Research of hydrogen saturation of magnesium and magnesium-aluminum films and the influence of a protective nickel coating on it

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Abstract. Experiments on the hydrogenation of Mg-Al films during their deposition by magnetron sputtering in a hydrogen atmosphere and subsequent gas-phase hydrogenation have been carried out. The hydrogen mass content and the rate of hydrogen desorption from the obtained metal hydride films have been determined. The key effect of the nickel protective coating on Mg-Al films for their use in hydrogen film accumulators is shown.

1. Introduction
The main disadvantages of powder metal hydride hydrogen storage systems are low thermal conductivity of the powder material, which leads to slow kinetics of hydrogen sorption / desorption, and uneven heating of the powder. These problems can be solved by using hydrogen storage systems based on metal hydride films deposited on resistive heated foil or a resistive layer deposited on a thin polymer film [1]. In addition to solving these problems, the proposed approach ensures greater operational safety (absence of fine powders) and the possibility of reducing both operating temperatures and the enthalpy of phase formation, which affect the energy efficiency of metal hydride systems [2].

The use of a compound of magnesium with aluminum as a hydride-forming material is promising and can significantly increase the operational characteristics of metal hydride storage systems [3]. In this work, a study of the hydrogen content and the kinetics of hydrogen desorption from "magnesium - aluminum" films with different percentages of these elements is carried out. It is shown that the nickel coating, which is also a catalyst for the adsorption process, has a significant effect on the characteristics of a "magnesium - aluminum" film hydrogen storage system.

2. Experiment details
The films are deposited using magnetron sputtering system on the PLAZMATEKH-M facility. Composite cathodes consisted of magnesium (99.5%) and aluminum (99.5%) plates with the required area ratio. Two methods of hydrogenation are used. First method is hydrogenation during the deposition of Mg-Al films in a hydrogen atmosphere (co-deposition). Second method is gas-phase hydrogenation (Sivert’s metod). Hydrogenated films are formed by co-deposition on resistive foil (X20H80 Nickel 80%, Chromium 20%). Surface area of the substrate is 4 or 8 cm². The Argon pressure is 0.3 Pa. The hydrogen with argon pressure P vary in the range 1 … 1.2 Pa, sputtering power vary in the range 300 … 500 W. The protective nickel (99.9%) coating is deposited over some Mg-Al films by using second magnetron sputtering system.
The volumetric method is used to determine the amount of released hydrogen. After deposition the samples are placed in the Sivert’s type facility. The chamber is pumped to a pressure below 1 \cdot 10^{-4} \text{ Pa}. The desorption of a low-melting and evaporating magnesium-based coating is carried out at a temperature of 300 °C with linear velocity of heating 9.17 °C/min and subsequent exposure during 2 hours. Before saturation the samples are activated with heating while high-vacuum pumping. The gas-phase hydrogenation is carried out at 300 °C for 2 hours. To take into account the gas released from the tooling and from the walls of the vacuum chamber, the pressure signal obtained during the experiment without the sample is subtracted from the obtained pressure signal with the sample. The heating unit with a thermocouple create the possibility of linear heating of the samples in a wide range of rates (5-50 °C / min). The Membrane-capacitive sensor MKS Instruments 628 with an operating pressure range of 0.001 - 10 Torr is used. The maximum hydrogen pressure 5 bar and maximum temperatures 650 °C.

3. Results
Deposited films consist from pure magnesium, magnesium and aluminum with Mg/Al atom ratio 1/1 and 9/1. Films thickness \( h \) and films mass \( m \) are given in the table 1.

| Coatings type | Sample       | \( h \), mkm | \( m \), mg |
|---------------|--------------|--------------|------------|
| Mg            | Mg1          | 4.8          | 5.6        |
| Mg            | Mg2          | 3.2          | 2.4        |
| Mg + Ni       | NiMg3        | 5.0          | 5.4        |
| Mg/Al=1/1     | Mg4          | 2            | 0.8        |
| Mg/Al=1/1 + Ni| NiMg6        | 6            | 9.2        |
| Mg/Al=9/1     | Mg5          | 4            | 3.5        |
| Mg/Al=9/1 + Ni| NiMg7        | 7            | 13.3       |

Hydrogen mass content \( w_{h2} \), maximum desorption rate and corresponding temperature \( V_{h2,max} \) and \( T_{vh2} \) and release time of 90% of the accumulated hydrogen \( t_{90} \) are given in table 2.

| Samples       | \( w_{h2} \), mass. % | \( V_{h2} \), mass. %/sec | \( T_{vh2} \), °C | \( t_{90} \), min | \( w_{h2} \), mass. % | \( V_{h2} \), mass. %/sec | \( T_{vh2} \), °C | \( t_{90} \), min |
|---------------|------------------------|--------------------------|------------------|----------------|------------------------|--------------------------|------------------|----------------|
| Mg1           | 5.37                   | 3.50E-03                 | 290              | 105            | 1.24                   | 7.96E-04                 | 245              | 75             |
| Mg2           | 2.98                   | 1.11E-03                 | 290              | 105            | 0.45                   | 5.20E-04                 | 200              | 105           |
| NiMg3         | 3.80                   | 5.20E-03                 | 153              | 75             | 5.30                   | 1.24E-02                 | 208              | 21             |
| Mg4           | 1.51                   | 1.02E-03                 | 273              | 120            | 0.77                   | 8.09E-04                 | 126              | 120           |
| Mg5           | 2.06                   | 1.24E-03                 | 300              | 75             | 0.28                   | 5.99E-04                 | 273              | 27            |
| NiMg6         | 5.50                   | 8.21E-03                 | 245              | 45             | 3.68                   | 6.69E-03                 | 172              | 23            |
| NiMg7         | 4.12                   | 7.01E-03                 | 181              | 45             | 3.54                   | 6.70E-03                 | 190              | 22            |

The time and temperature dependences of hydrogen desorption from samples without a protective nickel coating are shown in figure 1. The hydrogen content in gas-phase hydrogenated samples is much lower. Sample Mg1 was twice gas-phase hydrogenated and twice desorbed. Hydrogen mass content drop from 5.4% to 1.12% and 0.58%. Perhaps this is due to the oxidation of the films at the sorption / desorption temperatures. Which can lead to degradation of the hydrogen content during hydrogenation. It is important to note that the Mg1 sample was thermally desorbed immediately after deposition. The sample Mg2 was exposed to air for several tens of hours. The negative values of the rate of hydrogen desorption
from the Mg4 and Mg5 samples can be explained by the low mass of the coating at which the influence of the background signal is too great.

![Graph](image.png)

**Figure 1.** Dependence of the hydrogen mass content on the desorption time (a). Dependence of the hydrogen desorption rate on the desorption temperature for samples after co-deposition (Mg1, Mg2, Mg4, Mg5) and after gas-phase hydrogenation (Mg1gp1, Mg1gp2, Mg2gp1, Mg4gp1, Mg5gp1) (b).

The results of experiments with films with a protective Ni coating are shown in figure 2. The thickness of the nickel coating was in the range of 200-400 nm.

![Graph](image.png)

**Figure 2.** Dependence of the hydrogen mass content on the desorption time (a). Dependence of the hydrogen desorption rate on the desorption temperature for nickel coated samples after co-deposition (NiMg3, NiMg6, NiMg7) and after gas-phase hydrogenation (NiMg3gp1, NiMg6gp1, NiMg7gp1) (b).
The hydrogen content in the gas-phase hydrogenated samples is comparable to that in the samples with co-deposition. Which means the possibility of multiple recharging of these samples. It is also important to note that the presence of a Ni protective coating halved the time for leaving the hydrogen samples and reduced the position of the desorption peaks to temperatures of 150-200 °C.

Films containing aluminum show drop in hydrogen mass content after gas-phase hydrogenation. It can be explained by formation Al$_{12}$Mg$_{17}$ phase. This is confirmed by the fact that for sample with Mg/Al atom ratio 1/1 the $w_{h2}$ percentage drop is 33% that is greater than for sample with Mg/Al atom ratio 9/1 - 14%. The pure magnesium film tend to improve hydrogen mass content after gas-phase hydrogenation.

4. Conclusions
Fundamental changes in the saturation with hydrogen and the kinetics of desorption processes in Mg-Al films are associated with the deposition of a protective Ni coating on them which simultaneously acts as a catalyst. The mass content of hydrogen in such films can reach 5.4% without significant changes during desorption and subsequent gas-phase hydrogenation. The hydrogen release time decreases by 1.4 ... 5 times with a decrease in the temperature peak of desorption to 150-200 °C.

References
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