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Deuterium absorption in $Mg_{70}Al_{30}$ thin films with bilayer catalysts: A comparative neutron reflectometry study

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ABSTRACT

We present a neutron reflectometry study of deuterium absorption in thin films of Al-containing Mg alloys capped with a Ta/Pd, Ni/Pd and Ti/Pd-catalyst bilayer. The measurements were performed at room temperature over the 0–1 bar pressure range under quasi-equilibrium conditions. The modeling of the measurements provided a nanoscale representation of the deuterium profile in the layers at different stages of the absorption process. The absorption mechanism observed was found to involve spillover of atomic deuterium from the catalyst layer to the Mg alloy phase, followed by the deuteration of the Mg alloy. Complete deuteration of the Mg alloy occurs in a pressure range between 100 and 500 mbar, dependent on the type of bilayer catalyst. The use of a Ti/Pd bilayer catalyst yielded the best results in terms of both storage density and kinetic properties.

1. Introduction

Hydrogen-powered vehicles are foreseen as the ultimate solution to mitigate environmental impacts associated with transportation needs. Their practicality, however, depends on the development of a high capacity hydrogen storage system that can be charged quickly and efficiently at moderate pressures and temperatures (*P*,*T*). A hydrogen fuel-cell vehicle meeting these criteria could offer the advantages of electrical propulsion, while reaching ranges and refueling times comparable to gasoline vehicles. As part of the ongoing research on solid state hydrogen storage, absorption in Mg alloys have attracted a lot of interest. Mg offers high gravimetric and volumetric hydrogen densities, as well as a low cost due to its abundance. One of the main issues with Mg is the high operating temperatures (~300 °C) required for fast kinetics during absorption and desorption [1]. Therefore, recent efforts have focused on the addition of catalysts, formation of nanocrystalline phases (e.g. by ball-milling), and destabilization agents in order to improve the kinetics, and possibly the thermodynamics of hydrogen absorption [2–4]. The effectiveness of these approaches can be better assessed when a detailed nanoscale representation of the system is available. In that respect, thin Mg films constitute very interesting model systems to study fundamentals of absorption and catalysis as they can be synthesized with nanoscale layers of specific composition and dimension. Their synthesis, under well-controlled conditions, also minimizes detrimental contamination and surface oxidation.

It is well-known that a Pd layer improves the kinetics of hydrogen absorption in many metals [5–8] including thin MgAl films [9]. The Pd layer prevents the formation of an oxide layer, and is likely to lower hydrogen dissociation and diffusion barriers prompting atomic hydrogen spillover into the bulk hydrogen absorbing phase [10]. Improvement is achieved through a two-step mechanism involving absorption in the Pd layer and subsequent spillover in the main phase. This mechanism was evidenced by neutron reflectometry (NR) measurements on catalyzed $Mg_{70}Al_{30}$ thin films at room temperature and low pressure (<1.3 bar) [11]. The same NR experiments also revealed depletion zones near the $Mg_{70}Al_{30}$ interfaces, which were attributed to the elastic connection between the Mg alloy and adjacent layers. Deuterium concentration up to 5 wt.% was found in the $Mg_{70}Al_{30}$ layer, a significant value under these very mild conditions. At elevated temperatures Pd tends to form an alloy with the underlying Mg phase that hinders or prevents further hydrogen absorption. In order to reduce Pd alloying, the introduction of Fe, Ti or Ta interlayer underneath the Pd cap to form a bilayer catalyst has been considered [12–14]. Interestingly, the use of 5 nm Ta/5 nm Pd bilayer catalyst was also found to decrease the desorption temperature [14], and to improve the

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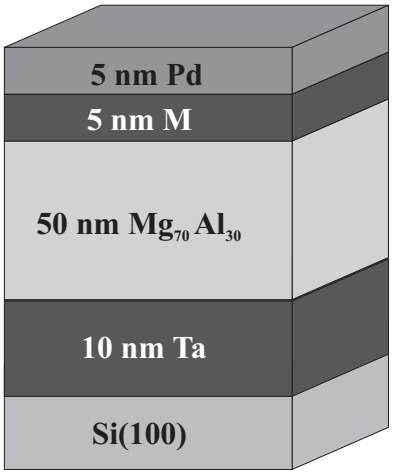

Fig. 1. Schematic of a film's structure; the symbol M in the top bilayer stands for Ta, Ni or Ti.

absorption rate at low pressures [11]. The improved kinetics at low pressure was attributed to a reduction of the nucleation barrier for the deuteration of the Mg alloy layer [11]. Similarly, the addition of metal interlayer was found to improve to various degrees the cyclability [13], and the kinetics [13,15]. The kinetics, in particular, was also found to depend on the enthalpy of solution (or formation) and thickness of the metallic interlayer, as found on interlayers exceeding 30 nm [15]. It should be pointed out that the use of a bilayer catalyst will affect the gravimetric storage capacity and materials costs as well. In this context, it appears important to get a better understanding of the mechanism by which minimal (5 nm M/5 nm Pd) bilayer catalysts involving different metals (M) could influence absorption properties.

In this report, we present NR measurements made on catalyzed $Mg_{70}Al_{30}$ thin films absorbing deuterium under quasi-equilibrium conditions. The measurements were performed in situ, at room temperature and over a 0–1 bar D_2 pressure range. NR is a powerful tool to determine the deuterium concentration profiles in the various layers with nanometer resolution [14,16,17]. The NR experiments were conducted on $Mg_{70}Al_{30}$ alloy films with catalyst bilayers containing M = Ta, Ni and Ti in order to investigate specifically the effect of these metals. A composition of 70 at.% Mg and 30 at.% Al was used as it was previously found to be optimal with respect to both capacity and kinetics [16,17]. Aluminum may also reduce the stability of the hydride, leading to improved dehydrogenation conditions [18,19]. We used X-ray reflectometry (XRR) to verify the film structure following the in situ NR measurements. XRR is a valuable complementary technique as it is not sensitive to deuterium and therefore provides information on the position of the metal atoms, i.e. metal interdiffusion.

2. Experimental

2.1. Sample preparation

The thin film samples used in this study were fabricated by co-sputtering onto a (1 0 0) silicon wafer in a confocal sputtering chamber (Orion 5 instrument from AJA International) operating at an Ar (purity 99.999% pure) pressure of 5×10^{-3} mbar, which had been previously evacuated to a pressure less than 3×10^{-8} mbar. The oxide was removed in situ by reverse etching the native oxide prior to film depositions. First a 10 nm Ta layer was deposited onto the wafer and, without interruption, a 50 nm $Mg_{70}Al_{30}$ layer was co-sputtered followed by 5 nm Ta (or Ni, Ti) and a 5 nm Pd top layer. The film structure is represented in Fig. 1.

2.2. In situ neutron reflectometry

The NR experiments were performed on the V6 horizontal reflectometer at the Helmholtz Zentrum, Berlin. This instrument is operated using a 0.466 nm neutron wavelength. The instrument involves an aluminum sample cell, allowing for in situ gas absorption measurements. The measurements were performed at room temperature, from a deuterium pressure of 1 mbar up to 1 bar, using ultra high purity deuterium (99.999%). Absorption under these mild conditions is relatively slow, allowing for quasi-equilibrium absorption measurements. Consequently, such NR experiments uniquely capture the evolution of the deuterium concentration profile during the absorption process, allowing for a detailed, i.e. nanoscale, representation of the absorption mechanism. This hydrogen profiling is usually not possible with other techniques, either at high temperature and/or on powder samples.

The NR reflectivity curves were measured in a specular configuration, i.e. with the interface of the films perpendicular to the scattering vector q_z. In this configuration, the neutron interaction with the films is reduced to a one-dimensional problem that can be described with a neutron index of refraction n analogous to optical reflectivity. The value of n depends on the strength of the interaction of neutrons with specific isotopes in the films and is given by [20]:

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

where λ is the neutron wavelength, N_j is the number density, b_j is the coherent nuclear scattering length, and the product $N_j b_j = S$ is the scattering length density (SLD) in layer j. The SLD depends on the elements and their isotopes present in the sample. Deuterium is used because of its large coherent scattering length, which leads to a significant increase in the layers' SLD upon absorption. The measured reflectometry curves were analyzed using the *Motofit* software involving genetic optimization with least square [21,22]. The analysis was performed using slab models, containing four to seven layers. The measured data were fitted by the models by varying the SLD, layer thickness, and interface roughness of each individual layer j. Total neutron reflection occurs up to a critical angle, or scattering vector q_c. The latter depends on the average scattering length density $\bar{S}$ of the materials such as [20]:

$$q_c = \frac{4\pi}{\lambda} \sin\theta_c = 4\sqrt{\pi \bar{S}} \tag{2}$$

This implies the critical edge angle increases as a result of deuterium absorption. Corresponding displacements of q_c were measured in short scans to quickly estimate the average amount of deuterium absorbed and identify quasi-equilibrium conditions. Typically, measurements over the $q = 0 - 0.5\ \mathrm{nm}^{-1}$ range were assumed in quasi-equilibrium when the critical edge, or the full NR curve, showed no major changes over a 1–2 h measurement period. Some measurements not satisfying this condition could not be fitted and were discarded. The deuterium content in each layer can be estimated from the scattering length density using the expression [6]:

$$C_D \cong \left[\frac{S_{M+D}}{S_{M(p=0)}} \frac{t_{M+D}}{t_M} - 1 \right] \frac{b_M}{b_D} \tag{3}$$

where S_{M+D} is the scattering length density of the deuterium-charged layer, $S_{M(p=0)}$ is the scattering length density of the layer in absence of deuterium, t_{M+D} and t_M are the corresponding thicknesses, and b_M and b_D are the scattering length of the metal and deuterium respectively.

2.3. X-ray measurements

X-ray reflectometry and diffraction measurements were also performed to confirm the structure and composition of the samples. These measurements were performed about 60 days following the NR measurements and hence, give some information on the stability of the absorbed phases. The measurements were made with a commercial Rigaku Ultima III X-ray diffractometer used in a high resolution configuration with the Cu $K_{\alpha 1}$ wavelength of 0.15406 nm.

3. Results

3.1. Neutron reflectometry

3.1.1. $Mg_{70}Al_{30}$/Ta/Pd

Neutron reflectivity curves and SLD profiles on the $Mg_{70}Al_{30}$/Ta/Pd sample are shown in Fig. 2. The corresponding SLD profiles, i.e. the SLD as a function of the direction z parallel to the surface normal of the film, are displayed in the insets. These insets provide a real space representation of the film. Fig. 2a refers to the as-prepared sample, as measured in air. The curve exhibits the characteristic Kiessig fringes associated with multiple reflections [23]. It was successfully fit using a four layers model. The scattering length density and the thickness of the $Mg_{70}Al_{30}$ phase are $2.2 \times 10^{-4}\ \mathrm{nm}^{-2}$ and 54 nm, respectively. The SLD corresponds to the value calculated from tabulated data ($2.2 \times 10^{-4}\ \mathrm{nm}^{-2}$) and the measured thickness is within 10% of the expected value (~50 nm). Following this measurement, deuterium was slowly