Influence of aluminum and tin on the mechanism of hydrogenation of $LaNi_5$-based intermetallides

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The interaction of hydrogen with the $LaNi_5$-based intermetallides containing different amounts of aluminum and tin was studied using the calorimetric titration technique. Based on the formal kinetic approach and X-ray diffraction data, a probable mechanism was proposed for the hydrogenation of the intermetallides in the temperature interval from 308 to 353 K. The phase of the α-solid solution in all the intermetallide—hydrogen systems is formed *via* similar mechanism. However, the mechanism of the β-hydride phase nucleation and growth changes dramatically when the content of the main group metal increases.

Key words: intermetallide, hydrogenation mechanism, rate-determining step, nucleation and growth, α-solid solution, β-hydride, formal kinetics.

Intermetallides (IM) synthesized by the substitution of some nickel atoms in $LaNi_5$ by the IIIA and IVA Group elements are promising materials for hydrogen accumulators, thermal pumps, and other similar devices. A practical interest in these compounds is due to their good absorption characteristics (*viz.*, low equilibrium pressure, high absorption capacity, and small hysteresis) and high durability toward impurities in hydrogen used in real technological processes.[1] Therefore, information on both the thermodynamics and kinetics and the mechanism of hydrogen absorption at different steps of hydrogenation of these compounds is needed for practical purposes. The published data on the mechanism of hydrogenation of intermetallides of the $CaCu_5$ structural type are very contradictory, first of all, because of methodical difficulties.[2—5]

It has been shown[6,7] that the technique of calorimetric titration with hydrogen[8] (combination of the partial hydrogenation method and differential Tian—Calvet microcalorimetry) developed at the Chair of High-Pressure Chemistry and Physics of the Moscow State University allows one to study the thermodynamics and mechanism of interaction of hydrogen with intermetallides containing different transition metal atoms.

In this work, we used calorimetric titration to study the mechanism of hydrogenation of the $LaNi_{5-x}M_x$ compounds containing aluminum and tin. The $LaNi_{4.9}Al_{0.1}$, $LaNi_{4.9}Sn_{0.1}$, $LaNi_{4.75}Al_{0.25}$, and $LaNi_{4.8}Sn_{0.2}$ intermetallides were chosen for the study.

Experimental

Intermetallides were prepared by electric arc melting of the high-purity metals in a blend (La, 99.8%; Ni, 99.96%; Al, 99.8%; and Sn, 99.8%) in a furnace with a nonconsumable electrode under the purified argon pressure. Testing weighing was carried out after melting to reveal whether the molecular composition of the melt prepared corresponded to the composition of the starting blend or not. The elemental composition of the resulting IM samples was determined by atomic emission spectroscopy with inductively-coupled plasma and molecular absorption spectroscopy. The phase composition of the samples prepared and the type and parameters of the crystalline lattice of the starting melts and their hydrides were determined by X-ray diffraction on a DRON-2 diffractometer with a copper cathode using a standard procedure. Silicon was added to the samples as reference.

The samples were pre-activated by ten hydrogenation—dehydrogenation cycles using the previously described technique of calorimetric titration with hydrogen.[9—11] The experimental setup consisted of a system of dosed gas supply to the reaction chamber and a DAK-1-1A differential microcalorimeter. The use of a differential calorimeter[12] made it possible to exclude corrections for the thermal effect related to the admission of hydrogen into the system and changes in the external conditions during prolonged experiments. During experiments, gaseous hydrogen was admitted to the calorimetric cell in portions of 0.0002—0.0003 moles with the simultaneous detection of the thermal effect of the reaction as a function of the time and amount of reacted H_2. Each next portion of hydrogen was admitted after the signal of the instrument returned to the zero line. Special purity grade hydrogen with the content of admix-

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tures 10^{-5} vol.%, which was prepared by desorption from the $LaNi_5$-based hydride phase at 363 K, was used for hydrogenation.

The Avraami—Erofeev equation[13] was used to study the mechanism of hydrogenation

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

where θ is the degree of hydrogenation of the IM sample, τ is the time of equilibration after a portion of hydrogen was admitted to the system, and n is the parameter characteristic of the nature of the limiting step.

The degree of hydrogenation of the sample (%) was calculated from the calorimetric titration data using the formula

$$\theta = \left(\sum_{i=1}^{k} W_i / W_{i\Sigma}\right) \cdot 100,$$

where W_i is the heat release after the ith portion of hydrogen was absorbed by the IM sample, and $W_{i\Sigma}$ is the integral heat release after the complete hydrogenation of the sample.

The W_i value was determined as a surface area between the experimental curve of the reaction thermal effect to the zero line, and the integral heat release was calculated by the summation of the differential W_i values.

Since hydrogen absorption by the IMs studied was not accompanied by an inductive effect, the time from the beginning of admission of the subsequent portion of hydrogen to the moment of returning of the thermal signal to the zero line was taken as the time of equilibration (τ) in the IM—H_2 system.

The Avraami—Erofeev equation was transformed into the $\ln[-\ln(1-\theta)] = k' + n\ln\tau$ form, plotted in the $\ln[-\ln(1-\theta)]$—$\ln\tau$ coordinates, and the kinetic parameter n was calculated as a slope ratio of each linear region of the plot. Based on the data obtained, we concluded about changes in the mechanism of hydrogenation depending on the hydrogen content in the metallic matrix. This method has previously been substantiated in detail.[6,13]

Results and Discussion

The p—c—T diagrams obtained in experiments on H_2 absorption by the $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ intermetallides at 308 K in the $\ln\tau$—$\ln[-\ln(1-\theta)]$ coordinates (hydrogenation degree of these IMs *vs.* time of equilibration) are compared in Figs. 1 and 2. The curve for the degree of hydrogenation of $LaNi_{4.9}M_{0.1}$ *vs.* time (see Figs. 1, *a* and 2, *a*) distinctly exhibits two linear regions with different slopes. The plots at 328 and 353 K are similar.

These curves have distinct inflection points, which can be indication that the limiting step changes during hydrogenation. Let us name the hydrogen content in the IM matrix, which corresponds to the inflection in the curve for the degree of hydrogenation *vs.* time, the "critical hydrogen content" C_H^{cr}. The C_H^{cr} values for $LaNi_{4.9}M_{0.1}$ at different temperatures are presented in Table 1. It is seen that at 308 K the mechanism of hydrogenation of

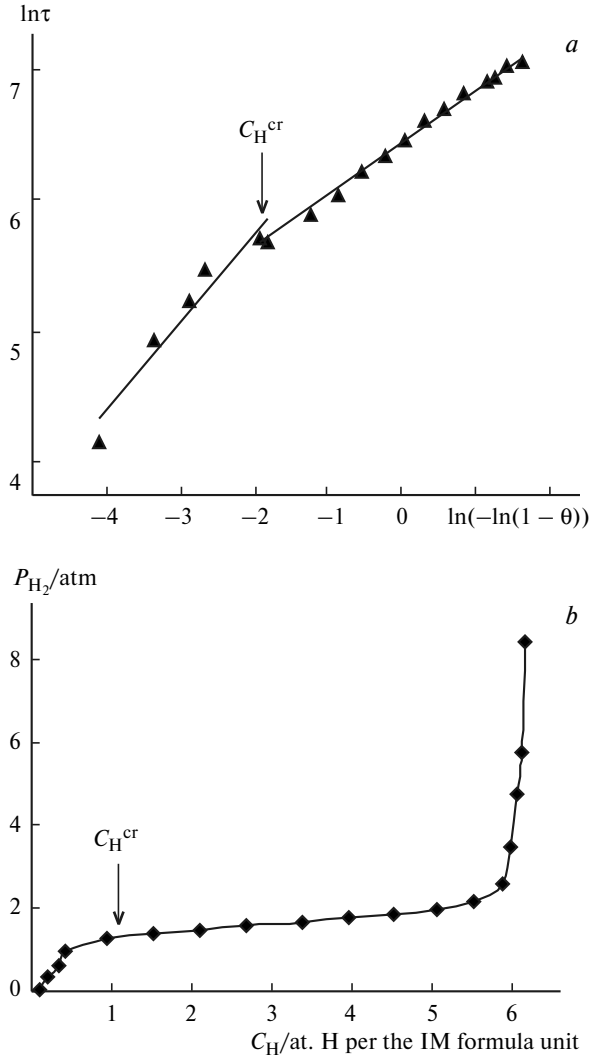

Fig. 1. Logarithmic plot for the degree of hydrogenation *vs.* time (*a*) and absorption isotherm (*b*) for the $LaNi_{4.9}Al_{0.1}$—H_2 system (T = 308 K).

$LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ changes at a hydrogen content of 0.9—1.1 at. H per the IM formula unit.

The kinetic parameter n for each linear region of the curves in Figs. 1, *a* and 2, *a* was determined using the least-squares method (see Table 1). The n value in the

Table 1. Critical hydrogen content in the metallic matrix and kinetic parameters of the $LaNi_{4.9}M_{0.1}$—H_2 systems

IM	T/K	C_H^{cr}	n_α	$n_{\alpha+\beta}$
$LaNi_{4.9}Al_{0.1}$	308	1.1	1.1±0.3	2.4±0.1
	328	0.8	1.4±0.4	3.0±0.3
	353	0.8	0.6±0.2	3.4±0.4
$LaNi_{4.9}Sn_{0.1}$	308	1.1	1.0±0.3	2.8±0.2
	328	0.7	1.1±0.4	2.7±0.3
	353	0.7	0.6±0.2	2.9±0.2

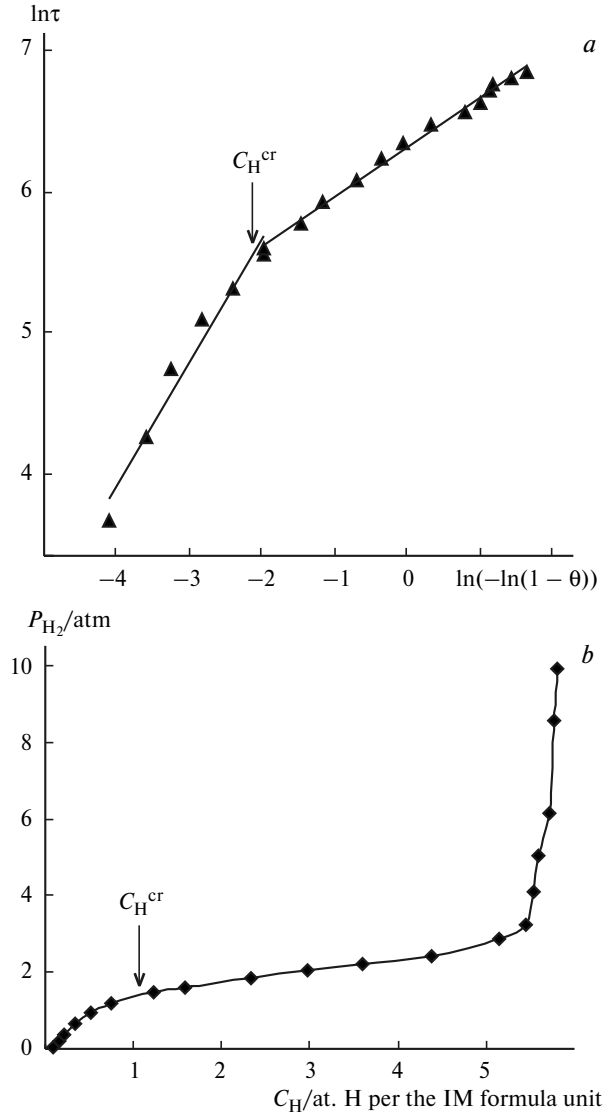

Fig. 2. Logarithmic plot for the degree of hydrogenation *vs.* time (*a*) and absorption isotherm (*b*) for the $LaNi_{4.9}Sn_{0.1}$—H_2 system (T = 308 K).

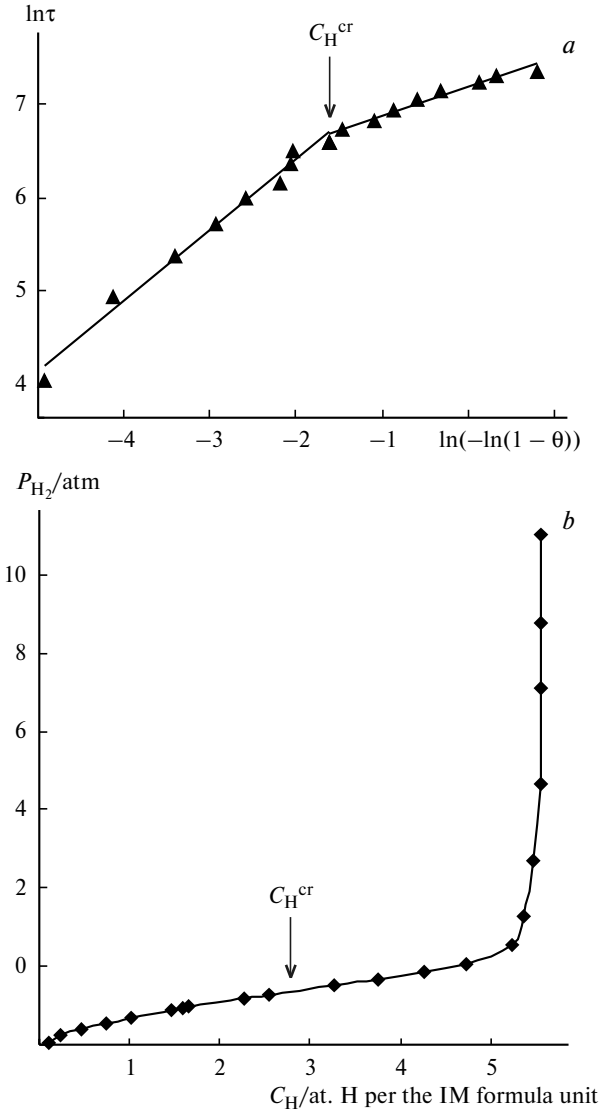

Fig. 3. Logarithmic plot for the degree of hydrogenation *vs.* time (*a*) and absorption isotherm (*b*) for the $LaNi_{4.8}Sn_{0.2}$—H_2 system (T = 308 K).

first region is close to unity, and in the second interval it ranges from 2.5 to 3.5. Based on the data in Table 1, we can conclude that the mechanism of hydrogenation of the $LaNi_{4.9}M_{0.1}$ IM remains almost unchanged with temperature.

Unexpected results were obtained in the study of the intermetallides with a high content of the main group metal. As in the case of $LaNi_{4.9}M_{0.1}$, the lnτ—ln[−ln(1 − θ)] plots exhibit one inflection point (Fig. 3). However, at 308 K the critical hydrogen content in the crystalline lattice of the $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ intermetallides is 2.6—2.8 at. H per the IM formula unit (Table 2). The temperature increase results in a sharp decrease in the C_H^{cr} values (*cf.* Figs. 3 and 4, see Table 2), which indicates, most likely, a change in the mechanism of hydrogenation of the $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ IMs with temperature. The kinetic parameter n in the whole 308—353 K temperature interval at the

Table 2. Critical hydrogen content in the metallic matrix and kinetic parameters of the $LaNi_{4.75}Al_{0.25}$—H_2 and $LaNi_{4.8}Sn_{0.2}$—H_2 systems

IM	T/K	C_H^{cr}	n_α	$n_{(\alpha+\beta)1}$	$n_{(\alpha+\beta)2}$
$LaNi_{4.75}Al_{0.25}$	308	2.7	1.1±0.2	1.0±0.2	2.7±0.4
	328	1.3	1.0±0.2	3.3±0.3	—
	353	0.7	0.8±0.2	2.6±0.2	—
$LaNi_{4.8}Sn_{0.2}$	308	2.6	1.2±0.2	1.1±0.2	3.1±0.5
	328	1.1	1.0±0.2	3.2±0.3	—
	353	0.9	1.3±0.3	3.1±0.4	—

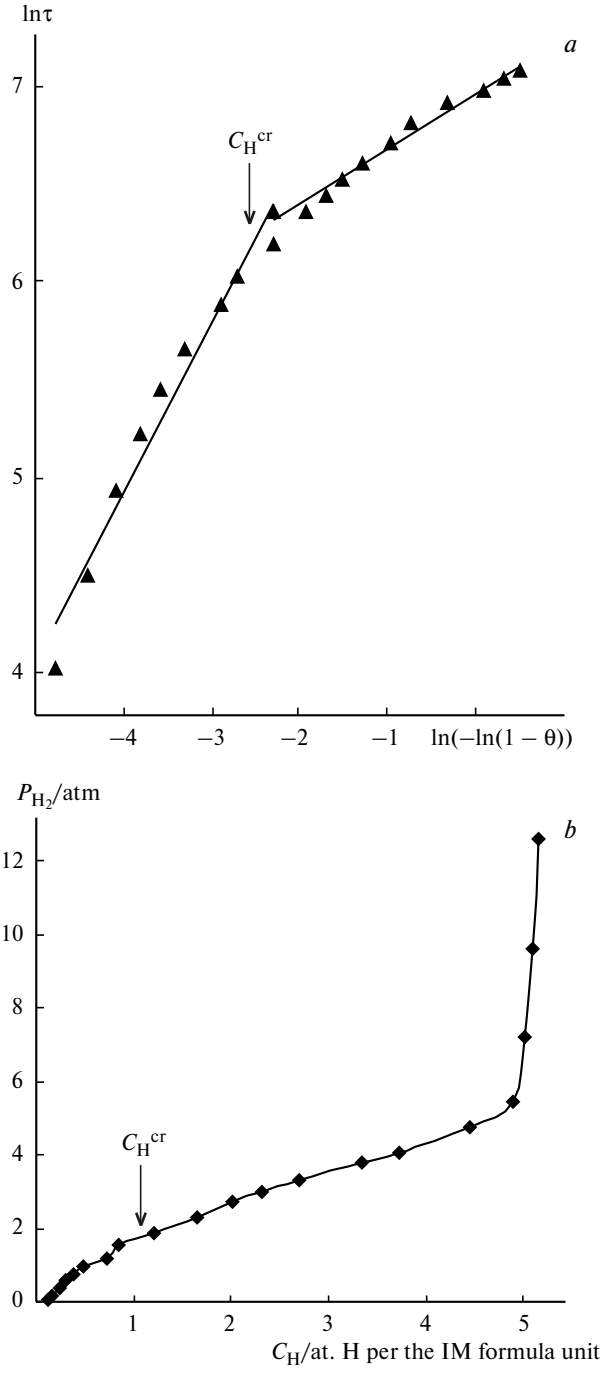

Fig. 4. Logarithmic plot for the degree of hydrogenation *vs.* time (*a*) and absorption isotherm (*b*) for the $LaNi_{4.8}Sn_{0.2}$—H_2 system ($T = 328$ K).

hydrogen content below the critical value approaches unity, whereas in the region after the inflection point it approaches three.

In order to explain the results obtained, the phase composition of the hydrides in which the hydrogen content corresponds to the critical value at 308 K was studied by X-ray diffraction. The hydride samples were stabilized by the treatment of their surface with carbon monoxide under 10—12 atm at 308 K.[14] According to the X-ray diffraction data, the $LaNi_{4.9}Al_{0.1}H_{0.9}$ and $LaNi_{4.9}Sn_{0.1}H$ samples are single-phase. Two phases were identified in the diffraction patterns of the $LaNi_{4.75}Al_{0.25}H_{2.8}$ and $LaNi_{4.8}Sn_{0.2}H_{2.6}$ samples (Table 3). The maximum content of hydrogen (at which the sample contains only the α-phase) in the crystalline lattice of $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ is 1.0 and 1.1 at. H per the IM formula unit, respectively.

Table 3. Phase composition and crystalline lattice parameters of the IM hydrides at the critical hydrogen content

Hydride	Phase composition of sample	Unit cell parameters/Å	
		a	*c*
$LaNi_{4.9}Al_{0.1}H_{0.9}$	α-Solid solution	5.025	3.987
$LaNi_{4.9}Sn_{0.1}H$	α-Solid solution	5.041	3.999
$LaNi_{4.75}Al_{0.25}H$	α-Solid solution	5.012	4.004
$LaNi_{4.75}Al_{0.25}H_{2.8}$	α-Solid solution	5.012	4.004
	β-Hydride	5.446	4.193
$LaNi_{4.8}Sn_{0.2}H$	α-Solid solution	5.040	3.994
$LaNi_{4.8}Sn_{0.2}H_{2.6}$	α-Solid solution	5.036	3.995
	β-Hydride	5.414	4.260

Based on the obtained results, we can propose the following mechanism of hydrogenation of the $LaNi_{4.9}M_{0.1}$ intermetallides. The value of the kinetic parameter *n* in the α-region close to unity suggests that the formation of a hydrogen solid solution in the crystalline lattice of the IMs under study is limited by a first-order reaction. According to the published data,[3,5,15,16] this reaction is, most likely, the dissociative chemisorption of H_2 molecules on the IM surface. When the hydrogen content equal to the critical value is achieved in the metallic matrix, the nucleation of the β-hydride phase begins. In the region of coexistence of two phases, the hydrogenation rate can be limited by several processes: (1) dissociative chemisorption of H_2 molecules on the IM surface; (2) diffusion of atomic hydrogen into the solid phase; (3) nucleation and growth of the β-hydride phase; and (4) diffusion of atomic hydrogen through the layer of the growing β-phase. Nucleation is most often the slowest stage of heterogeneous processes.[13,16] The value of the *n* parameter close to three, which was found in the second region of the kinetic curve, indicates that in the IM—H_2 systems the hydrogenation rate in the region of coexistence of two phases is also determined by the nucleation and growth rate of the β-phase, whose nuclei grow uniformly in three directions.

Based on the results obtained for the $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ IMs (see Table 2), we can assume that hydrogenation occurs in three steps. The formation of the phase of the α-solid solution, as in the previously considered case, is limited by dissociative chemisorption of H_2

molecules on the IM surface, which is indicated by the *n* value close to unity in this region (see Table 2). However, when the hydrogen content is above 1 at. H per the IM formula unit in the IM—H_2 systems, the β-hydride phase begins to form, and the growth of its nuclei exerts the main effect on the overall hydrogenation rate. The absence of a distinct inflection point in the plot (see Fig. 3, *a*) at the hydrogen content close to 1 at. H per the IM formula unit can be due to the fact that the kinetic parameter *n* in the two-phase region before the achievement of C_H^{cr} is still close to unity (see Table 2) because of the predominant one-directional growth of the formed nuclei of the hydride phase.[13,17] As the nuclei grow, they are overlapped, and at the critical hydrogen content the surface of the IM particle is completely covered with the β-hydride layer. After this, judging from the *n* value found, the reaction boundary begins to grow uniformly in three directions.[17]

Thus, the main difference in the mechanisms of hydrogenation of IMs with different concentrations of the main group metal is the following. For the $LaNi_{4.9}M_{0.1}$—H_2 systems, the critical hydrogen content determines the moment of phase transition, while in the $LaNi_{4.8}M_{0.2}$—H_2 systems, it corresponds to the change in the mechanism of nucleation of the hydride phase.

It is also worth to note that the hydrogenation of $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ with the temperature increase occurs only in two steps and becomes similar to that considered by us previously[6,7] for the $LaNi_{4.9}Al_{0.1}$ and $LaNi_{4.9}Sn_{0.1}$ intermetallides (see Table 2).

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