# General and Inorganic Chemistry

## Calorimetric investigation of the interaction in the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system

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The interaction of hydrogen with $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ was studied in a wide temperature range (308—393 K) using the technique of "calorimetric titration." The shape of the $p$—$C$—$T$ diagrams changes with temperature change. The values of enthalpy and entropy of hydrogenation of $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ were obtained for the first time by direct calorimetric investigations and $p$—$C$—$T$ measurements. The volume effects of the hydrogen absorption reaction are considered, and the $LaNi_{2.5}Co_{2.4}Mn_{0.1}H_{4.9}$ hydride is shown to retain the $CaCu_5$-type hexagonal structure.

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

Some intermetallic compounds (IMC) are materials with promising properties for preparation of metallohydride electrochemical current sources due to their ability to reversibly sorb hydrogen. The wide patent literature[1—3] is devoted to the multi-component $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ alloy; however, the data on the main thermodynamic parameters of reversible hydrogen absorption by this alloy are scarce.

In this work, we studied the interaction of the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ compound with hydrogen over the 308—393 K temperature range and plotted the $p$—$C$—$T$ diagram for the corresponding IMC—$H_2$ system.

### Experimental

The starting intermetallic compound $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ was prepared by alloying a blend of high-purity metals (La, 99.80%; Ni, 99.96%; and Co, 99.90%) in an electric-arc furnace with a permanent electrode under the pressure of purified argon. The required quantity of manganese was introduced in the form of Ni—Mn ligature.

The individual character of the alloy and related hydride phase was monitored by XRD and chemical analysis. The voltammetric analysis confirmed that the composition of the sample corresponded to the formula $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ presented. The X-ray phase analysis showed that the sample contained one phase with the hexagonal structure, whose parameters ($a$ = 5.049 Å, $c$ = 3.998 Å) were very close to those of the $LaNi_{2.5}Co_{2.5}$ alloy ($a$ = 5.048 Å, $c$ = 3.978 Å).[4]

Processes of hydrogen absorption and desorption were investigated using a Calve-type differential heat-conducting calorimeter. The calorimetric installation consisting of a DAK-1-1A calorimeter and a system for controlled admission of hydrogen has been described previously.[5] The procedure of calorimetric titration with hydrogen was used to determine the main thermochemical parameters of hydrogenation processes.[5—7]

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The amount of hydrogen consumed was determined from changes in the pressure of the system and calculated from the van der Waals equation. The hydrogen pressure was measured within the 0.1—2.5 MPa range by MO-16 and MO-25 calibrating manometers (accuracy class 0.4), and pressures below 0.1 MPa were measured by a VO calibrating vacuum gauge (accuracy class 0.4).

Hydrogen with a very low ($\leq 10^{-5}$ vol.%) concentration of impurities was used to study the hydrogenation process. An AMGV-06 portable calibrating instrument (Disperkhim) served as a hydrogen source. Prior to hydrogenation, samples were subjected to tenfold cycling in a hydrogen atmosphere at ~20 °C to obtain a fine powder with uniform granular size. Then, increasing temperature gradually, hydrogenation was carried out at 308, 328, 353, 373, and 393 K. The temperature in the thermostat was maintained constant with an accuracy of ±0.2 K. The corresponding results are presented in Table 1 and Fig. 1.

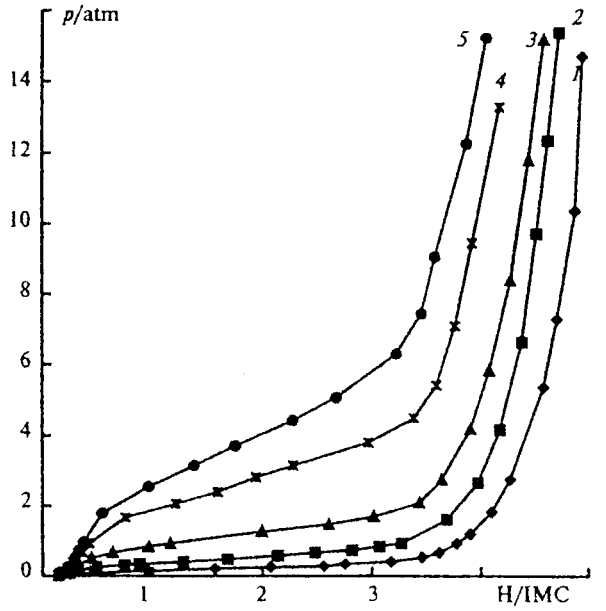


**Fig. 1.** Isotherms of hydrogen absorption in the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system: $T$/K = 308 (*1*), 328 (*2*), 353 (*3*), 373 (*4*), and 393 (*5*).

**Table 1.** Equilibrium pressures of absorption/desorption and hydrogen content per mole of IMC in the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system

| $T$/K | $p_{abs}$ | $p_{des}$ | $p_{abs}/p_{des}$ | H/IMC |
|---|---|---|---|---|
| | atm | | | |
| 308 | 0.25 | 0.23 | 1.10 | 4.90 |
| 328 | 0.50 | 0.45 | 1.10 | 4.70 |
| 353 | 1.20 | 1.10 | 1.10 | 4.68 |
| 373 | 2.50 | 2.00 | 1.25 | 4.42 |
| 393 | 4.20 | 3.00 | 1.40 | 4.06 |

## Results and Discussion

The thermodynamic parameters obtained for the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$-based hydride phase, dissociation pressure, and absorption capacity for hydrogen agree well with the data reported for $LaNi_{5-x}Co_x$ compounds with similar composition. However, this comparison is justifiable only in a narrow temperature range, since the studies[4,8—10] of hydrides of $LaNi_{5-x}Co_x$ alloys ($x$ = 2 to 3) were carried out, in the majority of cases, at 313 K. The absorption isotherms for the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ and $LaNi_{2.5}Co_{2.5}$ IMC[9,10] almost coincide at these temperatures: a low equilibrium pressure in the biphase region (0.30—0.35 atm), a small slope of the plateau increasing with temperature increase, and the absence of the second plateau, which is characteristic of cobalt-substituted compounds, are observed. Analysis of the isotherms in the $p$—$C$—$T$ diagram suggests that the absorption capacity of the alloy under study is lower than those of $LaNi_5$ or $LaNi_{4.7}Al_{0.3}$: 4.5—5.0 H atoms per mole of IMC were absorbed at 13—15 atm. Practically, the end of the plateau corresponds to the H/IMC value of ~3.8 at 308 K and ~3.5 at 353 K.

It is rather difficult to determine boundaries of the α-solid solution and regions of co-existence of the α- and β-phases in the 308—353 K temperature range on the phase diagram of interaction of $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ with hydrogen. This possibility, as in the case of the α+β→β-transition, appears at higher temperatures only. The change in the shape of isotherms with temperature increase indicates a change in the character of interaction of the intermetallide with hydrogen. It is of interest that the hysteresis of equilibrium pressures of absorption and desorption in the region of the α↔β-transition, which is observed for the majority of compounds of the structural $CaCu_5$-type, is virtually absent at 308 K and commences only at temperatures higher than 353 K.

When the temperature increases, the hysteresis loop is broadened (Fig. 2, see Table 1). The reduction of the hysteresis effect at low temperatures for cobalt-substituted IMC is usually related[11,12] to the fact that during hydrogenation of $LaCo_5$ the alloy volume increases by 11—13% only, whereas the $\Delta V$ value is 25—27% for $LaNi_5$.

The low equilibrium H pressure in the region of the plateau allowed us to study the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system at $T$ = 308 K by XRD. The interest in studying crystallographic changes induced by absorption is associated, in addition, with the possibility to determine boundaries of the α-phase, which can be hardly identified from the state diagram. To stabilize the composition, the method of "poisoning" the hydride phase by carbon monoxide[13] was used. The $LaNi_{2.5}Co_{2.4}Mn_{0.1}H_{4.9}$ hydride retains the hexagonal $CaCu_5$ structure in line with the published data.[9,10,14] The X-ray phase analysis shows that the $LaNi_{2.5}Co_{2.4}Mn_{0.1}H_{0.9}$ sample is biphasic. This indicates that the extension of the α-region is small, and the main part of the horizontal section on

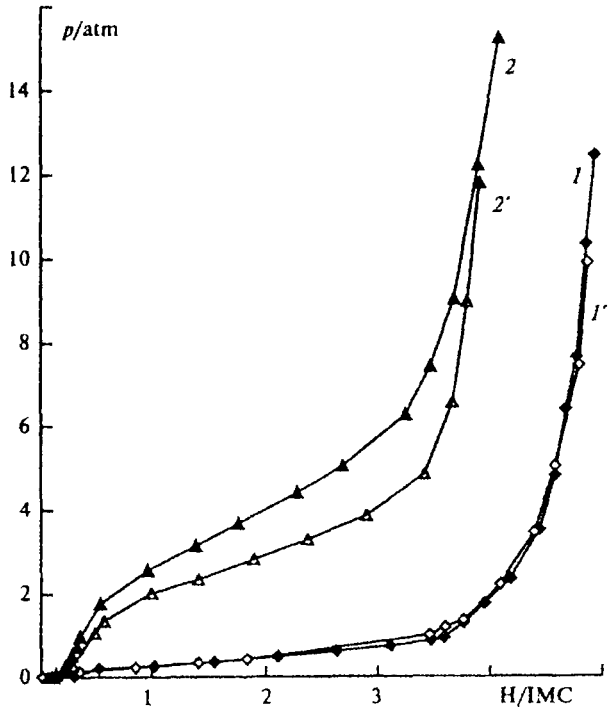


**Fig. 2.** Temperature dependence of the hysteresis value at equilibrium pressure of absorption/desorption in the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system: *1* and *2*, absorption; *1'* and *2'*, desorption; $T$/K = 328 (*1*, *1'*); 393 (*2*, *2'*).

the phase diagram falls on the biphase α+β-region, and that is significant for the determination of differential enthalpies and entropies of hydrogenation by the calorimetric method. A change in the cell volume with an increase in the amount of hydrogen in the matrix occurs almost only in the basis plane similar to $LaNi_{3.5}Cu_{1.5}$:[13] the $c_0$ parameter changes insignificantly (3%), and the main contribution to the change in volume comes from by the increase in the $a_0$ parameter (6.6%). For $LaNi_{2.5}Co_{2.4}Mn_{0.1}$, the increase in the alloy volume during the formation of β-hydride from the α-solid solution is 11—13%, and the total extension of the cell is 16.5%.

The values of enthalpies and entropies of hydrogenation were obtained from both $p$—$C$—$T$ measurements using van't Hoff's equation and calorimetric studies.

The temperature dependence of the equilibrium pressure is presented in Fig. 3. The pressure corresponding to the middle of the biphasic region in the $p$—$C$—$T$ diagram was used as the equilibrium value. After the results were processed by the equation

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

the changes in enthalpy ($\Delta H$) and entropy ($\Delta S$) of hydrogenation in the 308—393 K temperature range were calculated. The values obtained are presented in Table 2.

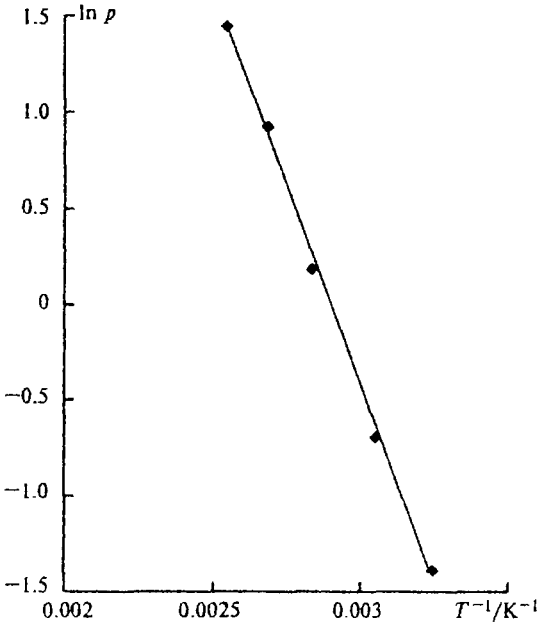


**Fig. 3.** Temperature dependence of the equilibrium pressure in the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system.

The calorimetric method was used for experimental determination of the differential enthalpies of hydrogenation ($\Delta H_{dif}$) in different regions of the phase diagram of $LaNi_{2.5}Co_{2.4}Mn_{0.1}H_x$. The curve of the differential enthalpies as functions of the amount of absorbed hydrogen has the pattern characteristic of hydrides of compounds of the structural $CaCu_5$-type. The $\Delta H_{dif}$ value in the region of invariant (α+β)-equilibrium is unchanged within the experimental error and independent of the degree of hydrogenation of the sample. Using the measured $\Delta H_{dif}$ values of the α→β transition and equilibrium hydrogen pressure for the composition corresponding to the middle of the plateau, we calculated changes in the differential entropy of hydrogenation ($\Delta S_{dif}$) at each temperature (see Eq. (1)). The $\Delta H_{dif}$ and $\Delta S_{dif}$ values found are presented in Table 2.

The $\Delta H$ and $\Delta S$ values obtained directly from the calorimetric measurements are independent of the choice

**Table 2.** Thermodynamic parameters of the $LaNi_{2.5}Co_{2.4}Mn_{0.1}$—$H_2$ system

| $T$/K | $\Delta H_{dif}$/kJ (mol $H_2$)$^{-1}$ | $\Delta S_{dif}$/J (mol $H_2$ K)$^{-1}$ |
|---|---|---|
| 308 | −37.4±1.7 | −109.9±5.6 |
| 328 | −38.0±1.5 | −110.2±4.6 |
| 353 | −39.6±1.6 | −113.7±4.6 |
| 373 | −39.7±1.6 | −114.0±4.3 |
| 393 | −40.6±1.6 | −115.2±4.2 |
| 308—353 | −35.3* | −102.8* |

* Calculated from the results of $p$—$C$—$T$ measurements.

of the $H/LaNi_{2.5}Co_{2.4}Mn_{0.1}$ ratio determining the equilibrium pressure in the middle of the plateau and, hence, more reliable. Therefore, it is possible to calculate the enthalpy and entropy values in the whole concentration region rather than only in the biphasic region where the α-phase reacts with hydrogen to form β-hydride. The $\Delta H$ and $\Delta S$ values measured by the calorimetric method and obtained from the $p-C-T$ diagrams coincide with the 95% confidence probability.

Because of low equilibrium hydrogen pressure on the plateau, the relative horizontal character of the plateau, and the almost complete absence of hysteresis in the 308—353 K temperature region, $LaNi_{2.5}Co_{2.4}Mn_{0.1}$ seems to be one of the most promising compounds for Ni-hydride batteries. However, since the absorption capacity of this alloy does not exceed 60—70% of the capacity of $LaNi_5$, the work on the development of an alloy with better properties should be continued.

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