Influence of high thermal conductivity addition on PCT-isotherms of hydrogen storage alloy

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Abstract. High reaction heat of an interaction between intermetallic compounds and hydrogen along with low thermal conductivity of fine dispersed metal hydride powders lead to crisis phenomena in metal hydride hydrogen storage facilities. Thus investigations of composite materials with improved heat transfer are of great interest for development of hydrogen storage technologies. A composite material was made of powders of activated La$_{0.9}$Ce$_{0.1}$Ni$_5$-alloy and copper. PCT-isotherms of hydrogen sorption and desorption was measured and compared for the composite and the pure alloy at temperature of 313, 333 and 353K. Values of $\Delta H$ and $\Delta S$ of the hydrogen sorption and desorption reactions were calculated, and temperature and pressure relaxation in the pure alloy and the composite material beds were studied. A significant difference between hydrogen storage behaviour of the pure alloy and the composite has been revealed.

1. Introduction
Development of metal hydride storage purification and compression systems is an important problem nowadays. However, the physicochemical properties of hydrogen storage alloys and the peculiarities of their interaction with hydrogen create obstacles to using hydrogen as power source. Intermetallic compounds (IMC) obtained by melting of the initial components in an inert atmosphere (the reason why they are called alloys) during the reaction with hydrogen are dispersed into powders with a particle size of about 1-10 µm. These powders have a low thermal conductivity (about 1 W/m·K) and a relatively high enthalpy of the hydrogen absorption reaction (25 – 70 kJ/mole H$_2$), which leads to a crisis of heat and mass transfer and a sharp decrease in the rate of hydrogen absorption or desorption [1]. In addition, a significant change in the volume of the crystal lattice of the IMC in the absorption and desorption of hydrogen causes sedimentation of particles under the action of gravity, self-condensation of backfill and accumulation of internal stresses. This leads to a change in the parameters of the interaction of large backfill IC with hydrogen compared to laboratory samples-scale effect [2].

In this work, the interaction with hydrogen of a composite material obtained from fine powders of IMC AB$_5$-type with composition of La$_{0.9}$Ce$_{0.1}$Ni$_5$ and copper was investigated. To obtain a fine powder of intermetallic compound for the preparation of the composite, it is possible to mechanically grind it in an inert or hydrogen atmosphere or by interaction with hydrogen during the activation of the sample. The second method is used in this work.

Activation of the IMC is a series of successive absorption and desorption cycles of hydrogen, which are carried out at excessive hydrogen pressure and a significant temperature drop. This involves dispersion of the alloy and reduction of the oxide film on the surface of the IMC particles, which
allows achieving the maximum capacity and reaction rate with hydrogen. The use of various additives and porous matrices of high-heat-conducting metal is one way to increase the thermal conductivity of metal hydride filling. Copper was chosen for heat transfer improvement by the following reasons: high thermal conductivity; inertness to hydrogen under experimental conditions; copper density is close to the density of IC, which allows to avoid stratification of the mixture during cycling; as we suppose plasticity of copper can compensate internal stresses that arise due to the increase in the volume of IMC particles during the reaction with hydrogen.

Figure 1. US-150 facility scheme: 1 – hydrogen vessel; 2 – 10 valves; 11 – vacuum vessel; 12 – hydrogen accumulator with LaNi₅; 13 – buffer autoclave; 14 working autoclave; 15,16 – manometers (0–15 MPa); 17 – pressure sensor (0-0.1 MPa);18,19 – pressure sensor (1-15 MPa); 20,21 – pressure sensor (0.1–1 MPa).

2. Experimental details
At the first stage the activation of the IMC sample was carried out by performing successive cycles of hydrogen absorption and desorption in the working autoclave of experimental facility US-150 (scheme is shown in Figure 1) at a temperature of 298 to 373 K and a pressure of hydrogen up to 10 MPa. Then the hydrogen sorption and desorption isotherms (PCT-isotherms) were measured by the Siverts method at a temperature of 313 K. The comparison of the obtained PCT-isotherms with the results of previous studies of this alloy showed their coincidence within the uncertainty of the method (Figure 2). Thus, the completeness of the sample activation was confirmed.

IMC powders after cycling with hydrogen actively interact with oxygen in the air and can be pyrophoric because of active metal surface and a certain amount of hydrogen remains in the powders even after strong vacuuming. So it is necessary to work with the powders in an inert atmosphere. Thus, the working autoclave with the sample was carefully vacuumed, filled with inert gas, disconnected from the facility and then placed in a dry box. Then, in the dry box the composite was prepared by mechanical stirring of 50 g of IMC powder and 450 g of copper. Further the composite was placed in the working autoclave and securely closed inside the dry box.

Powder of the electrolytic copper with a particle size of about 70 µm and a bulk density of about 1.6 g/cm³ was used for the preparation of the composite. Bulk density of the activated IMC
La$_{0.9}$Ce$_{0.1}$Ni$_5$ powder was about of 3.6 g/cm$^3$. The volume of the cylindrical working autoclave was 280 cm$^3$, so 500 g of the composite filled it completely. Previous studies of large samples of IMC showed that the mutual influence of particles significantly affected the PCT-isotherms. Therefore, the ratio of copper and IMC for the composite was chosen so that, on the one hand, to isolate the IMC particles from each other by copper, and, on the other hand, to preserve the accuracy of measurements.

![Figure 2. PCT-isotherms at 313K after activation. Comparison of the previous results (sorption and desorption, respectively) and new data (sorption and desorption, respectively).](image)

At the next stage, the autoclave with the sample was connected to the facility. The PCT-isotherms measurements of hydrogen sorption and desorption were carried out at temperatures of 353, 333 and 313K, and the relaxation times of temperature and the equilibrium pressure in the system composite-hydrogen were studied. The working autoclave was immersed in a liquid thermostat with a coolant based on polymethylsiloxane to maintain its temperature. Taking into account that the volume and density of the IMC particles during interaction with hydrogen vary considerably in contrast to the copper particles, the autoclave was located horizontally to avoid sedimentation of the composite particles under the action of gravity.

3. Results and discussion
The measured composite PCT-isotherm of absorption and desorption of hydrogen at temperatures 313, 333 and 353K were compared with the previously measured isotherms for the 50 g sample of IMC La$_{0.9}$Ce$_{0.1}$Ni$_5$ (Figure 3). The mass percentage of hydrogen absorbed and desorbed by the composite was calculated without taking into account the mass of copper for easy comparison.

Comparison of the PCT-isotherms shows that the maximum hydrogen content in the hydride decreases in the composite. Presumably, this is due to the fact that some particles of IMC were "sealed" in copper and did not interact with hydrogen. The equilibrium pressure of absorption and desorption of hydrogen by the composite decreases in comparison with the pure IMC, in addition, the angle of the absorption and desorption plateau increases. Dependency graphs of the equilibrium pressure logarithm as a function of the inverse temperature were built, and the values of enthalpy and entropy of hydrogen absorption and desorption were calculated using the Van’t Hoff’s equation (table 1). The values for hydrogen desorption are almost identical for the composite and pure IMC, but the enthalpy and entropy of hydrogen absorption by the composite are significantly lower. The assumption
that copper particles reduce or completely eliminate the mutual influence of IMC particles on each other has not been confirmed. Apparently, under experimental conditions, the plasticity of copper was insufficient to compensate for the stresses arising due to changes in the volume of IMC particles, which affected the PCT-isotherms.

Figure 3. Comparison of hydrogen absorption and desorption PCT-isotherms of the La$_{0.9}$Ce$_{0.1}$Ni$_5$ 50 g sample and the composite (absorption and desorption, respectively).

The characteristic relaxation times of temperature and the equilibrium pressure during absorption of hydrogen at a temperature of 353K are presented in Figures 4 and 5, respectively. It is clearly seen that the heat release in the absorption of hydrogen leads to less local overheating of the composite bulk. Due to the better thermal conductivity of the composite its temperature relaxation is almost 2 times faster than the temperature relaxation of the pure IMC: 14 and 24 minutes, respectively (Figure 4 a). The equilibrium pressure estimating in the system is much slower and has the limiting step: 35 minutes for the composite and 75 minutes for the pure IC (Figure 4 b).

At the last stage, the composite was extracted from the working autoclave to study its morphology. After the opening of the working autoclave, it was found that the sample was slightly compacted, and a small cavity was formed in the upper part of the autoclave at the hydrogen inlet at a horizontal arrangement. At the same time, the entire volume of the composite from the initial powder turned into a fairly stable formation (Figure 5). Similar agglomerations but more dense and resistant to the mechanical effects were found earlier in the study of large samples (up to 500 g) of pure intermetallic compounds in the lower part of the samples.
Table 1. Hydrogen sorption properties of the 50 g La$_{0.9}$Ce$_{0.1}$Ni$_5$ sample and the composite.

|                | Temperature, K | C(H$_2$)$_{max}$, wt. % | $\bar{P}_{eq}$, MPa | $\Delta H^\circ$, kJ/mole | $\Delta S^\circ$, J/mole K |
|----------------|----------------|--------------------------|---------------------|-----------------------------|-----------------------------|
| **Absorption** |                |                          |                     |                             |                             |
| La$_{0.9}$Ce$_{0.1}$Ni$_5$ sample | 313            | 1.3                      | 0.78                | 32.9±0.2                    | 121±1                       |
| 50 g sample    | 333            | 1.3                      | 1.58                |                             |                             |
| Composite (La$_{0.9}$Ce$_{0.1}$Ni$_5$ 50 g) | 313            | 1.2                      | 0.77                | 25.7±0.2                    | 99±1                        |
|                | 333            | 1.2                      | 1.41                |                             |                             |
|                | 353            | 1.2                      | 2.35                |                             |                             |
| **Desorption** |                |                          |                     |                             |                             |
| La$_{0.9}$Ce$_{0.1}$Ni$_5$ sample | 313            | 1.3                      | 0.44                | 31.2±0.2                    | 112±1                       |
| 50 g sample    | 333            | 1.3                      | 0.99                |                             |                             |
| Composite (La$_{0.9}$Ce$_{0.1}$Ni$_5$ 50 g) | 313            | 1.2                      | 0.42                |                             |                             |
|                | 333            | 1.2                      | 0.84                |                             |                             |
|                | 353            | 1.2                      | 1.66                |                             |                             |

Figure 4 a. Local temperature inside the bulk of the pure IMC and the composite during hydrogen absorption at 353K.

Figure 4 b. Estimates of equilibrium pressure during hydrogen absorption by pure IMC and the composite at 353K.
Figure 5. The composite after extraction from working autoclave.

4. Conclusions
The composite of IMC and copper powders has lower specific hydrogen content in the hydride compared to pure IMC. The addition of copper improves the thermal conductivity of the backfill and leads to a noticeable decrease in the relaxation time of the temperature and the equilibrium pressure of hydrogen absorption and desorption. The equilibrium pressure of hydrogen absorption and desorption in the composite is significantly lower; in addition, the slope of the absorption and desorption plateau increases compared to the pure IMC. The values for hydrogen desorption enthalpy and entropy are almost identical for the composite and pure IMC, but the enthalpy and entropy of hydrogen absorption by the composite are significantly lower. The assumption that copper particles reduce or completely eliminate the mutual influence of IMC particles on each other has not been confirmed. During hydrogen absorption and desorption the composite was slightly compacted and turned from the initial powder into a fairly stable formation.

Acknowledgments
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