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Hydrogen isotherms for annealed, un-activated $LaNi_5$ (273–333 K)

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ABSTRACT

Hydrogen absorption isotherms (273–333 K) have been measured for closely stoichiometric, annealed, un-activated $LaNi_5$, i.e., a virgin un-activated $LaNi_5$ sample was employed at each temperature. This is the first time that such isotherms have been measured for annealed, un-activated $LaNi_5$ at such low temperatures $\leqslant$298 K. After measurement of the initial absorption isotherms, the second absorption and desorption isotherms have been measured at each temperature. Van't Hoff plots have been made from these absorption and desorption plateau pressure data and, from these, ΔH_{plat} values have been obtained for the initial and subsequent absorption and desorption reactions. The $|\Delta H_{plat}|$ determined from the van't Hoff plot is smaller for the initial isotherm for the annealed, un-activated form of $LaNi_5$ than it is for activated $LaNi_5$.

1. Introduction

$LaNi_5$–H is the prototype intermetallic-H system [1,2] and information about it may be helpful in the understanding of other intermetallic-H systems. $LaNi_5$ has a hexagonal structure of the AB_5-type and other elements may be substituted into it in order to obtain desirable properties for specific H-storage tasks. AB_5–H systems are employed commercially as electrodes in Ni-metal hydride batteries.

It was first observed by Flanagan and Biehl [3] that relatively high temperature annealing, 1023 K, of previously activated $LaNi_5$ leads to a significantly greater absorption plateau, p_f, than that of its activated form. *Activated* refers to its condition after an initial cycle of hydriding/dehydriding. In one experiment Flanagan and Biehl [3] hydrided an annealed (1023 K), activated $LaNi_5$ sample to ≈50% and, then evacuated it prior to measurement of a complete absorption isotherm, i.e., it was half activated [3]. The absorption isotherm for this previously 50% hydrided $LaNi_5$ exhibited two different p_f values, one for the previously activated half and a significantly greater one for the un-activated half. Later Nomura et al. [4] found that p_f values are greater for annealed, un-activated $LaNi_5$ (453 K) which had been crushed into fine powder prior to the isotherm measurements. Both of these papers [3,4] concluded that, although p_f for hydride formation of the initial isotherm is significantly greater than for subsequent cycles, the decomposition plateau pressures, p_d, are nearly unchanged between the initial and subsequent desorption isotherms. More recently, others have measured initial and subsequent isotherms for un-activated $LaNi_5$ at single temperatures $\geqslant$298 K employing crushed material, e.g., [5–8], however, isotherms for annealed, un-activated $LaNi_5$ have not been systematically measured over a temperature range needed to construct a meaningful van't Hoff plot as will be done in the present research.

The emphasis will be on the thermodynamic aspects of H_2 isotherms for un-activated and activated $LaNi_5$; the microscopic aspects of the difference in the isotherms for activated and un-activated $LaNi_5$ have been carried out elsewhere. Microscopic details of $LaNi_5$ before and after the initial hydriding are useful for the interpretation of the present results. Kim et al. [9,10] have found from TEM studies that un-activated $LaNi_5$ nucleates to the hydride phase heterogeneously at defects and, after activation, nucleation occurs readily at dislocations and consequently the two phase co-existence p_{H_2} is less sloping for activated $LaNi_5$.

In a series of important papers Gray and co-workers [11–15] have determined dislocation densities from anisotropic line-broadening of diffraction patterns of both neutron and synchrotron radiation. The application of Krivoglaz theory by Wu et al. [11] to line broadening of hexagonal systems such as $LaNi_5$ has been regarded as a breakthrough [16]. The dislocations generated during the initial hydriding remain in the activated material during dehydriding. Complementary research has been carried out by Joubert and co-workers, e.g., [16,17].

Positron annihilation studies of activated $LaNi_5$ have shown that large vacancy concentrations are introduced during the initial hydriding of $LaNi_5$ [18] and these can be eliminated by annealing at ≈650 K whereas the dislocations are not removed until annealing at higher temperatures.

Luo et al. [19] found that ΔH_{plat} determined calorimetrically for H_2 absorption by un-activated $LaNi_5$ was equal, to within

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experimental error, to ΔH_{plat} for the activated form, -15.0 ± 0.1 kJ/mol $\frac{1}{2}H_2$ where ΔH_{plat} for absorption refers to the heat evolved from the reaction

$$\frac{1}{2}H_2(g, 1\ \mathrm{bar}) + (b-a)^{-1}LaNi_5H_a \rightarrow (b-a)^{-1}LaNi_5H_b \qquad (1)$$

where a and b are the H contents per mol $LaNi_5$ of the co-existing dilute and hydride phases, respectively.

This result was interpreted [19] as due to entropy production during the irreversible processes of plastic deformation and decrepitation of un-activated $LaNi_5$. This result supports the model of pressure hysteresis in metal hydrides as due to the irreversible free energy lost during plastic deformation [20] and is supported by the microscopic observations, e.g., [10,11].

In order to obtain the most reliable plateau thermodynamic parameters from isotherm data closely stoichiometric $LaNi_5$ must be employed and isotherms must be measured over a temperature range which is as wide as possible compatible with the requirement that there is no "plateau splitting" or other signs of $LaNi_5$ degradation during hydriding/dehydriding. It has been found that plateau splitting occurs during hydride decomposition at as low a temperature as 353 K [21]. Such splitting was avoided here by limiting the temperature of isotherm measurements to $\leqslant$333 K. In this research both absorption and desorption isotherms are measured from 273 K to 333 K employing annealed, un-activated $LaNi_5$.

The terminal hydrogen (H) solubilities (*THS*) increase with temperature for this annealed $LaNi_5$ [22] where *THS* refers to the H concentration where the hydride phase first appears during absorption or disappears during desorption. A plot of ln (*THS*) against 1/T [23] gives ΔH_{THS} as the slope, which at small H contents in the dilute phase, is equal to the sum of the enthalpies for hydride formation and for solution of (1/2) H_2(g) at infinite dilution of H, i.e.,

$$\Delta H_{THS} = -\Delta H_{plat} + \Delta H^{\circ}_{H} \qquad (2)$$

where consistent values must be employed, i.e., those for either absorption or desorption. $\Delta H_{THS} = 9.2$ kJ/mol H for absorption by annealed, activated $LaNi_5$ [22]. (The concentration unit employed for the *THS* does not affect ΔH_{THS}, e.g., it can be expressed as H/($LaNi_5$), mol ratio, or as (H atom)/(metal atom).) ΔH_{THS} mainly determines the value of *THS* since ΔS_{THS} is usually small [23]. Using *THS* = 9.2 kJ/mol H for annealed, activated $LaNi_5$ and $\Delta H_{plat} = -14.2$ kJ/mol H in Eq. (2), we obtain $\Delta H^{\circ}_{H} = -5.0$ kJ/mol H where -14.2 kJ/mol H has been employed for ΔH_{plat} rather than -15.0 kJ/mol H because the former is the value from the van't Hoff plot for hydride formation [22]. This value of ΔH°_{H}, -5.0 kJ/mol H, closely agrees with the experimental value for $\Delta H^{\circ}_{H} = -5.4$ kJ/mol H derived earlier from dilute phase isotherms for annealed $LaNi_5$ [22].

Because of the very large difference between absorption isotherms for annealed, un-activated and activated $LaNi_5$ it is of interest to determine isotherms for the former and to determine enthalpies for hydride formation and decomposition, ΔH_{plat}, from van't Hoff plots for the annealed, un-activated $LaNi_5$ and to compare these values to those derived from van't Hoff plots for H_2 absorption/desorption by activated $LaNi_5$.

2. Experimental

$LaNi_5$ was prepared at the Ames Laboratory of Iowa State University by arc-melting the elements. The purity of the Ni is 99.99% and the La is 99.95% including *oxygen*. During the preparation at Ames, the button was melted seven times inverting it after each melting. The arc–cast button was wrapped in Ta foil, sealed in an evacuated quartz tube and annealed at 1223 K for 100 h. It was shown from metallographic examination to be single phase and the XRD patterns showed that the angles of the reflections were equal for randomly selected regions within the ingot. The ratio of Ni-to-La in the $LaNi_5$ was 5.00 ± 0.01 based on electron microprobe analysis. Ingots of the $LaNi_5$ were broken up into several smaller pieces (not pulverized) before insertion into the reaction vessel; these pieces were massive compared to crushed material or to decrepitated particles resulting from activation.

Isotherms were measured in an all-metal apparatus with electronic diaphragm gauges (M.K.S) for H_2 pressure measurements. The temperatures were controlled with liquid baths to within ±0.2 K. The annealed, un-activated $LaNi_5$ samples were evacuated at the temperatures of the isotherms to be measured. The dual-cell calorimeter has been employed earlier [24] where it has been described in some detail.

3. Results and discussion

3.1. Dilute phase solubilities

It is difficult to measure dilute phase solubilities of H_2 in annealed, un-activated $LaNi_5$ since the solubilities are very small and the kinetics are slow. A dilute phase H_2 isotherm for annealed, un-activated $LaNi_5$ is shown in Fig. 1 (293 K) plotted as $p^{1/2}_{H_2}$ against H/($LaNi_5$); the solubility relation intersects the origin and is reasonably linear with a steep slope reflecting a small solubility. After completely forming the hydride phase and evacuating (303 K), a desorption isotherm was measured (293 K) for the same sample which indicates that the total amount of trapped H resulting from the activation process is $r_{trap} = H/(LaNi_5) = 0.44 \pm 0.02$ (Fig. 1).

After the first desorption isotherm was measured, this activated $LaNi_5$ was evacuated at 373 K (10 h) and a second absorption isotherm was measured (293 K) where it can be seen that p_{H_2} becomes measurable at $r \approx 0.15$ (Fig. 1) indicating that only a portion of the trapped H has been removed by evacuation at 373 K. After complete hydriding, a second desorption isotherm was measured which intersects the r axis at $r \approx 0.29$ indicating that H corresponding to $r = 0.29$ remains in the sample, i.e., if this 0.29 added is to the H trapped in the sample after evacuation at 373 K, $r = 0.15$, the total trapped H is $\approx$0.44 closely corresponding to the intercept of the initial desorption isotherm.

The region where $p_{H_2} \approx 0$ (Fig. 1) is likely to be due to H trapping in vacancies and vacancy clusters because it has been shown that large concentrations of these are produced by the activation process [25,26]. The interaction of H with vacancies is very strong [27] and this would be consistent with $p_{H_2} \approx 0$. Judging from work on Pd [27,28], H trapped in the stress fields of dislocations will be reflected by solubility enhancements in the dilute phase where

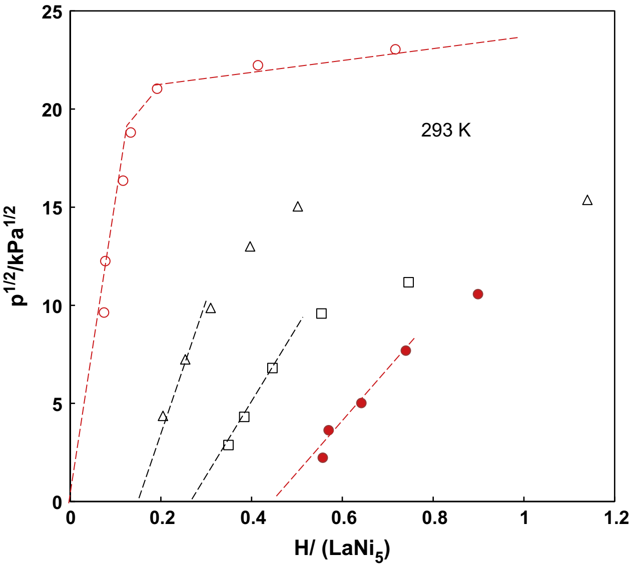

Fig. 1. Dilute phase solubilities at 293 K. ○, initial absorption; ●, initial desorption; △, second absorption after evacuation; □, 2nd desorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)