Thermodynamic properties of non-stoichiometric LaNi$_{x-1}$Cu–H systems

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Abstract

A series of non-stoichiometric LaNi$_{x-1}$Cu intermetallic compounds with $x = 5.0$ to 6.0 has been prepared and characterized by X-ray diffraction and shown to be single phase. The thermodynamics of hydrogen absorption and desorption by these compounds have been determined from their equilibrium hydrogen pressures and from the calorimetric measurement of their heats of reaction with H$_2$(g). For $x > 5.4$ the system appears to be above its critical composition for the co-existence of the dilute and hydride phases, in agreement with earlier results obtained from in situ X-ray diffraction. As x increases from 5.0 to 6.0, the hydrogen pressures corresponding to the plateaux, or else to the "plateau-like" regions, increase and the hydrogen capacities decrease. For the plateaux and plateau-like regions the calorimetrically measured enthalpies of reaction are found to increase in magnitude with x, whereas the corresponding entropy changes are nearly independent of x, and hence the enthalpy changes cause the observed increase of p_{H_2}. The hysteresis decreases with increasing x.

Keywords: La–Ni–Cu alloys; CaCu$_x$ phases; Non-stoichiometric compounds; Hydrogen sorption; p–c isotherms; Calorimetry

1. Introduction

Hydrogen absorption and desorption by non-stoichiometric intermetallic compounds of LaNi$_x$ were first systematically investigated by Buschow and van Mal [1]. (For convenience the terms intermetallic compound and alloy will be used interchangeably although the former expression is the more appropriate one for the AB$_x$ compounds which are the subject of this work.) They found that the plateau pressures of LaNi$_x$ increased with increasing x; this correlated with the decrease in unit cell size. They also showed that the plateau pressures no longer changed for $4.9 > x > 5.4$; this correlated very well with the unit cell size which was no longer a function of x for $4.9 > x > 5.4$, i.e. a two-phase compound was formed outside the homogeneity range. The plateau pressures are therefore an alternate method for the determination of the range of stoichiometry over which a single phase exists for a hydride-forming intermetallic compound.

Recent interest in non-stoichiometric AB$_x$–H systems has arisen because they have been shown to have promise as electrodes in rechargeable NiMH batteries in view of their facile electrochemical kinetics and stability towards cycling [2]. Structural, micro-structural and electrochemical studies have been carried out on these non-stoichiometric AB$_x$–H systems were A = La and B = (Ni + Cu) [2–6]. The purpose of this research is to characterize these systems thermodynamically.

The structural properties of the non-stoichiometric AB$_x$–H systems [3] are interesting because two B atoms occupy an A position in a dumbbell arrangement with the dumbbell axis oriented along the c-axis [3,6,7]. For the non-stoichiometric LaNi$_{x-1}$Cu intermetallics it is believed that the Ni atoms occupy the dumbbell positions and the Cu atoms preferentially occupy the spacious metal positions surrounding the dumbbells [3].

The fraction y of La atoms replaced can be calculated from [3]

$$y = \frac{x - 5}{x + 2} \tag{1}$$

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An increase of y was found to cause the lengths of the a-axis to decrease and the c-axis to increase. These dependencies were found to be linear except for the largest value of y, LaNi$_5$Cu, where the decrease in a is smaller than predicted from the linear relation.

Notten et al. [4] have measured hydrogen isotherms for LaNi$_{x-1}$Cu with $x = 5.0$, 5.2, 5.4 and 6.0 at 293 K, and also carried out in situ XRD measurements of the hydriding process which established the dependence of the lengths of the a- and c-axes on the hydrogen content. They found that an increase in x causes the plateaux pressures to increase and the phase boundaries to narrow such that the composition $x = 5.4$ is just within the miscibility gap. They found that for $x = 6.0$ the system is clearly above its critical composition because p_{H_2} and the lattice parameters show a continuous change with the hydrogen content of the alloy. Since the $x = 6.0$ compound does not have a plateau, p_{H_2} was evaluated at a hydrogen composition corresponding to the inflection point; the p_{H_2} evaluated in this way for $x = 6.0$ did not fit the linear correlation found for the lower values of x.

In the present research, isotherm measurements will be extended to include the $x = 5.6$ and 5.8 compounds in order to elucidate the behavior just above the critical value of x for the miscibility gap. In addition, reaction calorimetric measurements will be made of ΔH_H and ΔH_{plat} for the series of LaNi$_{x-1}$Cu intermetallics (single phase). The reaction calorimetric method yields more precise values of the enthalpies than those derived from van't Hoff plots of the equilibrium hydrogen pressures for intermetallic–H$_2$ systems and the former, in contrast to the latter method, gives values which are not directly affected by hysteresis [8,9].

In the two phase plateau region the reaction which occurs is given by reaction (2), or its reverse, and ΔH_{plat} is the corresponding enthalpy:

$$\frac{1}{2}H_2(g) + \frac{AB_xH_a}{(b-a)} \rightarrow \frac{AB_xH_b}{(b-a)} \tag{2}$$
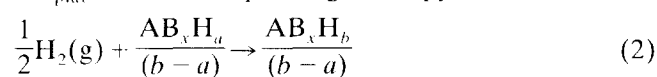
here a and b are the dilute and hydride phase boundaries in the co-existence region respectively. In single phase regions the reaction with H$_2$ is best represented as

$$\frac{1}{2}H_2(g) \rightarrow [H] \tag{3}$$

where [H] represents hydrogen dissolved in a dilute or a hydride single phase region.

2. Experimental

All of the compounds prepared had sharp XRD peaks and were single phase with the hexagonal hP6-CaCu$_5$ crystal structure. The samples were annealed

Table 1
Annealing temperatures, lattice parameters, and unit cell sizes (298 K) for unhydrided LaNi$_{x-1}$Cu alloys with $x = 5.0$ to 6.0

Alloy	T (K)	a (nm)	c (nm)	Unit cell (nm^3)
LaNi$_5$	1473	0.50152	0.39832	0.08676
LaNi$_4$Cu	1323	0.50394	0.40052	0.08809
LaNi$_{4.2}$Cu	1323	0.50252	0.40127	0.08776
LaNi$_{4.4}$Cu	1323	0.50102	0.40204	0.08740
LaNi$_{4.6}$Cu	1423	0.49984	0.40285	0.08716
LaNi$_{4.8}$Cu	1423	0.49868	0.40347	0.08690
LaNi$_{5.0}$Cu	1473	0.49775	0.40388	0.08666

under argon for one week at the appropriate temperatures between 1323 and 1473 K, as shown in Table 1. The samples were crushed to a coarse powder and then mixed with fine copper powder for better thermal conductivity in the calorimeter.

The samples were first evacuated at 573 K, hydrided at room temperature and then evacuated overnight at room temperature with a diffusion pump. The enthalpies for reactions (2) and (3) were determined from the heat evolved (or absorbed) from the absorption (or desorption) of H$_2$(g) by the intermetallic compound LaNi$_{x-1}$CuH$_n$. The calorimeter is a differential, twin cell, heat leak type which has been employed previously for investigations of the LaNi$_{5-z}$Mn$_z$–H [10] and ZrNi–H systems [11]. The calorimetric determinations were mainly carried out at 300 K, but several were carried out at 293 K. No difference was found between the measured enthalpies at these two temperatures. In single phase regions a measurement of q yields a relative partial molar enthalpy if a small increment of hydrogen, δn_H, is added or removed, i.e.

$$\left(\frac{q}{\delta n_H}\right)_{T,P} = \Delta H_H \tag{4}$$

where n_H is moles of H added or removed from the sample and the subscript P refers to hydrostatic pressure on the solid phase. Eq. (4) gives ΔH_{plat} values in the plateau region where, unless the plateau regions "slope", it is not necessary to add or remove small increments of H because the enthalpies, ΔH_{plat}, are integral ones and should be constant across the plateau; however, the calorimeter responds more linearly if the heats evolved or absorbed are not too large. The intermetallics were generally hydrided and dehydrided several times before the calorimetric measurements.

Relative partial entropies for absorption can be determined for single phase regions from

$$\Delta S_H = (\Delta H_H/T) - \frac{1}{2}R \ln p_{H_2} \tag{5}$$

and it is obtained in the two phase regions similarly but, if the enthalpy has been obtained from

calorimetry, the plateau pressure to be employed in the ln term is subject to some uncertainty because of hysteresis. It has been argued that a geometric mean plateau pressure is appropriate [8,9], i.e. $p = \sqrt{p_f p_d}$, where p_f and p_d are the plateau pressures for hydride formation and decomposition respectively. Experimental evidence has been given that this is the appropriate choice [12].

For each different intermetallic compound three to four complete series of calorimetric and equilibrium pressure measurements were carried out as a function of n (mol H/mol AB_x). Each series consisted of about 50 to 60 individual measurements of the heats evolved or absorbed.

3. Results and discussion

3.1. Lattice parameters and unit cell dimensions of the $LaNi_{x-1}Cu$ alloys (298 K)

When x increases for the $LaNi_{x-1}Cu$ alloys, it was found that the unit cell size decreases [3,4]. Two new compositions, $x = 5.6$ and 5.8, have been characterized by XRD in this research and their lattice parameters and unit cell sizes are shown in Table 1 along with the earlier values. In Fig. 1 the unit cell sizes have been plotted against y, the fraction of La atoms replaced by pairs of Ni atoms, calculated from Eq. (1). Because of the relatively small decrease in unit cell size with increasing y, if there is a linear relationship between the lattice constants and y, then there should be a closely linear relationship between the unit cell size and y. Deviation from a linear relationship for $y >$ 0.054 ($x > 5.4$) is apparent in Fig. 1, in agreement with the deviation found earlier for the lattice constants at $y = 0.125$ ($x = 6.0$) [3].

It was found that the unit cell size also decreased as the degree of non-stoichiometry increased for the

Fig. 1. Plot of unit cell size against y for (a) $LaNi_{x-1}Cu$ and (b) $LaNi_x$ [1] at 298 K where y is defined by Eq. (1).

binary $LaNi_x$ alloys, as shown in Fig. 1 [1,2]. The presence of one Cu atom per formula unit of $LaNi_{x-1}Cu$ increases the unit cell size compared with $LaNi_x$, but the variation of the unit cell size with y for both series [1,2] is caused by the non-stoichiometry. In the $LaNi_{x-1}Cu$ alloys there are two opposing effects: (i) the presence of pairs of Ni dumbbells on the crystallographic A-type positions causes a lattice contraction, while (ii) the Cu substitution on the B-positions causes a lattice expansion.

3.2. Activation and dilute phase hydrogen solubilities

Activation refers to the disintegration of an intermetallic compound into a fine powder as a result of hydriding and dehydriding. This is caused by the abrupt volume change accompanying the hydriding/dehydriding and the tendency for intermetallic compounds to undergo brittle fracture. After activation, the alloy is very active towards hydrogen uptake and evolution [13]. The solubility of hydrogen in a dilute phase of activated $LaNi_5$ does not obey Sieverts' law, $n = K_s \times p_{H_2}^{1/2}$. The reason for this has been attributed to hydrogen trapping at structural imperfections introduced by activation [14–16]. Recently, Notten and coworkers [17,18] have characterized the defects produced during hydriding of $LaNi_5$ by in situ XRD and TEM; plate-like defects were found to be introduced by hydriding and XRD pattern line-broadenings were attributed to these defects. Kisi et al. [19] and Lee and coworkers [20,21] have also employed TEM to examine the effects of hydrogen on $LaNi_5$. Both groups find that dislocations are introduced upon hydrogen absorption even in the dilute phase. After hydriding/dehydriding $LaNi_5$, Lee and coworkers found well-developed dislocation walls and slip bands.

There is no miscibility gap at 300 K for the $LaNi_{x-1}Cu$ alloys with $x > 5.4$ [4], and therefore it could be expected that these alloys would not fracture since an abrupt volume change does not occur as for $LaNi_5$ [13]. Examination of the alloys by optical microscopy after hydrogen absorption and desorption showed that the average particle size was significantly larger for the $x \geq 5.4$ alloys than for the $x = 5.0$ and 5.2 alloys which, after activation, became a finely divided powder similar to the activated parent compound $LaNi_5$. After hydrogen uptake and subsequent desorption, the particles of $LaNi_{x-1}Cu$ with $x > 5.4$ remained coarse and did not crumble even upon gentle application of pressure with a spatula. These results are consistent with the finding by one of the authors and his coworkers [4] that the $x = 5.4$ alloy composition is just within the miscibility gap at room temperature.

It was found that the dilute phase solubility of a pristine alloy with $x \geq 5.4$, e.g. $x = 5.6$, obeyed Sieverts' law and intersected the origin up to contents
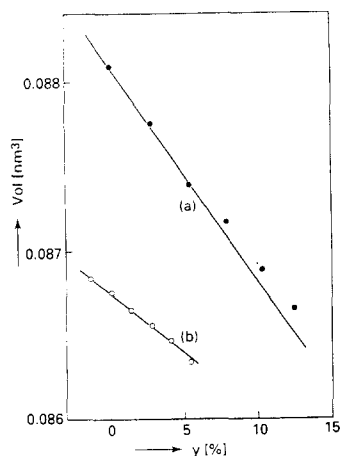
of $n \approx 0.3$ at 300 K but, after hydrogen was absorbed and desorbed several times in the dilute region (300 K), the solubility data no longer obeyed Sieverts' law. In view of this, it seems that even though the alloy–H system is above T_c and does not disintegrate after hydrogen absorption and desorption, the alloys, nonetheless, show some signs of activation resulting from solution of H_2 because some especially energetic sites seem to have been introduced. The calorimetric measurements along the isotherms were performed on fully activated samples.

4. Hydrogen isotherms

Isotherms are shown in Fig. 2 at 300 K for the various $LaNi_{x-1}Cu$ intermetallic–H systems. The plateau pressure of the stoichiometric compound $LaNi_4Cu$ is lower than that for the parent compound $LaNi_5$. This is in agreement with the increase in unit cell volume by substitutional Cu (compare plots a and b in Fig. 1) [3,22]. The plateau pressures for hydride decomposition are listed in Table 2 (300 K) and the isotherms shown in Fig. 2, where it is apparent that the plateau (plateau-like) pressures increase with x. For
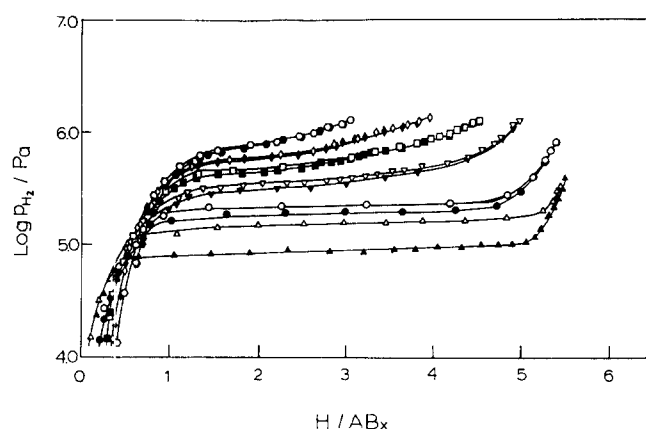
ternary stoichiometric alloys $AB_{5-z}M_z$, plots of $\log p_{plat}$ against X_M (fraction of M within the five B atoms) are linear when, for example, M = Mn [10], Cu [23] or Sn [24]. For the non-stoichiometric alloys plots of $\log p_{plat}$ against x for both the binary $LaNi_x$ and ternary $LaNi_{x-1}Cu$ intermetallics were found to be linear (293 K), with the same slope except for the composition of $x = 6.0$ for the ternary alloys [4]. This deviation from linearity is confirmed here by the inclusion of new data for the $x = 5.6$ and 5.8 alloys, which deviate increasingly from the linear relationship. The lack of linearity in the $LaNi_{x-1}Cu$ system for $x \geqslant 5.6$ is likely to be related to the corresponding lack of linearity in the relationship between the unit cell volume and y (Fig. 1). Fig. 3 shows a correlation between the logarithms of the plateau (plateau-like) pressures and the unit cell size. The plot is reasonably linear considering the spread in values for the alloy with $x = 5.0$, where hysteresis is significant. The near linearity of the plot results from the compensating degrees of non-linearity in the individual plots of the
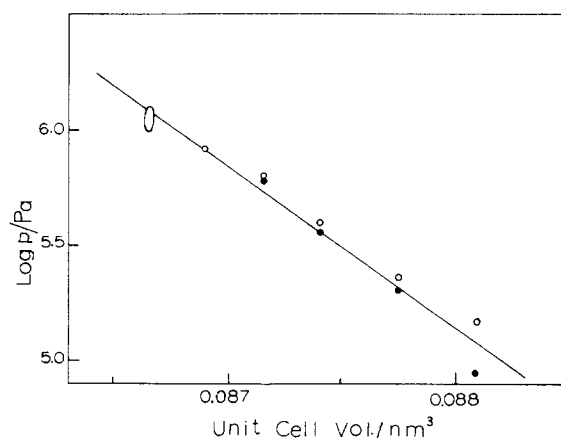

Fig. 3. Plot of the logarithms of the hydrogen plateaux pressures of the $LaNi_{x-1}Cu$ alloys at 298 K against unit cell size. For the alloys $x = 5.8$ and 6.0 with the highest plateau pressures there is no significant difference between the absorption and desorption pressures and only the open symbol is shown, but for the latter there was considerable difference between the different isotherms and this is shown by the elongated symbol. Open symbols are absorption and filled ones desorption.

Fig. 2. Hydrogen isotherms for $LaNi_{x-1}Cu$ alloys at 300 K. △, ▲, $x = 5.0$; ○, ●, $x = 5.2$; ▽, ▼, $x = 5.4$; □, ■, $x = 5.6$; ◇, ◆, $x = 5.8$; ○, ●, $x = 6$. Open symbols are absorption and filled ones desorption.

Table 2
Thermodynamic data for the plateaux and plateau-like regions of the $LaNi_{x-1}Cu$–H systems with $x = 5.0$ to 6.0 at 300 K

Alloy	p_{plat}^d (MPa)	$|\Delta H_{plat}|$ (kJ mol^{-1} H)	$|\Delta S_{plat}|$ (J K^{-1} mol^{-1} H)
$LaNi_5$	0.165	15.1 ± 0.2	56.1 ± 0.7
$LaNi_4Cu$	0.085	15.6 ± 0.2	54 ± 1
$LaNi_{4.2}Cu$	0.197	15.0 ± 0.2	53 ± 1
$LaNi_{4.4}Cu$	0.316	14.7 ± 0.3	55 ± 1
$LaNi_{4.6}Cu$	0.495	14.3 ± 0.3	54 ± 1
$LaNi_{4.8}Cu$	0.623	13.8 ± 0.3	53 ± 1
$LaNi_{5.0}Cu$	0.784	13.0 ± 0.3	52 ± 1

Data for $LaNi_5$–H are taken from Ref. [12] and data for the $x \geqslant 5.6$ alloys have been evaluated in the "plateau-like" region where there is an inflection point in the isotherms.

two quantities against x. The deviations are in the right direction for compensation because the unit cell volumes are larger than expected (Fig. 1) and the plateau pressures are smaller than expected from extrapolation of the linear relationship established for the $x = 5.0$ and 5.2 alloys (Fig. 4).

The critical point composition of the $LaNi_{x-1}Cu-H$ system was reported from careful in situ XRD measurements as slightly greater than $x = 5.4$ [4]. Hysteresis reflects the fact that there is a first order phase change when the hydride phase forms from the dilute phase or vice versa. The extent of hysteresis decreases with x. A linear extrapolation of the extent of hysteresis, $\frac{1}{2}RT \ln(p_f/p_d)$, against x indicates that it should disappear at $x \approx 5.5$, although a small "hysteresis-like" effect remains for $x \geqslant 5.6$ (this is not believed to be true hysteresis because it is clear from the in situ XRD results that two phases no longer exist for alloys with $x > 5.4$ [4]).

4.1. Calorimetrically measured enthalpies and derived entropies

4.1.1. Dilute phase

In the dilute region of the $LaNi_{x-1}Cu-H$ systems both p_{H_2} and ΔH_H depend strongly on $n = H/AB_x$ in the low concentration region (Figs. 5 to 7 and 9 to 11). For the stoichiometric compound, $x = 5.0$ (Fig. 5), as n increases from zero $|\Delta H_H|$ decreases in magnitude, abruptly reaching a minimum value, and then the enthalpies increase. The region of H contents where the $|\Delta H_H|$ values decrease with n increases in extent as x increases and the minimum gradually disappears as x increases. For the $x = 5.2$ alloy (Fig. 6) the initial region where $|\Delta H_H|$ decreases with n extends from 0

Fig. 4. Plots of the logarithms of the plateau decomposition pressures and $|\Delta H|$ against x at 298 K. Multiple symbols at the same x value indicate values from different isotherms. $|\Delta H|$ refers to the plateau values for $x \leqslant 5.4$ and for $x > 5.4$ plateau-like values of $|\Delta H_H|$.
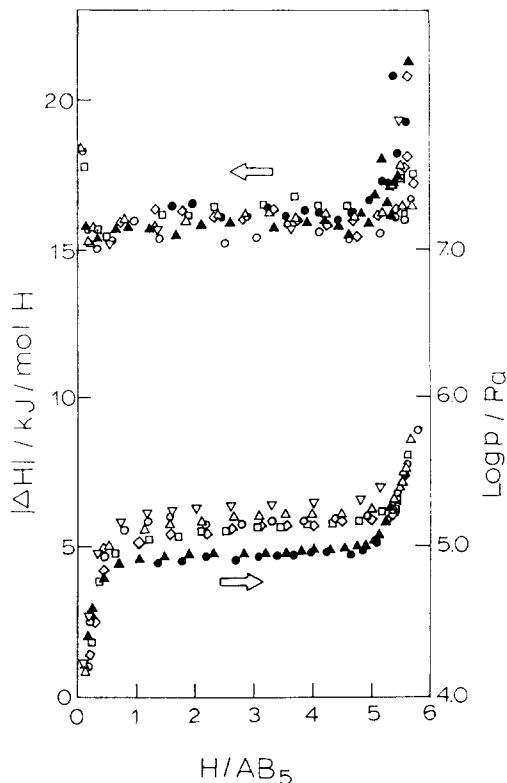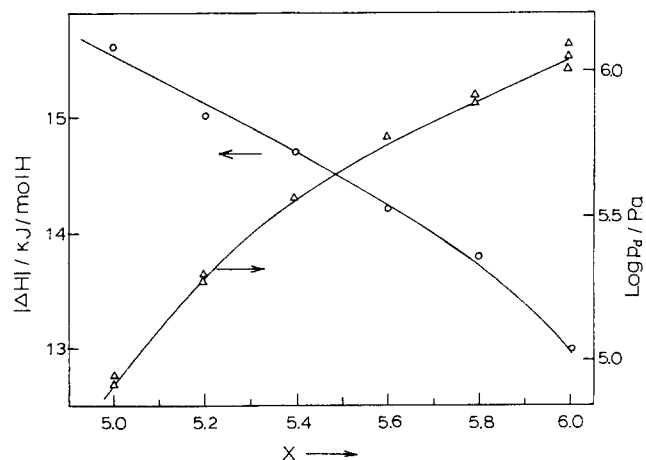
Fig. 5. Calorimetric and isotherm data for the $x = 5.0$ alloy (298 K). The upper and lower sets of data points refer to the calorimetric enthalpies and equilibrium hydrogen pressures respectively. The latter show the effect of repeated cycles of hydriding and dehydriding on the plateau pressures. Open symbols are for absorption and filled ones for desorption and the different symbols represent sequential isotherms; the same symbols are employed for the enthalpy change and the pressure data for a given run: $\triangledown$, $\blacktriangledown$, first run; $\triangle\blacktriangle$, second run; $\bigcirc$, $\bullet$, third run; $\Diamond$, $\blacklozenge$, fourth run; $\square$, $\blacksquare$, fifth run.

to 0.3, reaching a minimum at about 0.6, and with further increase of n $|\Delta H_H|$ increases.

For the $x = 5.4$ alloy the $|\Delta H_H|$ values fall with n and there is only a hint of a minimum near about 0.9 (Fig. 7). It is of interest to compare this $x = 5.4$ alloy with the $LaNi_{5.4}$ alloy because their non-stoichiometry is equal. Fig. 8 shows the binary non-stoichiometric $LaNi_{5.4}$ alloy, and in the dilute phase it more closely resembles the behavior of $LaNi_5-H$ than the $LaNi_{4.4}Cu-H$ system because a minimum is clearly seen.

At the alloy compositions $x \geqslant 5.6$ (Fig. 9) the extent of the initial region where the $|\Delta H_H|$ values decrease, and p_{H_2} increases, is appreciable. For the $x = 5.8$ alloy (Fig. 10) the minimum in ΔH_H values has disappeared.

The trends in behavior of the relative partial molar enthalpies with n for some metal–hydrogen systems will be reviewed for comparison with the results obtained here for the $LaNi_{x-1}Cu-H$ system. Pd–H is well-known to have a miscibility gap, and consequent-
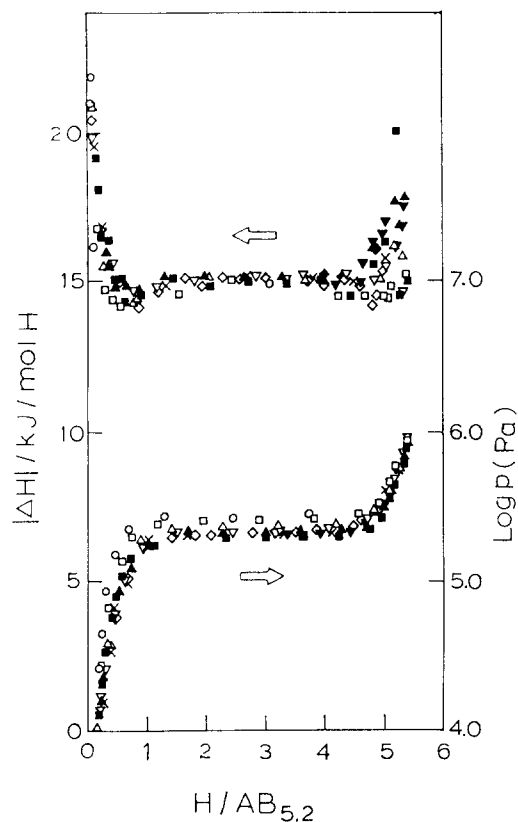
Fig. 6. Calorimetric and isotherm data for the $x = 5.2$ alloy (298 K). The latter show the effect of repeated cycles of hydriding and dehydriding on the plateau pressures. Open symbols are for absorption and filled ones for desorption and the different symbols represent sequential isotherms; the same symbols are employed for the enthalpy change and the pressure data for a given run: O, ●, first run; □, ■, second run; △, ▲, third run; ▽, ▼, fourth run; □, ■, fifth run; ◇, ◆, sixth run.
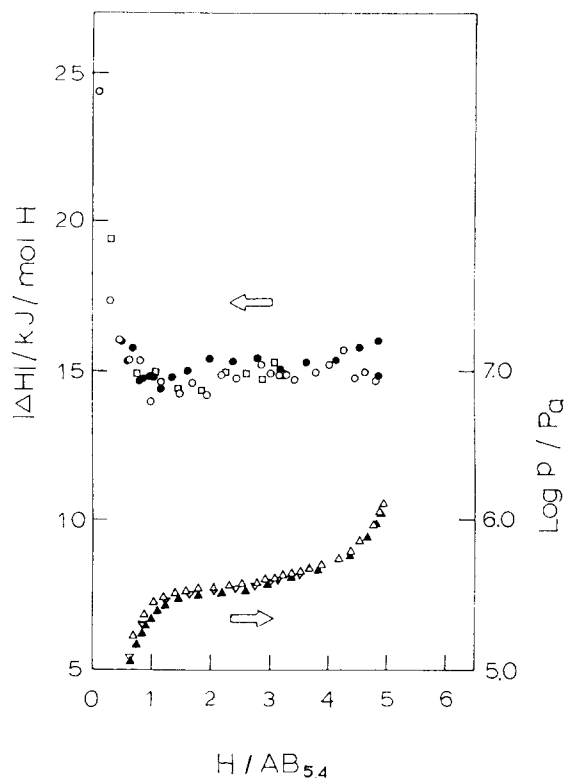
Fig. 7. Calorimetric and isotherm data for the $x = 5.4$ alloy (298 K). The latter show very small effects of repeated cycles of hydriding and dehydriding on the plateau pressures for hydride formation. O, ●, ΔH, first run; △, ▲, p_{H_2}, first run; □, ■, ΔH, second run; ▽, ▼, p_{H_2}, second run. Open symbols are for absorption and filled ones for desorption.

ly the partial enthalpies for its reaction with $H_2(g)$ become more exothermic as n increases due to the attractive H–H interaction [25,26] which leads to H–H condensation, i.e. hydride phase formation below T_c. Because the structure of the alloy sublattice does not change upon phase transition for a miscibility gap system, its free energy (G)–n relation is a single, continuous curve. Below T_c the requirement for the co-existence of two phases is that there must be a common tangent to this free energy curve at two different values of n. Rudman [27] has shown for metal–H miscibility gap systems that the requirement for the existence of such a common tangent is $(\partial \Delta H_H / \partial n)_T < 0$.

A miscibility gap system is usually characterized by a dome-shaped phase diagram and, if this is the case, there must be discontinuous changes in the values of $|\Delta H|$ and $|\Delta S|$ as n increases through the dilute/(dilute + hydride) and the (dilute + hydride)/hydride phase boundaries [28]. (In the dilute phase adjacent to the phase boundary $|\Delta H|$ refers to a partial value and in the adjacent two phase region to the integral

plateau value.) The magnitudes of the discontinuities depend on the steepness of the phase boundaries [28]. This is a consequence of the following equations which must hold at the boundaries [27,29]:

$$\frac{d \ln p_{plat}}{d(1/T)} = \left(\frac{\partial \ln p}{\partial(1/T)}\right)_n + \left(\frac{\partial \ln p}{\partial n}\right)_T \left(\frac{\partial n}{\partial(1/T)}\right)_{at\ a} \quad (6)$$

$$\Delta H_{plat} = \Delta H_H + \left(\frac{\partial \ln p}{\partial n}\right)_T \left(\frac{\partial n}{\partial(1/T)}\right)_{at\ a} \quad (7)$$

where the terms on the right-hand side refer to the single phase adjacent to the dilute/(dilute + hydride) phase boundary at composition a. Instead of discontinuities in the thermodynamic values at the phase boundaries, the experimental enthalpies are usually found to be continuous in the boundary regions due to the experimental conditions where ΔH_H values are measured over small increments of n and therefore "overlap" effects occur, i.e. δn and the corresponding q reflect both the plateau and the adjacent dilute phase. For example, when H_2 is absorbed the dose may lead partly to solution in the dilute phase and, after the terminal hydrogen solubility is exceeded, partly to some hydride phase formation. Since these two reactions have quite different enthalpies and
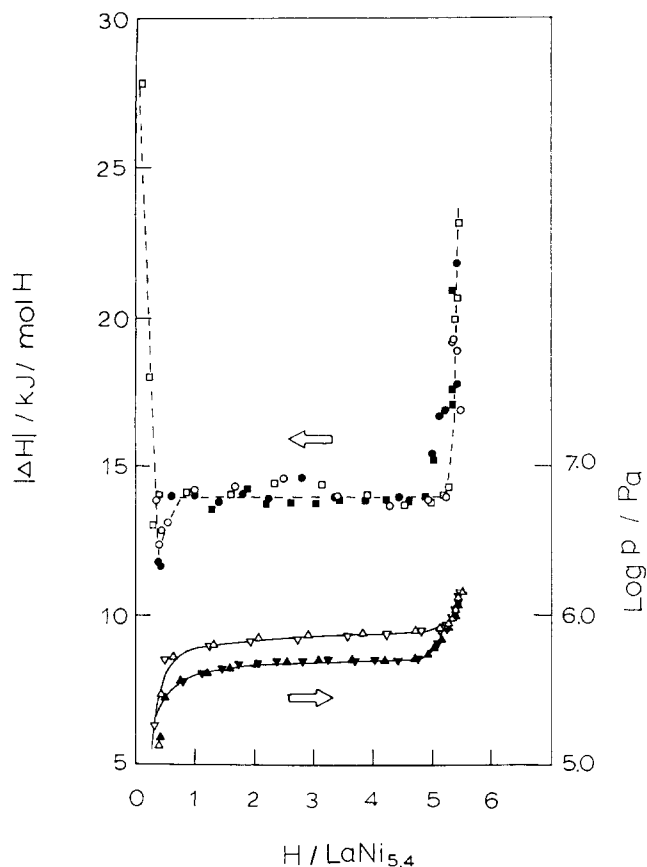
Fig. 8. Calorimetric and isotherm data for the single phase, non-stoichiometric $LaNi_{5.4}$ alloy (298 K). In contrast to the $LaNi_{4.4}Cu$ alloy, there are only two data points with enthalpies of greater magnitude than the plateau value and there is a minimum at the dilute/(dilute + hydride) phase boundary and a discontinuity in the desorption enthalpies at the (dilute + hydride)/hydride phase boundary. A two phase co-existence region is apparent from this phase boundary behavior. Open symbols are for absorption and filled ones for desorption.
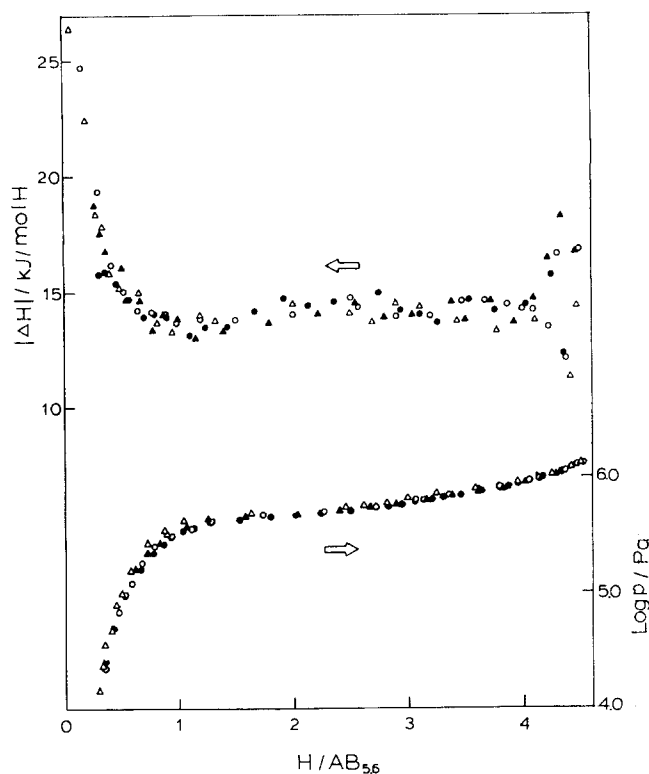

Fig. 9. Calorimetric and isotherm data for the $x = 5.6$ alloy (298 K). The first isotherm is not shown since it was slow and may not have represented equilibrium pressures: $\triangle$, $\blacktriangle$, second run; $\bigcirc$, $\bullet$, third run. Open symbols are for absorption and filled ones for desorption.

entropies, the measured values will be intermediate between the two rather than characteristic of one or the other phase, and therefore a discontinuity will be obscured. If, however, the δn increments are quite small and the discontinuity is large, indications of discontinuities become apparent because the $|\Delta H_H|$ values increase quite sharply with increasing n. Evidence for such discontinuities in $|\Delta H|$ in the miscibility gap system Pd–H are shown in Ref. [12].

Starting from the H-free metal, the partial entropies for solution of H_2 in the metal phase must decrease with n either for a miscibility or a structure transformation system, as shown, for example, by the data for Pd–H [30,31], because the ideal partial configurational entropy decreases as the fraction of sites becomes increasingly occupied [31].

An investigation of hydrogen absorption by the stoichiometric $LaNi_{5-z}Sn_z$ system was recently carried out [32]; the dilute and hydride phases were found to co-exist for z values up to 0.4 at $T \leqslant 373$ K. The

enthalpies for reaction of some of these alloys with H_2, e.g. $LaNi_{4.6}Sn_{0.4}$, were always lower in magnitude in the dilute phase than the plateau value, and for the other $LaNi_{5-z}Sn_z$ alloys, e.g. $LaNi_{4.8}Sn_{0.2}$, there were only one or two data points which were larger in magnitude than the plateau enthalpy, with the vast majority of the enthalpies smaller than the plateau values. Isotherms for the $LaNi_{4.8}Sn_{0.2}$–H system clearly show a critical point. These results contrast with the results for the present system, shown in Figs. 6, 7 and 9 to 11.

Compared with Pd–H and $LaNi_{5-z}Sn_z$–H, the dilute phase thermodynamic behavior of $LaNi_5$ is complex because of defects introduced by activation which mask the normally expected relations between $|\Delta H_H|$ and $|\Delta S_H|$ with n. Because of this, and because a critical point has not been unambiguously found, its thermodynamic behavior does not prove that $LaNi_5$–H has a miscibility gap. The structural behavior seems to suggest that it is a miscibility gap system, but even this aspect of its behavior is ambiguous because there is a small change in the alloy sublattice due to the transformation to the hydride phase [33].

The magnitudes of enthalpies of reaction of activated $LaNi_5$ with H_2 are greater than for the plateau value for the dilute phase from $n \to 0$ to 0.2. They then
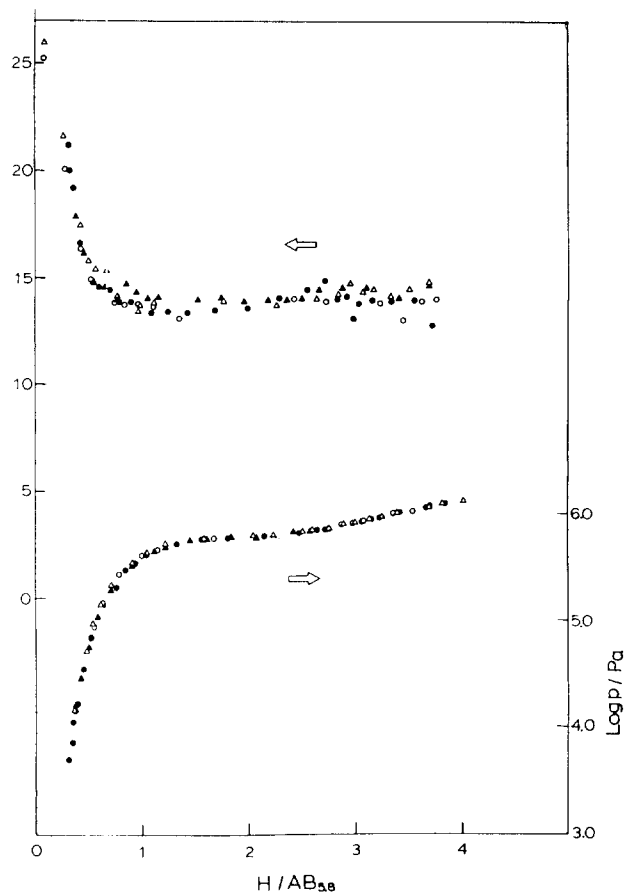
Fig. 10. Calorimetric and isotherm data for the $x = 5.8$ alloy (298 K). In contrast to the alloys with $x > 5.4$ there is no marked effect of cycling through hydride phase formation and decomposition on the absorption pressure. In these data a given run is shown as the same symbol for the calorimetric and equilibrium pressure data: △, ▲, second run; ○, ●, third run. (The first run was slow and is not shown because the data may not have at equilibrium.)

Fig. 11. Calorimetric and isotherm data for the $x = 6.0$ alloy (293 K). In contrast to the alloys with $x < 5.4$ there is no marked effect of cycling through hydride phase formation and decomposition on the absorption pressure. It can also be seen that there is no indication of any minimum in the enthalpies for $n < 1.0$, as seen in the $x = 5.0$ and 5.2 alloys. ○, ●, ΔH, first run; △, ▲, p_{H_2}, first run; □, ■, ΔH, fourth run; ▽, ▼, p_{H_2}, fourth run. (The second and third runs were carried out at different temperatures.) The second run was evacuated at 473 K for 12 h rather than the usual temperature of 298 K. This is reflected by the small displacement of the data for this run to larger n. Open symbols are for absorption and filled ones for desorption.

first decrease to a minimum, and then increase to the plateau value. Murray et al. [34] found that after evacuation of the activated LaNi$_5$ at 475 K, $\Delta H_H \approx -35$ kJ mol^{-1} H as $n \rightarrow 0$. The minimum was found at $n = 0.25$ where $\Delta H_H \approx -14.5$ kJ mol^{-1}H and the plateau started at 0.5 where $\Delta H_{plat} = -15.8$ kJ mol^{-1}H. It should be noted that about half of the $|\Delta H_H|$ values in the dilute region lie below the plateau value. Instead of evacuating at 475 K, if the activated LaNi$_5$ is evacuated at room temperature its behavior was similar except that the value at $n \rightarrow 0$ was somewhat less exothermic, i.e. -28 kJ mol^{-1} H [14]. The anomalously large enthalpies found in the dilute phase as $n \rightarrow 0$ for LaNi$_5$-H have been attributed to occupation of especially energetic sites introduced by activation. After these sites are filled, LaNi$_5$-H behaves more in accord with a miscibility gap system in that the enthalpies increase in magnitude and then there is an indication of a discontinuous change to the plateau value, but this is somewhat questionable due to "overlap effects".
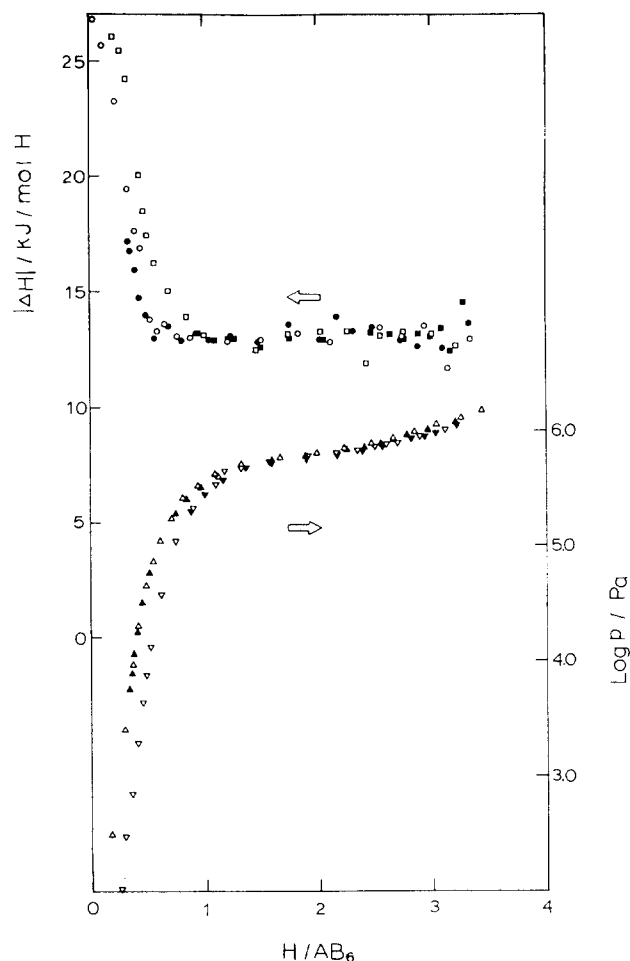
LaNi$_{x-1}$Cu-H systems with $x \geqslant 5.4$ differ from these representative systems because $|\Delta H_H|$ decreases as n increases from 0 for alloys with $x \geqslant 5.6$ (Figs. 9 to 11). This behavior does not satisfy the condition that $(\partial \Delta H_H / \partial n)_T < 0$ [27], and consequently cannot lead to a miscibility gap in these alloys which is consistent with the in situ XRD results [3] and the detailed isotherms (Fig. 12).

The most likely cause of the decrease of $|\Delta H_H|$ values over a relatively large range of n values from $n = 0$ (Figs. 9–11) is the selective occupation of interstices of different energies. These interstices must be an inherent feature of the structure of the LaNi$_{x-1}$Cu non-stoichiometric compounds. Evidence has been offered that the Cu atoms prefer to replace Ni atoms
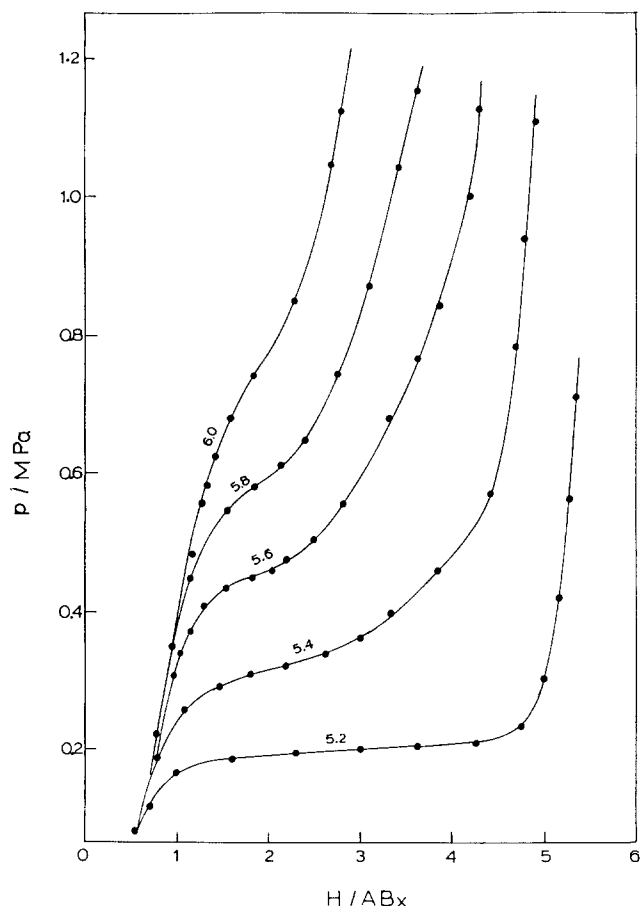
Fig. 12. Equilibrium decomposition pressure data plotted as p_{H_2} (298 K) instead of $\log p_{H_2}$ as in Fig. 1. (The $x = 5.0$ alloy is omitted because the purpose of the plot is to show the changes in the vicinity of the critical composition). The numbers on the isotherms are the values of x for the alloys. These data more clearly show that the miscibility gap must disappear at this temperature somewhere in the range $5.4 < x < 5.6$.

adjacent to the dumbbells because of the greater space in this region for the accommodation of the larger Cu atoms [3]. Thus the Cu solute is not distributed homogeneously within the Ni sublattice of the $LaNi_{x-1}Cu$ alloys. There is a marked anisotropy with increasing x, i.e. contraction of the a-axis and expansion of the c-axis [3]. This contrasts with the effect of substitional solute atoms on the stoichiometric alloys, e.g. $LaNi_{5-z}Sn_z$, where both axes expand with X_{Sn} [35]. In the $LaNi_{5-z}Sn_z$ alloys the thermodynamic behavior is normal for a miscibility gap system, and for this alloy system the Sn occupies Ni sites randomly and there are no dumbbell arrangements causing an anisotropic contraction. In the $LaNi_{x-1}Cu$ alloys there is a marked anisotropy which may be caused by the inhomogeneous distribution of Cu atoms which leads to different interstitial sizes in the vicinity of the dumbbells.

Hydrogen isotherms have been measured in amorphous and crystalline forms of the same alloys, e.g.

ZrNi [36], where it has been found generally that the amorphous forms do not form two phases, i.e. a plateau region is not observed despite comparable hydrogen solubilities in both forms. This absence has been explained theoretically as a consequence of the fact that a Gaussian spread in energies of the various interstices in the amorphous material exceeds the H–H interaction energy [37]. There is no reason to expect a continuous Gaussian distribution of site energies for the $LaNi_{x-1}Cu$ alloys as for amorphous materials, but there may be sets of sites with more negative energy for H occupation than the average, and the spread of their energies for H solution of the various sets of sites may exceed the H–H interaction. The interstices of different and more negative energies than the average are expected to be those near the dumbbells where the Cu atoms and the dumbbells cause local lattice expansion. This would explain why there is no hydride formation up to $n \approx 1.5$ for the $x \geq 5.4$ alloys, but not why miscibility gap behavior is absent after the energetic sites are filled, $n > 1.5$. After the energetic sites are apparently filled, the reaction enthalpies are relatively constant with n, indicating an absence or a masking of an H–H attractive interaction (Figs. 9 to 11). In the few cases where ΔH_H and ΔS_H have been measured over extensive single phase regions in crystalline alloys, e.g. ZrV_2 [38], the values of ΔH_H initially become more exothermic, pass through a minimum and then increase in value with n.

4.1.2. Hydride phase and hydride-like regions

Enthalpy changes for H_2 absorption and desorption have been measured by calorimetry in this research for the $LaNi_{x-1}Cu$ alloys for both absorption and desorption of H_2 over the whole range of n values accessible, up to around 10 bar (Figs. 5–7 and 9–11). For the stoichiometric Cu compound $x = 5.0$, the plateau enthalpy determined calorimetrically is -15.6 kJ mol^{-1} H (Table 2), and for $LaNi_5$ it is -15.1 kJ mol^{-1} H [39]. The more exothermic enthalpy change found for the Cu substituted stoichiometric compound reflects its larger unit cell compared with $LaNi_5$, and is also shown by its lower plateau pressure. The enthalpy for reaction (2) for the stoichiometric compound $LaNi_4Cu$ has also been determined from van't Hoff plots of the decomposition pressures and was found to be 16.9 kJ mol^{-1} H [22], which is larger in magnitude than the calorimetric value measured here. Hysteresis is not a large enough factor, $\frac{1}{2}RT \ln(p_f/p_d) = 670$ J mol^{-1} H, to explain the discrepancy, since it is expected that the calorimetric value plus one half of the hysteresis energy loss, i.e. 15.9 kJ mol^{-1} H, should be equal to the value obtained from the decomposition van't Hoff plot [8,9], i.e. 16.9 kJ mol^{-1} H [22]. Since the calorimetric values are more accurate, the previously reported value of 16.9 kJ mol^{-1} H must be in error.

The thermodynamic values determined by calorimetry for the non-stoichiometric $LaNi_{x-1}Cu$ alloys are shown in Table 2, where they have been evaluated from data at the midpoint of the plateau or at the inflection point for those alloys which are above T_c at 300 K. No systematic difference is found between the magnitudes of the enthalpies for H_2 absorption and desorption, which is expected in view of the results found for other metal–H systems [12].

Some typical results are shown in Figs. 5–7 and 9–11. Fig. 5 shows the data for $LaNi_4Cu$ which has a horizontal plateau and, after the initial cycle, only small hysteresis. The plateau enthalpy and entropy values are also quite constant for all of the $LaNi_{x-1}Cu$ alloys. The latter values are shown in Fig. 13 where, although it is not very apparent because of the profusion of data, the $x = 5.0$ and 5.2 alloys have values of ΔS_{plat} which are nearly constant with n, whereas there is a small increase in magnitudes for the alloys with $x > 5.2$.

Some scatter of data in the single phase regions is apparent in Figs. 5–7 and 9–11. In the single phase hydride region the desorption data exhibit greater values than the absorption ones. This is a general result found for other metal–H systems, e.g. Pd–H [12] and $LaNi_5$–H [34]. It is not found for the $LaNi_{x-1}Cu$ alloys with $x > 5.4$ where two phase regions are absent. It is caused because the presence of hysteresis allows desorption data to be obtained to lower values of n in the hydride single phase as compared with the absorption data.

In Fig. 6 are shown data for the $x = 5.2$ alloy where the minimum in $|\Delta H_H|$ values is clearly seen in the dilute range, and at the (dilute + hydride)/hydride phase boundary there is an increase in $|\Delta H|$ where again the desorption values are greater due to hysteresis because the desorption data remain in the single
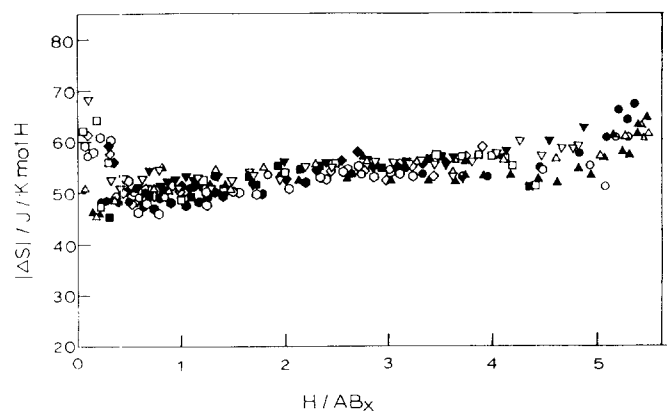

Fig. 13. Entropy changes for the alloys as a function of n at 298 K. △, ▲, $x = 5.0$; ○, ●, $x = 5.2$; ▽, ▼, $x = 5.4$; □, ■, $x = 5.6$; ◇, ◆, $x = 5.8$;   , $x = 6.0$. Open symbols are for absorption and filled ones for desorption.

phase to lower values of n than the corresponding absorption values.

Fig. 7 shows results for the $LaNi_{4.4}Cu$–H system which is just within the miscibility gap. It can be seen that there is only a hint of a minimum in the dilute phase and no clear trend in the β-phase region. For comparison, data for the non-stoichiometric $LaNi_{5.4}$–H system are shown in Fig. 8. There is a two phase co-existence region for this alloy, indicated by the minimum at the dilute/(dilute + hydride) phase boundary, and the clear indication of a discontinuity at the hydride/(dilute + hydride) phase boundary, especially for the desorption data which extends to lower values of n. The difference between these two alloys, each with the same degree of non-stoichiometry $AB_{5.4}$, is striking and must be attributed to the Cu substitution in the $LaNi_{4.4}Cu$ alloy.

Figs. 9 to 11 show results for the $LaNi_xCu$–H systems with $x = 5.6$, 5.8 and 6.0. The enthalpies ΔH_H are relatively constant from $n = 1.0$ to 4.2, which is suggestive of the existence of a plateau in this region, however, the p_{H_2}–n relation does not show a plateau but an inflection point or region (Fig. 12). It appears that while a region of hydrogen contents where the enthalpy of reaction with hydrogen is constant is a necessary requirement for the existence of a plateau, it is not a sufficient one.

It seems reasonable to treat the plateau enthalpies and the enthalpies in the plateau-like regions above T_c as similar quantities and to use them for correlations, e.g. Fig. 4. The plateau enthalpies which are integral quantities are related to the relative partial molar values for a miscibility gap system, i.e. quantities which would be measured if the alloy were to remain as single phase over the region of H contents from $n = a$ to b [40], e.g.

$$\Delta H_{plat} = \frac{1}{b-a} \int_a^b \Delta H_H \, dn \tag{8}$$

Figs. 9–11 show that the values of ΔH_H are nearly constant with n over an extensive range for the alloys which do not form two phases at 300 K. In keeping with this trend, it seems likely that the values of ΔH_H would be similarly constant for those alloys which do form two phases, e.g. $LaNi_{4.2}Cu$–H. For these alloys, therefore, from Eq. (8) it follows that $\Delta H_{plat} \approx \Delta H_H$. The plateau-like values of ΔH_H for the alloys with $x > 5.4$ are therefore quite similar to the ΔH_{plat} for the alloys with $x \leq 5.4$ because both are closely equal to the values of ΔH_H, and it is therefore appropriate to treat the values of ΔH of the various alloys above and below T_c as measurements of similar quantities.

If the data for the alloys are examined (Figs. 6, 7 and 9–11), there is seen to be a greater contribution to the relative chemical potential from the change of

entropy rather than enthalpy between $n = 1$ and 4.2, i.e. typically $T \Delta S_H$ changes by 2 kJ mol^{-1} H whereas ΔH_H changes by about 0.5 kJ mol^{-1} H. It can be seen in Fig. 13 that the $|\Delta S_H|$–n relations for the alloys are all rather similar and independent of whether the particular alloy forms two phases with hydrogen. The average values of ΔS_H or ΔS_{plat} found in the range from $n = 1$ to 4.2 are comparable with the values for a typical plateau in an AB$_5$ system, i.e. around -54 J K^{-1} mol^{-1} H [24,41]. The equality of ΔS_H and ΔS_{plat} values constitutes another justification for the similarity of the thermodynamic values above and below T_c for the purposes of correlation with, for example, x.

It is difficult to understand why the values of ΔH_{11} and ΔS_{11} act as plateau-like quantities for the LaNi$_{x-1}$Cu alloys with $x > 5.4$ and why they are similar to values typical of plateaux in the stoichiometric AB$_5$–H systems. An important contribution to the value of ΔS_H, but not to ΔS_{plat}, is the ideal partial configurational entropy, i.e. the distribution of H amongst the available interstices [40]. Normally in single phase regions the partial configurational entropy should vary significantly and continuously as a function of n. The most likely reason that it would remain relatively constant over a large range of n values is that there is a non-ideal configurational entropy which compensates for the variation of the ideal term, resulting in a nearly constant value.

5. Conclusions

To our knowledge the LaNi$_{x-1}$Cu systems with $x > 5.4$ are the first examples of systems having the AB$_5$ structure which dissolve hydrogen so extensively within single phase regions. This is of practical interest for metal hydride electrode materials because the absence of an abrupt lattice change is desirable for mechanical stability upon cycling [4,42]; it is also of fundamental thermodynamic interest. The extended range of single phase behavior would also be of interest for dynamic studies, e.g. a study of the dependence of diffusion constants on the hydrogen content.

In the dilute phase there is found to be an extensive region of solubility where the exothermicity of the ΔH_H values decreases with n, which is unlike the Pd–H and LaNi$_5$–H systems. This is attributed to an energy site distribution analogous to amorphous solids; the distribution might be centered about the dumbbell sites where the interstices would be larger than the normal ones. Such a distribution apparently decreases the effect of the H–H attractive interaction because two phases do not form for alloys with $x > 5.4$.

It has been found that when the degree x of non-stoichiometry increases in the LaNi$_{x-1}$Cu alloys, p_{H_2}

for the plateaux and "plateau-like" regions of these alloys increases and, since the accompanying ΔS values are all similar, it follows that ΔH must also decrease in exothermicity with x. This is consistent with the calorimetric determinations of these enthalpies. Hysteresis is found to decrease with increasing x until it is almost non-existent for the LaNi$_{5.4}$Cu–H, LaNi$_{5.6}$Cu–H, LaNi$_{5.8}$Cu–H, and LaNi$_{6.0}$Cu–H systems.

Fig. 12 shows a plot of p_{H_2} against n which indicates that there is no plateau for these alloys; this conclusion is not so apparent when $\ln p_{H_2}$ is plotted against n (Fig. 2), which is equivalent to plotting values of ΔH_{11} – $T \Delta S_H$ against n. There are no obvious indications of the presence or absence of a plateau region from the variation of the ΔH_{11} or ΔS_H against n for the various alloys.

Acknowledgements

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