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THE EFFECT OF GROUP III A AND IV A ELEMENT SUBSTITUTIONS (M) ON THE HYDROGEN DISSOCIATION PRESSURES OF $LaNi_{5-x}M_x$ HYDRIDES

by

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THE EFFECT OF GROUP III A AND IV A ELEMENT SUBSTITUTIONS (M) ON THE HYDROGEN DISSOCIATION PRESSURES OF $LaNi_{5-x}M_x$ HYDRIDES.

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Ternary modifications of the hydrogen absorbing alloy $LaNi_5$ have been found to have a large effect on the hydrogen dissociation pressure of the corresponding hydride.[1,2,3,4] Recently, we have studied a series of alloys $LaNi_{4.6}M_{0.4}$ (M = Al, Ga, In, Sn) to establish the effect of various group III A and IV A element substitutions on the dissociation pressures of their corresponding hydrides.[5] In this paper, we extend those results to include the alloys $LaNi_{4.6}Si_{0.4}$, $LaNi_{4.6}Ge_{0.4}$ and $LaNi_{4.4}B_{0.6}$. Further dissociation pressure measurements have been made on the alloy $LaNi_{4.6}Ga_{0.4}$ as well as two additional indium alloys. The data obtained for the three indium alloys appear to follow a linear correlation of lnP or ΔG with the amount of substituted element as has been previously observed for Al.[1,6]

Experimental

The experimental procedures and apparatus were essentially the same as described earlier.[7] The initial hydrogen absorption (i.e. "activation procedure") for the alloys in this study was performed at hydrogen pressures of from 150-400 PSIA.

Results

Desorption isotherms for the hydrides $LaNi_{4.6}Si_{0.4}H_y$ and $LaNi_{4.6}Ge_{0.4}H_y$ are shown in Fig. 1 for temperatures of 30° and 60°C. Isotherms were also obtained at 40°C but are not shown. An alloy of approximate composition $LaNi_{4.4}B_{0.6}$ was prepared and its x-ray powder diffraction pattern was indexed as hexagonal with a = 5.09 ± 0.01 Å and C = 3.69 ± 0.01 Å. A more detailed report on this newly discovered ternary alloy will be published elsewhere.[8] Desorption pressures were measured at five temperatures and at approximately the same composition for the hydride $LaNi_{4.4}B_{0.6}H_y$. From the data shown in Table I, the enthalpy and entropy of formation of the hydride were calculated to be -8.0 Kcal/mole H_2 and -23.4 cal/deg-mole H_2, respectively.

Table I.

Composition (H atom/mole $LaNi_{4.4}B_{0.6}$)	Temperature (°C)	H_2 Pressure (atm)
0.76	30.0	0.210
0.76	35.0	0.261
0.76	40.0	0.326
0.74	45.0	0.395
0.74	50.0	0.479

Two indium alloys of nominal composition $LaNi_{4.8}In_{0.2}$ and $LaNi_{4.7}In_{0.3}$ were also prepared. However, as will be explained in the discussion section, the actual compositions of the hexagonal AB_5-type phases were $LaNi_{4.95}In_{0.05}$ and $LaNi_{4.86}In_{0.14}$ as determined from their x-ray powder diffraction patterns. For $LaNi_{4.95}In_{0.05}$, a = 5.031 ± 0.002 Å and c = 3.991 ± 0.001 Å, while for $LaNi_{4.86}In_{0.14}$, a = 5.039 ± 0.003 Å and c = 4.018 ± 0.003 Å. Desorption isotherms for the indium samples were measured at three temperatures and their plateau pressures are given in Table II. Also given in Table II are plateau pressures measured for the hydride of $LaNi_{4.6}Ga_{0.4}$.

Table II

Composition	Temperature (°C)	Pressure (atm)
$LaNi_{4.95}In_{0.05}H_{2.5}$	30	1.37
$LaNi_{4.95}In_{0.05}H_{2.5}$	40	2.20
$LaNi_{4.95}In_{0.05}H_{2.5}$	60	4.83
$LaNi_{4.86}In_{0.14}H_{2.25}$	30	0.78
$LaNi_{4.86}In_{0.14}H_{2.25}$	40	1.17
$LaNi_{4.86}In_{0.14}H_{2.25}$	60	2.42
$LaNi_{4.6}Ga_{0.4}H_{2.5}$	30	0.49
$LaNi_{4.6}Ga_{0.4}H_{2.5}$	40	0.745
$LaNi_{4.6}Ga_{0.4}H_{2.5}$	60	1.71

The thermodynamic and crystallographic data for all of the group III A and IV A substituted alloys studied to date are summarized

in Table III.

Table III.

Alloy	$\Delta H_{\alpha\rightarrow\beta}$ $\frac{\text{kcal}}{\text{mole } H_2}$	$\Delta S_{\alpha\rightarrow\beta}$ $\frac{\text{cal}}{\text{mole } H_2\text{-deg}}$	calc ΔG for 20°	Alloy Cell Volume ($Å^3$)
$LaNi_{4.4}B_{0.6}$	-8.0	-23.4	-1.1	82.4
$LaNi_{4.6}Al_{0.4}$	-8.7	-26.1	-1.05	87.9
$LaNi_{4.6}Ga_{0.4}$	-8.4	-26.2	-0.7	88.1
$LaNi_{4.95}In_{0.05}$	-8.4	-28.3	-0.1	87.5
$LaNi_{4.86}In_{0.14}$	-7.6	-24.5	-0.4	88.4
$LaNi_{4.6}In_{0.4}$	-9.5	-26.5	-1.7	91.0
$LaNi_{4.6}Si_{0.4}$	-8.5	-27.3	-0.5	86.9
$LaNi_{4.6}Ge_{0.4}$	-8.2	-26.5	-0.4	87.8
$LaNi_{4.6}Sn_{0.4}$	-9.2	-26.2	-1.5	91.0

Figure 2 shows the approximately linear correlation observed for both the Al and In substituted systems of lnP versus amount of substituted element.

Discussion

The stoichiometries $LaNi_{4.95}In_{0.05}$ and $LaNi_{4.86}In_{0.14}$ were obtained by measuring the cell volumes accurately and then reading the In concentration from a plot previously obtained of cell volume vs In concentration.[9] The presence of an unknown second phase was noted by the appearance of 2 or 3 weak lines

in the x-ray powder diffraction pattern of the annealed alloys.

As can be noted from Table III, except for $LaNi_{4.4}B_{0.6}$, all the alloys follow the previously observed approximately linear correlation of decreasing free energy of formation of AB_5 hydrides with increasing cell volume.[1,6] However, a detailed examination of the data reveals a reversal of the trend for the two hydride pairs $LaNi_{4.6}Al_{0.4}H_y$ - $LaNi_{4.6}Ga_{0.4}H_y$ and $LaNi_{4.6}Si_{0.4}H_y$ - $LaNi_{4.6}Ge_{0.4}H_y$. For both pairs, there occurs a change in the electronic structure of the substituted element from empty 3d orbitals to filled 3d orbitals. Thus the observed reversal in hydride free energies may indicate the involvment of specific metal-hydrogen bonding properties in addition to the previously noted importance of metal-hydrogen[10] and hydrogen-hydrogen[11] distances on the dissociation pressure of the alloy hydrides.

The alloy $LaNi_{4.4}B_{0.6}$ clearly does not follow the above noted trend. Sandrock has suggested that the free energy may be more closely correlated with the "a" lattice parameter of the alloy rather than the cell volume.[12] $LaNi_{4.4}B_{0.6}$ would be consistent with this correlation. In any event, the further explanation of this notable exception to the cell volume correlation awaits a more precise structural determination.

Although no extensive measurements were made of absorption isotherms, some data points taken in order to compare the magnitude of hysteresis of the Group III A and IV A substituted hydrides with the parent hydride $LaNi_5H_6$ are shown in Table IV. The reason for the reduction in hysteresis in some of the alloys

compared to $LaNi_5$ is not clear, but is an important benefit in some proposed practical applications of metal hydrides.[13]

Table IV

Alloy	Temperature (°C)	H/mole alloy	P_{abs} (atm)	P_{des} (atm)	P_{a/P_d}
$LaNi_{4.6}Al_{0.4}$[a]	30	3.09	0.31	0.28	1.11
$LaNi_{4.6}In_{0.4}$	30	1.96	0.097	0.095	1.02
$LaNi_{4.4}B_{0.6}$	25	0.76	0.159	0.157	1.01
$LaNi_{4.6}Si_{0.4}$	30	1.58	0.73	0.67	1.09
$LaNi_{4.6}Si_{0.4}$	40	1.23	1.11	1.04	1.07
$LaNi_{4.6}Ge_{0.4}$	30	1.32	0.85	0.78	1.09
$LaNi_{4.6}Ge_{0.4}$	40	1.97	1.31	1.21	1.08
$LaNi_{4.6}Sn_{0.4}$[b]	20	2.41	0.078	0.079	0.99
$La_{1.05}Ni_{4.6}Sn_{0.4}$[b]	32	2.38	0.162	0.156	1.04
$LaNi_5$[c]	20	3.0	2.0	1.6	1.25

[a] from ref. 6

[b] two different samples

[c] from ref. 14

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