Enhancing metal hydride thermal conductivity by forming compacts

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Abstract. The development and implementation of metal hydride technologies face a number of challenges. One of the main problems is the low thermal conductivity of fine powders of hydride-forming materials. This feature, giving the relatively high values of the reaction heat of intermetallic compounds with hydrogen, leads to an increase in the cost of construction of vessels with metal hydrides and heat exchangers, which reduces the competitiveness of hydrogen-based technologies. One of the most promising ways to solve this problem today is the formation of compacts from metal hydride powders by pressing with additives that increase thermal conductivity. In this work, compacts based on AB5-type alloy with composition LaNi4.4Al0.3Fe0.3 prepared using various methods were studied and their properties were compared with the free bed of this alloy. Carbon nanofibers and nickel-foam were used as additives that improve the thermal conductivity of the compacts. The main methods of studying the properties of samples were measuring of hydrogen absorption and desorption PCT-isotherms and investigation of the temperature inside the samples during their heating and interaction with hydrogen. The compacts showed a noticeable improvement in thermal conductivity with a slight deterioration in hydrogen-adsorption properties, which is a promising result.

1. Introduction

Nowadays, hydrogen technologies using metal hydrides continue to develop actively and are used in various fields: energy storage [1], thermal energy storage [2], storage, purification and compression of hydrogen and others [3]. One of the main obstacles to the active introduction and market entry of devices based on metal hydrides is the low thermal conductivity of hydrogen-absorbing materials. The main reason for this is the dispersion of intermetallic compounds when interacting with hydrogen. The fact is that when hydrogen atoms are embedded in the internodes of the crystal lattice, its volume can increase by up to 25 %, and when hydrogen is released, it shrinks back. Due to the resulting stresses, the array of hydrogen-absorbing material is scattered into particles of the order of 10 microns, the sample density is reduced by half, and a fine dispersed powder bed with a porosity of about 50% is formed. The thermal conductivity of this bed is 0.1-0.5 W/m·K, and the enthalpy of the reaction with hydrogen can range from 20 to 70 and even higher kJ/mol, depending on the type of metal hydride. Since the absorption of hydrogen by metal hydrides is characterized by rapid kinetics, it is extremely difficult to remove the released heat. The bed overheats, which leads to an increase in the equilibrium pressure required for hydrogen absorption, and the reaction stops. When hydrogen is released, the reverse process occurs. Part of the hydride bed, which is located in the depth of the reactor far from the heated wall, is overcooled, which on the one hand slows the desorption kinetics, and on the other
hand reduces the equilibrium pressure below the minimum required for the consumer. Mathematical modeling methods are actively used to optimize geometry and heat transfer in metal hydride systems [4,5]. During long-term operation of hydride devices, redistribution of particles under the influence of gravity, the appearance of local seals, the accumulation of internal stresses, and agglomeration of particles can occur in such beds. All of the above impairs hydrogen absorption characteristics, reduces cyclic stability, and prevents devices from scaling from small laboratory samples to commercial ones. Thus, the problem of increasing the thermal conductivity of metal hydride backfills, as well as their mechanical stability, is of great interest.

In this work an AB5-type intermetallic compound (IMC) based on LaNi5 with the composition LaNi4.4Al0.3Fe0.3 was selected as the object of research. Alloys of this type have long been known and well-studied. They have a number of disadvantages, such as a relatively low gravimetric capacity (less than 1.5 %) and a high cost of raw materials. However, they have a number of key advantages that make their use in hydrogen storage systems relevant today [6]. These include a high volumetric storage capacity; conditions of interaction with hydrogen that are close to environmental conditions; the ability to vary the properties of the material in a wide range by changing the composition for each specific application; resistance to a number of impurities that may be present in hydrogen; relatively low values of the enthalpy of interaction with hydrogen; the ability to absorb hydrogen from mixtures selectively even at low partial pressure; safety. This intermetallic compound is a promising candidate for the development of hydrogen storage obtained by the biological way. The fact is that during dark fermentation, hydrogen is released in a mixture with CO2 and H2O at a partial pressure of less than 0.05 MPa. The LaNi4.4Al0.3Fe0.3 alloy is able to absorb hydrogen selectively at this pressure at room temperature with good kinetics, and the presence of aluminum in its composition increases its resistance to impurities. The dependence of the equilibrium pressure on the temperature allows compressing hydrogen using low potential heat. This makes possible to combine the functions of cleaning, storing and compressing hydrogen in one device without mechanical moving parts and with using of waste heat.

Materials suitable for solid-state hydrogen storage must meet specific requirements in order to be used in the development of hydrogen-based energy storage technologies. These materials should retain their properties in the field of interaction kinetics and capacity even after long cycling, however, in practice, powders tend to agglomerate, which reduces the efficiency of the system. One possible solution to this problem, which has been successfully tested for Mg-based systems [7,8], is the compaction of hydride powders into high-density pellets. Compacts made from hydride powders are usually made in cylindrical form after mixing with special additives to improve thermal conductivity and mechanical stability (for example, Al, Cu or carbon materials). The advantages of forming compacts include the fact that such materials can be handled more safely and are less prone to degradation due to air moisture and oxygen contamination. On the other hand, the high density of the compact can slow down the diffusion of hydrogen through the sample, worsen the reaction kinetics, and change the PCT-isotherms of hydrogen absorption/desorption. There is evidence in the literature that compacted systems tend to disaggregate as they cycle, returning to the initial state of free powder [9]. Therefore, the problem of mechanical stability of metal hydride compacts is also relevant.

2. Sample preparation
The raw material used was a 160 g IMC LaNi4.4Al0.3Fe0.3 ingot made by fusing pure metals (purity not less than 99.99 %) in an electric arc furnace in an argon atmosphere with a non-consumable tungsten electrode. Next, the ingot was placed in a working vessel of the US-150 setup and activated by successive cycles of absorption-desorption of hydrogen at a temperature of 373 K and a pressure of 3 MPa. A total of 10 cycles were performed, after which the PCT-isotherms of hydrogen absorption and desorption were measured at a temperature of 333 K. The coincidence of these isotherms with the results of previous studies of this IMC proved the completeness of activation and the quality of manufacture of the initial alloy.
Interaction with hydrogen results in dispersion of the alloy into a fine powder, as mentioned above. This powder is convenient for making samples and does not require additional mechanical processing. However, metal hydrides in this form are extremely pyrophoric even after prolonged vacuuming for 3 hours at a temperature of 353 K due to the residual hydrogen and the active metal surface, so it is not possible to work with them in the air immediately. The closed working vessel with the activated alloy powder was disconnected from the setup and placed in a dry box with an inert atmosphere. In the box, the powder was extracted and divided into three parts weighing about 50 g to prepare samples. Two parts were used for making compacts number 1 and 2, and the third was used for a control sample of free powder bed.

The compact number 1 was made in a dry box in an inert atmosphere. A heat-conducting matrix was made from a strip of 10 mm wide and 1.6 mm thick nickel foam, which was folded into a spiral, the diameter of which equaled the diameter of the working vessel and was 45 mm. The mass of the nickel foam was 3.174 g. Folding the sheet of nickel foam into a spiral is designed to provide a continuous metal matrix throughout the entire volume of the compact. At the next stage, the matrix was filled with activated LaNi4.4Al0.3Fe0.3 alloy powder weighing 49.752 g. The powder was carefully distributed through the matrix using vibration. Pressing was carried out directly in the working vessel in a dry box using a steel rod. The degree of compression was controlled by measuring the stroke of the rod, which was 5 mm, which corresponded to the degree of compression of 0.5 (i.e., the volume of the pore space was reduced by half, if we considered the alloy particles incompressible). The working vessel with the sample was closed in a dry box and connected to the control and measurement system of the US-150 setup to study its properties.

The sample of the compact number 2 could not be prepared in a dry box, since the method involved the use of a hydraulic press. To prevent the alloy powder from catching fire in the air, its surface was passivated. To do this, the powder was placed in a working vessel, into which a portion of air was released at a pressure of 0.05 MPa and kept for 12 hours at room temperature. After that, the pressure was brought to atmospheric pressure and the powder was kept for another 12 hours in a closed vessel at room temperature. Further operations were carried out in the air. The weight of the passivated alloy for the production of the compact 2 was 50.207 g. 10% carbon nanofibers (exact weight 5.086 g) were added to it and thoroughly mixed. The nickel foam matrix was made similarly to the compact 1 matrix, but, since the volume of sample 2 due to the addition of nanofibers was larger, the matrix was also increased (the weight of Nickel is 3.914 g). The matrix was placed in a mold whose diameter corresponded to the diameter of the working vessel of the US-150 installation. Then the nanofiber alloy powder was added to it in small portions and carefully distributed by vibration. The compact was pressed using a hydraulic press at a pressure of 30 MPa for 3 minutes. The resulting tablet was placed in a working vessel and reactivated. Since the surface of the IC particles interacted with air oxygen, an oxide film could appear on it, which inhibits the absorption of hydrogen. This is especially true for alloys containing aluminum. Re-activation consisted of two cycles of absorption-desorption of hydrogen at a temperature of 373 K and a pressure of hydrogen of up to 3 MPa.

3. Experimental details
For all three samples (control sample, compact 1, compact 2), PCT-isotherms of hydrogen absorption and desorption were measured at temperatures of 333 and 353 K. The measurements were made using the Sivert method on the US-150 installation, which allowed the study of samples weighing from 10 to 800 g at temperatures from 243 to 573 K and a pressure of up to 15 MPa.

The influence of the compact formation technique on the thermal conductivity of the metal hydride was studied in two ways: (i) comparison of the dynamics of heating samples from room temperature to 333 and 353 K in vacuum (pressure less than 100 PA); (ii) comparison of the dynamics of relaxation of the temperature of samples during desorption of a calibrated portion of hydrogen at a temperature of 353 K. The temperature inside the samples was measured using a thermocouple located in a steel case at 3 mm from the bottom along the axis of the working vessel.
For the first series of experiments, a working vessel with a sample was placed in a bath of a thermostat with liquid coolant at room temperature after prolonged vacuuming (at least 3 hours). After that, the thermostat was set to maintain a constant temperature of 333 or 353 K and the readings of the above-mentioned thermocouple were recorded in real time. The second series of experiments was conducted in several stages. First, hydrogen was gradually fed from the buffer vessel to the working vessel with the sample placed in the thermostat bath and heated to 353 K. The feeding was carried out until after the completion of hydrogen absorption (the pressure over the sample remained constant for 30 minutes), the equilibrium pressure in the system was 0.6 MPa. This pressure value corresponds to the inflection point on the PCT-isotherm at 353 K, at which the phase transition from the IMC to its hydride ends (the plateau region on the PCT-isotherm). Further absorption of hydrogen is possible due to physical sorption and requires a significant increase in the hydrogen pressure. Then the working vessel was closed, and all hydrogen was pumped out of the buffer vessel to a state of high vacuum. At the last stage, the working vessel with the sample was connected to an empty buffer and the temperature evolution was recorded as the hydrogen was desorbed.

Strictly speaking, the comparison of such temperature profiles is not completely correct, since the samples have different volumes, and, consequently, different contact area with the walls of the working vessel and the cover of the thermocouple. In addition, the hydrogen adsorption properties of the samples also differ. Nevertheless, these experiments provide valuable information about the prospects of various methods for forming metal hydride compacts in terms of improving their thermal conductivity.

4. Results and discussion
The hydrogen sorption properties of the samples are shown in Table 1. For ease of comparison, the capacity of the samples represented as calculated per pure metal hydride and per overall sample. For the compared sample, these values are the same, and for compacts 1 and 2, the capacity per sample is lower, since the mass of the matrices made of nickel-foam and carbon nanofibers, respectively, is taken into account. It is worth noting that the capacity of the compact 2 per pure metal hydride is noticeably lower in all cases. This was most likely caused by incomplete reactivation of the sample after its manufacture. In addition, too high compact forming pressure could lead to a loss of capacity, which led to an excessive decrease in porosity and hindered the diffusion of hydrogen into the compact.

| Sample          | T, K   | Peq abs, MPa | Peq des, MPa | C H₂, wt% per alloy | C H₂, wt% per sample |
|-----------------|--------|--------------|--------------|---------------------|---------------------|
| Compare         | 333    | 0.149        | 0.122        | 1.2                 | 1.2                 |
| Compact 1       |        | 0.157        | 0.116        | 1.1                 | 1.1                 |
| Compact 2       |        | 0.175        | 0.105        | 0.9                 | 0.8                 |
| Compare         | 353    | 0.228        | 0.269        | 1.2                 | 1.2                 |
| Compact 1       |        | 0.301        | 0.237        | 1.1                 | 1.0                 |
| Compact 2       |        | 0.314        | 0.225        | 0.9                 | 0.8                 |

The method of forming a compact also affects the equilibrium pressure of hydrogen absorption and desorption. As it can be seen from Table 1, the higher the pressure and the degree of compression in the manufacture of the sample, the higher the equilibrium pressure of hydrogen absorption and the lower the equilibrium pressure of hydrogen desorption. This leads to an increase in the pressure hysteresis (the difference between the pressure of absorption and desorption of hydrogen). In addition, the slope of the plateau on PCT-isotherms in the row "control sample" - "compact 1" - "compact 2" also increases. All of the above leads to deterioration of the hydrogen-adsorption properties of compacts and will negatively affect their use for various applications. Therefore, further research on
improving the methods of manufacturing compacts, as well as optimizing the ratio of IMC and various additives is very relevant.

The results of studying the thermal conductivity of samples are shown in Figures 1 and 2. Figure 1 shows two series of curves that represent the dependence of the temperature inside the sample on its heating time on the room temperature to 333 and 353 K, respectively. Curves with index 1 correspond to the control sample of free metal hydride bed, curves with indices 2 and 3 refer to samples of compact 1 and compact 2, respectively. It is clearly seen that the formation of compacts leads to a significant improvement in the thermal conductivity of the metal hydride backfill. The heating times of the compact 1 sample are approximately 30 % less than that of the control sample. The denser compact 2 with nanofibers has a heating time of almost 50% less than the control sample. The experimental data obtained indicate a significant increase in the thermal conductivity of compact samples, which has a positive effect on heat transfer.

Figure 1. Heating of the samples under vacuum.

Figure 2 shows the temperature profiles inside the samples during hydrogen desorption. Curve 1 corresponds to the control sample, curves 2 and 3 correspond to compacts 1 and 2, respectively. For ease of perception, the curves are slightly offset relative to each other. As it can be seen from the figure, a sharp drop in pressure in the working vessel when connected to an empty buffer leads to rapid cooling of samples by a value of about 10 K within a few seconds. Then the temperature relaxes as equilibrium is established in the system. In denser compacts, the temperature drops by a large amount, but its relaxation is noticeably faster as compared to the control sample. As in the case of heating samples under vacuum, compact 2 demonstrates the best thermal conductivity, and the rate of temperature relaxation is almost 50% higher than that of the control sample. The results of the experiments show that the formation of compacts for improving heat transfer in systems based on metal hydrides is promising.

Figure 2. Temperature evolution during hydrogen desorption.
Conclusions
In the course of this work, samples of two metal hydride compacts based on IMC with composition LaNi4.4Al0.3Fe0.3 were made using various methods and their hydrogen sorption properties and thermal conductivity were compared with a control sample of free powder bed of the same alloy. Compact 1 was manufactured by pressing activated alloy powder into a matrix of nickel foam in a dry box with an inert atmosphere. The degree of compression was about 50 %. Compact 2 was made in air from a mixture of the original alloy with the addition of 10 % carbon nanofibers and pressed into a matrix of nickel foam at a pressure of 30 MPa for 3 minutes. The degree of compression was about 80 %. After manufacturing, the sample was reactivated. The mass of the IMC LaNi4.4Al0.3Fe0.3 in all three samples was 50 g.

Measurement of PCT-isotherms of hydrogen absorption and desorption at temperatures of 333 and 353 K showed a noticeable difference in the hydrogen sorption properties of samples. The formation of compacts led to a decrease in the capacity, an increase in the pressure hysteresis and the slope of the PCT-isotherms plateau, which negatively affects their applicability in metal hydride devices. Moreover, negative trends increase with the increase in the degree of compression of the sample. Significant loss of capacity of compact 2 (up to 25 %) can be caused by incomplete reactivation or deterioration of diffusion inside the sample.

On the other hand, the study of the thermal conductivity of samples showed the prospects of compacts in terms of heat transfer. The heating time of the samples, as well as the time of temperature relaxation during hydrogen desorption, decreases with increasing density of the compact. For compact 1, these times are 25-30 %, and for compact 2, they are almost 50% lower than for the control sample of free filling. This is a very promising result from the point of view of the use of compacts in real devices.

Summing up, it should be concluded that the technology of forming metal hydride compacts is promising. However, a large amount of research is required to find optimal methods for manufacturing such materials. In addition, it is necessary to study further their mechanical stability during long-term use with a large number of hydrogen absorption-desorption cycles.

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