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Hydrogen uptake in Mg:C thin films

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Abstract

Magnesium:carbon films 25 nm thick, with approximately 40% carbon content and a 5 nm Pd capping layer, were co-sputtered in a dc magnetron sputtering chamber. The films were found to be X-ray amorphous. The hydrogen uptake was studied by *in situ* resistance measurements. The uptake showed one fast process with a time span of a few seconds followed by much slower resistance change, indicating structural relaxation. The isotherms show similar behavior as found in amorphous materials with a broad distribution of binding energies. A significant part of the film showed a reduction in the binding energy of hydrogen in MgH_2 that would yield a release temperature of ~200 °C at 1 bar.

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Keywords: Thin films; Hydrogen; Magnesium; Carbon

1. Introduction

There is currently a lot of interest in the high storage capacity of light metal hydrides. Magnesium is one of the lightest hydrogen storage material known; it is also abundant and inexpensive. The main problem with using magnesium as a storage material for hydrogen, is the high binding energy of hydrogen and the slow kinetics of uptake through the MgH_2 hydride that is formed at the surface of magnesium grains [1].

A lot of work has been done to solve the aforementioned problems. One method to improve the kinetics of the system is to reduce the Mg grain size using ball milling [2,3]. There it was shown that nanocrystalline Mg exhibited superior hydriding kinetics over larger grain sized Mg and additionally showing some lowering of the release temperature. This was further enhanced with the presence of Pd clusters on the Mg surface [4]. The improved kinetics have been explained with an increase in the specific Mg surface area and shorter diffusion pathways. Cheung et al. [5] calculated the binding energy of hydrogen in nanosized Mg grains. Those calculations indicated that the binding energy of H in MgH_2 lowered with Mg grain size but at the expense of storage capacity. The binding energy of the $Mg_{20}H_x$ was calculated for $x = 0$–40 and it was found that for $x < 10$ the removal of hydrogen became energetically unfavorable. Work has also been done to find hydrogen absorbing phases of Mg and another material with hydrogen binding energies lower than that of pure Mg such as $Mg(AlH_4)$ [6].

Another possible way to improve magnesium storage properties is to prepare composites of Mg and other materials such as Mg–C composite. There the binding energy can be influenced without forming a new phase. The Mg–C system has been studied thoroughly using ball milling techniques by Imamura et al. [7,8]. There Mg and Graphite was ball milled with and without various organic additives. Results show an improvement in the hydriding kinetics of Mg. This is attributed to the same effects as with pure Mg but additionally it is speculated that a charge transfer occurs between Mg and Graphite and this further enhances the kinetic properties [9,10]. Others have reported that the effect of carbon is to hinder oxygen back-diffusion to the Mg surface. Oxygen on the surface of Mg grains can hinder dissociative chemisorption of hydrogen thus hindering hydriding kinetics [11,12]. Mg has also been ball milled with various carbon structures such as carbon nanotubes [13] which has also enhanced the hydriding kinetics. Mg–C phases do exist [14] but are not reported to exist in any of the above-mentioned literature. In all of this work the effect of carbon on the binding energy of hydrogen in the MgH_2 is never quantitatively discussed although a

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decrease in binding energy is indicated and results generally show a distribution in the binding energy of the samples [15].

The aim of this work was to gain more information about the hydrogen uptake kinetics and change in hydrogen binding energy in Mg:C films. By cosputtering Mg and C, the structure consists of a network of random graphite planes or chains with magnesium material in between. Such a system could therefore exhibit improved kinetics, because of faster diffusion along the Mg:C:Mg interface, as well as a lowering of the binding energy due to the small grain size and possible clamping effects from the substrate.

2. Experimental

The samples were grown in a dc sputtering system that allows the measurement of the sample resistance during growth and under applied hydrogen pressure. The films were grown on specially prepared MgO(0 0 1) substrates which had Cr contacts pads on each end (see Fig. 1). The pads were pre grown at room temperature and were 100 nm thick. After growing the pads the substrate was placed on the sample holder and four probe wires were placed on top of the pads, two on each side. A mask was then placed on top of the sample holder, covering everything except the centre of the sample where the film was grown. The pads were connected by wires through a vacuum feedthrough to a Keithley 2400 resistance meter. The films were co-sputtered from Mg (99.995%) and C (99.95%) targets at room temperature while the resistance was measured. After growth the films were covered with a 5 nm layer of Pd to enhance the chemical absorption of hydrogen. The total thickness of the films was 30 nm including the Pd capping layer, measured by XRR measurements *ex situ*. The Mg:C composition of the samples, was determined to be approximately 40% C and 60% Mg by elastic recoil detection analysis (ERDA) measurements. All samples showed oxygen contamination after removal from growth chamber. Even with a 5 nm thick Pd layer covering the sample, an oxygen content of up to 60% could be observed. It was found that by covering the samples with more than 5 nm of Pd the oxygen content was reduced to approximately 10%.

In situ measurements are therefore required for the hydrogen uptake measurements. A residual gas analyzer was connected to the system to determine the composition of the residual gas. The partial pressure of oxygen was found to be in the order of $\sim 10^{-9}$ mbar with the basepressure $\sim 10^{-8}$ mbar. Oxidation of the sample during the measurements is therefore negligible. The hydrogen loading was performed *in situ* with a hydrogen gas of 99.999% purity. The loading was done at different temperatures from room temperature up to 423 K. The temperature was measured below the sample holder and was controlled by a Eurotherm 94C temperature controller with an accuracy of ± 2 K. Two capacitance pressure gauges in the range 0–10 mbar and 0–100 mbar were used to determine the applied hydrogen gas pressure. The gas was applied in two different ways, either by slowly increasing hydrogen pressure from vacuum to 25 mbar or by exposing the samples to a constant hydrogen pressure ranging from 6 mbar to 10 mbar for 2, 5 or 10 min. This was performed to study the kinetics of uptake and gain information on the extent of the hydride formation in the sample.

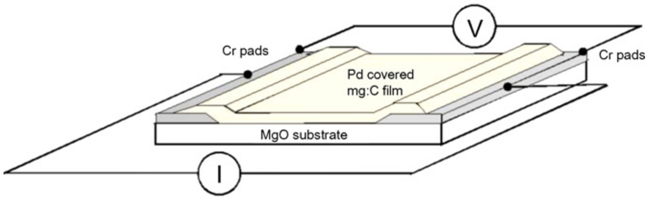

Fig. 1. Schematic of the grown sample. Cr contact pads are grown on each side of the substrate and wires connected to the pads. The Mg:C film is grown between the Cr pads and then covered with Pd.

3. Results and discussion

The kinetics of the hydrogen uptake at 90 °C is shown in Fig. 2. There the pressure was increased very fast to 7.7 mbar and held for different periods of time (2, 5 and 10 min) before it was decreased rapidly to 5×10^{-3} mbar and the resistance monitored.

The resistance increase in Fig. 2 and hence the uptake shows fast kinetics and that a large part of the film absorbs hydrogen in a very short time but further hydrogenation is a slow relaxation process. The desorption is also very fast until a certain pressure level is reached. There the desorption slows down and reaches equilibrium in a few hours, usually not reaching the same initial resistance value.

The measured resistance can be modeled with the following equation

$$R = \frac{V}{I} = R_{\mathrm{Pd}} + R_{\mathrm{MgH}_x} + R_{\mathrm{carbon}} + R_{\mathrm{interfaces}} \tag{1}$$

where R_{Pd} is the resistance of the Pd capping layer, R_{MgH_x} the resistance of the hydrogenated magnesium component, R_{carbon} the resistance of the carbon network in the sample and finally $R_{\mathrm{interfaces}}$ is the resistance of the interfaces between Mg and the carbon network.

In Fig. 3 the isotherm for a Mg:C sample at 70° is shown. The pressure was ramped slowly from base pressure up to 7.3 mbar and the resistance monitored as a function of time. The repeatability of the isotherms was found to be history dependent and also pressure profile dependent. In spite of this, three different zones of hydrogen uptake can be seen in all isotherms with the same pressure profile as the one in Fig. 3. These zones, A–C, can be seen in Fig. 3. The first zone (A) shows the uptake at the lowest pressure where hydrogen sites with the highest binding energy are being occupied possibly due to structural defects and vacan-

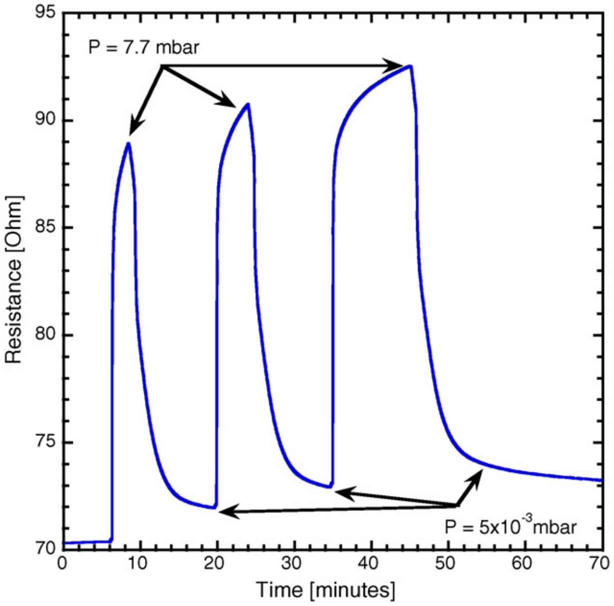

Fig. 2. The resistance response of the sample at 90 °C when a pressure pulse of 7.7 mbar is applied for different durations (2, 5 and 10 min).

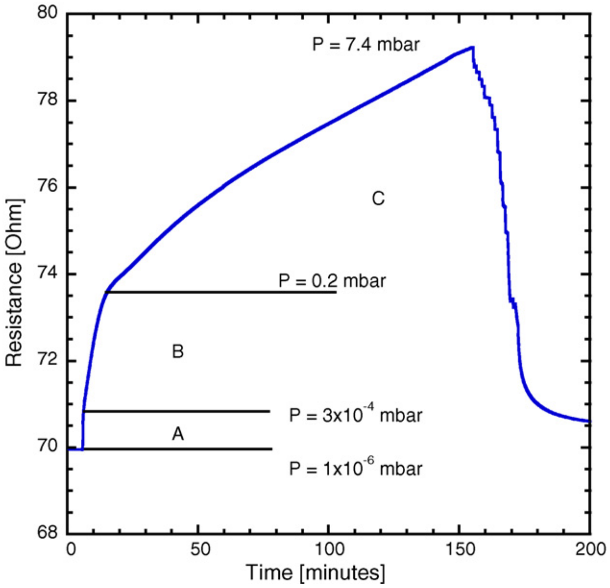

Fig. 3. The hydrogen absorption and desorption isotherms at 70 °C of a Mg:C sample. Three different uptake regions are seen in the isotherms and are labeled as A, B and C in the figure. The onset of MgH_2 formation for bulk is at $p = 0.2$ mbar for this temperature [19].

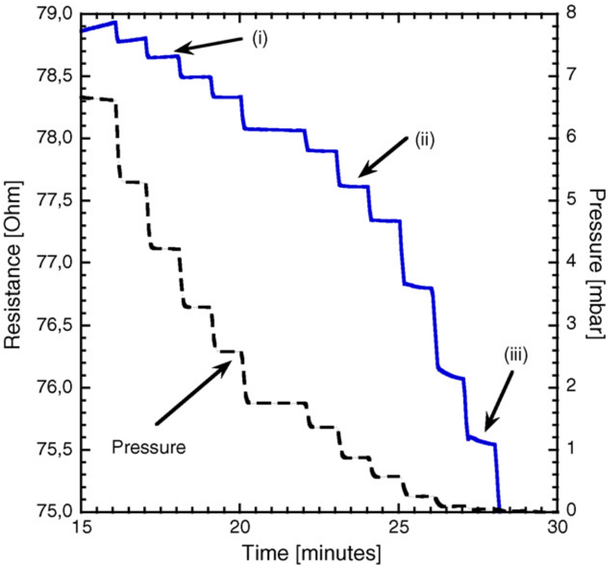

Fig. 4. The hydrogen pressure (dotted line) is decreased in steps and the resistance responce of the sample (full line) is shown. The resistance initially decreases rapidly for each step but at constant pressure it increases (i) or decreases (iii) depending on whether under or over-pressure is applied. At a certain pressure level the resistance change is stable (ii) indicating equilibrium state.

cies. In zone (B) the resistance change as function of applied pressure is decreased indicating a new uptake region possibly with occupation of similar sites but with lower binding energy. Then in zone (C) the uptake behavior changes again with appearance of definite equilibrium resistance levels but also followed with slow relaxation in resistance. This occurs at a pressure of 0.2 mbar, the plateau pressure of bulk MgH_2 at this temperature. The isotherm shows a typical uptake curve of amorphous materials with a distribution of site energies [16,17].

This amorphous behavior is shown further in Fig. 4 where response of the resistance to a stepwise decrease of pressure is plotted as a function of time. In the figure it can be seen that the resistance initially decreases rapidly at each step but at constant pressure it increases (i) or decreases (ii) depending on whether under or over-pressure is being applied. The pressure level where the resistance change is stable (ii) indicates a stable occupation of hydrogen in amorphous like energy distribution of sites. The fast resistance decrease corresponds to a certain region of the site energy distribution being depopulated. At under-pressure (iii) the depopulation relaxes the film, changing the site energy distribution slightly, creating new energy-levels that populate differently. This is a slow process due to the slow relaxation in resistance decrease.

The behavior in the Mg:C films is very different from the hydrogen uptake of pure Mg films [18]. There, a slow initial resistance increase, at low applied pressures is seen until the insulating MgH_2 phase starts to form at a certain pressure. At this pressure, a sharp increase in the resistance is observed followed by slow resistance increase at higher applied pressure. When the pressure is lowered the film dehydrogenates at a certain plateau pressure level [18].

It was not possible to obtain thermodynamic information using Van't Hoff analysis, from the measured isotherms, since the resistance change showed hysteresis depending on temperature, rate of applied pressure and previous hydrogenation history. This occurred in all isotherm zones A–C, both during hydrogenation and dehydrogenation.

However, the isotherm at 70° in Fig. 3 shows that hydride formation is occurring in the pressure range from 0.2 mbar to at least 7.4 mbar where the pressure was decreased. The binding energy at 7.4 mbar can be estimated by using the Van't Hoff relation, assuming that the values for entropy of solution are the same for this pressure range. The binding energy can then be calculated to be 0.32 eV/atom. This is a significant reduction in the binding energy of hydrogen in MgH_2 and is calculated to yield a release temperature of $\sim$ 200 °C at 1 bar. The sample shows further hydrogen uptake at higher pressures up to 100 mbar but with smaller resistance change indicating that a smaller volume of the sample has such low binding energy levels.

4. Conclusions

Growth of Mg:C films with 40% carbon content was performed. The growth process is a complicated process with difficulty in capping the sample to prevent oxidation in air. *In situ* measurements showed very fast kinetics of hydrogen compared to pure Mg films. The loading time is in a time span of a few seconds while slow relaxation is seen thereafter. During loading or unloading there is no defined plateau pressure behavior in the uptake curve although onset of MgH_2 hydride formation is seen. The thermodynamics of the Mg:C thin film is behaving like an amorphous material with a distribution of binding energies from bulk MgH_2 (-0.38 eV/atom) levels and to lower binding energy levels as low as -0.3 eV/atom in a small part of the sample.

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