

Hydrogen uptake in Mg-Pd thin films

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ABSTRACT

The article is focused on the study of the possibility to reduce the binding energy of hydride formation by alloying metal magnesium with transition metal palladium. Hydrogen uptake in Mg-Pd films, with composition ranging from $Mg_{0.95}Pd_{0.05}$ to $Mg_{0.5}Pd_{0.5}$ was investigated by in-situ resistance measurements. From the measurements p - ΔR - T a number of isotherms showing the enthalpy change were drawn. The data was then compared with the bulk values for MgH_2 and $PdH_{0.6}$. As a result, the authors were bound to conclude that the enthalpy change or the binding energy of hydride formation was reduced from -0.77 eV/ H_2 to -0.65 ± 0.5 eV/ H_2 .

1. INTRODUCTION

Hydrogen storage materials such as metal hydrides, chemical hydrides and nano-structured carbons have attracted considerable scientific attention in relation to their application in fuel-cell electric vehicles [1]. The latter have to be compact, light, safe and give affordable containment for on board storage. For development of high-performance hydrogen storage materials applicable to FCEV new materials with lighter elements have been looked for in recent years. It is expected that they are able overcome the disadvantages of conventional heavyweight metal hydrides.

One attractive light metal hydride is MgH_2 , because it is formed directly by the reaction of bulk Mg with gaseous hydrogen, reaching hydrogen concentrations up to 7.6 wt. % of hydrogen. However, there appear to be some disadvantages of MgH_2 for hydrogen storage due to its slow kinetics of hydrogen absorption-desorption and a relatively large amount of heat required to displace the hydrogen [2]. Indeed, the enthalpy change of magnesium hydride or binding energy of hydride formation, -0.77 eV/ H_2 , is too high compared to a hydride that releases hydrogen at pressure of 1 bar at room temperature (-0.4 eV/ H_2) [3]. Thus, the binding energy of hydrogen atoms needs to be reduced by 0.37 eV/ H_2 . The problem of slow kinetics of hydrogen absorption can be solved by depositing a catalytic layer, comprising such material as palladium, on the magnesium surface.

For further investigation of the matter, the hydrogen uptake in thin metallic films can be used. Only a few studies concerning the absorption of hydrogen into metal alloys have been carried out using this approach. Some of them are focused on detailed measurements of hydrogen uptake and description of hydrogen-hydrogen interaction in thin vanadium layers [4, 5]. These works represent initial studies of hydrogen uptake in multilayers by conductance measurements and introduce such basic thermodynamic properties of hydrides as enthalpy and entropy of formation. Until now the measurements have been performed for a limited number of alloys, such as vanadium and niobium, and for pure magnesium and palladium. Furthermore, enthalpy change bulk values for Mg and Pd hydride were stated. The present paper can be regarded as the first one to address the matter of enthalpy changes caused by the uptake of hydrogen in these thin film systems.

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The main objective of this paper is to investigate the behavior of Mg-Pd thin films exposed to hydrogen. The enthalpy change is compared to the bulk values for the magnesium and palladium hydride [6-8].

2. SAMPLE PREPARATION AND EXPERIMENTS

Mg-Pd thin films were grown on a polished MgO (001) substrate with DC magnetron sputtering under the condition of argon pressure of $3.6 \cdot 10^{-8}$ mbar. All samples were grown at room temperature with total thickness of 100 nm. The deposition rate during the process of growing equaled to 0.1 nm/s. Finally, the samples were covered with a 10 nm thick Pd layer, which served as a catalyst. Then, the sample was cleaved to dimensions of 10x5 mm for the in-situ resistance measurement. The resistance of the samples was measured with a resistance meter, which applies a 1-2 mA AC current and measures the voltage drop with a four-point probe technique. The sample temperature was controlled by the Eurotherm 94C heating unit driven by a feedback loop through a PID amplifier. A high vacuum pump lowered the pressure over the sample down to 10^{-6} mbar before hydrogen was introduced into the chamber. The pressure gauge was used to monitor hydrogen gas pressure. It was observed that with the increasing pressure the resistance of thin films tended to increase as well. The measurements carried out revealed that after unloading of hydrogen gas from the hydrogenation system the resistance of the sample returned to a value within 3.6% of the initial resistance value.

3. RESULTS AND DISCUSSIONS

3.1. Mg_{0.95}Pd_{0.05} film

In the current work, resistance measurements were used to monitor the hydrogen uptake in Mg_{0.95}Pd_{0.05} films. Two different pressure ranges were studied at the temperature of 60-100°C, the first pressure range being 0-1 mbar, the second one 0-10 mbar. According to the bulk data, MgH₂ formation begins at the pressure of at least 0.4 mbar and at the temperature of 60-100°C [2]. The hydrogenation pressure for bulk PdH_{0.6} was determined out of the solubility isotherms and it is higher than 60 mbar for the same temperature interval [9].

The phase diagram for Mg-Pd system shows that below the temperature of 540°C the Mg_{0.95}Pd_{0.05} alloy consists of solid solution of Mg and Pd. This means that in the pressure range 0-10 mbar only α -phase of PdH_{0.6} is present. For the chosen pressure ranges the behavior of MgH₂ can be expected at the low pressure range (p=0-1 mbar), while the behavior of PdH_{0.6} is expected at the high end of the high-pressure range (p=0-10 mbar).

The first experiments were performed at the low pressure range to prevent the samples from cracking and peeling, which is possible to happen during their exposure to extremely high hydrogen pressure. In the experiment the sample was heated up to a chosen temperature between 60-100°C. When the initial resistance had stabilized and the vacuum pressure inside the system had set below $\sim 10^{-6}$ mbar the hydrogen gas was introduced into the system.

Fig. 1 below shows the plot resistance versus time for a Mg_{0.95}Pd_{0.05} thin film sample.

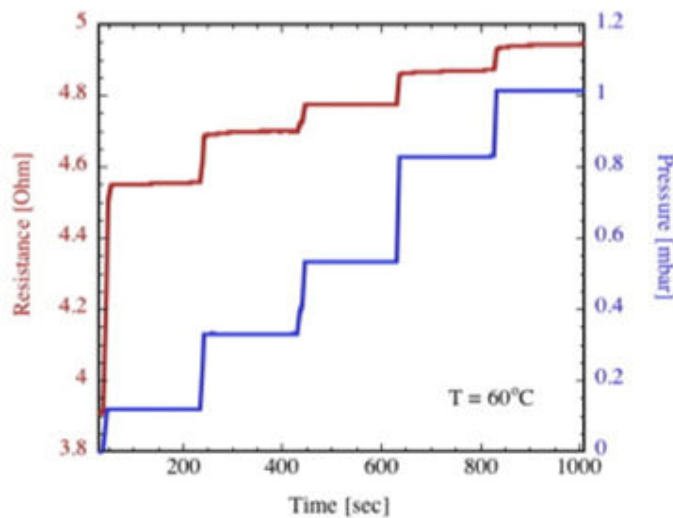


Fig.1. Kinetics of hydrogen uptake at T=60°C

The plot shows hydrogenation kinetics at low hydrogen concentrations and low hydrogen gas pressure. Fast and slow kinetics are visible in the thin film. The pressure is increased in steps and the resistance change is indicated.

Response to pressure increase shows fast and slow behavior. At this temperature the bulk Mg has a phase transformation hydrogenation pressure of 0.022 mbar which is higher than the pressure used here. The hydrogen should therefore enter the low concentration α -phase of the 100 nm MgPd layer or the Pd contact layers.

The fast resistance increase indicates that hydrogen can enter all parts of the sample relatively fast. The slow kinetics in the resistance change indicates the occurrence of a slow structural relaxation.

The repeatability of the measurement is therefore not good as it is in the case of a crystalline film. The initial resistance value increased at the rate of 5% when the hydrogen was removed.

Interface hydride is expected to be formed and since the hydride is an insulator the resistivity increases in proportion to the ratio of the sample reacted. However, in the low concentration α -phase the hydrogen atoms are very mobile and the sample is conducting, therefore the resistance gives good indication of the hydrogen concentration in the film.

This behavior can be easily perceived from the resistance isotherms presented in Fig.2, where the low concentration phase is characterized by a region of small resistance changes.

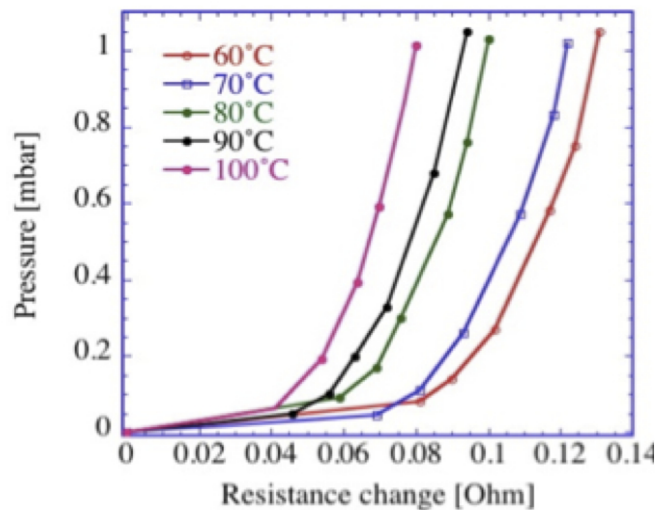


Fig.2. The p - ΔR - T isotherms for the $Mg_{0.95}Pd_{0.05}$ film.

It is difficult to obtain thermodynamic information from the resistance isotherms due to the lack of information concerning absolute hydrogen concentration. However, if the plateau pressure for the formation of the hydride is observed, the binding energy of hydride formation or enthalpy change (ΔH) of the system can be obtained using the Van't Hoff relation,

$$\ln p^{\frac{1}{2}} = \frac{\Delta H}{k_B T} - \frac{\Delta S}{k_B}$$

Here, p is the plateau pressure of hydride formation, T is the hydrogenation temperature, k_B is the Boltzman constant, ΔH and ΔS are the enthalpy and entropy changes, respectively.

The plateau pressure cannot be perceived from the resistance isotherms, but the resistance change is expected to increase much faster when the hydride formation starts. Fig.3 below shows the Van't Hoff or the Arrhenius plot, where the information of hydrogen concentration is not needed.

The data of the resistance change is plotted and analyzed, where the slope and intercept of the lines are the enthalpy change and the entropy change, respectively

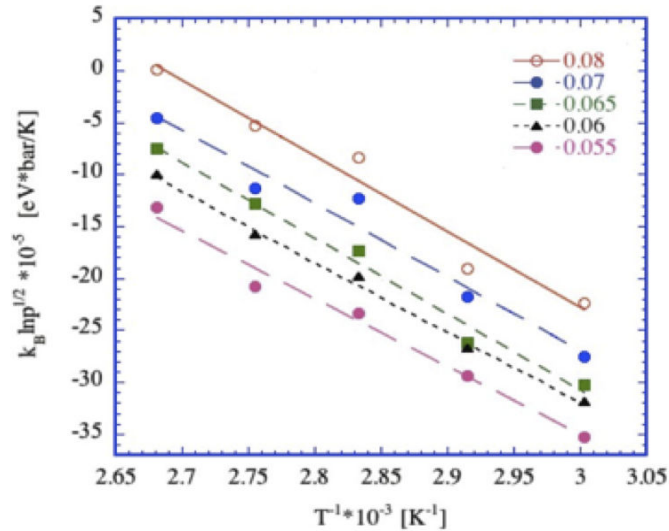


Fig. 3. Van't Hoff plot for Mg_{0.95}Pd_{0.05} film. The plateau pressure is plotted as a function of $1/T$. The slope and the intercept of the linear fits are the enthalpy change and the entropy change, respectively.

Fig. 4 represents the enthalpy plotted versus the resistance change. The enthalpy change for bulk Mg and Pd hydride are marked in the plot with the solid and the dashed lines, respectively. The filled circles in the plot represent the enthalpy changes in the pressure range of 0-1 mbar. The enthalpy changes vary from -0.65 to -0.70 eV/H₂. These indices are close to the bulk value of the MgH₂, -0.77±0.07 eV/H₂ [2] and are significantly smaller than the bulk value of the PdH_{0.6}, -0.4 eV/H₂ [6, 7]. The enthalpy changes in the pressure range of 0-10 mbar, depicted with the open circles in the figure, vary from -0.45 to -0.40 eV/H₂, which slightly differs from the value obtained for bulk PdH_{0.6} and is much higher than the enthalpy changes for bulk MgH₂.

The results show that we observe two types of behaviour. The magnesium behavior in the Mg_{0.95}Pd_{0.05} thin film is as follows: at low concentration it corresponds to low hydrogen gas concentration and shows a small resistance change. PdH_{0.6} or Mg-Pd-H behavior is as follows: at high concentration it corresponds to high hydrogen gas concentration and a larger resistance change.

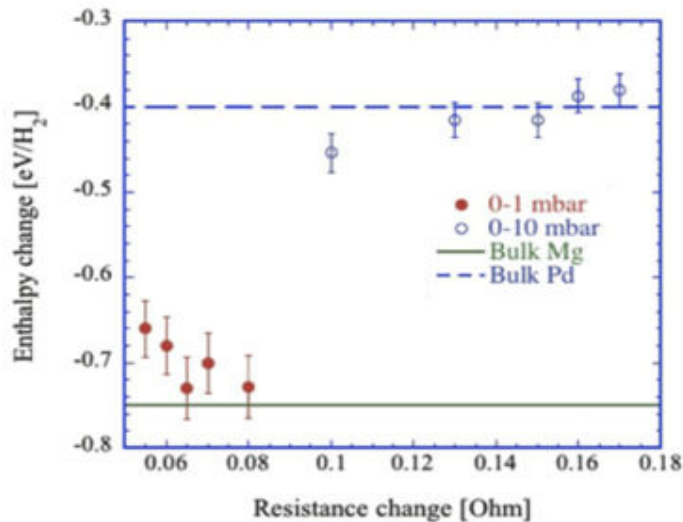


Fig.4. Enthalpy change for Mg_{0.95}Pd_{0.05} thin film as a function of the resistance change.

3.2. Mg_{0.5}Pd_{0.5} film

In this part, the in-situ resistance measurements were carried out for the purpose of investigation of the enthalpy

changes for the Mg_{0.5}Pd_{0.5} thin film, a large part of which had an alloy phase of Mg-Pd-H. The measurement procedure is similar to that described earlier for the Mg_{0.95}Pd_{0.05} thin film sample. Experimental work was performed in two different pressure ranges that we describe as low and high.

The first one is the pressure range of 0-1 mbar, the same as discussed in the previous section. The second one is much higher than previous one, and it is the pressure range of 0-100 mbar of hydrogen gas. The phase diagram for Mg-Pd system shows that below the temperature of 700°C the Mg_{0.5}Pd_{0.5} alloy is in the form of solid solution of Mg-Pd. Therefore, the high pressure values were chosen for examination as the Mg-Pd-H and PdH_{0.6} behavior is expected at pressure higher than 60 mbar, as was mentioned before. The hydrogen pressure increased in square root steps, and fast and slow resistance change behavior can also be observed. All measurement were repeated twice, the results were then compared. It allowed to reveal that the initial resistance values for the films increased by less than 5% from the first measurement to the last.

Thermodynamics information for the film was obtained through an Arrhenius plot, which is not given here. These values were deduced using the Van't Hoff relation. The slope on the Arrhenius plot gives the enthalpy change, while the intercept with the x-axis gives the entropy change.

Fig.5 represents the enthalpy change for both pressure ranges as a function of resistance change. The lines for the enthalpy change of bulk magnesium and palladium hydrides were also used for comparison.

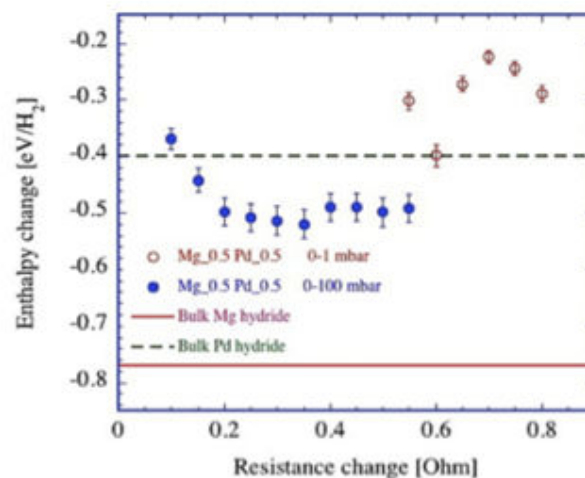


Fig.5. The enthalpy change versus resistance change plot for Mg_{0.5}Pd_{0.5}. The solid line shows the value of the enthalpy change for bulk MgH₂, while the dashed line presents the value of the enthalpy change for bulk Pd hydride.

However, the hydrogen in the film showed a strange concentration behavior in both pressure ranges. Here, the resistance change was the same for both pressure ranges. This indicates that the structure of the sample has possibly changed during the first measurement in the high pressure range. Two possible factors could have caused this change in the sample. The first one is segregation of the Mg-Pd phase by hydride formation of MgH₂ or PdH_{0.6} urged by high temperature. The second factor could be oxygen contamination in the sample. In the unaffected sample the enthalpy change equals to -0.20 eV/H₂, which is closer to the values for bulk PdH_{0.6} and indicates the presence of that phase in the given pressure range.

In the high pressure range (high temperature 60-200°C), where this value is determined to be between the values of the two bulk hydrides, the enthalpy change equals to -0.5 eV/H₂. Indication of that mixed behavior of MgH₂ and PdH_{0.6}, and the Mg-Pd-H phases can be observed here.

4. CONCLUSIONS

We have investigated the hydrogen uptake in the Mg_{0.95}Pd_{0.05} and the Mg_{0.5}Pd_{0.5} thin films with thickness of 100 nm. The results obtained are summarized as follows:

- In the Mg_{0.95}Pd_{0.05} film the enthalpy change or the binding energy of hydride formation decreased as a function of hydrogen concentration in the low hydrogen concentration regime. This indicates the occurrence of an attractive interaction in the film in a disordered phase. The binding energy is found to be -0.65 eV/H₂ in the low concentration regime, which is lower than the values for bulk MgH₂, and it was determined to be -0.40

eV/H₂ in the high pressure regime, which is closer to the bulk PdH_{0.6} and Mg-Pd-H behaviour.

- Hydrogen uptake in Mg_{0.5}Pd_{0.5} film was investigated in a low and high hydrogen pressure ranges. The enthalpy changes were deduced for both pressure ranges. However, the hydrogen in the film showed strange concentration behavior in both pressure ranges. This indicates that the structure of the sample has possibly changed during the first measurement in high pressure range. Two possible factors could have caused this change in the sample, they are segregation of the Mg-Pd phase or oxygen contamination in the sample. In the unaffected sample the enthalpy change equals to -0.20 eV/H₂, which is close to the values for bulk PdH_{0.6} and indicates the presence of that phase in the given pressure range. In the high pressure range (up to 200°C) where this value is determined to be between the values of the two bulk hydrides, the enthalpy change equals to -0.5 eV/H₂. Indication of that mixed behavior of MgH₂ and PdH_{0.6}, and the Mg-Pd-H phases can be observed here.
- The binding energy of hydride formation in the Mg_{0.95}Pd_{0.05} and the Mg_{0.5}Pd_{0.5} thin films is reduced to the value of -0.65±0.50 eV/H₂, as compared to the bulk data. This can be understood in the following way: the Pd or the mixture atoms disturb the potential well landscape of the Mg lattice as they reduce the potential depth. Since H atoms have to jump from one potential well to another, it is easy to diffuse through metal and to influence the changes in the binding energy of hydride formation. The second reason for the binding energy decrease could be the stress and strain in the thin films that are likely to increase the plateau pressure.
- This is the first attempt of performing hydrogen uptake measurements in Mg-Pd thin films. In this investigation we have taken some initial steps, which are believed to be necessary for further research of the given problem and a more detailed interpretation of the data obtained in the experiment.

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