Using the copper-foam for thermal conductivity improvement of La0.9Ce0.1Ni5-alloy bed during interaction with hydrogen

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Abstract. One of the main obstacles to the development of hydrogen energy is the problem of heat transfer inside metal hydride beds. Thus, the problem of increasing the metal hydride beds thermal conductivity is of great interest. This study is devoted to the investigation of the hydrogen sorption properties of an intermetallic compound placed in a matrix of foam material. Copper-foam with mass of 8 g was chosen as a matrix for 50 g of powder of activated AB5-type alloy with composition of La0.9Ce0.1Ni5. PCT-isotherms of hydrogen absorption and desorption were measured at temperatures 313, 333 and 353 K. Also, the dynamics of temperature change in the sample was studied when it was heated under vacuum conditions. The obtained data were compared with the results of previous studies conducted under the same conditions for samples of pure alloy and a mixture of alloy with copper powder. It has been concluded that the use of copper-foam to improve the thermal conductivity is promising, but it is necessary to take into account its influence on the hydrogen sorption properties of metal hydrides.

1. Introduction
Improvement of heat transfer inside the hydrogen storage systems based on metal hydride is one of the important tasks today. For this purpose, a number of different techniques can be used: improving the thermal conductivity of metal hydride beds, reducing the bed radius, increasing the surface area of heat exchange, optimizing the operating parameters of reactors, etc. [1]. The increase in thermal conductivity due to the use of foam materials from various metals as a matrix has been actively studied in recent years both experimentally and using various methods of mathematical modeling [2,3].

One of the disadvantages of such studies is that the thermal conductivity of the metal hydride beds and its hydrogen sorption properties are studied separately. In the simulation or experimental study of heat distribution in hydrogen storage reactors, data on PCT-isotherms, equilibrium pressure, enthalpy and entropy of hydrogen absorption and desorption are either taken from the literature or measured on small control samples. However, our previous studies have shown that the hydrogen sorption properties of metal hydride bed can be markedly different depending on its scale and geometry [4]. Therefore, the experimental measurement of PCT-isotherms and the study of heat distribution in conditions maximally close to the existing hydrogen storage reactors are important both in themselves and as a basis for subsequent mathematical modeling.

In this paper the measurements of PCT-isotherms of hydrogen absorption and desorption by a sample of activated powder of intermetallic compound (IMC) with composition of La0.9Ce0.1Ni5 weighing 50 g, placed in a matrix of copper-foam, were carried out. The mass content of hydrogen in the sample, the
enthalpy and entropy of hydrogen adsorption and desorption were calculated. In addition, the warm-up
time of the sample under vacuum conditions was studied. The obtained data were compared with the
results of similar experiments, which were carried out earlier, for two samples containing 50 g of the
same alloy: the first sample was pure IMC without additives and the second one was a mixture of the
alloy and copper powder [5].

2. Experimental details
Activation of the alloy, as well as all measurements in this work was made using the setup for measuring
PCT-isotherms US-150. This setup allows high accuracy measurements of hydrogen absorption and
desorption isotherms at a temperature of 243 to 673 K and a hydrogen pressure of up to 150 bars by the
Sievert’s method.

One of the sources of errors that can affect the accuracy of measurements is the history of the
samples. The time and surface area that comes into contact with the air, the disproportion and
decomposition during cycling with hydrogen, the inhomogeneity of the composition in large samples,
can affect the results of the PCT-isotherm measurements. Therefore, in order to obtain the most accurate
and reproducible data, all samples compared in this work were prepared from one batch of pre-activated
IMC. And the number of hydrogen absorption-desorption cycles for all samples was the same - 15.

The scheme of the working vessel in which the measurements were carried out is shown in figure 1. It is a steel cylinder with a height of 180 mm and a diameter of 45 mm, along the axis of which is a tube
with a diameter of 6 mm, into which the thermocouple is placed. The volume of the cylindrical part of
the working vessel is 280 cubic centimeters.

![Figure 1. Work vessel of the experimental setup: 1 – hydrogen inlet, 2 – top of the work vessel, 3 – tube for thermocouple, 4 – free volume for the sample.](image)

To prepare the sample, a porous matrix, made of copper-foam plates, was used. It was filled with
powder of activated IMC La0.9Ce0.1Ni5. The pore size of the foamed copper is larger than the particle
size of the activated alloy powder, that is, the powder is completely sieved through a layer of foam
material with prolonged vibration. For the manufacture of the matrix from a sheet of copper-foam with a thickness of 2.3 mm were cut out discs whose diameter coincides with the inner diameter of the working vessel and made up 45 mm. Because the axis of the vessel is a tube for thermocouple, which does not reach the bottom of the working vessel, all disks, except the lowest one, were to make a hole with a diameter of 6 mm. In result, the matrix consisted of 4 layers of copper-foam. The number of the layers was selected in such a way that the pore volume was sufficient to be filled with a powder of IMC with a mass of about 50 g. To ensure that during the filling of the matrix and further experiments, the layers of foamed copper did not diverge, and between them there was no continuous filling of IMC. The layers of foam copper were joined together by a thin copper wire, as shown in figure 2. The exact masses of the components were: m(Cu)= 8.061 g, m (La0.9Ce0.1Ni5) =50.743 g, sample weight: m = 58.804 g.

Figure 2. The copper-foam matrix.

3. Results and discussion
Hydrogen absorption and desorption isotherms obtained as a result of the experiment are shown in figure 3. The results of the calculation of the mass content of water, as well as enthalpy and entropy are presented in table 1.

Figure 3. Isotherms of hydrogen absorption and desorption at 313(--), 333(--(-)) and 353(--) K.
Table 1. Hydrogen sorption properties of the La0.9Ce0.1Ni5-alloy with the copper-foam matrix.

| Reaction | Temperature K | C(H2)max wt. % per IMC/per sample | Peq MPa | ΔHo kJ/mole | ΔSo J/mole K |
|----------|---------------|-----------------------------------|---------|-------------|--------------|
| Absorption | 313          | 1.3/1.1                           | 0.74    |             |              |
|           | 333          | 1.3/1.1                           | 1.32    | 26.3        | 100          |
|           | 353          | 1.3/1.1                           | 2.33    |             |              |
| Desorption | 313          | 1.3/1.1                           | 0.43    |             |              |
|           | 333          | 1.3/1.1                           | 0.89    | 31.5        | 113          |
|           | 353          | 1.3/1.1                           | 1.68    |             |              |

In the previous study [5], two samples containing 50 g of activated powder of the same alloy were studied, one of which was a control sample without any additives, and the second was added 450 g of copper powder. If we compare the obtained data with the results of previous ones (figure 4), we can find that at a temperature of 313 K the PCT-isotherms of all three samples are close. In this case, the sample with copper powder has a significantly lower relative capacity compared to others, and the angle of inclination of its hydrogen absorption plateau is the highest. At a temperature of 333 K the behavior of all three samples is different: the hydrogen absorption equilibrium pressure of the sample with copper powder addition is lower than that of the original IMC, but higher than that of the sample with copper-foam, and the slope of the plateau is the maximum among all samples. The equilibrium pressure of hydrogen desorption of the sample with copper powder is the lowest, and the plateau slope is the highest. The samples behave in a similar way at a temperature of 353 K, but the difference between the behavior of samples with copper powder and copper-foam is quite small.

![Figure 4. Comparison of the PCT-isotherms of three samples:](image)

The study of the heat distribution inside the sample with the copper-foam matrix was carried out by measuring the temperature change inside the sample when it was heated from room temperature to 333 K under vacuum. Further, the obtained data were compared with the experimental results under identical conditions for the pure IMC sample and the sample with the addition of copper powder (fig. 5).
Figure 5. Comparison of temperature inside the samples during heating from room temperature to 333 K.

As can be seen from the figure, the composite with copper powder has a minimum heating time compared to the composite with foam copper and pure alloy: 30, 60 and 90 minutes, respectively. The reason for this is that this sample was 90% copper powder, and it was self-compacted during cycling, which also increased its thermal conductivity.

Conclusions

In this paper we studied the behavior of samples prepared from 50 g of IMC with composition of La0.9Ce0.1Ni5 and copper in the form of foam (mass of copper 8 g) in interaction with hydrogen. The results were compared with the results of previous studies, which were carried out under similar conditions for a sample of 50 g of pure IMC and a mixture of 50 g of IMC with 450 g of copper powder. All three samples were prepared in a dry box of 200 g of pre-activated alloy in an inert atmosphere. The number of cycles of absorption-desorption of hydrogen for all samples was the same – 15. Thus, all factors affecting the hydrogen sorption properties of the samples, except for the amount and shape of the added copper, were excluded.

As a result, it has been found that the hydrogen sorption properties of samples with copper additives in the form of powder and foam differ markedly from the properties of the original IMC. The sample in which the powder of activated IMC was poured into a matrix of copper-foam has shown an improvement in thermal conductivity compared to the pure alloy, but to a lesser extent than the sample with copper powder. As with the addition of powder, the slope of the plateau on the PCT-isotherms increased and the equilibrium pressure decreased similar to the calculated values of enthalpy and entropy of hydrogen absorption. The maximum hydrogen content in the metal hydride was the same as in pure IMC. No agglomerations of particles in the sample with copper-foam after 10 cycles of absorption-desorption of hydrogen have been found. The matrix of copper-foam improves the heat distribution in metal hydride beds, while its mass is only about 15% of the sample mass. Thus, the use of foam materials in metal hydride systems is promising.

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