Journal of the Less-Common Metals, 45 (1976) 347 - 350

Short Communication

Hydrides of lanthanum–nickel compounds*

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(Received October 17, 1975)

The La–Ni system has recently been reinvestigated in the range 50 - 100 at.% Ni [1]. Six intermetallic compounds, listed in Table 1, were identified, and their structure and lattice parameters were determined. In view of the interesting, reversible hydriding characteristics of $LaNi_5$ [1 - 4], we undertook an investigation as to whether similar behavior would be exhibited by the other intermetallic phases in the La–Ni system. Of particular interest are the $LaNi_3$ and La_2Ni_7 compounds, because they have superstructures based on the hexagonal $LaNi_5$ cell. We have initiated a neutron-diffraction study of the hydride phases found in all the known La–Ni compounds and we will report our findings at a later date. In this communication, we wish to report on the absorption of hydrogen (in some cases deuterium) in five of the intermetallic compounds referred to above.

The La–Ni alloys were prepared from 99.9%-pure lanthanum and 99.95%-pure nickel. The samples, contained in 99.8%-pure alumina crucibles, were melted together under vacuum in an induction furnace. The homogenizing treatment consisted of repeated melting, crushing the samples and remelting once or twice, and finally sealing the resulting buttons in quartz ampules and heating to the appropriate temperature (as judged by the phase diagram in ref. 1) for periods ranging from 1 to 3 weeks. The compounds were identified by X-ray diffraction and the lattice parameters agreed well with those reported [1]. No major impurities were detected and only simple phases were indicated in the X-ray patterns.

The LaNi compound was hydrided by exposing a 12.762 g button, contained in a stainless steel boat, to 1 atm of ultra-pure hydrogen. Prior to admission of hydrogen the system had been evacuated to 10^{-3} Torr. On heating to 150 °C the rate of absorption became extremely rapid. The sample was further heated to 350 °C (accompanied by hydrogen evolution) and then cooled slowly to room temperature. The composition of the sample, $LaNiH_{2.60}$, was calculated from the known volume of the system and

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*This study was supported by a grant from Norges Teknisk-Naturvitenskapelige Forskningsrod (NTNF).

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TABLE 1

Lanthanum–nickel alloys

Compound	Structure	Structure type
LaNi	orthorhombic	CrB
$LaNi_{1.4}$	orthorhombic	unknown
$LaNi_2$	cubic	$MgCu_2$
$LaNi_3$	rhombohedral	$PuNi_3$
La_2Ni_7	hexagonal	Ce_2Ni_7
$LaNi_5$	hexagonal	$CaCu_5$

the pressure change; the final pressure was 0.64 atm. On heating to moderate temperatures, 300 - 400 °C, it was found that hydrogen was desorbed with difficulty. Because of the apparent high stability of the hydride, we did not attempt any high-pressure work on LaNi. An X-ray pattern of the sample could be indexed on the basis of an f.c.c. lattice, $a = 5.64$ Å. This is close to the value expected for $LaH_{2.6}$ [5] and we suspected at first that the intermetallic compound had decomposed to give $LaH_{2.6}$ and Ni. However, no lines due to metallic nickel were found in the pattern and $LaNiH_{2.60}$ appears to be a hydride phase. Further study is in progress.

$LaNi_2$ was hydrided in a similar fashion at 250 °C, heated further to 400 °C and cooled slowly in hydrogen to room temperature. The composition of the sample was $LaNi_2H_{2.51}$ at a final pressure of 0.72 atm. The sample was reheated to 252 °C and a desorption isotherm was determined. A plateau pressure of ≈ 0.005 atm was indicated, and by varying the temperature whilst monitoring the plateau pressure, ΔH for the reaction

$$LaNi_2(s) + H_2(g) \rightarrow LaNi_2H_2(s)$$

was calculated to be -13.0 ± 1 kcal/mole by the usual procedure of plotting $\log P_{\text{plateau}}$ *vs.* $1/T$. The reaction was repeated with deuterium rather than with hydrogen and the composition of the sample was $LaNi_2D_{2.52}$ at a final pressure of 1 atm. When placed under 10 atm of D_2 at room temperature, this sample continued to absorb gas until a final composition of $LaNi_2D_{4.10}$ was reached. $LaNi_2$ has the cubic $C15$-type structure [1] with 8 molecules/unit cell and a total of 41 tetrahedral sites. The maximum composition, if all tetrahedral sites are filled, is therefore $LaNi_2H_{5.125}$. It is probable that this composition can be approached by increasing the hydrogen pressure.

$LaNi_3$, when hydrided at 200 °C, followed by slow cooling in hydrogen to room temperature, resulted in a hydride of composition $LaNi_3H_{2.80}$, under a final pressure of 0.53 atm. Another $LaNi_3$ sample was hydrided at room temperature by exposure to 50 atm H_2 pressure. Absorption took place immediately and was accompanied by considerable evolution of heat. The composition of this sample was $LaNi_3H_{5.3}$ under 50 atm H_2 pressure. A preliminary desorption study of this sample indicated behavior similar to that found in the $ErCo_3$–H system [6], although the equilibrium pressures were much lower (below 1 atm).

La_2Ni_7 was deuterided at 200 °C and gave a deuteride of composition $La_2Ni_7D_{5.74}$ when cooled to room temperature under a final pressure of 0.58 atm. Further D_2 absorption was accomplished by exposing the sample to 10 atm pressure. However, the final composition will not be known until the neutron-diffraction pattern has been obtained and the sample analyzed.

$LaNi_5$ absorbed deuterium to a composition corresponding with $LaNi_5D_{6.0}$ under a pressure of 10 atm. This is in good agreement with the earlier observations on the corresponding hydrogen absorption for $LaNi_5$ [1 - 4].

A cellular model has recently been proposed to account for the heat of formation in transition metal alloys [7, 8]. In this model, the heat of formation, ΔH, is assumed to be derived from two contributions, one being positive and reflecting the discontinuity in the density of electrons, n_{ws}, at the boundary between dissimilar atomic cells, and the other being negative and originating in the difference in chemical potential, φ^*, for electrons at the two types of atomic cells. ΔH may be estimated by the formula:

$$\Delta H = \mathrm{f}(c)\ [Q(n_{\mathrm{ws}}^{1/3})^2 - P\mathrm{e}(\Delta\Phi^*)^2] \tag{1}$$

where ΔH is in kcal/g at. alloy, P and Q are constants and $\mathrm{f}(c)$ is a concentration function discussed in ref. 8. Values for Q and P, as well as for the parameters n_{ws}, and Φ^* may also be obtained from ref. 8.

With the additional assumption that hydrogen in metals may be treated as a metallic atom, the model has been applied to binary hydrides [7] and also to ternary hydrides [4, 9]. For ternary hydrides, a simple expression for the heat of formation may be written:

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta H(AB_n) \tag{2}$$

where $\Delta H(AB_nH_{2m})$ is the heat of formation of the ternary hydride, $\Delta H(AH_m)$ is the heat of formation of the stable binary hydride, $\Delta H(B_nH_m)$ is the heat of formation of the unstable binary hydride (*i.e.*, element B does not normally form a stable hydride) and $\Delta H(AB_n)$ is the heat of formation of the intermetallic compound, AB_n. ($n \geqslant 1$)

Equation (2) has been used to estimate the heats of formation of the various hydride phases found in the La–Ni system. The results are shown in Table 2. The heats of formation of the alloys were estimated using eqn. (1) and the heats of formation of LaH_2 and LaH_3 were obtained from ref. 10. The way in which the ternary hydride is broken down in eqn. (2) is at present somewhat arbitrary. Considerations of the actual crystal structure, the interatomic distances, and atomic volumes, must be made in making the appropriate choice. The entropy change in forming hydrides is almost entirely due to the entropy loss of hydrogen as a molecular gas and it is, therefore, not surprising that this change is nearly constant, around 30 cal/deg. mole H_2, for all hydrides [4, 9]. This being the case, it is clear that it is possible to formulate the stability criterion for hydrides in terms of ΔH only. If, for example, one requires the transformation pressure of the

TABLE 2

Heats of formation of ternary hydrides in the La–Ni system

Hydride (AB_nH_{2m})	$\Delta H(AH_m)$ (kcal/mole)	$\Delta H(B_nH_m)$ (kcal/mole)	$\Delta H(AB_n)$ (kcal/mole)	$\Delta H(AB_nH_{2m})$ (kcal/mole H_2)
$LaNiH_3$	−49.6	0	− 7.4	−28.1
$NaNi_2H_5$	−60	0	−12.3	−19
$LaNi_3H_5$	−60	0	−14.8	−18.1
$LaNi_{3.5}H_4^*$	−49.6	0	−15.7	−17.0
$LaNi_5H_6$	−60	0	−16.8	−14.4

*Assumed composition, $La_2Ni_7H_8$, is written as $LaNi_{3.5}H_4$.

hydride reaction to be 1 atm at room temperature, *i.e.*, $\Delta G = 0$, this will correspond with $\Delta H - T\Delta S \cong -9$kcal/mole H_2 [4, 9]. For ternary hydrides, consideration of eqn. [2] and the entropy argument leads to a rule of reversed stability; the more stable the binary compound which is being hydrided, the less stable will be the ternary hydride [4, 9]. The calculations in Table 2 for the LaNi system support this conclusion. There is a gradual increase in the stability of the intermetallic compound as the nickel concentration increases from LaNi to $LaNi_5$, as seen by the decrease in negative values values for $\Delta H(AB_n)$. There is a corresponding decrease in the stability of the resulting ternary hydride, as evidenced by the decrease in negative values for $\Delta H(AB_nH_{2m})$. Our experimental data are in qualitative agreement with this trend. The order of decreasing stability of the hydrides, deduced from the dissociation measurements, is $LaNiH_3 > LaNi_2H_5 > LaNi_3H_5 > LaNi_{3.5}H_4 > LaNi_5H_6$.

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