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HYDROGEN UPTAKE IN Mg–Pd THIN FILMS

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Рассматривается вопрос о возможности снижения энергии, наблюдаемой при образовании гидрида, в сплаве металлического магния с переходным металлом палладием. Абсорбция водорода в тонких пленках Mg–Pd с составом, варьирующимся от $Mg_{0,95}Pd_{0,05}$ до $Mg_{0,5}Pd_{0,5}$, исследована методом измерения сопротивления в режиме «in-situ». Экспериментальные данные были использованы при вычислении зависимости $p-\Delta R-T$, что позволило построить изотермы, подтверждающие изменение энтальпии. Сопоставив полученные данные с основными значениями для MgH_2 и $PdH_{0,6}$, авторы показали, что при изменении энтальпии в исследованных структурах энергия, наблюдаемая при образовании металлического гидрида, стремится к уменьшению значений от $-0,77$ эВ/H_2 до $-0,65 \div -0,5$ эВ/H_2.

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The work 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. Experimental data were used to calculate the dependence $p-\Delta R-T$ and isotherms showing the enthalpy change were drawn. The data were 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 down to $-0.65 \div -0.5$ eV/H_2.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

INTRODUCTION

Hydrogen storage materials such as metal hydrides, chemical hydrides and nanostructured 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 to overcome the disadvantages of conventional heavy-weight 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.

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].

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1. 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 and oxidation protection layer. Then, the samples were cleaved to dimensions of 10×5 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 controller. A turbomolecular pump lowered the pressure over the sample down to 10^{-6} mbar before hydrogen was introduced into the chamber. A capacitance pressure gauge was used to monitor hydrogen gas pressure. It was observed that with the increasing hydrogen pressure the resistance of thin films tended to increase as well. The measurements carried out revealed that after unloading the hydrogen gas from the hydrogenation system the resistance of the samples changed within 3.6 % of the initial resistance value.

2. RESULTS AND DISCUSSIONS

2.1. $Mg_{0.95} Pd_{0.05}$ 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, MgH_2 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 of 0–10 mbar only α-phase of Pd–H system is present. For the chosen pressure ranges the behavior of MgH_2 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 ($p > 60$ mbar).

The first experiments were performed at the low pressure range to prevent the samples from cracking and peeling, which is possible to happen due to lattice expansion and stress formation. 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.
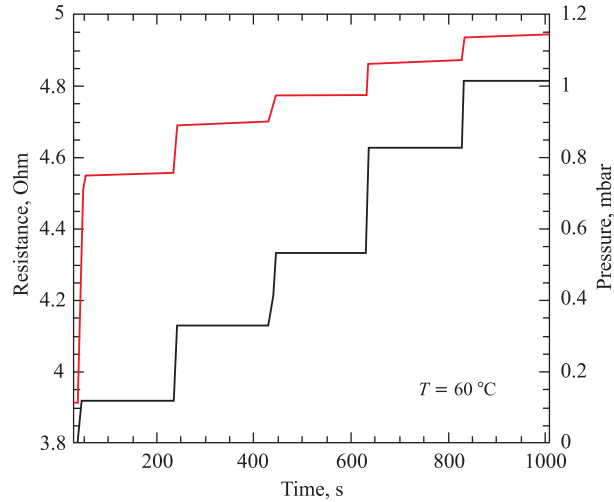
Fig. 1. Kinetics of hydrogen uptake at $T = 60\,°\text{C}$

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

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 material layer or the Pd capping layer.

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 ocurrence of a slow structural relaxation. The repeatability of the measurement is therefore not good as it is in the case of a crystalline film since the initial resistance value increased by 5 % when the hydrogen was removed.

MgH_2 hydride could be formed at the Pd, MgPd interface in similar way as seen in Pd capped Mg films [4], however low concentration Pd alloying of Mg could move that boundary throughout the whole film. Since the MgH_2 hydride is an insulator the resistivity increases in proportion to the ratio of the sample reacted.

The resistance isotherms are presented in Fig. 2, where the low concentration phase is characterized by a region of small resistance changes.

It is difficult to obtain thermodynamic information from the resistance isotherms due to the lack of information concerning absolute hydrogen concentration. How-

ever, 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 in Fig. 2, since the resistance change is not seen to increase much faster when the hydride formation starts. Here, Fig. 3 below shows the Van't Hoff or the Arrhenius plot analysis from the isotherm data, where the information of hydrogen concentration is implied by the resistance change.

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.

Figure 4 represents the enthalpy obtained from the analysis 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/H$_2$. These indices are close to the bulk value of the MgH$_2$, -0.77 ± 0.07 eV/H$_2$ [2] and are significantly smaller than the bulk value of the PdH$_{0.6}$, –0.4 eV/H$_2$ [6, 7]. The enthalpy changes in the
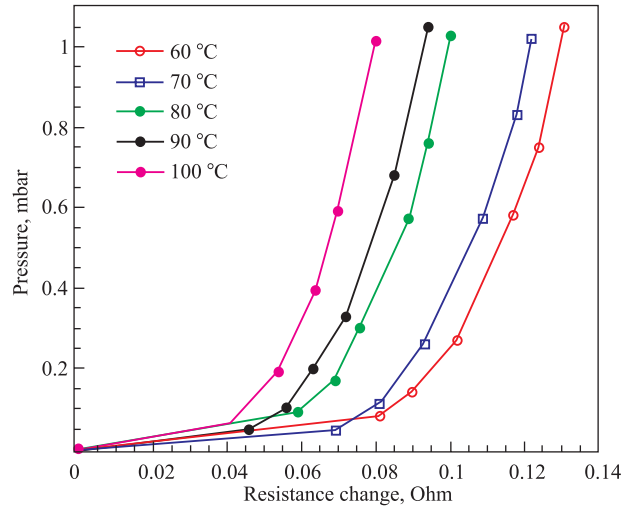

Fig. 2. The $p-\Delta R-T$ isotherms for the Mg$_{0.95}$Pd$_{0.05}$ film

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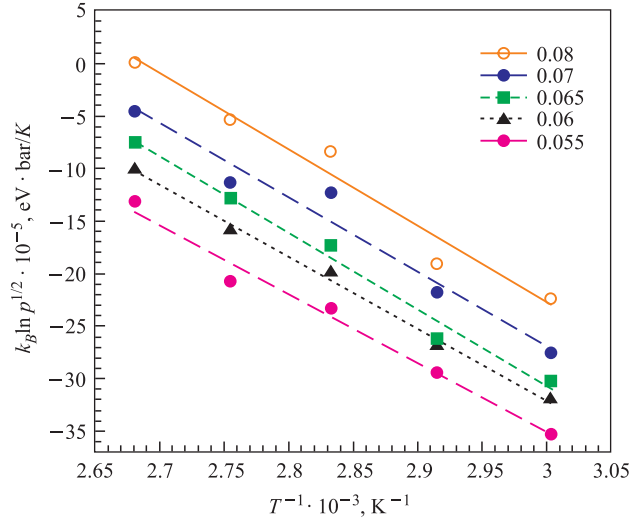
Fig. 3. Van't Hoff plot for $Mg_{0.95}Pd_{0.05}$ film. The plateau pressure is plotted as a function of $1/T$. The slope and the intercept of the linear fits are the enthalpy change and the entropy change, respectively
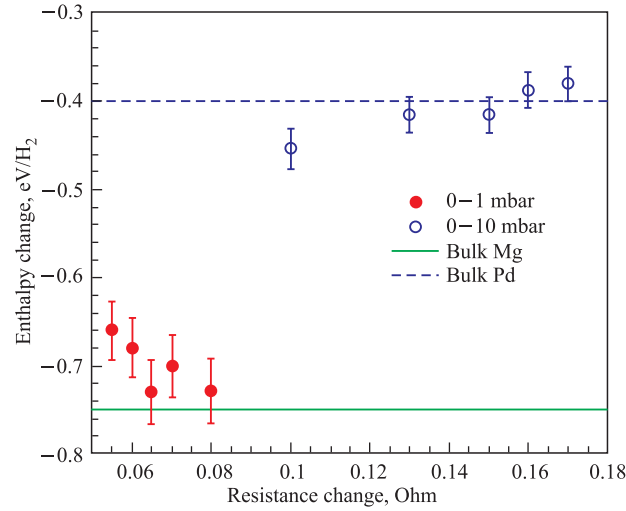

Fig. 4. Enthalpy change for $Mg_{0.95}Pd_{0.05}$ thin film as a function of the resistance change

pressure range of 0–10 mbar, depicted with the open circles in the figure, vary from –0.45 to –0.40 eV/H_2, which slightly differs from the value obtained for bulk $PdH_{0.6}$ and is much higher than the enthalpy changes for bulk MgH_2.

The results show that we observe two different entalphy behaviours in the $Mg_{0.95}Pd_{0.05}$ thin film: at low gas pressure it corresponds to MgH_2 phase formation showing small resistance change indicating small formation volume of MgH_2 phase possibly only at the interface. At higher gas pressures the behavior corresponds to formation of new MgH_2 phase with lowered enthalpy change or binding energy and also at the same time possible contribution from the hydrogen uptake of the low concentration α–PdH_x phase.

The formation of new MgH_2 phase with lowered enthalpy change or binding energy is due to the clamping stress induced by the substrate and lattice expansion of MgH_2 phase already formed in the film [10].

2.2. $Mg_{0.5}$ $Pd_{0.5}$ 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 the 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 $700\,^{\circ}C$ 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 measurements were repeated twice, the results were then compared. It allowed one to reveal that the initial resistance values for the films increased by less than 5 % from the first to the last measurement.

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.

Figure 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.

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 MgH_2 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/H_2, which is
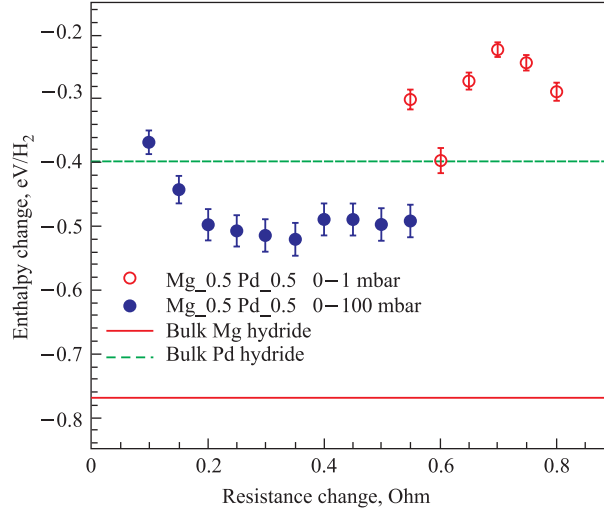
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Fig. 5. The enthalpy change versus resistance change plot for $Mg_{0.5}Pd_{0.5}$. The solid line shows the value of the enthalpy change for bulk MgH_2, while the dashed line presents the value of the enthalpy change for bulk Pd hydride

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/H_2. Indication of that mixed behavior of MgH_2 and $PdH_{0.6}$, and the Mg–Pd–H phases can be observed here.

CONCLUSIONS

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

1) In the $Mg_{0.95}Pd_{0.05}$ film the enthalpy change or the binding energy of hydride formation is found to be –0.65 eV/H2 in the low concentration regime, which is lower than the values for bulk MgH_2. In the high pressure regime it was determined to be $–0.40$ eV/H_2, which is due to the clamping stress induced by the substrate and lattice expansion of MgH_2 phase already formed in the film [10].

2) The $Mg_{0.5}Pd_{0.5}$ film was affected by hydrogen induced Mg–Pd phase segregation. The enthalpy changes were deduced for both pressure ranges. In the unsegregated sample at low concentration the enthalpy change equals to

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-0.20 eV/H_2, which is lower than the values for bulk $PdH_{0.6}$ but closer to the PdH_x α-phase value and indicates the presence of those phases in the given pressure range. The Pd alloying hinders the formation of the MgH_2 phases in the low-gas pressure range. In the high-pressure range or in the highly phase segregated sample the enthalphy value is -0.5 eV/H_2 that indicates hydrogen induced segregation and formation of clamped MgH_2 phase in the film.

This is the first attempt of performing hydrogen uptake measurements in Mg–Pd thin films using resistance as a H-concentration probe. 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. Hydrogenography [10] of this alloy system is expected to give improved informtion on the the hydrogen uptake and segregation mechanism.

REFERENCES

1. *Zuttel A., Schlapbach L.* Hydrogen-Storage Materials for Mobile Applications // Nature (London). 2001. V. 414, No. 6861. P. 353–358.
2. *Bogdanovic B., Ritter A.* Active MgH_2–Mg Systems for Reversible Chemical Energy Storage // Angewandte Chemie Int. (Germany). March 1990. V. 29, Issue 3. P. 223–234.
3. *Oskarsson F.* Master's Thesis: Theoretical Calculations of Hydrogen in Magnesium and Magnesium Hydride with and without Impurities. Reykjavík: University of Iceland, Department of Chemistry, 2003. P. 13
4. *Stillesjo F., Olaffson. S.* Hydride Formation in Mg/Ni Multilayers, Studied by Hydrogen Profiling and Volumetric Measurements // Zeitung der Physikalische Chemie. 1993. V. 181. P. 87.
5. *Gislasson H. P. et al.* Hydrogen Interactions in Ultrathin Two-Dimensional Vanadium Layers // Journal of Magnetism and Magnetic Materials. North-Holland, 2001. P. 478–480.
6. *Fukai Y.* The Metal-Hydrogen System: Basic Bulk Properties. New York, 1993. P. 123.
7. *Zaluska A. et al.* Nanocrystalline Magnesium for Hydrogen Storage // Journal of Alloys and Compunds. 1999. V. 288. P. 217–225.
8. *Bogdanovic B.* Thermodynamic Investigation of the Magnesium–Hydrogen System // Journal of Alloys and Compounds. 1999. V. 282. P. 84–92.
9. *Griessen R.* The Physics of Hydrogen in Metals. Amsterdam: Vrije Universiteit, Faculty of Sciences, 1999.
10. *Silveira M. G. et al.* Effect of H-Induced Microstructural Changes on Pressure-Optical Transmission Isotherms for Mg–V Thin Films // International Journal of Hydrogen Energy. 2010. V. 35, Issue 13. P. 6959–6970.

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