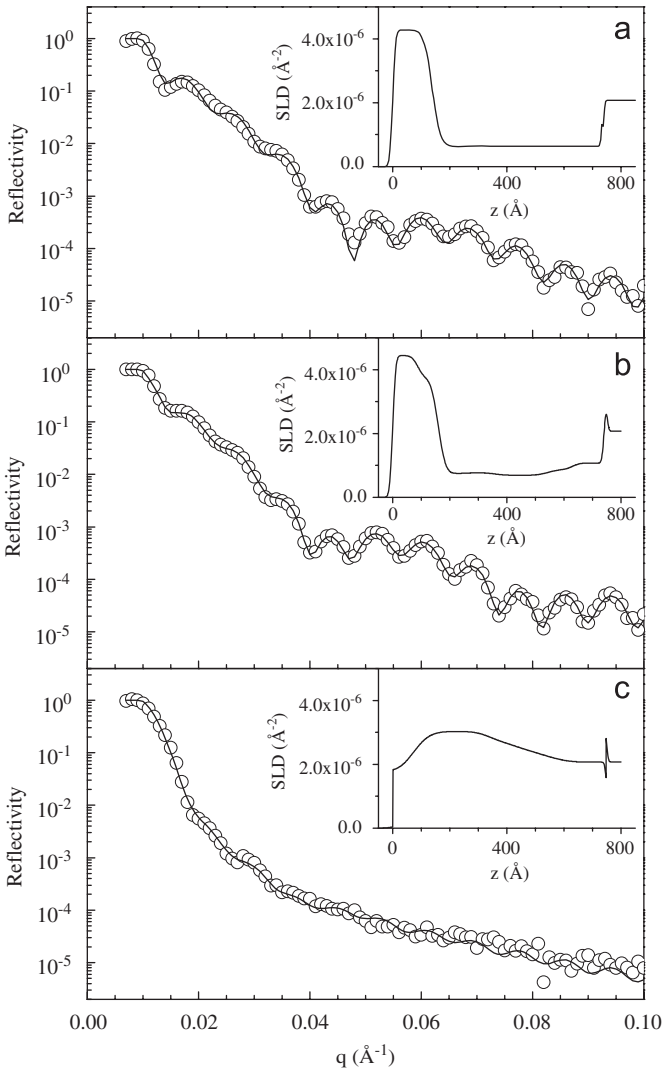


**Fig. 1.** Reflectivity curve of a Pd-covered $Mg_{0.6}Al_{0.4}H_y$ thin film on a Si substrate: (a) after hydrogen absorption ($y$=0.85), measured at 295 K, (b) measured at 448 K ($y$=0.65), and (c) measured at 295 K, after annealing at 473 K for 24 h ($y$=0). Open circles represent experimental data, the solid lines represent fits, and the insets show the corresponding SLD profile.

In order to get more insight into the interdiffusion process and separate the desorption from the interdiffusion process, we investigated the film structure of a $Mg_{0.7}Al_{0.3}H_y$ film, which has been fully desorbed before the interdiffusion sets in. The NR experiments were performed in the following way: the sample was heated up to 473 K, held at the same temperature for some time, then it was cooled to 295 K and the NR measurement began. This allowed us to get a precise snapshot of the interdiffusion process. The NR data could be collected in a large $q$-range with very good statistics because the interdiffusion process does not continue at temperatures below 295 K.

Fig. 2 shows the NR scans of a hydrogen-absorbed $Mg_{0.7}Al_{0.3}$ film after annealing at 473 K: (a) for 1 h, (b) for 3 h, and (c) for 9 h. The corresponding SLD profiles are shown in the insets. The data in Fig. 2 could only be fit properly with the same 7 box model as mentioned above. As can be deduced from Fig. 2(a), the hydrogen of the $Mg_{0.7}Al_{0.3}$ film is desorbed after 1 h annealing at 473 K with the Pd layer still intact. After 3 h at 473 K (Fig. 2b), the SLD at the location of the Pd layer had decreased from 4 to $3.5\times10^{-6}$ Å$^{-2}$ and at the same time the SLD of the MgAl in contact with the Pd layer had increased. This certainly proves the Pd interdiffusion into the

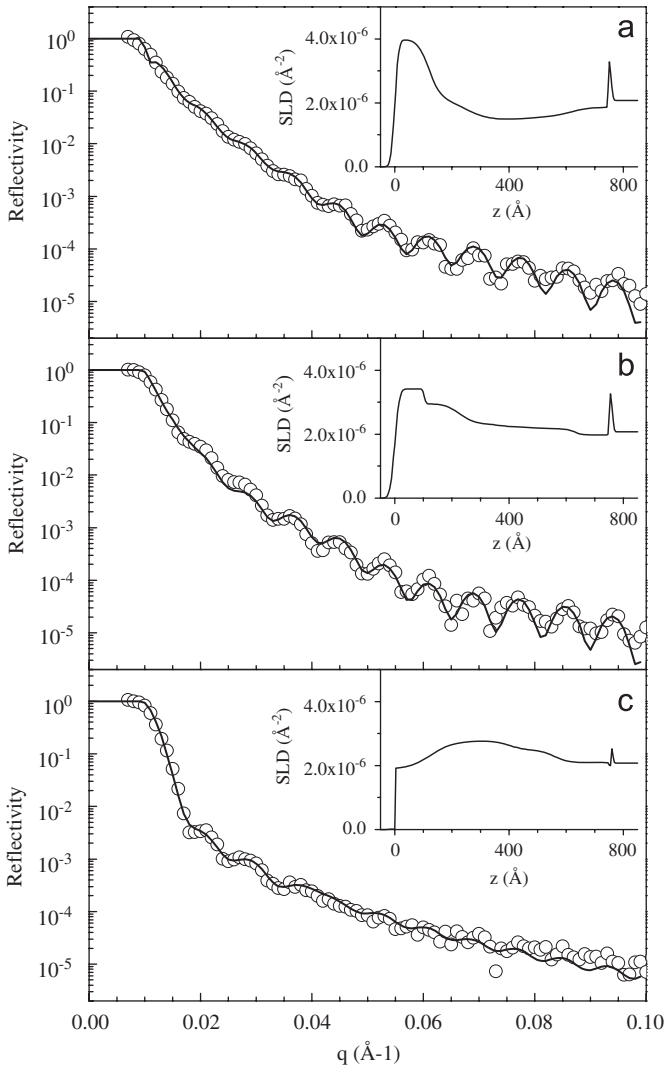


**Fig. 2.** Reflectivity curve of a Pd-covered $Mg_{0.7}Al_{0.3}H_y$ thin film on a Si substrate: (a) after 1 h annealing at 473 K, (b) after 3 h annealing at 473 K, and (c) after 9 h annealing at 473 K. Open circles represent experimental data, the solid lines represent fits, and the insets show the corresponding SLD profile.

MgAl layer. After a 9 h annealing (Fig. 2c), the Pd layer cannot be observed anymore. Interestingly, the Pd distribution is not homogeneous but shows a maximum in the center of the film.

To study the influence of the hydrogen absorption/desorption on the interdiffusion we also annealed an as-prepared $Mg_{0.6}Al_{0.4}$ film at 473 K for 24 h. The difference in the NR curves can be seen in Fig. 3, where (a) represents the as-prepared state and (b) after a 24 h annealing at 473 K. The main effect of the annealing is the increase of the Pd/MgAl interface roughness from 1.5 to 3 nm. However, the Pd layer does still exist in contrast to a $Mg_{0.6}Al_{0.4}$ film that has been charged with hydrogen and also annealed at 473 K for 24 h (Fig. 1c). The reason for the enhanced interdiffusion in the films that have once been charged with hydrogen is probably the well-known effect of hydrogen to distort the film structure by e.g. creation of voids or pores.

## 4. Conclusion

We have studied the hydrogen desorption properties of thin Pd-capped $Mg_{70}Al_{30}$ and $Mg_{60}Al_{40}$ films. The hydrogen is dissolved homogeneously in the MgAl layers with no hydrogen present in the Pd cap layer. By annealing the MgAl films at 473 K

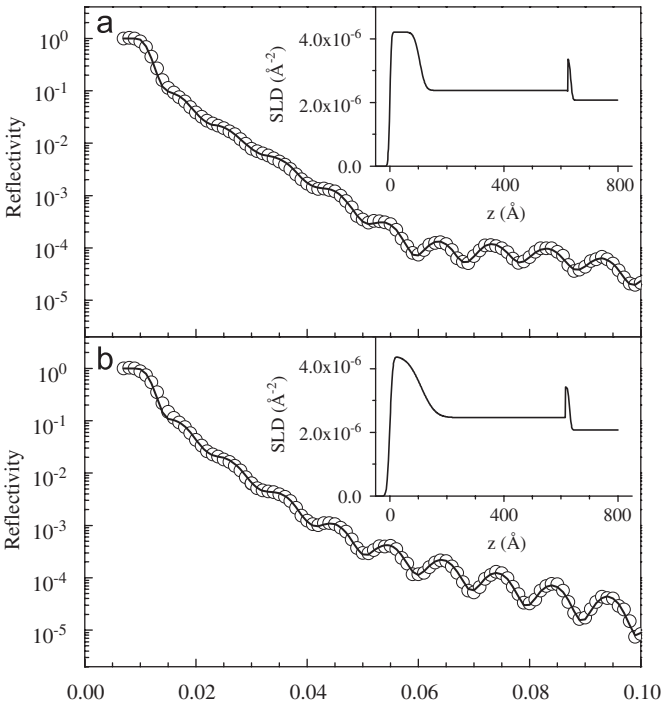


**Fig. 3.** Reflectivity curves of a Pd-covered $Mg_{0.6}Al_{0.4}$ thin film on a Si substrate: (a) as-prepared, (b) after 24 h annealing at 473 K. Open circles represent experimental data, the solid lines represent fits, and the insets show the corresponding SLD profile.

for more than 9 h, the film structure is destroyed by interdiffusion of the Pd into the MgAl layer. Interestingly, the Pd layer is not destroyed when annealing an as-prepared hydrogen-free MgAl film. We have shown that NR gives detailed information on the hydrogen profile within a thin film and that NR reveals structural changes which are important in terms of recyclability of a hydrogen storage material.

## Acknowledgment

The research presented herein is made possible by a reflectometer jointly funded by Canada Foundation for Innovation (CFI), Ontario Innovation Trust (OIT), Ontario Research Fund (ORF), and the National Research Council Canada (NRC). We acknowledge the great dedication of Zin Tun (CNBC), Mitch King (AECL), Paul Adams (AECL), Derrick West (NRC), John Fox (CNBC), and the whole CNBC technical group to design, build, and commission D3.

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