THE EFFECT OF MISCHMETAL ON BEHAVIOUR OF $LaNi_5$-TYPE HYDRIDES

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Due to extremely high bulk density of hydrogen atoms at ambient temperature and pressure intermetallic compounds (IMC) hydrides are widely used as media for compact and safe hydrogen storage. Modification of intermetallics composition allows user to adapt metal-hydride materials to specific technical requirements. As a rule, it is necessary that intermetallide reversibly and fast absorb large amounts of hydrogen at 270-310 K. This temperature range is the most popular for application tasks. Other requirements for potential hydrogen storage systems include the lowest possible enthalpy values for hydrogenation and dehydrogenation. The lower the ΔH value, the less heat is used for endothermic hydrogen emission from hydride so that it reduces the energy consumption of the metal hydride storage system. The material cost and availability are the essential factors of their choosing for wide application.

It is well known that La substitution in the $LaNi_5$–type alloys by Ce or Mm (commercial mixture of rare-earth metals) affects significantly equilibrium pressures of hydrogen absorption and desorption, hysteresis parameters and hydrogenation/ dehydrogenation enthalpies. Moreover, doping $LaNi_5$-based alloys with mischmetal reduces the time of hydrogen interaction equilibrium. In could possibly be due to the presence of other rare-earth metals (REM) in the mishmetal composition, such as Pr and Nd. The substitution of rare-earth metals for mishmetal contributes to the considerable cost reduction of metal-hydride materials.

In this work we studied the interaction in the systems $La_{0,75}Mm_{0,25}Ni_5$—H_2 and $La_{0,5}Mm_{0,5}Ni_5$—H_2, where Mm consists of 56 wt% Ce, 26 wt% La, 11 wt% Nd, 5 wt% Pr, 2 wt% the other metals, in the temperature range 273-308 K. The corresponding P-C isotherms are shown on Fig. 1 and 2.

As it is notable, the increase of mishmetal content in IMC have little effect on its hydrogen sorption capacity, but it significantly increases the equilibrium pressure and plateau slope, as well as the hysteresis of sorption/desorption pressures.

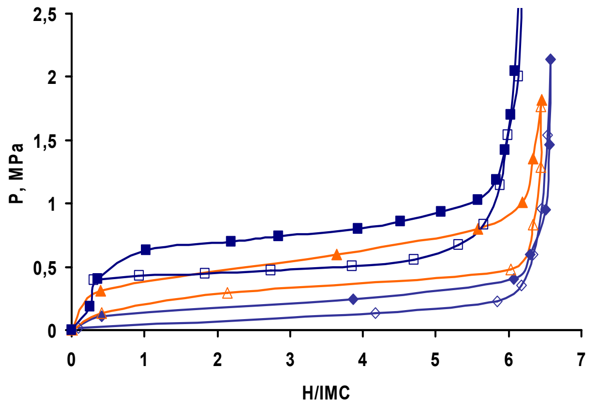

Fig.1. P-C isotherms in system $La_{0,75}Mm_{0,25}Ni_5$—H_2: closed symbols — absorption, open symbols — desorption. Diamonds — 273 K, triangles — 295 K, squares — 308 K.

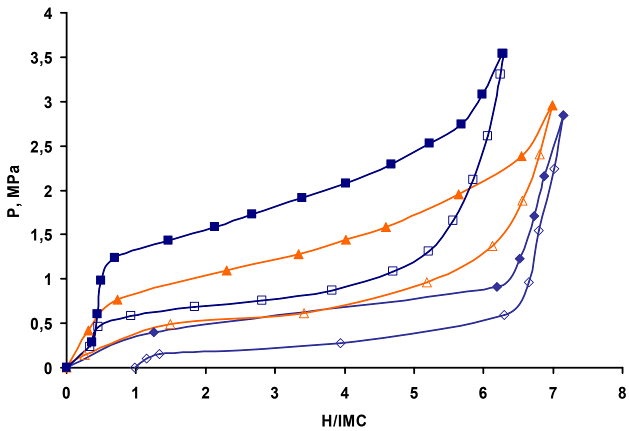

Fig.2. P-C isotherms in system $La_{0,5}Mm_{0,5}Ni_5$—H_2: closed symbols — absorption, open symbols — desorption. Diamonds — 273 K, triangles — 295 K, squares — 308 K.

To study the influence of mishmetal amount in intermetallic compounds on thermodynamic properties of hydrogenation/ dehydrogenation and hydrogen desorption dynamics from the corresponding hydrides, the technique of partial hydrogenation was used in combination with Tian-Calvet microcalorimetry. The technique of the direct experimental determination of partial molar absorption/ desorption enthalpies allows us to obtain more precise ΔH values of the system processes against the usual P-C-T method for thermodynamic functions evaluation. The enthalpy reaction value in the region of invariant (α+β)-equilibrium is constant within the experimental error and is not affected by the hydrogenation degree of the sample. That is why in order to calculate the IMC hydrogenation and dehydrogenation enthalpies the average enthalpy value is calculated in two-phase region. For the system $La_{0,75}Mm_{0,25}Ni_5$—H_2 $\Delta H_{\alpha\rightarrow\beta}$ makes -29,3±1,4 kJ/mol H_2, $\Delta H_{\beta\rightarrow\alpha}$ equals 28,8±0,6 kJ/mol H_2, whereas the P-C-T measurements gave ΔH sorption -25,9±0,1 kJ/mol H_2, ΔH desorption 28,6±0,1 kJ/mol H_2. The higher the equilibrium pressures of the intermetallide hydrogenation and dehydrogenation and its hysteresis, the more the corresponding ΔH values vary, which are obtained using direct calorimetry and Van't Hoff methods. For the system $La_{0,5}Mm_{0,5}Ni_5$—H_2 $\Delta H_{\alpha\rightarrow\beta}$ makes -28,3±1,3 kJ/mol H_2, $\Delta H_{\beta\rightarrow\alpha}$ equals 26,3±1,2 kJ/mol H_2, whereas the P-C-T measurements gave ΔH sorption -21,2±0,1 kJ/mol H_2, ΔH desorption 22,3±0,1 kJ/mole H_2. In the row $La_{1-x}Mm_xNi_5$ the increase of mishmetal content leads to reduction of the heat effect of hydride formation reaction.

Another advantage of microcalorimetric technique is the ability to monitor the dynamics of equilibrium achievement in the system using the heat generation and heat absorption curves. In this work for the samples of different mishmetal content there were examined the characteristic curves of heat power absorption against the timescale when desorbing hydrogen in 1, 5 and 10 cycles. As you can see from fig. 3 the more mishmetal contains the IMC hydride, the higher the hydrogen emission rate. The $La_{0,5}Mm_{0,5}Ni_5$ hydride shows lack of induction period on the first cycle already, but also shows high rate of hydrogen desorption.

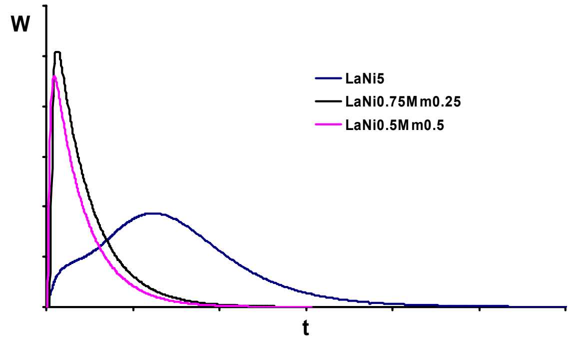

Fig. 3. Heat absorption curves for the first cycle desorption..

Therefore, the intermetallic compounds doped with mishmetal due to their thermodynamic and kinetic characteristics have a good prospect to be used as a system for hydrogen storage and transportation.