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Calorimetric investigation of hydrogen interaction with intermetallic compounds at pressure up to 2000 atm

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Abstract

Investigations of the AB_5 and AB_2-type systems ($Ce_{0.8}La_{0.2}Ni_5$–H_2 and $Ti_{0.9}Zr_{0.1}Cr_{1.0}Mn_{1.0}$) using calorimetric measurements for hydride formation and decomposition and simultaneous measurements of P–C isotherms in the temperature range 333–433 K have been made. The combined installation includes a heat-conducting Tian–Calvet type calorimeter coupled with high gaseous pressure apparatus which allows measurement of the heat effects up to 2500 atm and demonstrates the possibilities of calorimetry and the choice of the object to be measured.

Keywords: Intermetallic compounds; Hydrogen interactions; Calorimetry

1. Introduction

With the large hydrogen capacity and high equilibrium pressure available in $CeNi_5$-based intermetallic compounds, they take a particular place among hydride-forming intermetallic systems being perspective objects of study for their application in heat pumps and thermosorption compressors. The $CeNi_5$–H_2, $Ce_{0.8}La_{0.2}Ni_5$–H_2, $Ce_{0.8}La_{0.2}Ni_{4.7}Cu_{0.3}$–$H_2$ systems were studied in detail in the temperature range 273–343 K [1] by means of high gaseous pressure technique [2]. P–C isotherms were measured in this temperature range and were used for calculation of the thermodynamic functions $-\Delta H_{\mathrm{abs}}$, ΔH_{des} [1]. However, the direct calorimetric measurements were not carried out for these systems in view of the high equilibrium pressures in these systems requiring a combination of the calorimetric apparatus with the high gaseous pressure technique for these calorimetric measurements.

The results of a direct calorimetric study of the $Ti_{0.9}Zr_{0.1}Cr_{1.0}Mn_{1.0}$–$H_2$ and $Ce_{0.8}La_{0.2}Ni_5$–H_2 systems using the combined experimental apparatus are presented for the first time in this work.

2. Experimental details

Investigation of the $Ce_{0.8}La_{0.2}Ni_5$–H_2 system consisted of calorimetric measurements of hydride formation and decomposition and simultaneous measurements of P–C isotherms in the temperature range 333–433 K. The experimental installation includes a heat-conducting calorimeter of Tian–Calvet type coupled with a high gaseous pressure apparatus.

The differential enthalpies of absorption and desorption $|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|$ were measured in the $Ce_{0.8}La_{0.2}Ni_5$–H_2 system with using a method of calorimetric titration, with average increment of hydrogen, being 5–6×10^{-4} mol.

The pressure in the working cell of the calorimeter reached 2000 atm and the experimental apparatus used for creation of that pressure includes a vacuum system, a system for hydrogen purification and preliminary compression using a metal hydride accumulator, a system for high pressure creation, a ‘pressure transmission medium-hydrogen’ separator with a shift gauge and a cell containing the sample placed in calorimeter. The silicon oil which provides the transmission of pressure to hydrogen was compressed to 250 MPa by a UNGR hydraulic pump.

The high pressure experimental apparatus used in our work has the following parameters: working pressure up to 250 MPa, working temperature: 77–673 K, separator gas volume: 90.34 cm^3, maximum hydrogen compression degree: 30, sample mass: 1–1.5 g, measurement accuracies of pressure: 0.1–0.4%, temperature: 0.2–1 K, volume: 0.02 cm^3, hydrogen content in hydrides: 5×10^{-3} mass%. The hydrogen accumulator, based on a Ti–Fe–V alloy, accomplishes purification of hydrogen from 99.99 to 99.9999%. A more detailed description of the high pressure experimental apparatus can be found in Ref. [2].

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The composition determination of the hydride phases formed was carried out volumetrically with the help of a computer code using a high pressure hydrogen state equation. The state equation was chosen on the basis of the literature and our own experimental data on hydrogen compressibility along with a number of theoretical P–V–T expressions [3,4]. The accomplished analysis permitted us to determine that in the temperature range 100–1000 K and pressure range 0–300 MPa, the maximum calculation accuracy (0.1–0.5%) is provided by using the modified van der Waal's equation proposed in Ref. [5]:

$$(P + a(p)/V^2)[V - b(p)] = RT \tag{1}$$

where

$$a(p) = \exp\{a_1 + a_2 \ln(p) - \exp[a_3 - a_4 \ln(p)]\} \tag{2}$$

$$b(p) = \sum b_i \ln(p) \tag{3}$$

$$\alpha(T) = \alpha_0 + \alpha_1 T + \alpha_2 T^2 \tag{4}$$

Values of a_i, b_i and α_i are cited in Ref. [5].

The accuracy of the calculations depends considerably on taking into account the sample expansion during its hydrogen saturation. Preliminary calculations showed at 200 MPa, the error caused by an indefinite sample volume could reach 10%. In order to minimise this error, we used the assumption (for the compounds studied in this work) of a linear dependence of the sample volume on hydrogen content. In addition, we checked the calculated values against our own X-ray experimental data.

The heat effect corresponding to enthalpy of reaction was calculated using equation:

$$Q = S*A/\Delta n*10^{-6} \tag{5}$$

where A is sensitivity of device (mJ mm^{-2}), S is the area under the heat flow curve (mm^2), Δn is quantity of hydrogen absorbed (moles)

The calorimetric measurement error was taken as $\sigma^2 = \Sigma\, \Delta^2[n(n-1)]^{-1}$, where Δ is the measurement deviation from the mean value and n is the number of measurements.

3. Results and discussion

The differential molar enthalpies of absorption and desorption $|\Delta H_{\text{diff}}^{\text{abs(des)}}|$ have been determined from the heat effects of reaction:

$$Ce_{0.8}La_{0.2}Ni_5H_x + Y/2H_2 \Leftrightarrow Ce_{0.8}La_{0.2}Ni_5H_{x+y} \tag{6}$$

The $Ce_{0.8}La_{0.2}Ni_5$–H_2 system was investigated in the temperature range of 333–433 K and the P_e–X and $|\Delta H_{\text{diff}}^{\text{abs(des)}}|$–$X$ dependencies (P_e = hydrogen equilibrium pressure, $X = H/Ce_{0.8}La_{0.2}Ni_5$) were obtained (Table 1; Figs. 1a,b and 2a,b). As can be seen on the curves of P_e–X, three regions can be selected: the α-solution, the plateau corresponding to reversible reaction:

$$\alpha \text{ sol.} + H_2 \Leftrightarrow \beta\text{-hydride} \tag{7}$$

and the β-hydride. With the experimental temperature increased from 333 to 433 K, the boundaries, in which the hydride phases coexist, change noticeably. Specifically the α-solution, upper limit increases significantly with increasing temperature. At the same time the values of $\Delta H_{\text{diff}}^{\text{abs(des)}}$ decreased slightly in this temperature range.

One should pay a special attention to one of the obtained results, namely the difference in values of absorption and desorption enthalpies at constant temperature:

$$|\Delta H_{\text{diff}}^{\text{abs}}| < \Delta H_{\text{diff}}^{\text{des}}$$

That is the calorimetric measures enthalpy changes directly and there can be measurable differences in the enthalpy changes on the two plateau of a hysteresis loop owing to variations in the end of a phase compositions. This result is in agreement with information given in Ref. [6], where the conditions of the two-phase coexistence in metal–hydride type systems are examined in application to calorimetry.

In contrast with calorimetry [7], the temperature variation of plateau pressures or end phase compositions (P–C–T methods) gives enthalpies, which directly depend on the hysteresis value, because van′t Hoff plots are directly affected by the dissipation energies. Strictly speaking accurate results from van't Hoff plots are limited to single-phase regions, or when the value of hysteresis is negligible.

Table 1
The thermodynamic parameters of the $Ce_{0.8}La_{0.2}Ni_5$–H_2 system

T (K)	ΔH_{diff} (Abs)±σ [kJ mol^{-1} H_2]	ΔH_{diff} (Des)±σ [kJ mol^{-1} H_2]	P_e (atm)		Ref.
			Abs	Des	
333	20.8±0.9	23.1±0.9	208	74	Present work
393	18.8±0.9	21.5±1.2	450	240	Present work
	$-\Delta H_{\text{abs}}$ [kJ mol^{-1} H_2]	$-\Delta H_{\text{des}}$ [kJ mol^{-1} H_2]			
0–343	18.9±0.6	23.8±0.3			[1]

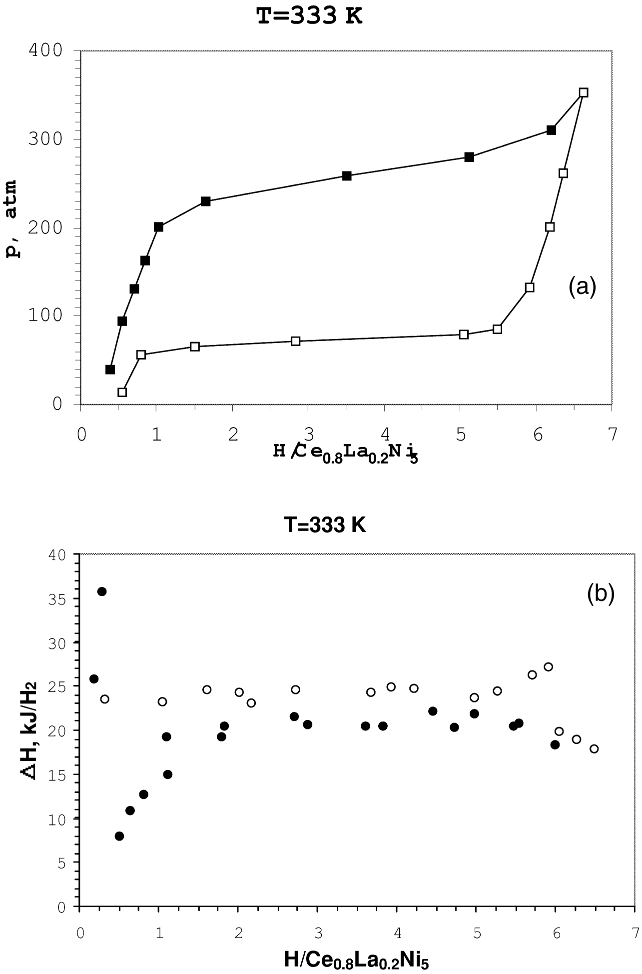

Fig. 1. Pressure–composition isotherms for the $Ce_{0.8}La_{0.2}Ni_5$–H_2 system (a) and $|\Delta H_{\mathrm{diff}}|$ as function of hydrogen contents (b) at 333 K. Closed symbols: absorption, open symbols: desorption.

Nevertheless, the results of measurements of heat effects by direct calorimetric method and by P–C–T method, presented in Table 1 are in satisfactory agreement.

It must be born in mind that the measurements had to be carried out in temperature range of 333–433 K, however, at 433 K an unexpected result was obtained. The absorption capacity and character of isotherm changed dramatically indicating disproportionation of intermetallic compound.

It was anticipated that the Laves phase structure compounds are stable under these conditions and in view of this, $Ti_{0.9}Zr_{0.1}Mn_{1.0}Cr_{1.0}$ was chosen for study. The $Ti_{0.9}Zr_{0.1}Mn_{1.0}Cr_{1.0}$–$H_2$ system was investigated in the temperature range of 313–393 K and the dependence of absorbed and desorbed hydrogen from hydrogen equilibrium pressure (X–P_e) and $|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|$–$X$ dependence was measured simultaneously. The experimental data are presented in Figs. 3 and 4.

The obtained dependencies are typical for the processes in the sense that three regions corresponding to three

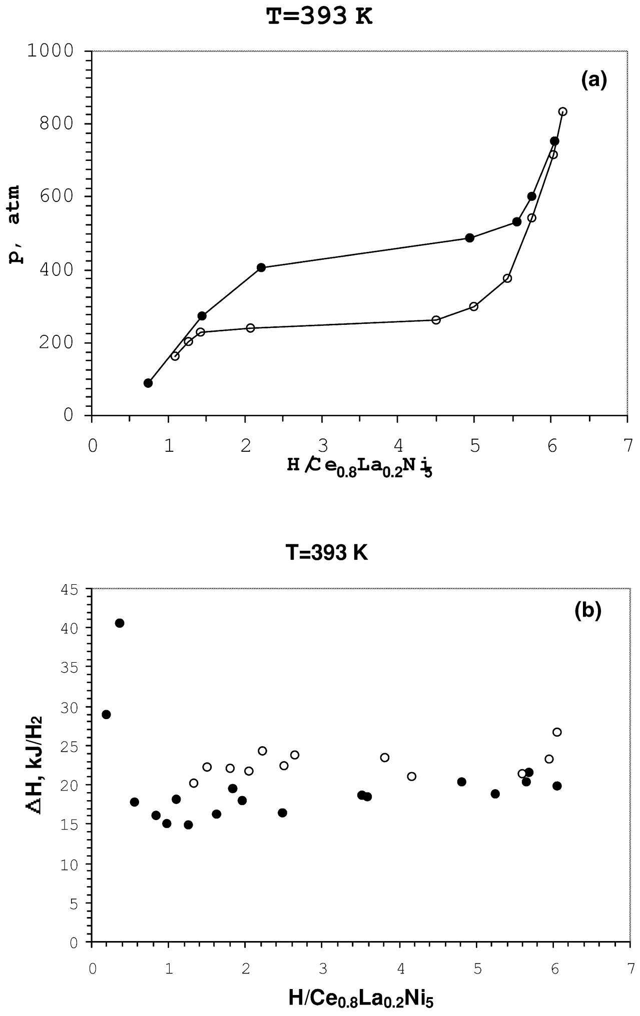

Fig. 2. Pressure–composition isotherms for the $Ce_{0.8}La_{0.2}Ni_5$–H_2 system (a) and $|\Delta H_{\mathrm{diff}}|$ as function of hydrogen contents (b) at 393 K. Closed symbols: absorption, open symbols: desorption.

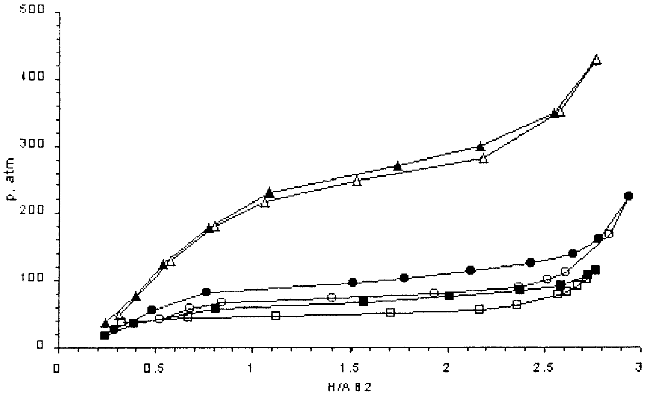

Fig. 3. Pressure–composition isotherms for the $Ti_{0.9}Zr_{0.1}Cr_{1.0}Mn_{1.0}$–$H_2$. Closed symbols: absorption, open symbols: desorption. Squares: 313 K, circles: 333 K, triangles: 393 K.

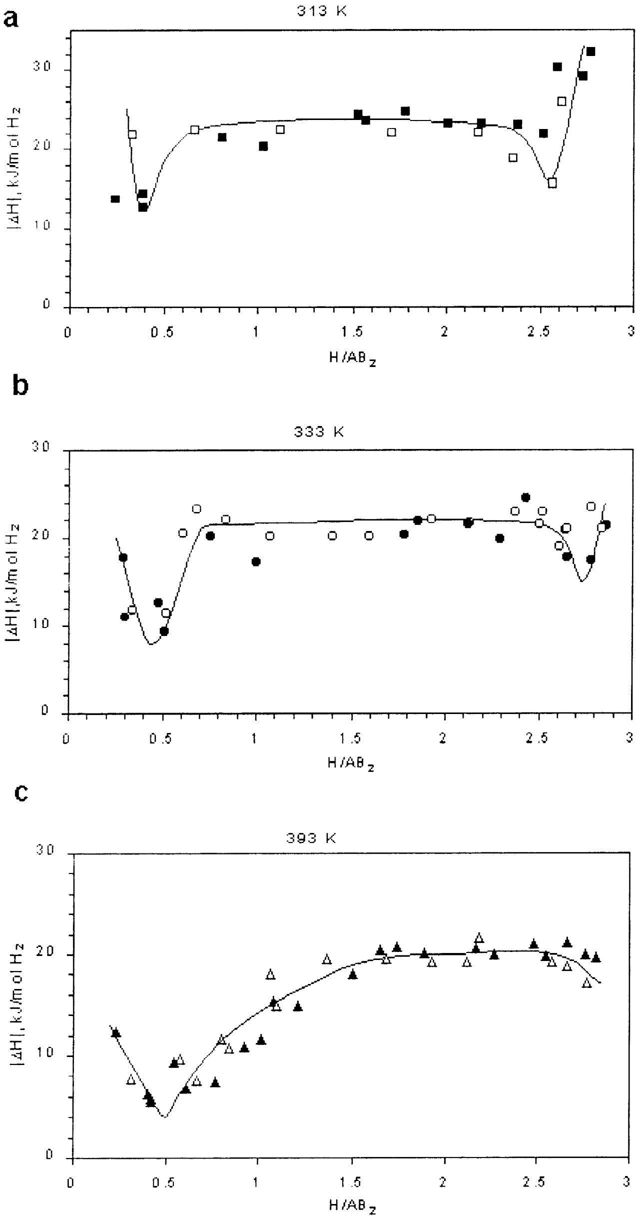

Fig. 4. Differential molar enthalpy $|\Delta H_{\mathrm{diff}}|$ as function of hydrogen contents in the 313–293 K temperature region. Closed symbols: absorption, open symbols: desorption.

stages of processes can be selected on the obtained curves: the α-solution region, the 'plateau' region, corresponding to reversible reaction (7) and β-hydride region. It holds for curves describing the change of heat effect at the absorption and desorption and to curves of P_e–X.

At the change of the experimental temperature the existence boundaries of different hydride phases change too. This behavioral pattern particularly shows itself on sloping regions corresponding to α-phase, and here this dependence has a complex character owing to chemosorption of hydrogen atoms on the IMC surface that precedes α-solution formation (concentration range of $0 \leq x \leq 0.5$). The different molar enthalpies of absorption (desorption) have been determined from the heat effects of reaction:

$$\mathrm{Ti}_{0.9}\mathrm{Zr}_{0.1}\mathrm{Cr}_{1.0}\mathrm{Mn}_{1.0} + y/2\mathrm{H}_2 \leftrightarrow \mathrm{Ti}_{0.9}\mathrm{Zr}_{0.1}\mathrm{Cr}_{1.0}\mathrm{Mn}_{1.0}\mathrm{H}_{x+y}$$

As have been shown earlier, direct calorimetric measurements were not carried out for systems with so high equilibrium pressures, however, taking into consideration a large number of investigations of Ti–Mn–H_2 systems it can be expected that two hydride phases form also for the $\mathrm{Ti}_{0.9}\mathrm{Zr}_{0.1}\mathrm{Cr}_{1.0}\mathrm{Mn}_{1.0}$–$H_2$ system. However, as can be seen from Figs. 3 and 4, there are no reasons to consider such kind of hydride formation in this case even at the lowest experimental temperature of 313 K. All of three calorimetric curves have only one 'plateau' and differential molar enthalpies of absorption and desorption corresponding to different experimental temperatures are:

$$|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|_{313\ \mathrm{K}} = 22.2\ (23.1)\ \mathrm{kJ\ mol^{-1}\ H_2}$$

$$|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|_{333\ \mathrm{K}} = 21.1\ (21.8)\ \mathrm{kJ\ mol^{-1}\ H_2}$$

$$|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|_{393\ \mathrm{K}} = 19.3\ (20.0)\ \mathrm{kJ\ mol^{-1}\ H_2}$$

that is to say the decreasing differential molar enthalpies occur with increasing experimental temperature. While the existence of the hysteresis loop on the P_e–X curves of AB_5-type compound correlates with the difference in values of absorption and desorption enthalpies at the constant temperature, the slight hysteresis loop for curves P_e–X corresponding to endo and exothermal processes in the $\mathrm{Ti}_{0.9}\mathrm{Zr}_{0.1}\mathrm{Cr}_{1.0}\mathrm{Mn}_{1.0}$–$H_2$ system is leveled for curves describing $|\Delta H_{\mathrm{diff}}^{\mathrm{abs(des)}}|$–$X$ dependencies, and difference in mean values of $|\Delta H_{\mathrm{diff}}^{\mathrm{abs}}|$ and $|\Delta H_{\mathrm{diff}}^{\mathrm{des}}|$ is in range of measurement error.

It is known that calorimetric studies of hydrogen interaction with IMC is a most precise determination of the reaction enthalpy for a wide temperature range. The combined installation presented in our work, allows to measure the heat effects in the pressure range up to 2500 atm and essentially extends the possibilities of calorimetry and choice of the object to be measured.

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