Structural Changes of Thin MgAl Films During Hydrogen Desorption

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We used Neutron Reflectometry (NR) to study the structural changes of thin Pd-capped $Mg_{0.7}Al_{0.3}$ alloy films during hydrogen desorption. The reflectometry experiments were performed on the newly commissioned D3 reflectometer at NRU in Chalk River. 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 films were co-sputtered onto a Si(100) 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 for the different compositions, and the Pd was sputtered at a rate of 0.1 nm/s. 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. The films were adsorbed with hydrogen in a dedicated high-pressure furnace at 430 K for 20 hours at 6.8 MPa.

Recent (NR) experiments on thin MgAl films [1] 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 [1] showed that the $Mg_{0.6}Al_{0.4}$ films are desorbed at slightly higher temperatures (473 K). Along with hydrogen desorption an interdiffusion of the Pd into the $Mg_{0.6}Al_{0.4}$ 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 [2]. In order to separate the desorption from the interdiffusion process we investigated the film structure of a $Mg_{0.7}Al_{0.3}Hy$ 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, hold at that temperature for a certain time, then it was cooled down to 295 K and the NR measurement started. 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.

NR scans of a previously hydrogen-absorbed $Mg_{0.7}Al_{0.3}$ film that has been desorbed at 448 K, are shown in Fig. 1 after annealing at 473 K a) for 1 hour, b) for 3 hours, and c) 9 hours. The open circles represent experimental data, the solid lines represent fits, and the insets show the corresponding SLD profile. In order to fit the data 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 7 independent layers and for each box the SLD, thickness, and interface roughness was varied to optimize the fit.

The SLD of the absorbed $Mg_{70}Al_{30}$ film is 3.5×10^{-7} Å^{-2} [1,2], the SLD of the desorbed film is 2×10^{-6} Å^{-2}. So, we can conclude from Figure 1a) that the hydrogen of the $Mg_{0.7}Al_{0.3}$ film is fully desorbed after one hour annealing at 473 K with the Pd layer still intact. After 3 hours at 473 K (Figure 1b) the SLD at the location of the Pd layer has decreased from 4 to 3.5×10^{-6} Å^{-2} and at the same time the SLD of the MgAl in contact with the Pd layer has increased. This nicely proves the Pd interdiffusion into the MgAl layer. After a 9 hour annealing (Figure 1c) the Pd layer cannot be observed anymore. This detailed information on structural changes gained by NR, is very important in terms of recyclability of hydrogen storage materials.

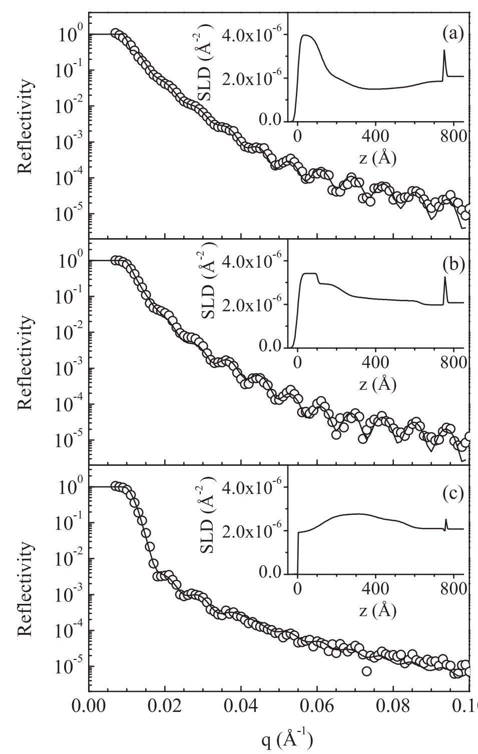

Fig 1. *Reflectivity curve of a desorbed Pd-covered $Mg_{0.7}Al_{0.3}$ thin film on a Si substrate a) after 1 hour annealed at 473 K, b) after 3 hours annealing at 473 K, and c) after 9 hours annealing at 473 K. Open circles represent experimental data, the solid lines represent fits, and the insets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

References

[1] H. Fritzsche, M. Saoudi, J. Haagsma, C. Ophus, E. Luber, C. T. Harrower, and D. Mitlin, Appl. Phys. Lett. 92, 121917 (2008)

[2] H. Fritzsche, M. Saoudi, J. Haagsma, C. Ophus, C. T. Harrower, D. Mitlin, Nucl. Instr. and Meth. A 600, 301 (2009)