ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 210–211

Journal of
ALLOYS
AND COMPOUNDS

Calorimetric study of hydrogen interaction with $LaNi_{3.92}Al_{0.98}$

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Abstract

The interaction of hydrogen with $LaNi_{3.92}Al_{0.98}$ has been investigated by means of the calorimetric method. $P–X$ and $\Delta H–X$ isotherms at pressures up to 60 atm in the temperature range 319–605 K have been determined. The existence of two hydride phases and the decrease of ΔH value with increasing temperature has been established.

Keywords: Hydrogen; Alloys; Calorimetry

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1. Introduction

The influence of temperature on the thermodynamical parameters of the interaction of hydrogen with intermetallic compounds (IMC) has been rather poorly studied up to now. Recent investigation of $Zr_{0.8}Ti_{0.2}CrFe–H_2$ system has revealed [1] a noticeable change of absorption (desorption) reaction enthalpies in the temperature range of 318–584 K. For further studies in this field we have chosen the $LaNi_{3.92}Al_{0.98}–H_2$ system. The choice of this IMC is explained by the fact that the substitution of 20% nickel by aluminium in $LaNi_{4.9}$ leads to the decrease of the desorption equilibrium pressure, which favours the work goal — an investigation of the change of $\Delta H_{dif}^{abs(des)}$ of the hydrogen interaction with $LaNi_{3.92}Al_{0.98}$ using the calorimetric method in the temperature range of 319–605 K under hydrogen pressures up to 60 atm.

2. Experimental

The method and the calorimetric apparatus have been previously described [2]. The sample alloy was prepared by arc melting of electrolytic lanthanum, nickel and aluminium. The cell parameters of starting IMC crystallising in $CaCu_5$ structure type are $a=5.02\pm0.02$ and $c=4.10\pm0.02$ Å, and are close to those of $LaNi_4Al$ cited in the literature [3]. For all measurements we used the same quantity of the sample, equal to 3711×10^{-6} mole. The measurement error was been 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.

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

$$LaNi_{3.92}Al_{0.98}H_x + y/2\ H_2 \Leftrightarrow LaNi_{3.92}Al_{0.98}H_{x+y}$$

The $LaNi_{3.92}Al_{0.98}–H_2$ system was investigated in the temperature range of 319–605 K and the $P_e–X$ and $|\Delta H_{dif}^{abs(des)}|–X$ dependencies (P_e—hydrogen equilibrium pressure, $X=H/LaNi_{3.92}Al_{0.98}$) were obtained. The experimental data are presented in Fig. 1 and Table 1.

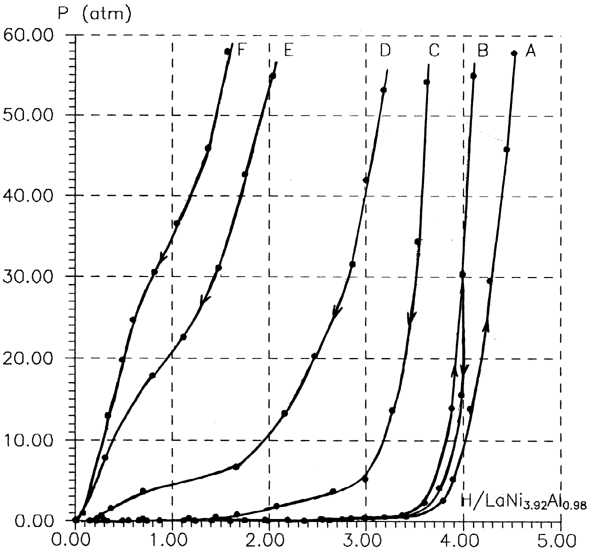

Fig. 1. Pressure–composition isotherms for the $LaNi_{3.92}Al_{0.98}–H_2$ system: absorption (→), desorption (←), A—319 K, B—336 K, C—407 K, D—523 K, E—566 K, F—605 K.

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0925-8388/97/$17.00
PII S0925-8388(96)02884-8

Table 1
The temperature dependence of the enthalpy for the $LaNi_{3.92}Al_{0.98}$–H_2 system

Temperature [K]	Range[a]	$(\|\Delta H_{dif}{}^{abs(des)}\| \pm \sigma)$ [kJ (moleH_2)$^{-1}$]
319	$0.2 \leq X \leq 1.2$	49.2±0.9
	$1.4 \leq X \leq 3.4$	41.8±0.4
336	$0.3 \leq X \leq 1.0$	46.6±1.0
	$1.3 \leq X \leq 3.6$	41.3±0.5
407	$0.2 \leq X \leq 1.6$	46.5±0.3
	$1.7 \leq X \leq 3.1$	40.9±0.3
523	$0.9 \leq X \leq 2.3$	42.3±0.7
566	$0.8 \leq X \leq 1.3$	42.8±0.9
605	$1.0 \leq X \leq 1.2$	37.9±0.6

[a] Error in ranges = ±0.1

The result for 319 K proved to be very close to the literature data [4] in the composition range $0 < X < 3.3$, but detailed investigation revealed two intervals of constant $|\Delta H_{dif}{}^{abs(des)}|$ values. As can be seen from the data in Table 1, one of them corresponds to the concentration range of $0.2 \leq X \leq 1.2$, where $|\Delta H_{dif}{}^{abs}| = 49.2 \pm 0.9$ kJ (mole H_2)$^{-1}$ and the other to $1.4 \leq X \leq 3.4$ with $|\Delta H_{dif}{}^{abs}| = 41.8 \pm 0.4$ kJ (mole H_2)$^{-1}$. The reason for this is the formation of two hydride phases with compositions $LaNi_{3.92}Al_{0.98}H_{\sim 1}$ and $LaNi_{3.92}Al_{0.98}H_{\sim 4}$.

With the experimental temperature increased to 336 K the boundaries within which the hydride phases exist change negligibly, but the $|\Delta H_{dif}{}^{abs(des)}|$ value for the monohydride phase decreases dramatically and in the range of $0.3 \leq X \leq 1.0$ becomes equal to 46.6±1.0 kJ (mole H_2)$^{-1}$, whereas the value stays unchanged for the range in which the tetrahydride phase exists. Fig. 1 shows that at $3.0 \leq X \leq 4.0$ $P_e{}^{abs} > P_e{}^{des}$ and $|\Delta H_{dif}{}^{abs}| > \Delta H_{dif}{}^{des}$, while their mean values are practically indistinguishable.

At 407 K the first plateau range increases to $0.2 \leq X \leq 1.6$ but $\Delta H_{dif}{}^{des}$ in this range does not change (Table 1). Simultaneously the second plateau, referring to tetrahydride, shortens to $1.7 \leq X \leq 3.1$ with a slight decrease of $\Delta H_{dif}{}^{des}$.

The increase in temperature to 523 K leads to the transformation of two plateaux into one in the range of $0.9 \leq X \leq 2.3$ with $\Delta H_{dif}{}^{des} = 42.3 \pm 0.7$ kJ (mole H_2)$^{-1}$. At 566 K this enthalpy value stays unchanged and the plateau range shortens to $0.8 \leq X \leq 1.3$. In the α-solution region we did not notice any decrease of $|\Delta H_{dif}{}^{abs(des)}|$ with increasing X at 319, 336 and 407 K, but when only one hydride phase exists at $523 \leq T \leq 566$ K the isotherms show a minimum of solution enthalpy characteristic for AB_5–H_2 systems [5,6]. The shape of isotherms in the β-solution region is analogous to that described earlier [5,6]. The only exception is the absence of the discontinuity of $\Delta H_{dif}{}^{des}$ at T = 523 K observed for AB_5–H_2 systems.

The measurement at 605 K showed that there is a decrease of desorption rate, noticed earlier in $LaNi_{3.85}Cu_{1.07}$–H_2 [7]. The residual hydrogen content is $X \sim 0.5$. The $\Delta H_{dif}{}^{des}$ value, having a minimum at $X = 0.75$, increases up to 37.9±0.6 kJ (mole H_2)$^{-1}$ and it is clearly seen (Table 1) that it stays unchanged in a narrow range of $1.0 \leq X \leq 1.2$. Then it increases to 42 kJ (mole H_2)$^{-1}$ ($X = 1.3$) and decreases to 35 kJ (mole H_2)$^{-1}$ at $X = 1.6$. Such a behaviour shows that the temperature T = 605 K is very near the critical value, but additional experiments are needed to determine its exact value.

For compositions with the same content of hydrogen we have found (Table 1) a decrease of $|\Delta H_{dif}{}^{abs(des)}|$ with increasing temperature. This is greater for the first plateau (from 49.2 at 319 K to 46.5 kJ (mole H_2)$^{-1}$ at 407 K) than for the second plateau in the same temperature range. After the transformation of both plateaux in the range of 523–605 K the trend of decreasing desorption enthalpy value is preserved (from 42.3 to 37.9 kJ (mole H_2)$^{-1}$). The obtained results prove one more time that calorimetric studies of hydrogen interactions with IMC allow a most precise determination of the reaction enthalpy for a wide temperature range.

Acknowledgments

This work was supported in part by the Russian Foundation for Basic Research Grant No. 95-03-08787.

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