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Hydrogen isotherms for $LaNi_{4.6}M_{0.4}$ alloys where M=group 4A elements

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Abstract

Hydrogen isotherms have been measured for activated $LaNi_{4.6}M_{0.4}$ alloys from 300 to 473 or 493 K where M=Si, Ge, Sn. Thermodynamic parameters have been obtained from the isotherms using van't Hoff plots for hydride formation and decomposition. The ΔH_{plat} values are more exothermic than for the parent compound, $LaNi_5$, but the ΔS_{plat} values are similar. As for the $LaNi_{5-x}Sn_x$ alloys, $LaNi_{4.6}Ge_{0.4}$ and $LaNi_{4.6}Si_{0.4}$ have a greater resistance towards degradation than the parent compound.

Keywords: Hydrogen isotherms; $LaNi_5$; Alloys

1. Introduction

It is well known that $LaNi_5$ degrades during continued hydriding/dehydriding at elevated temperatures, e.g. Ref. [1]. In an effort to have AB_5 alloys with greater resistance towards degradation than $LaNi_5$, a series of $LaNi_{4.6}M_{0.4}$ alloys have been prepared and characterized by H_2 isotherm measurements with M=Si, Ge and Sn.

It has been shown previously that M=Sn alloys have lower plateau pressures and a greater resistance to degradation than the parent compound, $LaNi_5$ [2–6]. Hysteresis for the activated forms of these alloys decreases significantly with increase of *x*. Other members of group 4A elements, i.e. Si and Ge, will be substituted into $LaNi_5$ in order to learn if they also have desirable properties for H_2 storage with regards to plateau pressures and resistance towards degradation.

Isotherm measurements of these systems have been previously carried out by Mendelsohn et al. [7] on all three of the $LaNi_{4.6}M_{0.4}$ alloys but only over a very limited temperature range, i.e. 303 and 313 K. Percheron-Guegan et al. [8] measured an isotherm for a $LaNi_{4.5}Si_{0.5}$ alloy at 303 K and Witham et al. [9] determined isotherms at a few temperatures near ambient for a series of $LaNi_{5-x}Ge_x$ alloys. Meli et al. measured dynamic H_2 isotherms at several temperatures for $LaNi_{4.7}Si_{0.3}$ and $LaNi_{4.5}Si_{0.5}$ alloys [10].

2. Experimental

The $LaNi_{4.6}M_{0.4}$ alloys were prepared at the Ames Laboratory of Iowa State University by arc-melting the elements. The purity of the Ni was 99.99% and the La 99.96% including oxygen. The buttons were melted several times inverting them after each melting. The arc-cast buttons were wrapped in Ta foil, sealed in an evacuated quartz tube and annealed at 1223 K for 100 h. The alloy ingots were shown to be single phase from metallography and the powder X-ray diffraction (XRD) patterns showed that the angles of the reflections were equal for randomly selected regions within the ingot.

The isotherms for the $LaNi_{4.6}Sn_{0.4}$ alloy had two sections in their plateaux which was not a 'splitting' because they appeared for the initial absorption plateau. This is probably due to a gross inhomogeneity which could not be removed by the annealing treatment. For this reason another sample was also employed which did not exhibit any anomalies; this was obtained from HCI (Hydrogen Consultants, Inc.) and had been employed earlier [4].

Isotherms were measured in an all-metal apparatus using electronic diaphragm gauges (M.K.S. Instruments). The temperatures were controlled with liquid baths to within ±0.2 K.

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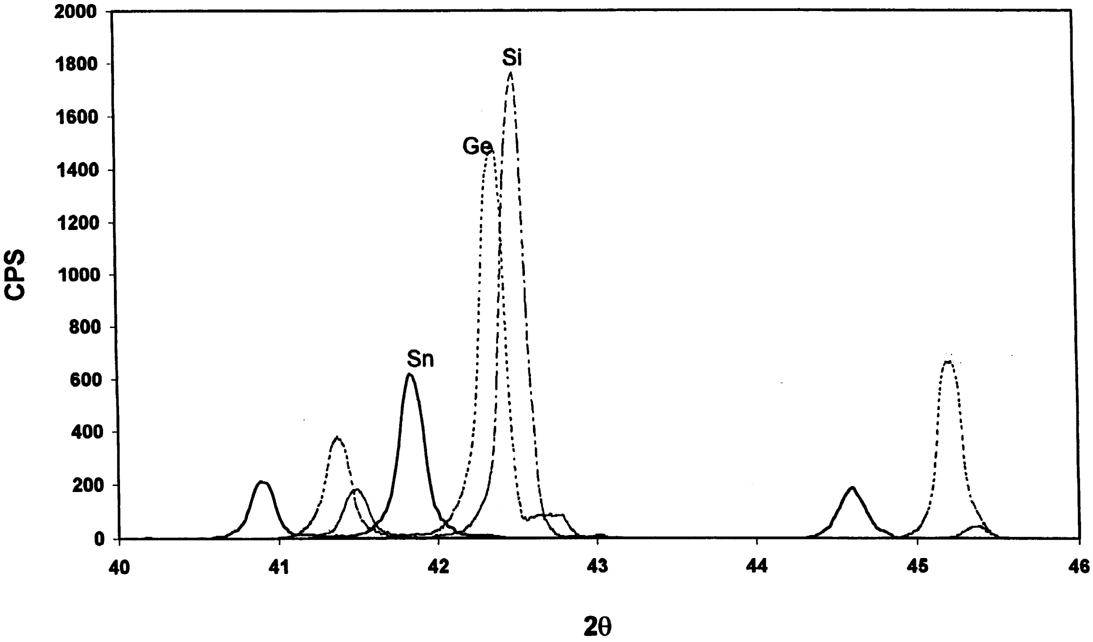

Fig. 1. XRD patterns for H-free, unactivated $LaNi_{4.6}M_{0.4}$ alloys (298 K); the reflections appear rather broad because of the narrow 2θ scale. The three different alloys are identified on the figure.

3. Results and discussion

3.1. XRD determination of lattice parameters

The XRD patterns are shown in Fig. 1 for unactivated, H-free alloys at 298 K. The results are shown in Table 1 where it can be seen that the lattice parameters and unit cell sizes increase in the order: $LaNi_5$, $LaNi_{4.6}Si_{0.4}$, $LaNi_{4.6}Ge_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$. The parameter and unit cell size for $LaNi_{4.8}Sn_{0.2}$ are also shown which are closer to the other $LaNi_{4.6}M_{0.4}$ alloys than the $LaNi_{4.6}Sn_{0.4}$ alloy. The lattice parameters for $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ do not differ very much but the latter parameters are definitely greater than the former.

3.2. Hydrogen isotherms for $LaNi_{4.6}M_{0.4}$ at 373 K

An initial, activation isotherm is shown for the $LaNi_{4.6}Si_{0.4}$ alloy (373 K) with the subsequent isotherm and, as usual for AB_5–H systems, the initial absorption isotherm has a greater plateau p_{H_2} than the subsequent ones but the desorption plateau is nearly the same (Fig. 2). A total of 11 isotherms were measured on this alloy from 300 to 493 K.

Table 1
Lattice parameters and unit cell volume by XRD for the $LaNi_{4.6}M_{0.4}$ alloys

Alloy	a_0 (nm)	c_0 (nm)	V (nm^3/10^{-3})
$LaNi_5$	0.5006	0.3993	86.75
$LaNi_{4.6}Si_{0.4}$	0.5023	0.3995	87.26
$LaNi_{4.6}Ge_{0.4}$	0.5036	0.4009	88.03
$LaNi_{4.6}Sn_{0.4}$	0.5091	0.4069	91.23
$LaNi_{4.8}Sn_{0.2}$	0.5057	0.4018	89.01

An initial, activation isotherm is shown for the $LaNi_{4.6}Ge_{0.4}$ alloy (373 K) with the subsequent isotherm. As expected, the initial absorption isotherm has a greater plateau p_{H_2} than the subsequent ones and the desorption plateau is nearly the same. A total of 23 isotherms were measured for this alloy from 300 to 503 K and some at 373

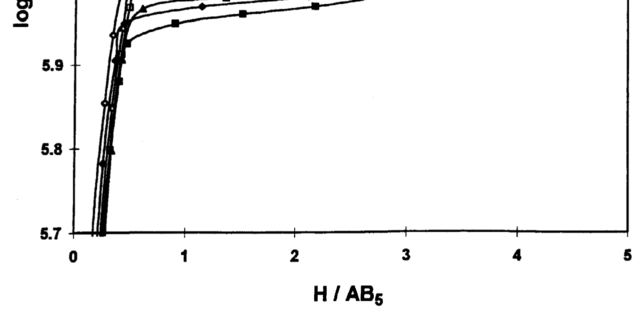

Fig. 2. Hydrogen isotherms for the $LaNi_{4.6}Si_{0.4}$ alloy at 373 K. ◊, Isotherm for unactivated alloy; △, second isotherm; □, measured after an isotherm measured and 'soaked' at 473 K, 15 h at 112 bar. Open symbols represent absorption and filled ones desorption.

K are shown in Fig. 3. The activation absorption isotherm has only a few points and the initial points before the plateau may have some error because of the slow kinetics. The absorption plateau is relatively greater than the subsequent ones as compared to the isotherms for the $LaNi_{4.6}Si_{0.4}$ alloy (Fig. 2).

Isotherms were measured for the $LaNi_{4.6}Sn_{0.4}$ alloys from both sources, Ames and HCI, and they had similar pressures over the first half of the plateaux but the alloy from Ames had somewhat higher pressures in the latter half. Isotherms for the $LaNi_{4.6}Sn_{0.4}$ alloy (HCI) were measured in 1993, 1995 and 1998 and, in each case, the sample was obtained from the same arc-melted ingot and a small decrease in the plateau pressures over time was noticed, i.e. an aging effect.

A series of isotherms (373 K) for each of the activated $LaNi_{4.6}M_{0.4}$ alloys, M=Ge and Sn, and for activated $LaNi_5$ are shown in Fig. 4; the $LaNi_{4.6}Si_{0.4}$ alloy is not included because its isotherms are very close to those for the $LaNi_{4.6}Ge_{0.4}$ alloy. First of all, it can be seen that under identical conditions $LaNi_5$ shows plateau splitting but the others do not. The desorption plateau for $LaNi_5$ splits for the initial, activation isotherm (not shown). The capacities of the $LaNi_{4.6}M_{0.4}$ alloys are smaller than for $LaNi_5$. The plateau pressures decrease from $LaNi_5$ to $LaNi_{4.6}Ge_{0.4}$ to $LaNi_{4.6}Sn_{0.4}$. The plateau pressure of $LaNi_{4.6}Sn_{0.4}$ is much lower than those for the $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ alloys (Fig. 4) whose plateau pressures are closer to that of $LaNi_{4.8}Sn_{0.2}$. This is consistent with the unit cell size of $LaNi_{4.8}Sn_{0.2}$ being closer to the other $LaNi_{4.6}M_{0.4}$ alloys than the $LaNi_{4.6}Sn_{0.4}$ alloy (Table 1).

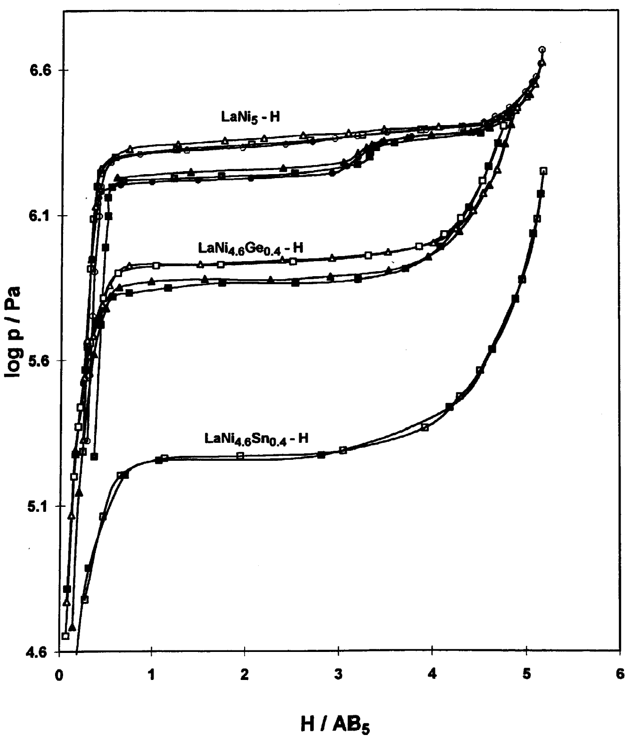

Fig. 4. Hydrogen isotherms for activated $LaNi_5$, $LaNi_{4.6}Ge_{0.4}$ and $LaNi_{4.6}Si_{0.4}$ alloys (373 K). The different symbols show different isotherms for each.

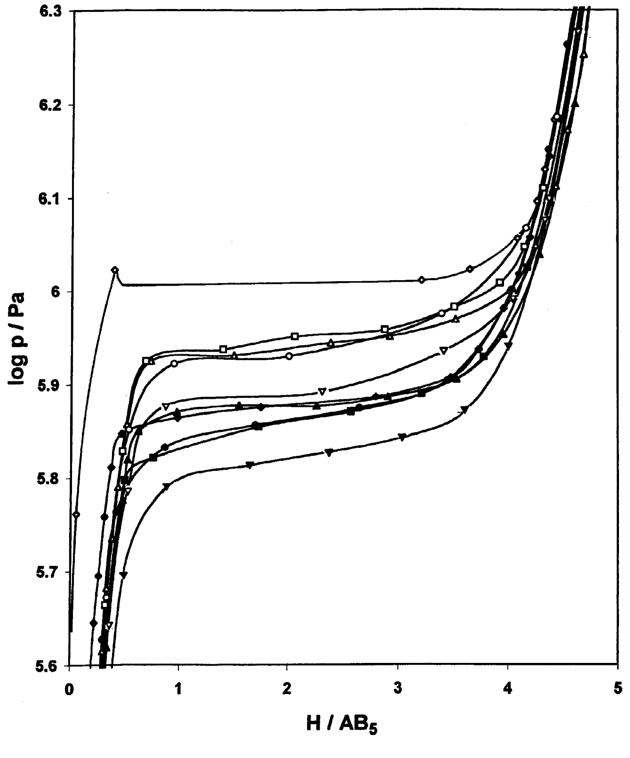

Fig. 3. Hydrogen isotherms for the $LaNi_{4.6}Ge_{0.4}$ alloy at 373 K. ◊, Isotherm for unactivated alloy; △, second isotherm; □, measured after nine previous cycles at temperatures and soaking at 473 K for 44 h at 116 bar ($H/AB_5=3.5$); ○, isotherm after soaking at 493 K for 25 h at 118 bar ($H/AB_5=3.5$); ▽, isotherm after soaking at 503 K for 24 h at 110 bar. Open symbols represent absorption and filled ones desorption.

3.3. Isotherms at various temperatures and van't Hoff plots for the $LaNi_{4.6}M_{0.4}$ alloys

Fig. 5 shows isotherms for activated forms of the alloys. The low temperature isotherms were measured before the higher temperature ones in order to avoid any possible effects of degradation in the lower temperature data (300 to 373 K). There is a decrease in plateau widths as the temperatures are increased. At the higher temperatures the $LaNi_{4.6}Si_{0.4}$ alloy has greater plateau pressures than the $LaNi_{4.6}Ge_{0.4}$ alloy but at 300 K they have very similar ones. In view of this, the enthalpy for hydride formation should be slightly greater for the former as compared to the latter.

The corresponding van't Hoff plots are shown in Fig. 6 for the $LaNi_{4.6}M_{0.4}$ alloys and they extend from 303 to 373 K where only liquid temperature baths were employed. The derived thermodynamic parameters are tabulated in Table 2. The plateau enthalpies are as expected, i.e. more exothermic than for $LaNi_5$, and the entropies are in the range expected for AB_5–H systems, 54±2 J/K mol

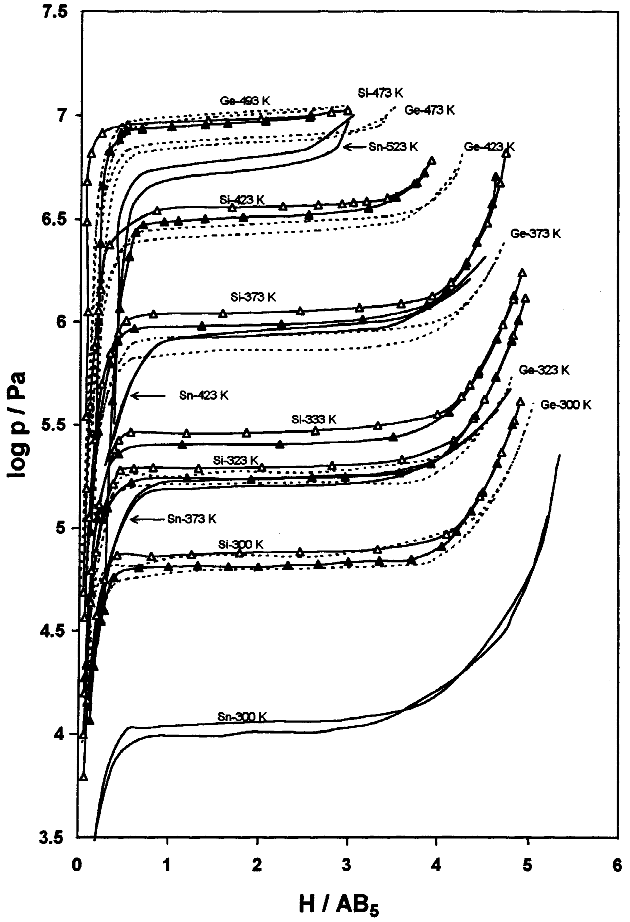

Fig. 5. Hydrogen isotherms for the $LaNi_{4.6}M_{0.4}$ alloys at different temperatures. Continuous curves without data points, $LaNi_{4.6}Sn_{0.4}$; dashed curves without data points, $LaNi_{4.6}Ge_{0.4}$; △, $LaNi_{4.6}Si_{0.4}$. The isotherms are labeled in the figure, e.g. Ge-373 K refers to $LaNi_{4.6}Ge_{0.4}$ at 373 K.

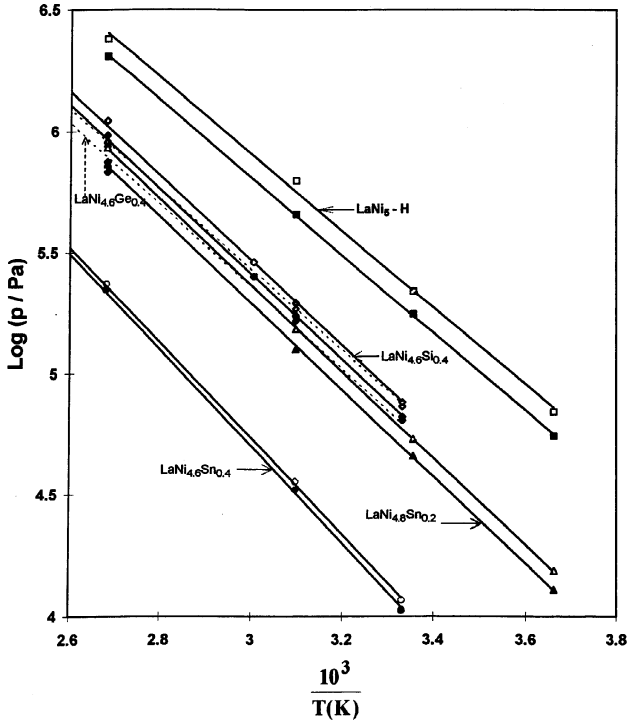

Fig. 6. van't Hoff plots for the $LaNi_{4.6}M_{0.4}$ alloys compared to $LaNi_5$ [6] and to $LaNi_{4.8}Sn_{0.2}$.The dashed lines without data points represent the van't Hoff plots for the $LaNi_{4.6}Ge_{0.4}$ alloy. Open symbols are for absorption and filled ones for desorption.

$1/2H_2$, for the T-range centered about 350 K [4], the following values of the absorption thermodynamic parameters were determined by Mendelsohn et al. [7] using isotherms at rather closely spaced temperatures: $\Delta H^{f}_{plat} = -17.8$, -17.1 and -19.2 kJ/mol $1/2H_2$ for $LaNi_{4.6}Ge_{0.4}$, $LaNi_{4.6}Si_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$, respectively and $\Delta S^{f}_{plat} = -57.1$, -55.4 and -54.8 J/K $1/2H_2$ for the same alloys. Desorption values were not determined. While the agreement with the present results (Table 1) is reasonable, it is interesting that the entropy change is more negative for the $LaNi_{4.6}Ge_{0.4}$ alloy than the expected value of -54 ± 2 J/K mol $1/2H_2$ [4] and the enthalpy is consequently more negative than found here (Table 1), i.e. a somewhat anomalous entropy implies a spurious ΔH_{plat}. This may be an illustration of a general rule for AB_5–H systems.

If the equilibrium plateau pressure is taken as $\sqrt{p_f p_d}$ where p_f and p_d are the formation and decomposition plateau pressures [11] and ΔS_{plat} is -54 J/K mol $1/2H_2$ at ≈350 K [4]. The plateau enthalpies can be calculated on this basis using

$$\Delta H_{calc,\,plat} = T(R \ln \sqrt{p_f p_d} - 54). \tag{1}$$

Although it is apparent Eq. (1) predicts that there is a temperature dependence in the calculated values because $|\Delta S_{plat}| = 54$ J/K mol $1/2H_2$ is appropriate at a temperature centered about 350 K, there is only a difference of 0.1 J/K mol $1/2H_2$ for $|\Delta S_{plat}|$ using plateau pressures at 373 or 323 K. It is clear from Table 2 that the calculated values of $|\Delta H_{plat}|$ are very close to the average for absorption and desorption making the approximate method quite convenient and probably more accurate than experimental values based on a limited number of closely spaced sets of plateau pressures/temperatures.

The loss of work due to hysteresis can be computed from the expression

Table 2

Thermodynamic parameters for $LaNi_{4.6}M_{0.4}$ and for $LaNi_5$ and $LaNi_{4.8}Sn_{0.2}$ where $|\Delta H_{plat}|$ is in units of kJ/mol $1/2H_2$ and $|\Delta S_{plat}|$ is in units of J/K mol $1/2H_2$

Alloy	ΔH^{f}_{plat}	ΔH^{d}_{plat}	$\lvert\Delta H_{calc,\,plat}\rvert$	ΔS^{f}_{plat}	ΔS^{d}_{plat}
$LaNi_5$	−15.1	15.3	15.3	−54.2	53.7
$LaNi_{4.6}Si_{0.4}$	−16.8	17.1	16.6	−54.8	55.2
$LaNi_{4.6}Ge_{0.4}$	−16.1	17.0	16.8	−52.2	53.9
$LaNi_{4.6}Sn_{0.4}$	−19.0	19.1	18.9	−54.3	54.4
$LaNi_{4.8}Sn_{0.2}$	−17.0	17.1	17.0	−54.0	54.2

$$\frac{1}{2}RT\ln(p_f/p_d) \qquad (2)$$

where p_f and p_d are the plateau pressures for hydride formation and decomposition, respectively. Using the expression for the loss of work, the hysteresis is about 150 J/mol 1/2H_2 (323 K) for the M=Ge and Si alloys which is quite small; the value for the $LaNi_{4.6}Sn_{0.4}$ alloy is even smaller than this but that for the $LaNi_{4.8}Sn_{0.2}$ alloy is also about 150 J/mol H_2.

3.4. Degradation of $LaNi_{4.6}M_{0.4}$ alloys

As shown by Sandrock et al. [12] an effective test for stability is to hold an AB_5 alloy at a large H content at an elevated temperature, ‘soaking’. After such soaking it was shown that $LaNi_{5-x}Mn_x$ alloys degraded rather quickly at 573 K [13]. The degradation was shown by the failure of the subsequent desorption isotherms (≥573 K) to coincide with the absorption isotherm in the dilute phase, by slow kinetics and by anomalous behavior of isotherms measured subsequently at lower temperatures. In the parent compound, $LaNi_5$, degradation is accompanied by plateau splitting [1].

The $LaNi_{4.6}M_{0.4}$ alloys resist degradation more effectively than either of the above which is the principal reason why the $LaNi_{5-x}Sn_x$ alloys have been used for practical applications, e.g. Ref. [14]. Luo et al. [5] found that after the $LaNi_{4.8}Sn_{0.2}$ alloy was ‘soaked’ at, e.g. 523 K for 72 h at 140 bar, there was no evidence for any degradation. The degradation of the $LaNi_{4.6}Sn_{0.4}$ alloy has not been examined until now.

The two different (Ames and HCI) $LaNi_{4.6}Sn_{0.4}$ samples were subjected to soaking, e.g. 523 K for 24 h at 103 bar, and in both cases there was no effect on the subsequent isotherms at 373 K except for a small lowering of the desorption plateau pressure.

Soaking the $LaNi_{4.6}Ge_{0.4}$ alloy at 118 bar for 24 h at progressively higher temperatures 473 K, 493 K did not cause any changes in the subsequent isotherms (373 K) measured after soaking at each temperature but there was a lowering of the plateau pressures after soaking at 503 K (Fig. 3).

The $LaNi_{4.6}Si_{0.4}$ alloy was soaked at 473 K for 15 h at 112 bar and there was no change in the subsequent isotherm (373 K) except for a small decrease in p_d and increase of hysteresis (Fig. 2). This was also found for another sample ‘soaked’ at the same temperature.

4. Conclusions

Isotherms have been measured and thermodynamic parameters determined for $LaNi_{4.6}M_{0.4}$ alloys. The $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ alloy–H systems have similar plateau pressures while the latter has a slightly greater H capacity. Both have significantly greater plateau pressures than $LaNi_{4.6}Sn_{0.4}$–H. The $LaNi_{4.6}M_{0.4}$ alloys are quite resistant to degradation by ‘soaking’ at elevated temperatures although there is a slight decrease of p_d for the $LaNi_{4.6}Sn_{0.4}$ and $LaNi_{4.6}Si_{0.4}$ alloys after soaking. Both p_f and p_d were ≈12% lower after a 503 K soaking, but there was no loss in capacity.

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References

[1] S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, J. Alloys Comp. 253–254 (1997) 226.
[2] S. Lambert, D. Chandra, W. Cathey, F. Lynch, R. Bowman, J. Alloys Comp. 187 (1992) 113.
[3] J. Cantrell, T. Beiter, R. Bowman, J. Alloys Comp. 207–208 (1994) 372.
[4] S. Luo, W. Luo, J. Clewley, T. Flanagan, L. Wade, J. Alloys Comp. 231 (1995) 467.
[5] S. Luo, W. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Alloys Comp. 231 (1995) 473.
[6] S. Luo, J. Clewley, T. Flanagan, R. Bowman, L. Wade, J. Alloys Comp. 267 (1998) 171.
[7] M. Mendelsohn, D. Gruen, A. Dwight, Inorg. Chem. 18 (1979) 3343.
[8] A. Percheron-Guegan, C. Lartique, J. Achard, J. Less-Common Metals 109 (1985) 287.
[9] C. Witham, R. Bowman, B. Fultz, J. Alloys Comp. 253–254 (1997) 574.
[10] F. Meli, A. Zuettel, L. Schlapbach, J. Alloys Comp. 190 (1992) 17.
[11] T. Flanagan, C.-N. Park, W. Oates, Prog. Solid State Chem. 23 (1995) 291.
[12] G. Sandrock, P. Goodell, E. Huston, P. Golben, Zeit. Phys. Chem. N.F. 164 (1989) 1285.
[13] W. Luo, S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, J. Alloys Comp. 202 (1993) 147.
[14] R. Bowman, P. Karlmann, S. Bard, Brilliant Eyes Ten-Kelvin Sorption Cryocooler Experiment, 1997, JPL Publication 97-14.