Experimental research of film hydrogen accumulator model

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Abstract. For the experimental research of hydrogen sorption / desorption processes, a model of a film hydrogen accumulator with a tape foil carrier has been developed and manufactured. Experiments were carried out to study the sorption / desorption (S / D) of hydrogen on a model of a film battery with a tape carrier (NiCr foil 20-50 microns with a titanium coating of 10-15 microns and a magnesium coating of 2-5 microns).

The high energy intensity of hydrogen (heat of combustion 141.9 MJ / kg) and its environmental friendliness make this type of energy carrier the most preferable when creating energy systems of the future. The method of storing hydrogen in the form of metal-hydrides is promising and actively developing. There are metal-hydride hydrogen storage systems on the market based on fine powders. The disadvantages of powder hydrogen storage systems are the high inertia of the process of its release and the uneven heating of the powder. The use of film metal hydride hydrogen accumulators as an energy carrier solves all of the above problems. For the experimental research of hydrogen S / D processes, models of a film hydrogen accumulator with a tape foil carrier with coatings of titanium hydride and magnesium hydride have been developed and manufactured. The research of the model can be divided into several stages:

- Preparation of the energy carrier for the coating deposition process. Nichrome foil wrapped on a cylindrical shell. Then the surface is treated to give a relief that serves as gas supply/discharge channels. After that, the foil was weighed, and then placed in the working chamber of the «PLASMATECH-M» facility.

- Deposition of a hydride-forming coating. For preliminary cleaning of the surface, a glow discharge in an argon atmosphere is used. Further, the technological process of coating deposition takes place using a magnetron sputtering system or an electric arc source in a hydrogen atmosphere.

- Determination of the mass and thickness of the hydride applied to the foil, as well as verification of the adhesive properties of the resulting coating by the method of lattice notches.

- Assembly of battery components. The coated foil is tightly wrapped on a hollow cylinder attached to the bracket of the flange with vacuum electric leads. Then the flange is attached to the working chamber of the thermal vacuum facility, where the heating and saturation operations of the model are performed. In figure 1 and 2 represents models of a hydrogen film accumulator with various energy carrier heating systems.

- Testing of the sorption and desorption parameters of the film battery on the test stand. Four carriers were tested: MAK1, MAK2 with a titanium coating applied from an electric arc source plasma (EAS) and MAK5, MAK6 based on a magnesium coating with a protective nickel layer (table 1). To determine the possibility of cycling, after desorption, the models were saturated by the gas diffusion method at a hydrogen pressure of up to 5 atm. abs. and then re-thermodesorbed.
Figure 1. Model diagram of a hydrogen film battery heated by a halogen lamp: 1 – thermocouple, K-type; 2 – power supply electrodes of the KGT lamp; 3 – halogen lamp; 4 – carrier mounting bracket; 5 – body; 6 – carrier with metal-hydride coating; 7 – vacuum valve; 8 – connecting flanges.

Figure 2. Model diagram of the film battery with resistive heating (without inter-turn insulation): 1-thermocouple, K-type; 2 – power electrodes of resistive heating; 3 – central stud; 4 – body; 5 – carrier with metal hydride coating; 6 – vacuum valve; 7 – connecting flanges.

Table 1. Characteristics of MAK 1, MAK 2, MAK 5, MAK 6.

| Carrier | Foil thickness, microns | Foil width, mm | Foil length, mm | Coating weight, gr. | Coating thickness, microns | Mechanical processing |
|---------|------------------------|----------------|----------------|---------------------|---------------------------|-----------------------|
| MAK1    | 50                     | 20             | 3029           | 2,6626              | 9.6                       | no                    |
| MAK2    | 20                     | 20             | 3013           | 3,1407              | 11.5                      | yes                   |
| MAK5    | 50                     | 20             | 3000           | 0.263               | 1.8                       | no                    |
| MAK6    | 50                     | 20             | 3005           | 0.6281              | 4.3                       | no                    |

Determination of the mass fraction of desorbed hydrogen $w_{H_2}$ in models with a titanium coating was carried out using the volumetric method. The pressure was determined by the MKS Instruments membrane-capacitive sensor. To account for the released gas from the chamber equipment, the background signal was subtracted from the received signal (taken when the model was warmed up without the applied coating). Initially, the heating was carried out by a halogen lamp up to 500 degrees Celsius and then kept at this temperature, figure 3 and figure 4. Then a circuit with resistive heating of a titanium-coated foil was assembled, figure 5, 6. The heating of the MAK1tv1-res and MAK2tv2-res models took place in several stages, without intermediate saturation. The total mass fraction of the released hydrogen is shown in table 2

Figure 3. The dependence of the mass fraction of desorbed hydrogen on the temperature for MAK1tv1, MAK1tv2.

Figure 4. The dependence of the mass fraction of desorbed hydrogen on the temperature for MAK2tv2.
Figure 5. The dependence of the mass fraction of desorbed hydrogen on the temperature for MAK1tv₁res.

Figure 6. The dependence of the mass fraction of desorbed hydrogen on the temperature for MAK2tv₂res.

When testing models with a magnesium coating, a scheme for determining the thermal desorption spectrum (TDS) [2] was implemented with an Extorr XT-100 residual gas analyzer calibrated according to a known flow. These models were heated with a halogen lamp to 350 °C and then kept at this temperature, figure 7 and figure 8.

Figure 7. Thermal desorption spectra for MAK5tv₁, MAK5tv₂ and MAK5tv₃.

Figure 8. Thermal desorption spectra for MAK6tv₁, MAK6tv₂.

As a result of the conducted studies of several film models of hydrogen accumulators, the following conclusion can be made:

The titanium-based coating has a high adhesion to the substrate. In the process of S/D of hydrogen using indirect heating, in which there were periodically problems with accidents due to the shunt metal
coating on the insulators that occurs during the heating of the chamber, the mass content of hydrogen after re-saturation is minimal. In the case of resistive heating of the titanium coating, it was possible to re-saturate it to 2% (a series of successive heats without intermediate saturation), with a theoretical maximum of 4%.

Table 2. Model research results.

| Carrier   | t, min | T, °C | \( w_{I2}, \% \) | heating   | Processes in working chamber                      |
|-----------|--------|-------|-----------------|-----------|--------------------------------------------------|
| MAK1tv1   | 30     | 500   | 0,14            | indirect  | Activation(1h) + saturation(90min) - heating up  |
| MAK1tv2   | 70     | 500   | 0,12            | indirect  | Activation(1h) + saturation(90min) - heating up  |
| MAK1tv1 res | 150   | 500   | 1,31            | direct    | Activation(1h) + saturation(90min) - heating up  |
| MAK2tv2   | 45     | 500   | 0,36            | indirect  | Activation(1h) + saturation(90min) - heating up  |
| MAK2tv2 res | 90    | 300   | 2               | direct    | Activation(1h) + saturation(90min) - heating up  |
| MAK5tv1   | 50     | 350   | 1,52            | indirect  | TDS                                              |
| MAK5tv2   | 50     | 350   | 1,61            | indirect  | saturation(15h) - TDS                            |
| MAK5tv3   | 50     | 350   | 1,06            | indirect  | Activation(1h) + saturation(120min) - TDS        |
| MAK6tv1   | 50     | 350   | 1,05            | indirect  | TDS                                              |
| MAK6tv2   | 45     | 300   | 0,72            | indirect  | Activation(1h) + saturation(90min) - TDS         |

The magnesium-based coating has slightly worse adhesion. Thanks to the protective nickel layer, it became possible to repeatedly re-saturate the coating on a long-length tape carrier with a mass content of hydrogen equal to ~ 70% of the mass content of hydrogen in the coating deposited in the hydrogen atmosphere. In the case of indirect heating of the magnesium coating, it was possible to re-saturate it to 1.6% with a theoretical maximum of 7.6%. To increase the hydrogen content, magnesium coatings must be saturated at higher hydrogen pressures.

References
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