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Equilibria in $Ce_xLa_{1-x}Ni_{5-y}Al_y$–H_2 systems at subcritical and supercritical parameters

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Abstract

Equilibria in $Ce_xLa_{1-x}Ni_{5-y}Al_y$–H_2 systems ($x=0$–0.8; $y=0$–0.6) were studied in a wide pressure range from 0.1 to 40 MPa. Isotherms, isobars and polytherms were investigated. It has been established for a narrow interval of alloy compositions ($x \geqslant 0.5$ and $y \leqslant 0.1$) that a metastable hydride phase occurs in these systems. The metastable phase exists both for supercritical thermodynamic parameters and for subcritical thermodynamic parameters.

The conditions of metastable-state formation (stable hydride heating in hydrogen at a constant or increasing high pressure) are probably induced by factors similar to those defining the phenomena of the "immobilized hydride phase" and the "aged hydride phase".

1. Introduction

As is well known the hydrogen–intermetallics systems are under detailed investigation since their amazing property of absorbing hydrogen reversibly at moderate temperatures and pressures was discovered [1–3]. The $LaNi_5$–H_2 system and its derivatives $A_xLa_{1-x}Ni_{5-y}T_y$–H_2 have been studied much more thoroughly than other systems [1, 4–8] (A≡Ca, rare earth metals; T≡Co, Fe, Mn, Al, Cu, Ti etc.). All the systems mentioned above may be characterized by the occurrence of only one hydride phase (the so-called β phase) containing up to about one hydrogen atom per one atom of metal, *e.g.* $LaNi_5H_{6.7}$ [9–12].

However, recent investigations [6–8, 13–21] show that phase diagrams of these systems are not as simple as generally believed. In particular, anomalies were noted by Shilov *et al.* [8] in the course studying the isotherms for $LaNi_5$–H_2. These anomalies, in the opinion of Shilov *et al.*, give evidence of the existence of five hydride phases in this system. It was shown in our previous work [17] that the well-established sloping plateau in equilibrium isotherms of $Ce_{0.2}La_{0.8}Ni_5$–H_2 systems does not correspond to three-phase equilibrium $\alpha+\beta+H_2$ in the temperature interval 250–400 K but rather corresponds to an irregular solid solution of hydrogen in the intermetallic compound; the β phase really exists only at temperatures lower than the critical value of 248 K. It has been noted [6, 7, 14–16, 18] that some

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characteristic irreproducibility is observed in the isotherms. This irreproducibility is induced by sorption–desorption cycling of the system [6, 15, 16, 18] ("immobilized hydride phase" creation according to refs. 15 and 16) or by long-term ageing of the specimen in a hydrogen atmosphere ("aged hydride phase" creation according to ref. 14).

The present work is devoted to an investigation of equilibria in Ce_x-$La_{1-x}Ni_{5-y}Al_y$–H_2 systems ($x=0$–0.8; $y=0$–0.6) over a wide pressure range. This intermetallic alloy was chosen because it is characterized by a drastic dependence of plateau pressure on x and y [12]. Isotherms, isobars and polytherms were investigated.

2. Experimental details

As is known, such equilibria are commonly investigated by the method which is defined as the "classic" method in the present paper. The "classic" method includes only isotherms to be studied by the well-known Sieverts technique, *i.e.* first preliminary activation of a sample, next constant-temperature conditioning by thermostat and finally both sorption and desorption procedures to be carried out at a constant temperature T_1. Sorption–desorption procedures are controlled usually by both continuous recording of pressure and measurement of the volume of the sorbed–desorbed portions of the hydrogen. The maximum pressure of sorption–desorption procedure is denoted as P_1 (Fig. 1).

In addition to "classic" experiments which were carried out in each case, another experimental method to be defined as the "alternative" method

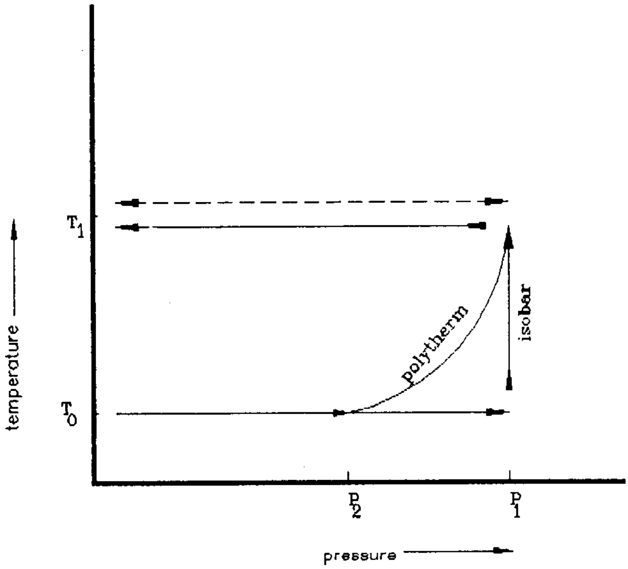

Fig. 1. Schematic curves obtained from " classic" (– – –) and "alternative" (——) experiments for studying the equilibria in hydrogen–intermetallics systems.

was used in this paper. The "alternative" experiment includes preliminary activation of a sample, next its saturation by hydrogen at room temperature T_0 and pressure P_2, followed by heating in a closed volume up to T_1 (this process leads to a pressure rise up to P_1) and finally an isothermal desorption procedure at T_1. Isobaric heating ($P_1 = P_2$) instead of polythermal heating was used too.

The "alternative" method is of interest because it simulates the reaction route which is realized during hydrogen thermosorption compressor operation [16]. It becomes possible to observe not only the pressure hysteresis usually studied in "classic" experiments but also phenomena related to the approach to equilibrium from the unusual side.

Our experiments were carried out in the pressure interval from 1×10^{-2} to 40 MPa and in the isotherm temperature interval from 240 to 473 K. The experimental equipment, sample preparation, calculation procedures and main "classic" results have been described earlier [12, 17].

The X-ray powder diffraction (Cu Kα radiation) was carried out on original and after-experiment samples. The diffractometer DRON-3M (Minpribor, Russia) was used. This analysis confirmed that all the samples were single phase.

3. Results and discussion

Desorption isotherms for the $LaNi_5$–H_2, $Ce_{0.5}La_{0.5}Ni_5$–H_2 and $Ce_{0.7}La_{0.3}Ni_5$–H_2 systems at room temperature and at 373 K are shown in Fig. 2. The experimental points determined by the "classic" method are denoted by the open symbols. The full symbols correspond to the experimental points obtained by the "alternative" method. These data were chosen for presentation in Fig. 2 because they form the most characteristic pattern.

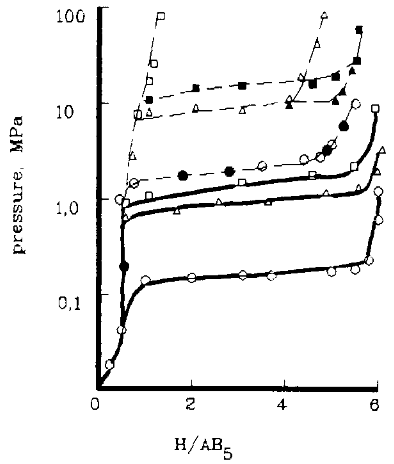

Fig. 2. Desorption isotherms for hydrogen–intermetallics: ○, $LaNi_5$, "classic"; ●, $LaNi_5$, "alternative"; △, $Ce_{0.5}La_{0.5}Ni_5$, " classic"; ▲, $Ce_{0.5}La_{0.5}Ni_5$, "alternative"; □, $Ce_{0.7}La_{0.3}Ni_5$, "classic"; ■, $Ce_{0.7}La_{0.3}Ni_5$, "alternative"; ——, 293 K; – – –, 373 K.

One can see that the 373 K "classic" plateau length is larger than the 293 K value (for $LaNi_5$ and $Ce_{0.5}La_{0.5}Ni_5$) and there is no plateau at $T_1 = 373$ K for $Ce_{0.7}La_{0.3}Ni_5$. An increase in cerium content in the $Ce_xLa_{1-x}Ni_5$ alloy leads to a dramatic decrease in the plateau length during the rise in temperature. In other words, the critical temperature decreases with increase in x. For example, our experiments have established the critical temperature value to be only 360 ± 10 K in the case of $Ce_{0.7}La_{0.3}Ni_5$ and near 480 K in the case of $LaNi_5$.

"Alternative" saturation results in an increase in the solubility of hydrogen in $Ce_{0.7}La_{0.3}Ni_5$ at 373 K. Accordingly, the "alternative" isotherm differs from the "classic" isotherm. It was essential that varying the maximum saturation pressure P_1 in the range from 4 to 40 MPa did not influence the experimental results.

The "classic" and "alternative" procedures were repeated in different sequences up to six times; all the desorption points were reproduced with an accuracy of about 3%. The X-ray analysis showed that the before-experiment and after-experiment samples both contained only the intermetallics phase AT_5. There was a difference in the X-ray reflection widths, similar to those observed in other studies [6, 15].

The phenomena described cannot be defined by the usual hysteresis. Indeed, the hysteresis would cause only the opposite result, namely a fuller saturation by hydrogen at higher temperatures, *i.e.* a larger plateau length in "classic" isotherms. Sorption and desorption plateau pressures for several systems are shown in Table 1. One can see from Table 1 that actual pressure hysteresis in these systems does not exceed 30%. It seems that the most likely interpretation of the phenomena observed is hydride phase formation in a metastable state at supercritical temperatures and pressures. The conditions of this state formation (heating of the stable hydride in hydrogen at a high pressure) are related, in our opinion, to those described earlier [6–8, 14–16].

The present investigation has established, as a result of studying the "classic" and "alternative" isotherms for the described values of x, y, temperatures and pressures, that the difference between "classic" and "alternative" isotherms occurs only upon the following conditions:

$x \geqslant 0.5$

$y \leqslant 0.1$

$323\ \text{K} \leqslant T_1 \leqslant 423\ \text{K}$

The results may be presented as a three-dimensional diagram plotted in Fig. 3. One can see a surface limited by configuration points according to an intermetallics–H_2 equilibrium. The points A, B, C, D, E, F and G are located at this surface. The temperature T_c is the critical temperature. The other surface, which is limited by the line IHKLMNI, corresponds to the metastable state. It is apparent that the metastable state exists both at supercritical and partially at subcritical conditions.

TABLE 1

Characteristic temperatures and plateau pressures of several $Ce_xLa_{1-x}Ni_{5-y}Al_y$–H_2 systems

Intermetallics	Critical temperature T_c (K)	Lamination temperature T_L (K)	Middle plateau pressure (MPa) (obtained by the "classic" method)			
			293 K		373 K	
			Absorption	Desorption	Absorption	Desorption
$LaNi_{4.6}Al_{0.4}$	>500	–	0.05	0.03	0.70	0.61
$LaNi_5$	480	–	0.20	0.18	2.0	1.9
$Ce_{0.2}La_{0.8}Ni_{4.98}Al_{0.02}$	460	–	0.49	0.42	5.2	5.1
$Ce_{0.5}La_{0.5}Ni_5$	420	360	1.2	1.0	10.0	9.6
$Ce_{0.6}La_{0.4}Ni_5$	380	360	2.0	1.4	12.1	11.7
$Ce_{0.7}La_{0.3}Ni_5$	360	340	2.1	1.6	–	–
$Ce_{0.7}La_{0.3}Ni_{4.95}Al_{0.05}$	380	360	1.6	1.3	12.7	12.4
$Ce_{0.7}La_{0.3}Ni_{4.6}Al_{0.4}$	480	–	0.32	0.27	3.9	3.7

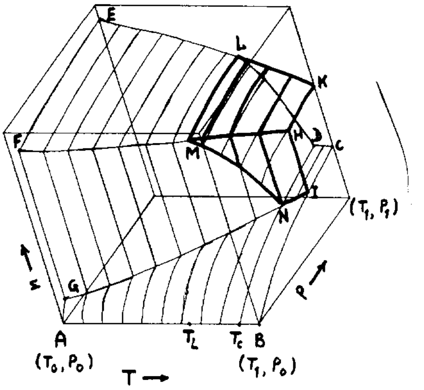

Fig. 3. Three-dimensional pressure–temperature–hydrogen content diagram for the intermetallics–hydrogen system which contains a metastable hydride phase.

Figure 2 allows one to follow the routes of stable-state and metastable-state formation. For example, let us consider the formation of the two states at T_1 and P_1.

In the "classic" experiment the sample is heated preliminarily in vacuum from T_0 to T_1 ($A \rightarrow B$) and then it is saturated at T_1 by raising the hydrogen pressure to P_1 ($B \rightarrow I \rightarrow C$). As a result the equilibrium state is created in the form of a supercritical solid solution of hydrogen in intermetallics.

In the "alternative" experiment the sample is preliminarily saturated at T_0 by raising the hydrogen pressure to P_1 ($A \rightarrow G \rightarrow F \rightarrow E$) and then it is heated to T_1 at a constant pressure. On heating, the configuration point moves along the route ($L \rightarrow K$) on the metastable surface IHKLMNI instead of the route according to equilibrium ($L \rightarrow D \rightarrow C$). Point L is the lamination point. The lamination point is determined as the point of a boundary line where lamination of a phase surface into equilibrium and metastable surfaces occurs. As a result the metastable state is created in the form of a solid solution of hydrogen in the hydride phase.

As has already been noted in this paper, all the phase diagrams of the systems $Ce_xLa_{1-x}Ni_{5-y}Al_y$–H_2 where $x \geq 0.5$ and $y \leq 0.1$ form a pattern similar to that shown in Fig. 3. In particular, characteristic values of such diagrams are listed in Table 1 for several systems.

As far as the $Ce_{0.7}La_{0.3}Ni_5$–H_2 system is concerned, it has been established that "metastable" and "equilibrium" surfaces come together when the temperature increases above 373 K. These surfaces merge together at 423 K and the metastable state disappears. The section shown in Fig. 3 corresponds to $T_1 = 400$ K.

If we analyse the reasons defining the limitation of the metastable-state-bearing intermetallics composition by the conditions $x \geq 0.5$, $y \leq 0.1$ and 324 K$\leq T \leq$423 K, it may be noted that there is a relationship between these conditions and the critical parameters in hydrogen–intermetallics systems. For instance, the critical temperature in the $LaNi_5$–H_2 system is about 480

K. The last value is essentially larger than the upper limit of existence of the metastable state. These conditions are probably related to factors similar to those defining the phenomena of the "immobilized hydride phase" and the "aged hydride phase".

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