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# Calorimetric Study of Interaction in the Systems $LaNi_{4.9}Al_{0.1}$–$H_2$ and $LaNi_{4.9}Sn_{0.1}$–$H_2$

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**Abstract**—Interaction of hydrogen with the intermetallic compounds $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ was studied by Tian–Calvet differential heat-conducting microcalorimetry. In the range 308–353 K these compounds exhibit a low equilibrium hydrogen pressure in the region of the plateau, a fairly high absorption capacity, and an insigificant hysteresis of the absorption/desorption pressures in the two-phase region of the *P–C–T* diagram. The enthalpies of hydrogenation of the intermetallic compounds were calculated from the results of the calorimetric experiment and by the van't Hoff equation; the entropies and Gibbs free energies of hydrogenation in the range 308–353 K were calculated. The probable mechanism of the interaction of hydrogen with the intermetallic compounds was suggested.

One of the most pressing problems of the modern hydride-absorption technology is recovery of hydrogen from gas mixtures formed in the course of petrochemical synthesis. However, recovery of hydrogen from such mixtures is relatively difficult, because the partial pressure of hydrogen in them at 25–30°C usually does not exceed 0.5–1 atm. Therefore, the only way to recover hydrogen from such gas mixtures is to use intermetallic compounds (IMCs) over which the hydrogen pressure does not exceed the above-indicated level and desorption at 50–70°C is sufficiently fast.

For solving this interesting problem, much promise is shown by multicomponent intermetallic compounds derived from $LaNi_5$ by substitution of a part of nickel atoms (less than 20%) by Al or Sn.

Interaction of hydrogen with intermetallic compounds $LaNi_{5-x}Al_x$ $(0.3 < x < 1.0)$ is described in the literature in sufficient detail [1–5]. It is known that at a low (~5 at. %) Al content the equilibrium hydrogen pressure in the region of the plateau decreases by a factor of more than 2, with no appreciable changes in the absorption capacity of IMC [4].

It is noted in recent papers that partial replacement of Ni atoms in the $LaNi_5$ lattice by Sn atoms improves the service properties of the intermetallic compounds. Compounds $LaNi_{5-x}S_x$ $(0.1 < x < 0.5)$ exhibit a low equilibrium hydrogen pressure, a high absorption capacity, and a small absorption/desorption pressure hysteresis in the two-phase range at temperatures close to room temperature [6–8].

It should be emphasized that, despite a great deal of data on multicomponent intermetallic compounds containing Al or Sn, in most cases the consideration is restricted to plotting of the *P–C–T* diagrams and calculation of the enthalpies of hydrogenation by the van't Hoff equation. At the same time, the mechanism of interaction of hydrogen with these compounds and the effect of small additions of Al and Sn on this mechanism are not yet understood.

In this work, using differential heat-conducting microcalorimetry, we studied the interaction of hydrogen with $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$. The equilibrium in the systems intermetallic compound–$H_2$ was studied by "calorimetric titration" with hydrogen [9, 10]. This procedure has certain advantages over the common procedures for plotting the *P–C–T* diagrams. In particular, with this procedure the calorimetric experiment furnishes information not only on the hydrogenation thermodynamics, but also on the mechanism of interaction in the system intermetallic compound–$H_2$ [11–13].

The equilibrium in the systems $LaNi_{4.9}Al_{0.1}$–$H_2$ and $LaNi_{4.9}Sn_{0.1}$–$H_2$ was studied at 308, 328, and 353 K. The absorption–desorption isotherms are shown in Fig. 1. It is seen that at 308 K the plateau in the *P–C–T* diagrams is practically horizontal, and the absorption capacity in the two-phase region is about 5 atm $H_2$ per mole of intermetallic compound. The equilibrium hydrogen pressure in the middle of the two-phase region of the *P–C–T* diagram and the

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[†] Deceased.

**Table 1.** Effect of temperature on the characteristics of hydrogenation of intermetallic compounds

| Compound | $T$, K | at. H/(mol IMC) | $P_{abs}$, atm | $P_{abs}/P_{des}$ |
|---|---|---|---|---|
| $LaNi_{4.9}Al_{0.1}$ | 308 | 5.2 | 1.6 | 1.2 |
| | 328 | 4.9 | 3.8 | 1.3 |
| | 353 | 4.1 | 9.5 | 1.2 |
| $LaNi_{4.9}Sn_{0.1}$ | 308 | 4.8 | 2.1 | 1.4 |
| | 328 | 4.5 | 4.3 | 1.3 |
| | 353 | 4.0 | 9.7 | 1.2 |

absorption capacity in these systems are given in Table 1. It should be noted that with increasing temperature the absorption capacity of the compounds for hydrogen decreases, and the slope of the plateau increases.

Figure 2 illustrates the influence of metals substituting nickel in $LaNi_5$ on the capability of the alloys to absorb hydrogen. These results suggest that the Al-containing compounds show more promise for various branches of the hydride-absorption technology because of their lower equilibrium hydrogen pressure at temperatures close to room temperature and of their higher absorption capacity as compared to the tin-containing samples (Fig. 2).

Luo *et al.* [8] note that at temperatures close to room temperature the reversible absorption in the systems $LaNi_{5-x}Sn_x$–$H_2$ ($x$ = 0.05–0.5) occurs with a minor hysteresis of the equilibrium pressure in the range of equilibrium of the α and α + β phases. They also report that the value of the hysteresis is proportional to the tin content in the IMC lattice. Our previous studies showed that in the system $LaNi_{4.8}Sn_{0.2}$–$H_2$ at 308 K there is practically no absorption/desorption pressure hysteresis [11]. However, studies of the equilibrium in the system $LaNi_{4.9}Sn_{0.1}$–$H_2$ revealed hysteresis even at 308 K (Fig. 1). The $P_{abs}/P_{des}$ ratios characterizing the absorption/desorption pressure hysteresis are listed in Table 1.

Our procedure allows a highly accurate calculation of the thermodynamic parameters of hydrogenation of intermetallic compounds at a specific temperature, whereas calculation by the van't Hoff equation gives only the enthalpy of hydrogenation averaged over a certain temperature range. The enthalpies of hydrogenation of intermetallic compounds determined from the calorimetric experiment at 308, 328, and 353 K are listed in Table 2. By the van't Hoff equation we also estimated the average enthalpy of hydrogenation for the examined temperature range, $\Delta H_{308-353}$. For

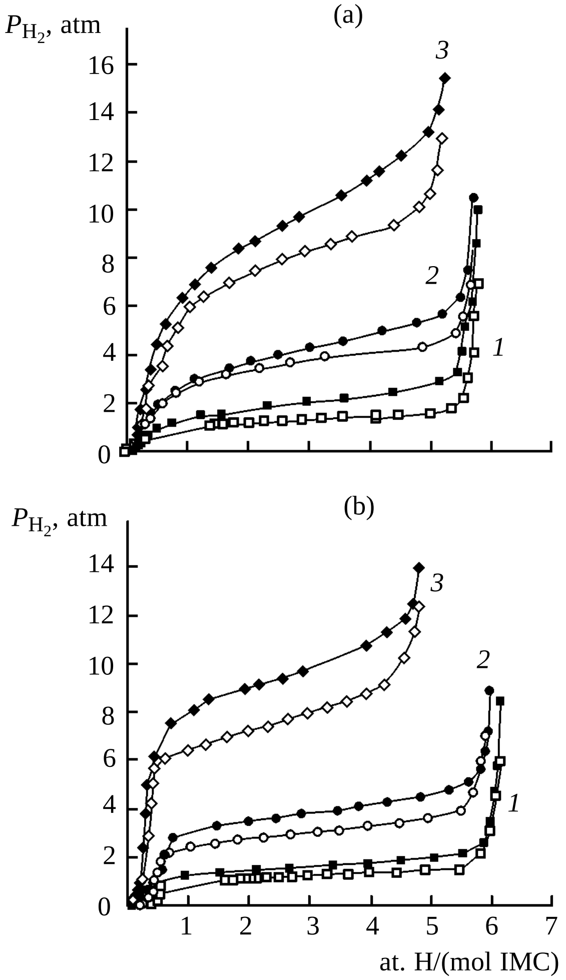

**Fig. 1.** Isotherms of hydrogen absorption/desorption with (a) $LaNi_{4.9}Sn_{0.1}$–$H_2$ and (b) $LaNi_{4.9}Al_{0.1}$–$H_2$ at (*1*) 308, (*2*) 328, and (*3*) 353 K. Dark symbols refer to absorption, and clear symbols, to desorption.

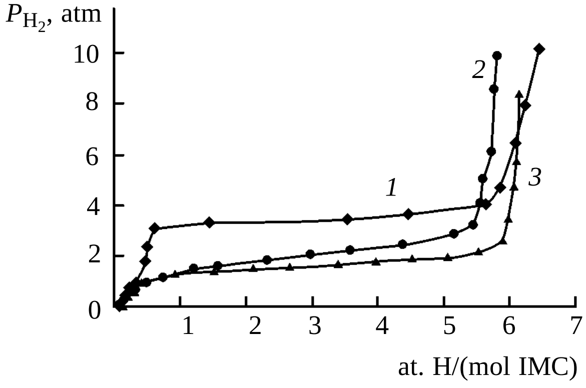

**Fig. 2.** Influence of metals substituting nickel on the equilibrium hydrogen pressure over intermetallic compounds and their absorption capacity at 308 K: (*1*) $LaNi_5$, (*2*) $LaNi_{4.9}Sn_{0.1}$–$H_2$, and (*3*) $LaNi_{4.9}Al_{0.1}$–$H_2$.

**Table 2.** Thermodynamic parameters of hydrogenation of intermetallic compounds

| Compound | $T$, K | $\Delta H_{dif}$, kJ/(mol $H_2$) | $\Delta S_{dif}$, J/(mol $H_2$ K) | $\Delta G$, kJ/(mol $H_2$) |
|---|---|---|---|---|
| $LaNi_{4.9}Al_{0.1}$ | 308 | –32.6 ± 0.8 | –115.7 ± 5.6 | 3.2 ± 0.6 |
| | 328 | –33.5 ± 1.9 | –120.8 ± 6.0 | 6.1 ± 0.7 |
| | 353 | –35.3 ± 3.3 | –129.9 ± 5.2 | 10.5 ± 1.0 |
| $LaNi_{4.9}Sn_{0.1}$ | 308 | –31.6 ± 2.4 | –114.7 ± 5.7 | 3.7 ± 0.7 |
| | 328 | –33.4 ± 1.8 | –122.1 ± 6.6 | 6.6 ± 0.5 |
| | 353 | –34.1 ± 2.7 | –124.8 ± 6.3 | 9.9 ± 1.1 |

$LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ this quantity is –35.3 and –32.3 kJ/(mol $H_2$), respectively. Thus, the values calculated by the van't Hoff equation and directly from the calorimetric data reasonably agree with each other and also with our previous data for $LaNi_{4.75} \cdot Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ [11] and with the published data for $CaCu_5$-type intermetallic compounds [14–17].

Using the results of the calorimetric experiment, we also calculated the entropy and Gibbs free energy of hydrogenation of $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ at the hydrogen content corresponding to the two-phase region of the *P*–*C*–*T* diagram. The results are listed in Table 2. It should be noted that with increasing temperature the deviation of $\Delta G$ from zero grows. This fact is the thermodynamic substantiation of the increase in the slope of the plateau, observed in the phase diagrams of the systems in question (Fig. 1). It is interesting that the entropies of hydrogenation do not differ significantly from the entropy of dissociation of hydrogen in a vacuum [130 J/(mol K)]. This fact suggests that chemisorption of the hydrogen molecule followed by its dissociation on the surface of the intermetallic compound contributes most to the $\Delta S$ of hydrogenation.

Heterogeneous equilibria are often described in the formal kinetics by the Avraami–Erofeev equation

$$[-\ln(1 - \theta)]^{1/n} = k\tau,$$

where $\theta$ is the degree of conversion, and $\tau$ is the reaction time [18]. The method of taking the logarithm of the Avraami–Erofeev equation, used in our laboratory, allows us to apply the results of the calorimetric experiment to study of the interaction mechanism in the systems intermetallic compound–hydrogen in various areas of the phase diagram. This method was described in more detail in [12, 13].

The plot of the degree of hydrogenation vs. interaction time in the coordinates $\ln\tau$–$\ln[-\ln(1-\theta)]$ consists of two linear sections with different slopes (Fig. 3). The parameter n calculated as the slope relative to the ordinate determines the mechanism of hydrogen interaction with the intermetallic compounds, and the inflection point corresponds to the change in the limiting stage of hydrogenation.

In Fig. 3 the plot of the degree of hydrogenation vs. time is compared with the P–C–T diagrams of the systems under consideration at 308 K. For 328 and 353 K, the dependences were similar. As seen from these data, for all the compounds the limiting stage changes at the boundary between the regions of the $\alpha$-solid solution and of the invariant equilibrium when particles of the $\beta$-hydride start to form in the system.

The kinetic parameter $n$ for each section of the plot can be determined by the least-squares method (Table 3). Our calculations showed that in the region of the $\alpha$ phase $n$ does not exceed 1.0, i.e., the hydrogenation rate is limited by diffusion of gaseous hydrogen into the bulk of the solid phase. For the second section, $n$ is within 2.0–3.5, which suggests that in the region of the plateau the major influence on the reaction rate is exerted by the formation and growth of the $\beta$-hydride nuclei [19]. In Table 3 is also given the "critical" hydrogen concentration, i.e., the hydrogen content in the solid matrix at which the limiting stage of hydrogenation changes. Our results are fully similar to those described in [20] and confirm the fact that formation of the $\beta$-hydride phase is accompanied by a change in the character of bonding between the intermetallic compound and hydrogen [21].

## EXPERIMENTAL

The intermetallic compounds were prepared by fusion of the high-purity metals (La 99.8%, Ni 99.96%, Al 99.8%, Sn 99.8%) in an electric arc furnace with a permanent electrode under purified nitrogen. The ingot was weighed after fusion to be sure that the composition of the alloy corresponds to that of the charge. For all the samples the combustion loss did not exceed 1.5%. The samples were single-phase, which was checked by X-ray phase analysis with a DRON-2 diffractometer ($CuK_\alpha$ radiation).

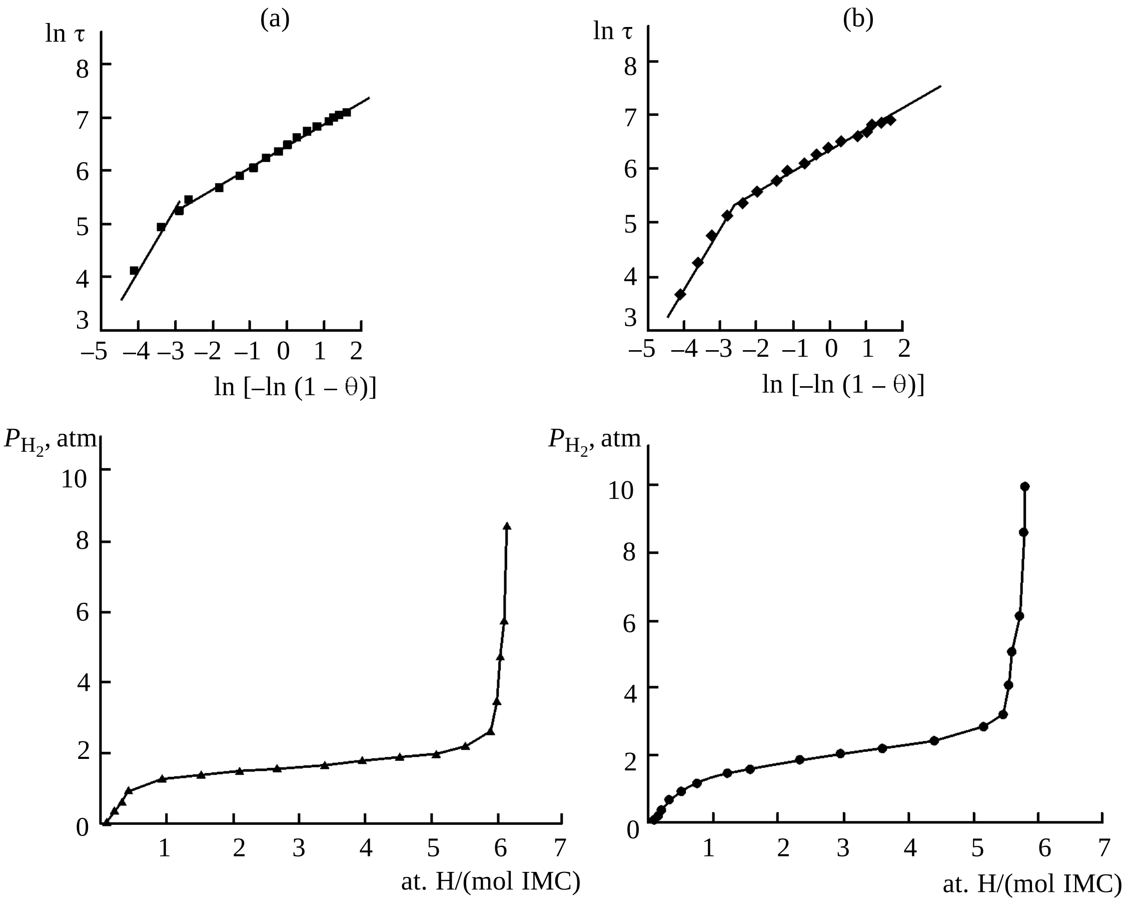

**Fig. 3.** Comparison of the time dependences of the degree of hydrogenation and the *P–C–T* diagrams for the systems (a) $LaNi_{4.9}Al_{0.1}$–$H_2$ and (b) $LaNi_{4.9}Sn_{0.1}$–$H_2$ at 308 K.

The equilibrium absorption of hydrogen with intermetallic compounds was studied by Tian–Calvet differential heat-conducting calorimetry. The experimental setup consisted of a DAK-1-1A calorimeter and a unit for dosing gas to the reaction chamber. Hydrogenation of $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ was studied by “calorimetric titration” with hydrogen–a procedure developed at our laboratory and described in detail elsewhere [9, 10].

Hydrogen was generated by desorption from the hydride phase; the content of impurities did not exceed $10^{-5}$ vol %. The source of ultrapure hydrogen was an AMGV-06 portable standard apparatus produced by Disperkhim Research and Production Private Company.

Alloy samples placed in the calorimeter cell were preliminarily activated by tenfold hydrogenation/dehydrogenation at 308 K to obtain a uniform disperse powder with a particle size of 3–5 μm. Then hydrogen was fed to the calorimeter cell in $10^{-5}$–$10^{-4}$ M portions, and simultaneously the thermal effect corresponding to this portion was recorded.

The amount of reacted hydrogen was determined from the pressure change in the system and calculated by the modified van der Waals equation. The hydrogen pressure below 0.1 MPa was measured with a VO reference vacuum gage (precision class 0.4), and

**Table 3.** Critical hydrogen concentration in the metal matrix $H/IMC_{cr}$ (mol/mol) and kinetic parameters of the system intermetallic compound–$H_2$

| Compound | *T*, K | $H/IMC_{cr}$ | $n_\alpha$ | $n_{(\alpha+\beta)}$ |
|---|---|---|---|---|
| $LaNi_{4.9}Al_{0.1}$ | 308 | 0.94 | 1.1 ± 0.3 | 2.4 ± 0.1 |
| | 328 | 0.75 | 1.4 ± 0.4 | 3.0 ± 0.3 |
| | 353 | 0.33 | 0.6 ± 0.2 | 3.4 ± 0.4 |
| $LaNi_{4.9}Sn_{0.1}$ | 308 | 0.75 | 1.0 ± 0.3 | 2.8 ± 0.2 |
| | 328 | 0.52 | 1.1 ± 0.4 | 2.7 ± 0.3 |
| | 353 | 0.40 | 0.6 ± 0.2 | 2.9 ± 0.2 |

in the range 0.1–2.5 MPa, with an MO-25 reference manometer (precision class 0.4).

The temperature in the calorimeter thermostat was maintained to within ±0.2 K.

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