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STUDIES OF SORPTION-DESORPTION PROCESSES IN THE $Ce_xLa_{1-x}Ni_5$-H_2 SYSTEM BY DSC

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ABSTRACT

The dependence of the integral enthalpy of hydrogenation (or dehydrogenation) of the intermetallic compounds (IMCs) $Ce_xLa_{1-x}Ni_5$ ($x = 0$, 0.05, 0.1 or 0.3) on pressure in the range 0.5–6 MPa was studied by the method of differential scanning calorimetry. It has been shown that at $x = 0$ and $x = 0.05$ the absorption (or desorption) proceeds via the formation of a stable intermediate hydride phase.

INTRODUCTION

The use of intermetallic compounds (IMCs) based on $LaNi_5$ as sorbents for hydride accumulators and hydride thermosorption compressors [1,2] leads to the necessity of studying the physico-chemical properties of these compounds including the thermal characteristics of the hydrogen sorption–desorption.

There is a considerable number of published studies on the thermodynamics of the interaction between hydrogen and $LaNi_5$ and some of its derivatives [1,3–18]. The data are generally obtained from P–c–T diagrams constructed according to the well-known Siverts method, as well as from the calculations based on Miedema's equation [15]. Results of direct calorimetric experiments have also been published [5–7,13,18].

The purpose of this research is to study the influence of pressure on the value of the integral enthalpy of hydrogenation–dehydrogenation in the IMC series having a varying cerium content. This would make it possible for the first time to obtain systematic data about the influence of an alloying addition and external parameters on the thermodynamics of the H_2–IMC system.

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Because calorimetry is a direct method, the errors typical of the usual enthalpy calculations from P–c–T data are not present [15]. In this case, the use of an instrument working in the differential mode can exclude the main experimental errors which are connected with a number of problems, such as the thermal effect of gas introduction into the cell, the pressure changes during the experiment, etc. [6].

EXPERIMENTAL

The hydrogen sorption–desorption experiments were carried out in a pressure differential scanning calorimeter (system DSC 910) of a TA 990 instrument (DuPont, U.S.A.). A pre-used IMC was activated by heating under 5 MPa pressure, followed by 2- to 3-fold cycling. The sample mass was about 100 mg. Heating rates of about 0.5 K min^{-1}, 1 K min^{-1}, 2 K min^{-1}, 5 K min^{-1}, 10 K min^{-1} and 20 K min^{-1} were used at a hydrogen pressure of 0.5–6 MPa.

The hydrogen pressure was maintained with a precision of better than $\pm 1\%$. Hydrogen was purified by diffusion through membranes of a palladium alloy which ensure a purity of better than 99.999 99%.

The samples of the intermetallic compounds were prepared by melting together stoichiometric quantities of high-purity metals in a vacuum furnace with radiation heating. The homogeneity of the samples was confirmed by X-ray diffraction, and the stoichiometry of the composition was checked by chemical analysis. Each sample containing cerium was alloyed with the same small quantity of aluminium. The compositions of the samples used corresponded to $LaNi_5$, $Ce_{0.05}La_{0.95}Ni_{4.98}Al_{0.02}$, $Ce_{0.1}La_{0.9}Ni_{4.98}Al_{0.02}$ and $Ce_{0.3}La_{0.7}Ni_{4.98}Al_{0.02}$.

RESULTS AND DISCUSSION

Typical DSC curves of hydrogen absorption and desorption by $LaNi_5$ are presented in Fig. 1 using a common scale and with the coordinates of change in thermal flux dQ/dT versus temperature T (K). The hydrogen desorption is followed by an endo effect with a clear peak-splitting. In this case, the shape of the curves is unchanged when the heating rate changes from 0.5 K min^{-1} to 20 K min^{-1}. An increase in the heating rate causes the temperature range of the process to shift towards a more high-temperature zone, but the temperature interval between the peak minima remains constant and is about 8–10° for a hydrogen pressure of 30 MPa (see Fig. 2).

The hydrogen absorption is accompanied by an exo effect, but the peak splitting of the DSC curve can only be observed at a heating rate of 0.5 K min^{-1}.

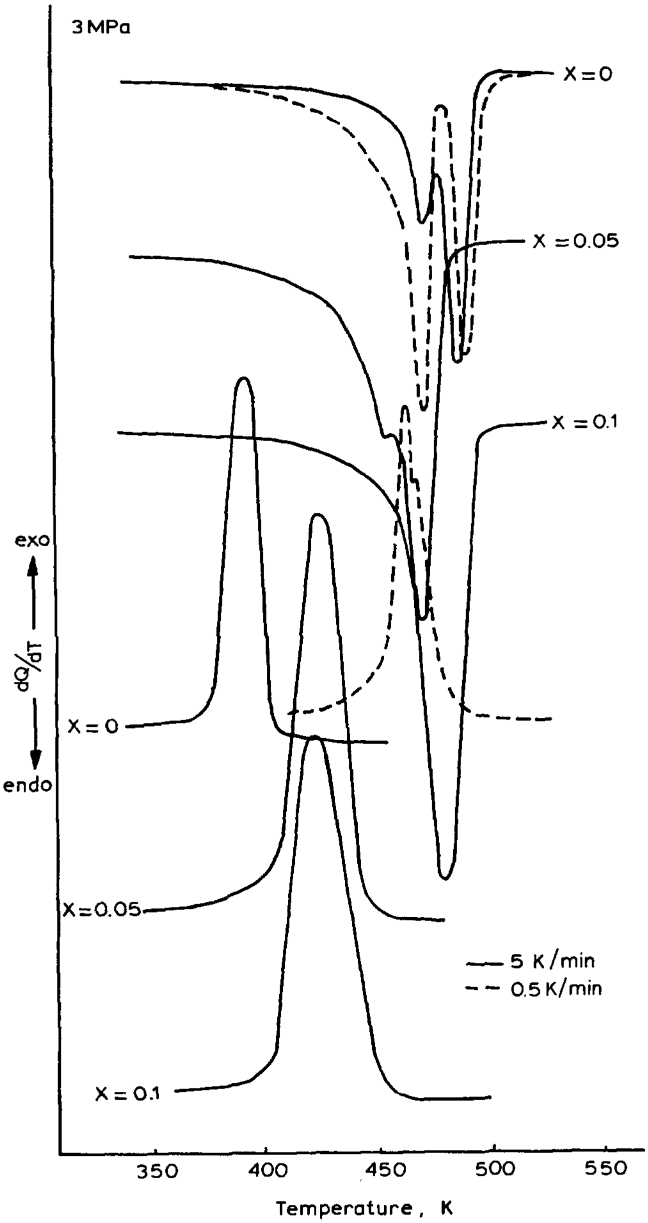

Fig. 1. Selected DSC curves for the $Ce_xLa_{1-x}Ni_5-H_2$ system.

During the hydrogen desorption, the temperature of the maximum deviation of the DSC curve decreases by 10 K when the heating rate changes from 20 K min^{-1} to 0.5 K min^{-1}; in the absorption this temperature decrease is 30°. The hysteresis of the maximum deviation temperatures in absorption and desorption is 8 K (at a heating rate of 0.5 K min^{-1} and a hydrogen pressure of 3 MPa).

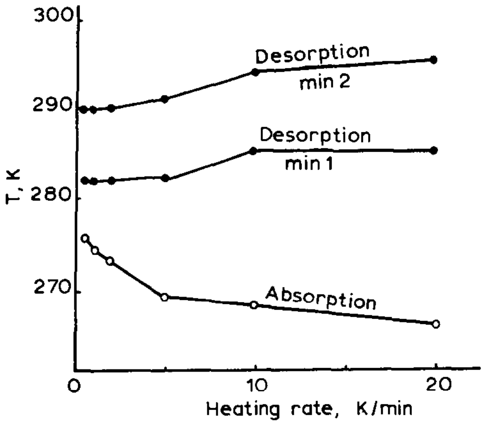

Fig. 2. Dependence of the maximum deviation temperature of the DSC curves on the heating rate in the $LaNi_5$–H_2 system ($P = 3.0$ MPa).

The data obtained confirm the proximity of the hydrogen desorption to equilibrium and show that the peak splitting of the DSC curve is not connected with the kinetic characteristics of the IMC hydride decomposition.

An increase in the cycling pressure increases the splitting effect of the endo peaks, and the processes shift towards a higher temperature zone which corresponds to the data of the P–c–T diagrams.

The results of the measurements of the integral enthalpy are given in Fig. 3 with the coordinates ΔH (kJ mol^{-1} IMC) and pressure P (Pa), for $LaNi_5$ as an example.

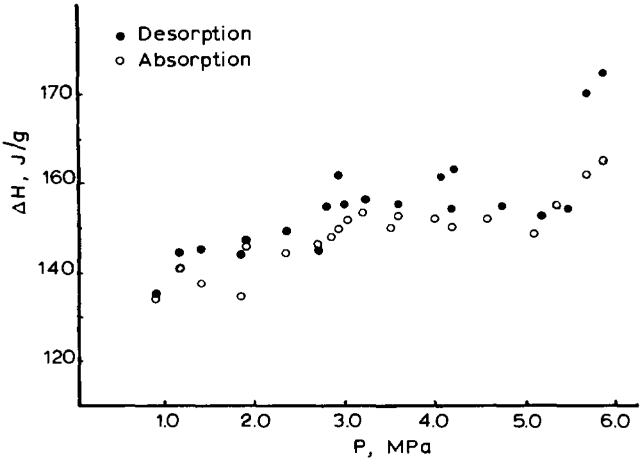

Fig. 3. Integral hydrogenation–dehydrogenation enthalpy for the $LaNi_5$–H_2 system at different hydrogen pressures.

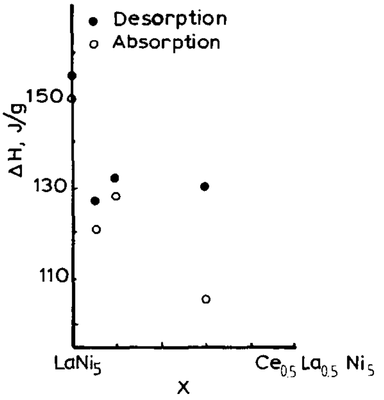

Fig. 4. Dependence of integral enthalpy on cerium content at $P = 3.0$ MPa.

According to the data obtained $\Delta H_{abs} < |\Delta H_{des}|$, which is connected with the hysteresis character of the hydrogen sorption by the IMC and agrees with published data [3,6]. The clearly observed hysteresis of temperature intervals and integral enthalpies is a consequence of the pressure hysteresis [3].

The pressure dependence of the integral enthalpies for hydrogen sorption in other IMCs is just the same. When the pressure goes up to 6 MPa it increases by 17% for $Ce_{0.05}La_{0.95}Ni_{4.98}Al_{0.02}$, by 27% for $Ce_{0.1}La_{0.9}Ni_{4.98}Al_{0.02}$ and by 60% for $Ce_{0.3}La_{0.7}Ni_{4.98}Al_{0.02}$ (in the last case, in the range 2–4 MPa).

Figure 1 also shows the change in the character of the DSC curve when cerium is partially substituted for lanthanium: at $x = 0.05$ only, a weak splitting of the desorption peaks remains; but when the cerium content increases, a full confluence of the peaks takes place. The increase in cerium content causes a decrease in the temperature of the maximum deviation of the DSC curve at constant pressure, e.g. $P = 3$ MPa and $x = 0$ conforms to $T_{abs} = 371$ K; $P = 3$ MPa and $x = 0.3$ conforms to $T_{abs} = 322$ K. It is noteworthy that the $|\Delta H|$ decreases at the same time (Fig. 4).

According to the available data [14] from P–c–T measurements, ΔH_{des} ($CeNi_5$–H_2) = 14.1 kJ mol^{-1} H_2 and ΔH_{des} ($LaNi_5$–H_2) = 31.9 kJ mol^{-1} H_2.

In our research, for the system $LaNi_5$–H_2, $d(\Delta H)/dx \approx 25$ kJ mol^{-1} H_2 in the studied range for absorption of 6 mol H_2, which is considerably less than in ref. 14.

In our opinion, such a divergence is caused by the shortcomings in the method of calculating ΔH from P–c–T data as mentioned above. To support this, one can cite the considerable fluctuations in the calculated ΔS_{des} values, 80–109 J K^{-1} mol^{-1} H_2, obtained in ref. 14 by processing the P–c–T diagrams for similar systems which differed in the alloying addition content.

It is also of interest to note the irregular dependence of ΔH on the cerium content, with a marked anomaly at $x = 0.05$. This anomaly might be explained by the simultaneous coexistence of small quantities of cerium and aluminium additions, but such an explanation is hardly exhaustive.

The influence of cerium on the DSC curves emphasises once again the non-kinetic nature of splitting the DSC peaks in $LaNi_5$–H_2. The sorption–desorption in this system probably proceeds through the formation of an intermediate hydride phase of composition $LaNi_5H_{3.4}$. The appearance of such a phase has been noticed before [19,20]. In ref. 13, in a calorimetric experiment, the authors observed a splitting of the sorption–desorption peak in the $LaNi_5$–H_2 system, but did not suggest the cause of this effect. The results of our study suggest that the peak splitting in the DSC curve is caused by the formation of an intermediate hydride phase; the replacement of some of the lanthanium by cerium, whose metal radius is 2.8% larger, causes a decrease in the stability of this intermediate phase and its eventual disappearance.

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REFERENCES

1 J.C. Archard and A. Percheron-Guegan, Entropie, 20 (1984) 43.
2 V.V. Solovey, Izv. Vuzov S.S.S.R., Ser. Energ., (1984) 57.
3 T.B. Flanagan, Metal Hydrides, Proc. NATO Adv. Study Inst., Rhodes, (1981) 361.
4 T.B. Flanagan, C.A. Wulff and B.S. Bowerman, J. Solid State Chem., 34 (1980) 251.
5 R.P. Wemple and C.J. Northrup, Thermochim. Acta, 12 (1975) 39.
6 M.L. Post, J.J. Murray and J.B. Taylor, Int. J. Hydrogen Energy, 9 (1984) 137.
7 J.J. Murray, M.L. Post and J.B. Taylor, Metal Hydrogen Syst., Proc. Int. Symp., Oxford, 1983, p. 445.
8 H. Diaz, A. Percheron-Guegan, J.C. Archard, C. Chatillon and J.C. Mathieu, Int. J. Hydrogen Energy, 4 (1974) 445.
9 A.L. Shilov, M.E. Kost and N.T. Kuznetsov, J. Less-Common Met., 144 (1988) 23.
10 A.L. Shilov, M.E. Kost and N.T. Kuznetsov, Dokl. AN S.S.S.R., 283 (1985) 947.
11 Che Guang-Can, Yu Yu-de and Liang Jing-kui, Acta Phys. Sin., 33 (1984) 770.
12 Yu.B. Patrikeev, Yu.Z. Levinskiy, V.V. Badovskiy, Yu.M. Finliand and O.A. Bachtina, Zh. Phys. Chim., 60 (1986) 1344.
13 R.A. Sirotina, A.P. Savschenkova, V.V. Burnaschova, I.F. Beliaeva and K.N. Semenenko, Zh. Obsch. Chim., 58 (1988) 2526.
14 F. Pourarian and W.E. Wallace, Int. J. Hydrogen Energy, 10 (1985) 49.
15 A.L. Shilov, L.N. Paduretz and M.E. Kost, Zh. Phys. Chim., 59 (1985) 1857.
16 A.L. Shilov, L.N. Paduretz and M.E. Kost, Zh. Phys. Chim., 57 (1983) 555.

17 H.H. Van Mal, K.H.J. Buschow and A.R. Miedema, J. Less-Common Met., 35 (1974) 65.
18 W.H. Hubbard, P.L. Rawlings, P.A. Connick, P.E. Stedwell and R.A.G. O'Hare, J. Chem. Thermodyn., 15 (1983) 785.
19 T. Masumoto and A. Matsushita, J. Less-Common Met., 123 (1986) 135.
20 E. Akiba, K. Nomura and S. Ono, J. Less-Common Met., 129 (1987) 159.