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Early deuteration steps of Pd- and Ta/Pd- catalyzed Mg₇₀Al₃₀ thin films observed at room temperature

Christopher Harrower^{a,b}, Eric Poirier^c, Helmut Fritzsche^{c,*}, Peter Kalisvaart^{a,b},
Sushil Satija^d, Bulent Akgun^{d,e}, David Mitlin^{a,b}

^aChemical and Materials Engineering, University of Alberta, Alberta T6G 2V4, Canada

^bNational Research Council Canada, National Institute for Nanotechnology, Edmonton, Alberta T6G 2M9, Canada

^cNational Research Council Canada, SIMS, Canadian Neutron Beam Centre, Chalk River, Ontario K0J 1J0, Canada

^dNational Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD 20899, USA

^eDepartment of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

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ABSTRACT

Deuterium absorption in Mg₇₀Al₃₀ thin films coated with a Pd layer and a Ta/Pd bilayer were investigated using in situ neutron reflectometry at room temperature and deuterium pressures up to 1.3 bar. The approach used provides a detailed profile, at the nanoscale, of the deuterium content inside the specific layers that constitute the films. It is found that Mg₇₀Al₃₀ can store up to 5 wt.% under these mild conditions following a two-step mechanism. The latter involves the deuteration of the top and bottom catalyst layers first, followed by the main Mg₇₀Al₃₀ layer. The presence of deuterium throughout the films in the early absorption stages evidences atomic deuterium spillover from the catalyst layers. The addition of a Ta layer between the Pd and Mg₇₀Al₃₀ was found to allow observable absorption at a pressure 10 times lower than on the Ta-free sample, without affecting the storage capacity. Our measurements imply that this improvement in kinetics is due to a lowering of the nucleation barrier for the formation of the hydride phase in the Mg₇₀Al₃₀ layer.

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1. Introduction

Magnesium and its alloys are amongst the most promising candidates for solid-state hydrogen storage applications owing to their high hydrogen capacity of 7.6 wt.% and their low cost [1]. The main drawback seen by Mg is the high temperature, on the order of 300 °C typically required to obtain fast hydrogen absorption and desorption kinetics. This temperature is deemed too high for mobile applications and its reduction by means of catalysts addition and nanostructuring is now widely investigated [2–5]. The

hydrogenation of magnesium is commonly described with two models: (i) a nucleation and growth model where the hydride grains may impinge before the whole Mg particle is hydrided and (ii) the three-dimensional diffusion-controlled shrinking-core model, where a continuous layer of hydride forms immediately on the surface and reduces significantly the hydride formation because of the reduced diffusion rate through the hydride layer [6]. The addition of catalysts may alter significantly the hydriding kinetics by lowering hydrogen dissociation and diffusion barriers [7]. To investigate these effects, thin films are very interesting model systems which

* Corresponding author.

allow incorporation of catalysts in a well controlled manner at the nanoscale. Recent studies of hydrogen absorption in Mg thin films capped with a Pd catalyst layer showed that absorption is possible near ambient temperature and pressure [8]. A theoretical study suggested room temperature absorption on such systems may be promoted by a spillover mechanism from the Pd into the Mg alloy phase [9]. Nevertheless, a detailed representation of the hydrogen absorption mechanism in such systems lacks of experimental measurements at the nanoscale. Neutron reflectivity (NR) has proved to constitute a powerful tool for profiling the hydrogen or deuterium content with nanometer resolution in the distinct layers that constitute films [10,11]. It has recently been shown using NR that the use of a Ta/Pd bilayer catalyst on a $\text{Mg}_{70}\text{Al}_{30}$ film layer improves its kinetics properties [12], leading to hydrogen desorption at 100 °C compared to 170 °C for a single Pd layer [13]. The addition of Ta did not lead to a diminution of the gravimetric hydrogen storage capacity of the film, a somehow expected consequence of catalytic enhancement. The effect of the Ta catalyst layer on the absorption properties at room temperature remains, however, an open question. In order to investigate the absorption mechanism and the effectiveness of a Ta/Pd bilayer as a catalyst for room temperature absorption, we used NR to observe and compare the deuteration mechanism of two $\text{Mg}_{70}\text{Al}_{30}$ thin films with a Pd-layer and Ta/Pd-bilayer catalyst, respectively. We chose the $\text{Mg}_{70}\text{Al}_{30}$ alloy because it is the composition with the optimum desorption properties as was determined in previous studies [13,14]. The measurements were performed in situ at distinct stages of the absorption process, under quasi-equilibrium conditions, from the early deuteration steps in catalyst layers up to the full saturation of the samples. The concentration profiles thus obtained offer new insights in how absorption proceeds on such metal systems, and how the use of certain catalysts may lead to improved materials.

2. Experimental

To study the influence of a Ta catalyst layer, we compare a 50-nm thick $\text{Mg}_{70}\text{Al}_{30}$ film capped with a 10-nm thick Pd catalyst layer with a 50-nm thick $\text{Mg}_{70}\text{Al}_{30}$ film capped with a 5-nm/5-nm thick Ta/Pd bilayer. The thin film samples used in this study were fabricated by co-sputtering onto a native oxide (100) silicon wafer in a confocal sputtering chamber (Orion 5 instrument from AJA International) [15] 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. First a 10-nm Ta buffer layer was deposited onto the wafer and, without interruption, a 50-nm $\text{Mg}_{70}\text{Al}_{30}$ layer was co-sputtered followed by either a 10-nm Pd layer or a 5-nm Ta/5-nm Pd bilayer. The sample structure is depicted in Fig. 1. The investigated films have the same structure as previously reported [12,16], i.e., no intermetallics in the as-prepared state and the first absorption cycle. The microstructure consists of a supersaturated solid solution of Al in Mg with a strong texture along the surface normal, i.e., Mg (002) is parallel to Si(100), but we do not observe a single crystal growth. The HCP structure of the Mg is maintained with a contracted lattice parameter due to Al in solution. The

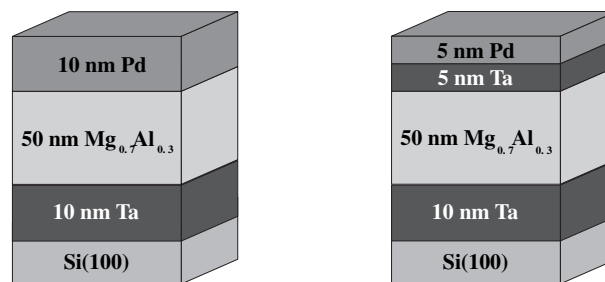


Fig. 1 – Illustration of the structure of the film with the single Pd catalyst layer (left) and the Ta/Pd catalyst bilayer (right).

lattice parameter follows a Vegard's law wherein the lattice contracts proportional to the Al concentration in the Mg. A contracted lattice is only noticed in the as-prepared material and is not noticed in the material once hydride – the Al precipitates out of MgH_2 and remains as a precipitate.

Neutron Reflectometry (NR) experiments were conducted on the NG7 reflectometer at the National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg MD, USA. This instrument has a resolution of $\Delta q/q = 4\%$ using a 4.75-Å wavelength. The deuterium absorption was performed in situ, using an aluminum sample cell, at room temperature from a deuterium pressure of $\sim 10^{-4}$ mbar up to 1.3 bar using ultra high purity deuterium (99.999%). The reflectivity curves were measured at grazing incidence, in specular geometry as a function of the incident angle θ . 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 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 [17]:

$$n^2 = 1 - \frac{\lambda^2}{\pi} N_j b_j \quad (1)$$

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) of the layer. The SLD of each layer depends on their elements and their isotopes in the sample [18,19]. Deuterium is used because of its large coherent scattering length, which leads to a dramatic increase in the layers' SLD, creating a strong contrast in the SLD of the deuterated layers with respect to the as-prepared material. Total reflection of neutrons occurs up to a critical scattering vector q_c calculated as [17]:

$$q_c = \frac{4\pi}{\lambda} \sin \theta_c = 4\sqrt{\pi N b} \quad (2)$$

The evolution of q_c upon deuteration is a good indicator of the average deuterium content in the film. Short measurements showing the movement of the critical edge upon deuteration were helpful in monitoring the absorption kinetics. Typically, the measurements over the $q = 0 - 0.1 \text{ \AA}^{-1}$ range were considered as quasi-equilibrium when the kinetics was sufficiently slow, i.e., with the critical edge, or the full NR curve showing no major changes over a 1–2 h measurement

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