General and Inorganic Chemistry

Calorimetric investigation of interactions in the $LaNi_{4.75}Al_{0.25}$—H_2 and $LaNi_{4.8}Sn_{0.2}$—H_2 systems

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The interaction of hydrogen with intermetalic compounds $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ has been studied in the temperature range 308—353 K by the calorimetry titration method. The mechanism of hydrogenation was investigated. It was shown that, as the temperature increases, the initial concentration of hydrogen in the metal lattice needed for β-hydride formation decreases. It was assumed that this effect is related to the concentration of $H^{\delta+}$ atoms, which "oxidize" the metallic matrix according to the scheme $H^{\delta+} + M^0 \rightarrow H^{\delta-} + M^+$. The enthalpy and entropy of hydrogenation for the $LaNi_{4.75}Al_{0.25}$—H_2 system were calculated from the *p-C-T* curves and the calorimetry results. The thermodynamic parameters of the $LaNi_{4.8}Sn_{0.2}$—H_2 system were obtained for the first time.

Key words: intermetallic compound, calorimetry, hydrogen absorption, *p-C-T* diagram, enthalpy of reaction, entropy of reaction.

Since some intermetallic compounds (IMC), in particular, $LaNi_5$, can reversibly absorb hydrogen, they are used for the production of anodes for nickel—metal hydride accumulators. However, cyclic electrochemical absorption of hydrogen is accompanied by partial destruction (degradation) of a metal hydride electrode and a substantial decrease in its capacity. Thus the capacity of a $LaNi_5$-containing anode diminishes by 60% after 100 electrochemical charge/discharge cycles.[1] This drawback precludes the use of $LaNi_5$-based alloys in devices that should withstand tens of thousands of absorption—desorption cycles.

Partial replacement of nickel by aluminum giving $LaNi_{5-y}Al_y$ alloys ($y < 1.0$) increases their stability but decreases the capacity with respect to hydrogen.[2,3]

In recent years, publications have appeared indicating that doping of the $LaNi_5$ alloy with small amounts of tin diminishes the degradation of the $LaNi_{4.8}Sn_{0.2}H_x$ phase during the repeating absorption—desorption cycles without substantial decrease in the capacity.[4,5] Nevertheless, the influence of doping with small amounts of tin and aluminum on the thermodynamic characteristics of $LaNi_{5-y}R_y$ alloys (R = Al or Sn) and on the mechanism of interaction of these compounds with hydrogen has not been described in the literature.

In this work, we study the influence of small amounts of added tin and aluminum on the interaction of $LaNi_{5-y}R_y$ alloys (R = Al, Sn, y = 0.2; 0.25) with hydrogen at 308—353 K, construct phase diagrams for the corresponding IMC—hydrogen systems, and determine the main thermodynamic characteristics of hydrogenation of the compounds under study.

Experimental

The starting compounds were prepared by fusing together a batch of high-purity metals (La 99.8%, Ni 99.96%, Al 99.8%, Sn 99.8%) in an arc-melting furnace with a nonconsumable

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1841—1844, October, 1999.

electrode in an atmosphere of purified argon. The monophase composition of the resulting samples was confirmed by powder X-ray diffraction analysis and the correspondence to the formula presented above was confirmed by the atomic absorption and inductively coupled plasma methods.

Hydrogen absorption and desorption were studied by Tian—Calvet differential heat-conductive calorimetry. The experimental setup consisted of a DAK-1-1A calorimeter and a system for controlled introduction of hydrogen.[6] Hydrogenation of $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ was studied using a procedure of calorimetric titration with hydrogen developed in our laboratory and described in detail in previous publications.[7—9]

The quantity of absorbed hydrogen was determined from the pressure change in the system and calculated by the modified van der Waals equation. Hydrogen pressures below 0.1 MPa were measured by a VO standard pressure indicator (class of accuracy 0.4), and pressures ranging from 0.1 to 2.5 MPa were measured using an MO-25 standard manometer (class of accuracy 0.4). Hydrogen with a content of impurities not exceeding 10^{-5}% (v/v) was employed to study hydrogenation. A standard portable AMGV-06 device (joint-stock "Disperkhim" company) was used as the source of extra pure hydrogen. Prior to the work, the samples were subjected to ten absorption—desorption cycles at 308 K in order to obtain a homogeneous powder with a particle size of 3—5 μm. Then hydrogenation at 308, 328, and 353 K with gradual temperature increase was carried out and phase diagrams were constructed. The temperature in the thermostat was maintained constant with an accuracy of ±0.2 K.

Results and Discussion

Figure 1 shows the *p-C-T* diagrams obtained at various temperatures for the $LaNi_{4.8}Sn_{0.2}—H_2$ and $LaNi_{4.75}Al_{0.25}—H_2$ systems. It can be seen that at 308 K, the intermetallic compounds studied exhibit a high absorption capacity with respect to hydrogen (more than 5 H atoms per mole of IMC) at a low (0.9—1.1 atm) equilibrium pressure in the region of equilibrium between the α- and β-phases (Table 1). As the temperature is raised, the capacity slightly decreases and the equilibrium pressure of hydrogen in the region of two-phase equilibrium increases; the boundary between the α-solid solution and the assumed equilibrium region between the α- and β-phases develops more clearly on the absorption isotherm (see Fig. 1). The plateaus in the phase diagrams of the compounds studied at low temperatures show slight slopes. At higher temperatures, the slope of the plateau gradually increases (see Fig. 1).

It should also be noted that the presence of Al in a metallic matrix decreases the equilibrium pressure in the $LaNi_5—H_2$ system to a greater extent than the same amount of Sn. As the temperature increases, the discrepancy between the p_{equil} values becomes more pronounced (see Fig. 1).

The hysteresis of the absorption—desorption pressures in the plateau region, which is observed for the majority of compounds of the $LaNi_5$ type in the $LaNi_{4.8}Sn_{0.2}—H_2$ system, becomes visible at temperatures above 308 K (Fig. 2, Table 1). The absence of hysteresis at low temperatures for the compounds $LaNi_{5-y}Sn_y$ is due to the fact that the volume expansion of the metallic matrix upon hydrogenation is smaller than that in the case of $LaNi_5$.[4,5,10]

The boundary between the α-solid solution and the region of the invariant equilibrium between the α- and β-phases in the *p-C-T* phase diagrams of the compounds studied in the 308—353 K temperature range is not sufficiently clear-cut (see Fig. 1). This border can be distinguished by taking the double logarithm of the Avraami—Erofeev equation; this method has been described in detail in previous publications.[7,8] Using this method, the concentration of hydrogen in the solid phase can be determined

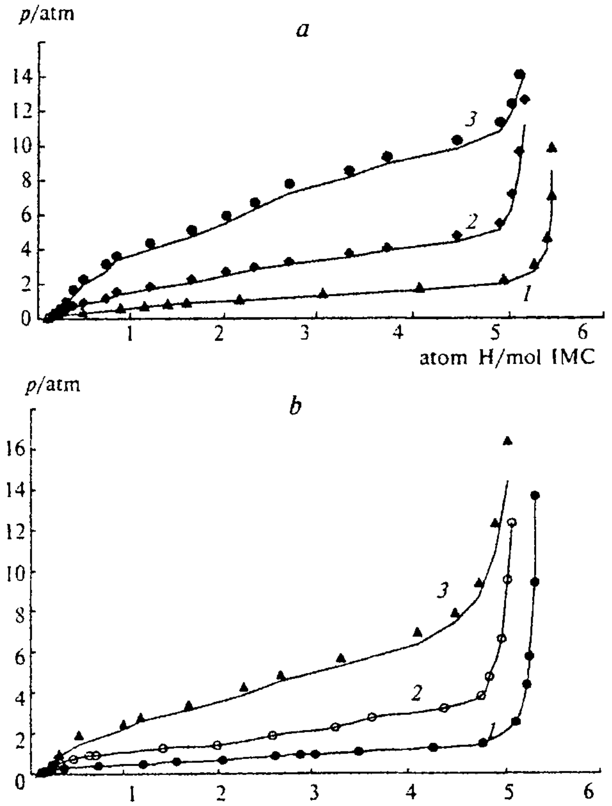

Fig. 1. Isotherms of hydrogen absorption in the $LaNi_{4.8}Sn_{0.2}—H_2$ (*a*) and $LaNi_{4.75}Al_{0.25}—H_2$ (*b*) systems at 308 (*1*), 328 (*2*), and 353 K (*3*).

Table 1. Effect of temperature on the equilibrium pressure and the content of hydrogen during absorption in the $LaNi_{4.75}Al_{0.25}—H_2$ and $LaNi_{4.8}Sn_{0.2}—H_2$ systems

T/K	$LaNi_{4.8}Sn_{0.2}$			$LaNi_{4.75}Al_{0.25}$	
	H/IMC	p_{abs}/p_{des}	p_{eq}/atm	H/IMC	p_{eq}/atm
308	5.2	1.1	1.4	5.1	1.2
328	4.9	1.2	2.7	4.7	2.0
353	4.6	1.5	7.7	4.5	4.9

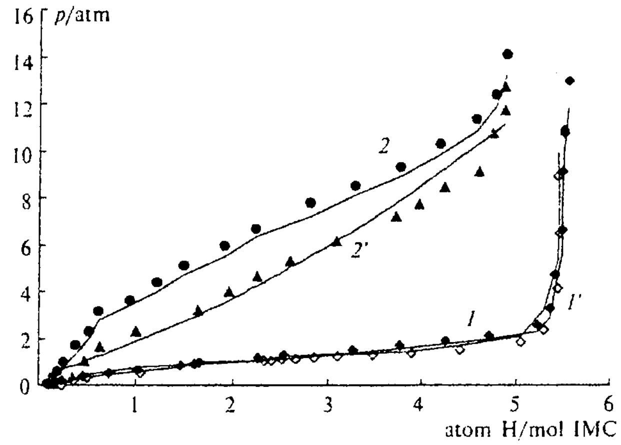

Fig. 2. Absorption—desorption curves in the $LaNi_{4.8}Sn_{0.2}—H_2$ system at 308 (*1* and *1'*) and 353 K (*2* and *2'*).

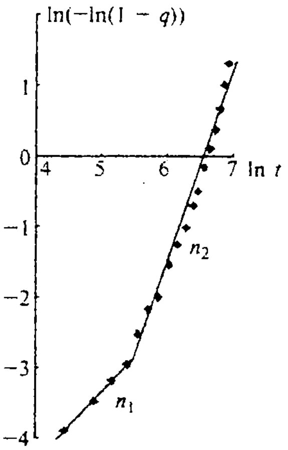

Fig. 3. Logarithmic dependence of the degree of hydrogenation of $LaNi_{4.8}Sn_{0.2}$ on the time of equilibration (T = 353 K).

with high reliability. At this concentration, the diffusion mechanism of hydrogenation, typical of the α-solid solution region, is replaced by a mechanism of "chemical reaction of nucleation and growth of the nuclei of a nascent phase," which describes the interaction of hydrogen with IMC in the region of two-phase equilibrium.

In the plot that shows the degree of hydrogenation of $LaNi_{4.8}Sn_{0.2}$ *vs* the time of equilibration, two straight sections can be clearly seen (Fig. 3). The calculated tangents n of the slope of each straight section on the kinetic curve confirm the assumption that the inflection point is matched by replacement of the rate-determining step of hydrogenation (Table 2). It is known that for $0.5 < n < 2.5$, the reaction rate is governed mainly by the diffusion of hydrogen inside the solid bulk, whereas for $n > 2.5$, the nucleation and the growth of nuclei of the β-hydride becomes the rate-determining step of the process.[11,12] As the temperature increases, the inflection point on the time dependence of the degree of hydrogenation shifts to lower concentrations of hydrogen in the solid phase (see Table 2). For instance, at 308 K, the diffusion step in the $LaNi_{4.75}Al_{0.25}—H_2$ system continues up to 3.1 H atom per mole of IMC, which corresponds to the plateau region in the phase diagram, while at 353 K, the content of hydrogen in the solid phase is only 0.6 H atom per mole of IMC (see Fig. 1). Similar results were obtained for the $LaNi_{4.8}Sn_{0.2}—H_2$ system (see Table 2). The effect of temperature on the mechanism found here is apparently due to the fact that at higher temperatures the "oxidation" of the metallic matrix by hydrogen proceeds at lower concentrations of the "oxidant": the $H^{\delta+}$ atoms,[13] and, therefore, the formation of the β-hydride starts at a lower degree of hydrogenation of the intermetallic compound.

The van't Hoff's equation

$$RT\ln p = \Delta H - T\Delta S \qquad (1)$$

was used to calculate the enthalpies (ΔH) and entropies (ΔS) of hydrogenation of the intermetallic compounds $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.8}Sn_{0.2}$ in the 308—353 K temperature range. The calculation was carried out by a statistical method of regression analysis using a linear approximation of Eq. (1) in $\ln p = f(1/T)$ coordinates. The pressure corresponding to the composition in the center of the assumed plateau region in the p-C-T diagram and given in Table 1 was taken to be the equilibrium pressure.

The calculated ΔH and ΔS values for hydrogenation in the 308—353 K temperature range are presented in Table 3. The data obtained in the study of $LaNi_{4.75}Al_{0.25}$

Table 2. Slope tangents (n_1, n_2) for the straight sections of kinetic curves and the hydrogen contents at the inflection points for $LaNi_{4.75}Al_{0.25}—H_2$ and $LaNi_{4.8}Sn_{0.2}—H_2$

T/K	$LaNi_{4.75}Al_{0.25}—H_2$			$LaNi_{4.8}Sn_{0.2}—H_2$		
	H/IMC	n_1	n_2	H/IMC	n_1	n_2
308	3.1	1.4±0.2	4.5±0.4	2.6	1.3±0.2	3.1±0.5
328	1.4	0.9±0.2	3.4±0.4	1.2	1.0±0.2	3.2±0.3
353	0.5	0.7±0.2	2.9±0.1	0.4	1.4±0.3	3.1±0.4

Table 3. Thermodynamic characteristics of the $LaNi_{4.75}Al_{0.25}—H_2$ and $LaNi_{4.8}Sn_{0.2}—H_2$ systems

T/K	$LaNi_{4.75}Al_{0.25}—H_2$		$LaNi_{4.8}Sn_{0.2}—H_2$	
	ΔH_{dif}	ΔS_{dif}	ΔH_{dif}	ΔS_{dif}
308	−33.7±2.6	−110.9±5.5	−33.5±2.4	−111.7±5.7
328	−35.9±2.2	−115.2±5.7	−33.4±2.5	−110.0±5.5
353	−36.5±1.9	−116.6±5.4	−33.5±2.4	−111.8±5.9
	(−31.4±2.6)	(−102.9±4.8)	(−35.2±2.4)	(−115.4±5.4)

Note. The enthalpies and entropies calculated from p-C-T diagrams are given in parentheses. The ΔH_{dif} values are expressed in kJ (mol of $H_2)^{-1}$; ΔS_{dif} is in J (mol of H_2 K$)^{-1}$.

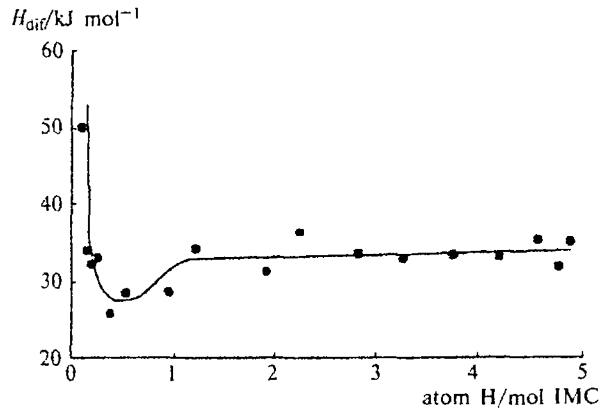

Fig. 4. Differential enthalpy of hydrogenation of $LaNi_{4.8}Sn_{0.2}$ *vs* the amount of hydrogen absorbed (T = 353 K).

are well correlated with the ΔH and ΔS values presented in previous publications[14—16] for compounds of the $LaNi_{5-y}Al_y$ type.

The enthalpies and entropies of hydrogenation found from the p-C-T diagrams depend on the ratio of H atoms to IMC moles that is normally matched by the equilibrium pressure in the center of the "apparent" plateau region. Therefore, in this study, we calculated the thermochemical characteristics for the hydrogenation of the compounds in question using the data of a calorimetric experiment, whose results seem to be more reliable and objective.

The curve for the dependence of the differential enthalpy (ΔH_{dif}) on the amount of hydrogen absorbed has a shape typical of hydrides derived from compounds of the $CaCu_5$ structural type (Fig. 4). It follows from this dependence that in the region of invariant (α + β) equilibrium, ΔH_{dif} is constant to within the experimental error and does not depend on the degree of hydrogenation of the IMC (see Fig. 4). The resulting values for the differential enthalpy in the region of coexistence of two phases were used to calculate the differential entropies (ΔS_{dif}) of hydrogenation from Eq. (1) (see Table 3). It should be noted that the thermodynamic characteristics of the hydrogenation process found from direct calorimetric measurements and those calculated from the p-C-T diagrams differ by 3—5%, which is within the error of the methods used.

The low equilibrium pressure of hydrogen in the plateau region, the relatively horizontal position of the two-phase region, and the relatively high absorption capacity (more than 5 H atoms per mole of IMC) make the compounds under study interesting as regards their potential use in nickel—metal hydride cells.

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Received November 11, 1998;
in revised form April 14, 1999