Ti-catalyzed Mg(AlH$_4$)$_2$: a reversible hydrogen storage material

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Abstract

Mg-Al thin films with a compositional gradient are co-sputtered from off-centered magnetron sources and capped with a thin Pd layer. We study their hydride formation by monitoring their optical transmission during hydrogenation under defined pressure and temperature conditions. We find that Mg(AlH$_4$)$_2$ is already formed from the elements at p(H$_2$) = 1 bar and T = 100°C. A thin layer of Ti acts as a catalyst. Doping of Mg-Al with Ti has a negative influence on hydrogen absorption.

Key words: Mg, alanate, hydrogen storage materials, thin films, combinatorial research

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1 Introduction

A key issue for the large scale use of hydrogen as an energy carrier is the availability of a safe and effective way to store it reversibly [1]. Light-weight complex hydrides are promising for this purpose due to their large storage capacity. However, applications are still hindered by the high temperatures needed for abs/desoption of hydrogen. Bogdanovic et al. showed that Ti-doped $NaAlH_4$ can be cycled reversibly under moderate conditions [2]. This stimulated the investigation of many other complex systems. Generally, studies of (de)hydrogenation are performed on chemically synthesized and subsequently ball milled bulk hydrides. In this work we follow a novel approach based on the optical an electronic changes induced by hydrogen in thin films. This method exploits the fact that many metal-hydrogen systems undergo a metal-insulator transition and an opening of an optical band gap during hydrogenation [3–5]. To span a large range of possible compounds, the thin films are sputtered as compositional gradients of the elemental metals.

For this study, we choose the Mg-Al system. Apart from the pure metallic Mg and Al, the α-Mn $Mg_{17}Al_{12}$ and the fcc Mg_2Al_3 phases are present at room temperature in the Mg-Al phase diagram. Figure 1 is a summary of the hydrogenation properties of the Mg-Al system reported in the literature [6]. Various sample preparation methods (bulk, ball milled, microcrystalline) have been used. The atomic H content z in $MgAl_yH_z$ is displayed as a function of y = [Al]/[Mg]. For y = 0, the hydride formed is the rutile phase α-MgH_2. With increasing Al content, $z \leq 2$ for $y < 2$. Given the uncertainty in the data, we conclude that $MgAl_yH_z$ segregates in MgH_2 and Al for $y < 2$. The only known Mg-Al hydride is the magnesium alanate, $Mg(AlH_4)_2$ (i.e. y = 2), which

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exhibits an advantageous gravimetric density of 9.3%. This compound has been successfully synthesized by chemical reaction and its thermal desorption behavior has been studied [7,8]. However, to use magnesium alanate as an hydrogen storage material, it is important that it can be formed directly from the metallic elements Mg and Al at a moderate H_2 pressure.

In this work, we study the hydrogenation properties of Mg-Al thin films with compositional gradients by means of optical transmission and electrical resistivity. The film are characterized in the as-deposited, metallic state, and after hydrogenation. Also, the effects of Ti doping of our film on the final hydrogenation state and on the minimal hydrogenation temperatures are discussed.

2   Experimental

Samples (later referred to as "Mg-Al" samples) consist of a Mg-Al compositional gradient layer (100 nm thick in center) covered with a 1 nm Mg layer and capped with 10 nm Pd to promote hydrogen dissociation and absorption. To study the influence of Ti as a catalyst/dopant on the hydride formation, we deposited two other set of samples. "Ti doped" samples consist in a Mg-Al gradient doped with a mean 3 at.% co-deposited Ti in the Mg-Al layer. In "Ti covered" samples, a 5 nm Ti homogeneous buffer layer is deposited between the Mg-Al and Pd layers. Films are sputtered on 70 mm long glass substrates at room temperature with a 6 source magnetron sputtering apparatus (AJA). The argon pressure is $3 \cdot 10^{-3}$ mbar, the background pressure less than 10^{-8} mbar. The chemical composition range is adjusted by varying the angle of both Mg and Al sources relatively to the sample normal. Sputter rates in the center of the sample are determined *in situ* before deposition by

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a quartz crystal monitor. Total thickness is measured every 5 mm by stylus profilometry. Compositions are determined by measuring the thickness of pure metallic Mg and Al gradient samples deposited separately. This method has been checked by performing Rutherford Backscattering Spectrometry (RBS) on simultaneously deposited layers on glassy carbon substrates.

After deposition, metallic films are transferred to an hydrogen loading cell for pressures up to 10 bar with 3 inch view ports to monitor optical transmission. The whole cell is placed in an oven, whose temperature is controlled up to 300°C by means of a PT100 sensor and a PID controller. Up to 3 different samples can be loaded in the cell under exactly the same conditions. A 150W diffuse light source illuminates the samples from the substrate side, and a 3 channel (RGB) SONY XC-003 charged-coupled device (CCD) camera records the transmitted light through the substrate. Images of the abs/desorption process are taken at different time intervals Δt (1 s $< \Delta t <$ 1000 s) depending on the overall kinetics of the Mg-Al gradient sample. Images are subsequently analysed with MATLAB to get averaged RGB signals and the total intensity over the full range of composition and their temporal evolution. For resistivity measurements, separated zones are created every 3 mm prior to deposition by means of a mask glued on the glass substrate. In each zone, four gold pins connected to a KEITHLEY 2000 multimeter measure resistivity by the Van der Pauw method [9]. Results are corrected for the influence of the Pd over-layer and the thickness variation within the Mg-Al gradient. X-ray diffraction (XRD) measurements are performed in a BRUKER D8 spectrometer using Cu K$_{\alpha}$ radiation in a θ-2θ configuration.

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3 Results and Discussion

3.1 *As-deposited state*

In the as-deposited state, Mg_xAl_{1-x} gradient samples are completely opaque and exhibit a shiny metallic surface. X-ray diffraction (XRD) patterns reveal the presence of an hcp Mg phase for compositions x > 0.5 and a fcc Al phase for x < 0.35 (Fig. 2). On the other hand, the electrical resistivity shows a broad parabolic maximum centered on x = 0.49, with a maximal (fitted) resistivity of 47 $\mu\Omega cm$. This is characteristic for a conduction dominated by electron-impurity scattering and thus reflects the disorder of the Mg-Al mixture. There is no indication for the formation of another alloy phase at an intermediate composition, neither in the XRD spectra, nor in the resistivity measurements. These observations fit well with other studies of Mg-Al layers deposited by magnetron sputtering [10], which report highly supersaturated single phase solid solutions of Al in Mg (0.7 < x < 1) and Mg in Al (0 < x < 0.2) and a single phase amorphous or microcrystalline glassy metal in the 0.45 < x < 0.5 range.

3.2 *Hydrided state*

After hydrogenation, some regions of the gradient sample have become transparent (Fig. 3). Mg-rich parts show a high transmission for compositions x > 0.5. We attribute this effect to the formation of MgH_2, as this hydride is a colorless insulator with a band gap of 5.6 eV [11]. The segregated Al in Mg_xAl_{1-x} is dispersed in MgH_2 for x > 0, leading to a decreasing transmission with de-

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creasing x. At x < 0.5, MgH_2 forms insulating clusters in a metallic Al matrix. Assuming that the increasing absorption is due to the metallic Al matrix, we fit the transmission with a Lambert-Beer law: $T \propto \exp(-k(1-x)) \propto \exp(kx)$. By extrapolation to the background, we find a limit for Mg hydride formation at x = 0.31 ± 0.01. However, transmission does not vanish completely in the Al rich region. After background substraction due to residual transmission of MgH_2, we find a peak within a compositional range of 0.27 < x < 0.36 with a maximum at x = 0.32 ± 0.01. This composition is in agreement with an Al:Mg ratio of 2 (x = 0.33), suggesting that $Mg(AlH_4)_2$ has been formed.

Theoretical calculations predict that Mg-alanate should be a wide band insulator [5]. However, transmission remains low. We therefore performed in situ XRD measurements in this range and found an increase of the Al(111) peak intensity and a shift of the lattice parameter toward the bulk value during annealing and hydrogenation: an increase in the Al grain size hinders the Mg-alanate formation and explains the low transmission.

To confirm the formation of $Mg(AlH_4)_2$, we measured the conductivity of our film in the hydrided state. As observed optically, we found that the Mg-rich part becomes insulating, with a percolation threshold of Al in MgH_2 at x = 0.61. Moreover, an additional dip in conductivity at a composition x = 0.32 is also present [12], although this composition is far below the percolation threshold and thus should be fully conductive. This is consistent with the formation of the insulating $Mg(AlH_4)_2$ phase at this composition.

To find the temperature for which hydrogenation starts, we follow the transmission of the Mg-Al, Ti doped and Ti covered gradients samples under a constant hydrogen pressure of 1.1 bar from room temperature up to 120 °C

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with a heating rate of 3K/hr. After cooling down under hydrogen atmosphere, we dehydrid the film in air with the same heating rate up to 200 °C. Figure 4 shows the temperature and composition dependence of the transmission of a Mg-Al gradient sample (Fig. 4b) compared to that of a Ti doped Mg-Al gradient sample (Fig. 4a). We observe the following features: (i) Both films start to hydride at the same composition of x = 0.62 around room temperature. (ii) For low temperatures (T < 80°C) the region where MgH_2 forms is slightly smaller in the Ti doped sample than in the pure Mg-Al film. This can be seen in Fig. 4c) for a x = 0.5 composition. (iii) Ti doping lowers the hydriding temperature of the Mg-rich part (Fig. 4c), x = 0.7). (iv) However, the main difference comes from the Al-rich region. The Ti doped sample stays non transmittive for x < 0.35, and hence no formation of $Mg(AlH_4)_2$ is found (Fig. 4c), x = 0.33).

An advantage of using thin films is that in contrast to bulk, they offer the opportunity to discriminate between the different roles of additives. Either as a destabilizing dopant, or as a catalyst on the surface. Figure 5 shows a comparison of the transmission of samples with and without a Ti buffer layer during hydrogen absorption at $p(H_2) = 1.1$ bar and desorption in air. Absorption is similar for both samples. However, the desorption temperature is lowered by about 100 °C if a 5 nm Ti layer is present between the Pd and the Mg-Al layer. This suggests that Ti catalyzes the decomposition of $Mg(AlH_4)_2$ when it is located at the film surface.

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4 Conclusion

By means of optical transmission and electrical resistivity measurements, we demonstrate the formation of MgH_2 and $Mg(AlH_4)_2$ within well-defined compositional ranges in Mg_xAl_{1-x} gradient films. Furthermore, we determine the minimal hydriding temperature as a function of x. Reversible formation of $Mg(AlH_4)_2$ is possible from the metallic elements below $100°C$ when using a Ti buffer layer. In contrast, doping with metallic Ti suppresses the formation of $Mg(AlH_4)_2$. However, it favors the formation of MgH_2 for all Mg molar fractions above the Al percolation threshold (x > 0.61).

The results point to the potential of Mg alanate as a reversible hydrogen storage material and illustrate the great advantage of the compositional gradient method for the search of new light-weight metal hydride storage materials.

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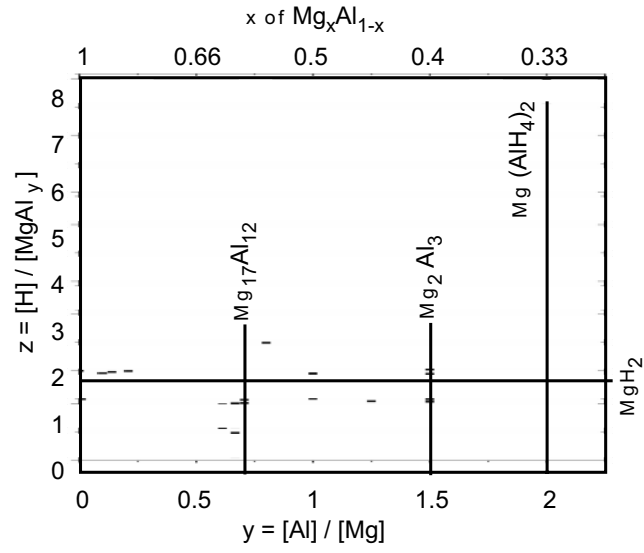
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Fig. 1. Summary of studies reporting on the hydriding of $MgAl_yH_z$ [6]. The atomic hydrogen content z in $MgAl_yH_z$ is plotted as a function of y = [Al]/[Mg]. The top scale shows the Mg molar fraction used throughout this paper.
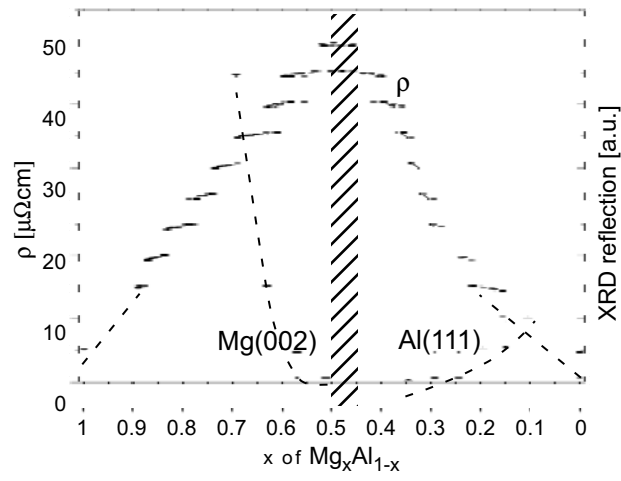
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Fig. 2. Filled circles: resistivity ρ; down triangles: intensity of the out-of-plane Mg(002) XRD reflection, up triangles: intensity of the out-of-plane Al(111) XRD reflection as a function of Mg content x.
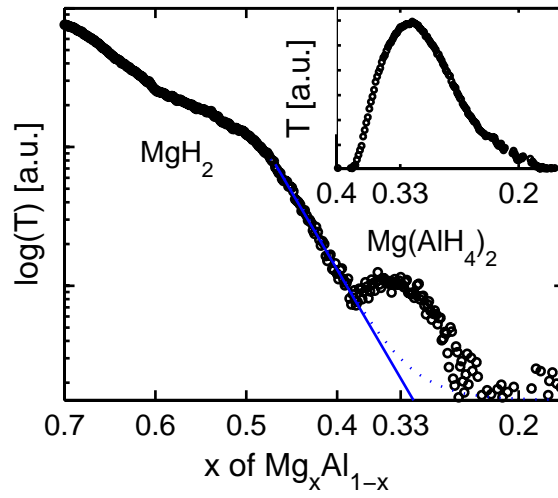
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Fig. 3. Hydrogenated Mg-Al gradient sample after 40h, T = 110°C, p(H$_2$) = 1.1 bar: red channel transmission as a function of composition. Full line: Lambert-Beer fit of the Al absorption; Dotted curve: assumed background. Inset: After substraction of the MgH$_2$ contribution, the optical transmission peak at a composition corresponding to Mg(AlH$_4$)$_2$.
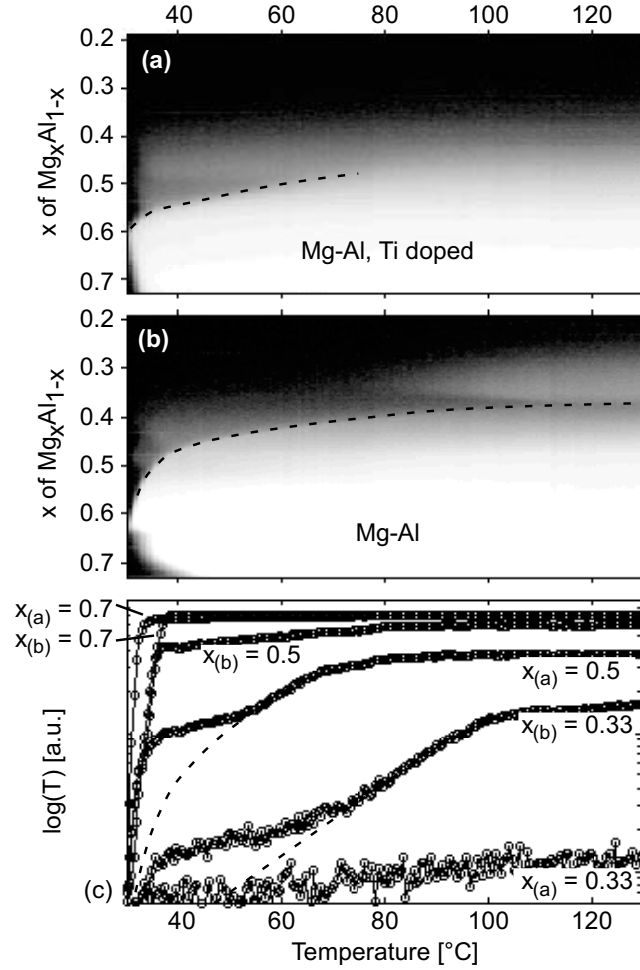
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Fig. 4. Contour plot of the transmission as a function of temperature and composition for (a) a Mg-Al gradient doped with 3% of Ti and (b) a Mg-Al gradient sample during hydriding ($p(H_2) = 1.1$ bar, heating rate: 3K/hr). The dashed lines indicate the region in which MgH_2 is formed. In (c), the transmission for three compositions $x_{(i)}$ of samples (a) and (b) is given as a function of temperature. Dashed lines: corrected transmissions for internal reflections in the hydrogen cell.
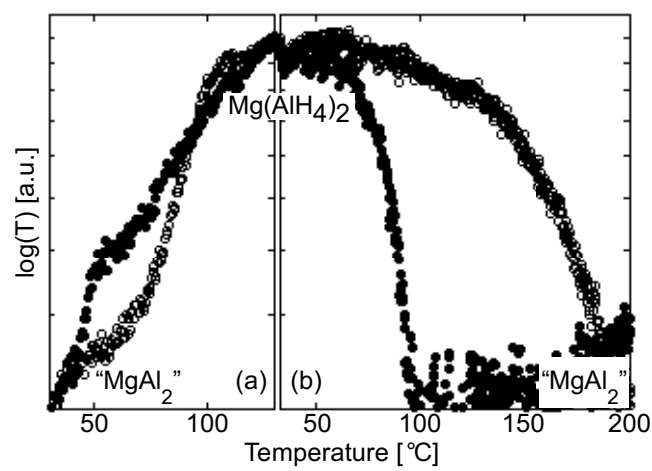
Fig. 5. Transmission as a function of temperature at a nominal MgAl$_2$ composition during (a) hydrogen absorption at p(H$_2$) = 1.1 bar and (b) desorption in air. Open circles: without a 5 nm Ti buffer layer. Filled circles: with a 5 nm Ti buffer layer.

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