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Split Plateaux in the $LaNi_5$–H System and the Effect of Sn Substitution on Splitting

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Abstract

Split plateaux corresponding to the appearance of an additional, γ, phase, which have been observed elsewhere, have been found in this research for closely stoichiometric $LaNi_5$. The plateaux were found to be very horizontal at lower temperatures before splitting occurs. Some splitting in the decomposition plateau was found even at 273 K after cycling at more elevated temperatures. A virgin sample showed a small amount of splitting of the decomposition plateau at 373 K and this splitting increased markedly for the second cycle and its extent became nearly constant after about 5 or 6 cycles at 373 K. Van’t Hoff plots were made using data from the split plateaux. Split plateaux were not found for any of the $LaNi_{5-x}Sn_x$ alloys which were examined at 373 K, i.e., those with $x \geq 0.05$, after cycling where $LaNi_5$ exhibited split plateaux for the first cycle.

Keywords: $LaNi_5$; $LaNi_{5-x}Sn_x$; Split plateau

1. Introduction

Many pressure–composition isotherms have been reported in the literature for $LaNi_5$ which was not very close to the stoichiometric 1-to-5 ratio of La-to-Ni and where there is an accompanying significant plateau sloping. Closely stoichiometric $LaNi_5$ will be employed here which was prepared by the Ames Laboratory of Iowa State University.

One motive of the research was to establish whether the so-called split plateaux corresponding to the appearance of an additional, γ, phase [1–7] occur for closely stoichiometric $LaNi_5$ where, in the absence of splitting, its plateaux were found to be very horizontal.

It was also planned to determine whether split plateaux occur at 373 K for $LaNi_{5-x}Sn_x$ alloys with $x \geq 0.05$ under the same conditions where $LaNi_5$ exhibits split plateaux. A few words should be said about these Sn substituted AB_5 alloys. The $x=0.2$ alloy has been shown to be have a greater stability towards degradation during thermal cycling and towards “soaking” at elevated temperatures [8,9], i.e., storage at high H contents and elevated temperatures, than the parent compound. The stability of the $x<0.2$ alloys towards thermal cycling or soaking have not been determined. The degree of hysteresis is relatively small for the $x=0.2$ alloy.

2. Experimental

$LaNi_5$ was 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 was 99.95% including oxygen. 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 to be single phase from metallography and the XRD patterns showed that the angles of the reflections were equal for samples from randomly selected regions in the ingot. The ratio of Ni-to-La in the $LaNi_5$ was 5.00 ± 0.01 based on electron microprobe analysis. The $LaNi_{5-x}Sn_x$ samples with $x=0.2$ and 0.1 were also prepared at Iowa State University using a similar procedure and then they were annealed in vacuo at 1223 K for 120 h. The alloys were also subjected to

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elemental analysis and the results have been reported elsewhere [9]. The $x=0.05$ alloy was prepared at the University of Vermont by arc-melting equal amounts of the $x=0.0$ and 0.10 the alloys from the Ames Laboratory and then annealing the resultant alloy in a sealed quartz vessel for 96 h at 1133 K.

Three different samples from the main batch of stoichiometric $LaNi_5$ were employed. The first $LaNi_5$ sample (A) was hydrided and dehydrided 43× for isotherm measurements without raising its temperature above 323 K. After these isotherms were measured, some were measured at more elevated temperatures where splitting would be expected to occur.

Isotherms for sample (B) were measured initially at 353 K and then measured at 373 K to search for splitting as described below.

Isotherms for the third sample (C) were measured initially at 373 K in order to examine the isotherms for splitting.

The P_{H_2} versus $n=(H/AB_5)$ data were determined volumetrically in an all-metal apparatus. Temperatures were controlled with fluid baths. The $P_{H_2}-n$ data were corrected for non-ideality of the $H_2(g)$ and for the volume expansion of the alloy due to interstitial H.

XRD studies were performed on the same bulk materials as the $p–c–T$ studies for $x=0.00$, 0.05, 0.010 and 0.020 in $LaNi_{5-x}Sn_x$ using a SCINTAGX$_1$ automated powder diffractometer in the theta–theta mode (silicon solid state detector) and Cu K_α, radiation. The description of the sample handling techniques are described elsewhere [10].

3. Results and discussion

3.1. Splitting of plateaux and degradation of $LaNi_5$

Some of these observations, e.g., the occurrence of sloping plateaux, the reduced capacity which accompanies splitting and the occurrence of splitting at low temperatures after it has taken place at higher temperatures, have been made earlier, e.g., [6,7]. Because the observation of splitting of the plateaux in the $LaNi_5–H_2$ system is still somewhat controversial and because the experimental conditions of the present and earlier research [6,7] differ somewhat, it is useful to re-characterize splitting using a closely stoichiometric sample. Further characterization of the splitting, which has not been reported elsewhere, will be described.

In this paper splitting will refer to the decomposition plateau only because it was not very apparent in the formation isotherm. Sample A was employed for the following set of experiments where it was found that there was no indication of splitting after a total of 43 complete cycles of hydride formation and decomposition at $T\leq323$ K. The temperature was then increased, and a total of four isotherms were measured at progressively higher temperatures from 353 K to 373 K. The splitting became more obvious with increased temperature. After isotherm measurements at 373 K, the sample was cooled, and an isotherm measured at 298 K showed some splitting and a reduced capacity; the plateau for hydride formation, which did not show appreciable splitting, showed a greater slope than before. The sample was then reheated to 373 K where an isotherm was measured which showed increased splitting accompanied by a capacity loss. Fig. 1 shows an isotherm at 323 K before the sample had been heated above 323 K compared to an isotherm at 323 K after splitting had been observed at 373 K. It can be seen that there is splitting and sloping plateaux which were not observed before the sample had shown splitting at 373 K although a total of 43 isotherms had been previously measured at $T\leq323$ K. It was found that the kinetics for desorption were significantly faster in the split between the two plateau regions than on either side of the split and the kinetics were slightly faster in the plateau on the high H content side than on the lower H content plateau indicating perhaps a more profound structural change for $\gamma\rightarrow\alpha$ than for $\beta\rightarrow\gamma$ phase change.

Virgin sample B was introduced and isotherms measured as shown by the flow chart in Fig. 2. A series of isotherms were measured between 323 K and 373 K. The purpose of which was to monitor the effect of heating and isotherm measurement at 373 K on the isotherms subsequently measured at 323 K. The capacities decreased and the splitting increased progressively at 323 K after each isotherm measurement at 373 K particularly after the last one because during the isotherm at 373 K the sample had been ‘‘soaked’’ for 12 h at $n=5.7$. After measurement of a total of four isotherms at 373 K, the sample was then cooled to 298 and to 273 K for isotherm measurements. These both exhibited sloping, splitting and reduced capacities. The observation of splitting at 273 K is noteworthy.

Isotherms for sample C were measured consecutively at 373 K. There was found to be a small indication of splitting for the first decomposition plateau and then, for the subsequent isotherms, the splitting became more prominent.

For sample C the splitting was examined as a function of the n value at the start of the desorption. The results are shown in Fig. 3 where it seems that the location of the split increases as the starting value of n for the desorption increases, however, the difference between n at the start of the desorption and at the split does not seem to be a fixed value.

Hysteresis, $\frac{1}{2}RT\ \ln\ (p_f/p_d)$, of the split plateaux after about 8 cycles at 373 K is about 60 J/ mol $\frac{1}{2}H_2$ for $n>3.5$ and about 200 J/ mol $\frac{1}{2}H_2$ for $n<3.0$ found for sample C. For the same sample at 323 K it was 300 J/ mol $\frac{1}{2}H_2$ under conditions where there was little splitting. Hysteresis scans were carried out in the region $n<3.0$ and $n>3.5$. In

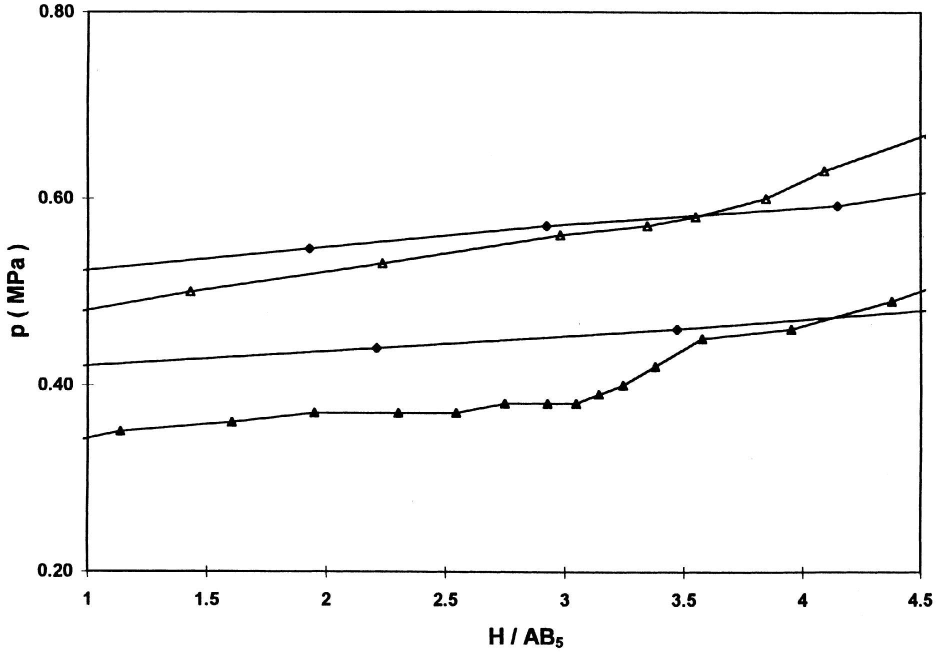

Fig. 1. Hydrogen isotherms at 323 K for $LaNi_5$ before and after the appearance of splitting in isotherms measured at 373 K. ◇, before any measurements at $T>323$ K; △, after splitting had been observed at 373 K. The data are plotted directly as PH_2 rather than log pH_2 so that the splitting is more apparent. The two upper curves represent absorption and the two lower ones desorption.

both ranges the scans were rather horizontal but, in the higher content range, the scan was nearly reversible over the range from $n=4.5$ to 3.9.

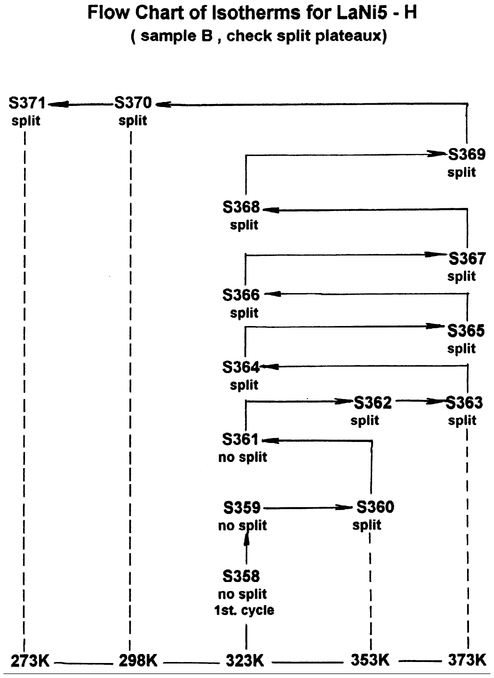

Fig. 2. Flow chart for Sample B showing the appearance of splitting. The first isotherm for this sample is designated as S358.

3.2. van't hoff plot for $LaNi_5$–H

The data characterizing the split plateaux were employed to construct a van't Hoff plot and Fig. 4 shows the results where the data for decomposition appear to reflect the splitting, i.e., except for the data at 323 K, the split plateau data bracket the values which would be expected from extrapolation of the lower temperature decomposition plateau data which do not exhibit splitting.

3.3. Splitting of plateaux for $LaNi_{5-x}Sn_x$ alloys

The plateau pressures for the $LaNi_5Sn_x$–H system decrease with increase of X_{Sn}. In order to determine whether these alloys also exhibit splitting, consecutive isotherms were measured at 373 K because at this temperature the parent compound exhibited a small a degree of splitting during the initial cycle and significant splitting for subsequent ones (Fig. 3).

The isotherm measurements commenced with the $X_{Sn}=0.2$ followed by the 0.10 and 0.05 alloys. The $X_{Sn}=0.2$ did not show any splitting after cycling 2× at 373 K. The $X_{Sn}=0.1$ also did not show any splitting after four consecutive cycles at 373 K and its capacity did not change with the cycling. The $X_{Sn}=0.05$ alloy, whose stoichiometry is the closest to the parent compound, also did not show any splitting after four consecutive cycles at 373 K (Fig. 5). Two cycles were then carried out at 393 K where there was a very faint indication of splitting but then

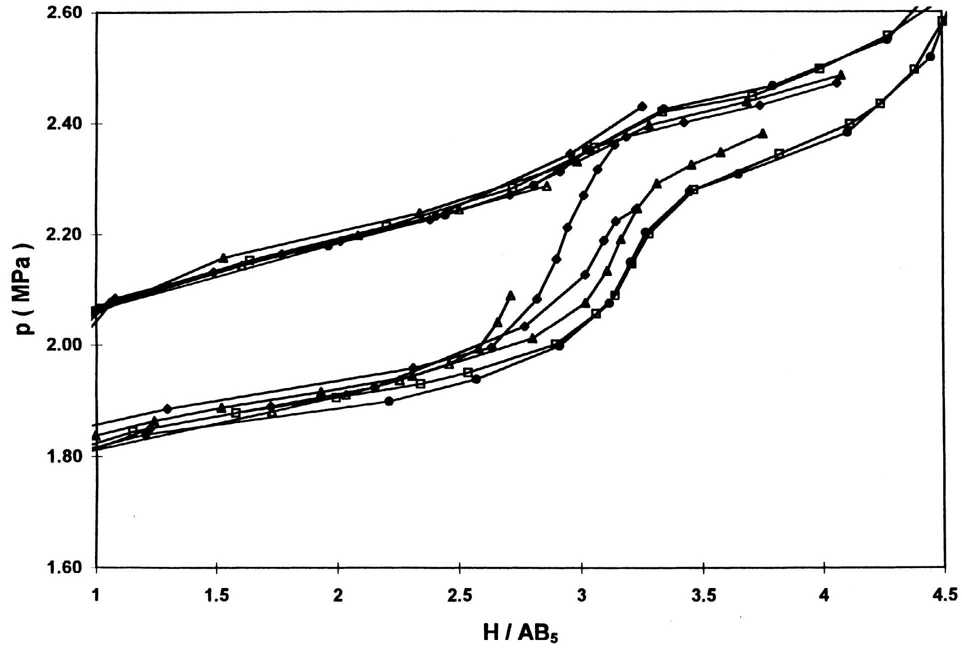

Fig. 3. Isotherms at 373 K measured for Sample C. The shifting position of the split in the desorption plateau reflects the starting point of the desorption. The value of *n* where the absorption was stopped and desorption commenced is shown after the symbol. ◇, *n*=4.0; △, *n*=4.10; □, *n*=4.6; □, *n*=4.8; △, *n*=2.9; ◇, *n*=3.3; where the same symbols are used for absorption and desorption. The lower curves are for desorption and the upper ones for absorption.

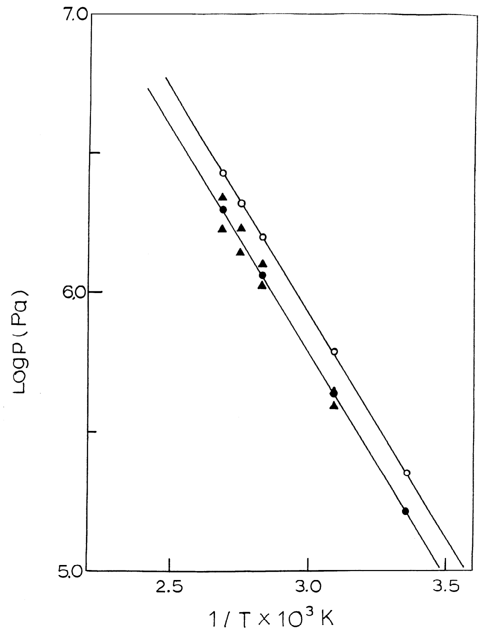

Fig. 4. Van't Hoff plot for $LaNi_5$–H (samples A and B). The straight lines are for the van't Hoff plot established at lower temperatures. The filled circles show desorption data for a sample which did not show significant splitting. The filled triangles show data for split plateaux and, except for 323 K, these data bracket the van't Hoff plot determined at lower temperatures. Open symbols represent absorption and filled ones desorption.

two more cycles at 373 K showed no splitting. The capacity was also found to be unchanged by cycling. This is a rather remarkable result considering that the $X_{Sn}=0.05$ alloy has such a small amount of Sn and its hysteresis is similar to the parent compound.

3.4. XRD characterization

All of the XRD patterns indicate that only a single phase is present for the various H-free AB_5 samples following the measurement of the isotherms described above, i.e., no evidence for the γ-phase was found. The XRD peaks were quite narrow with the FWHM being $\leqslant$0.16 degrees for the two $LaNi_5$ samples. The $LaNi_{5-x}Sn_x$ alloys generally had peaks with FWHM as narrow as 0.04 to 0.06 degree. There were no extra peaks and all normally appearing peaks were between $2\theta=20$ to 80° even when the data were expanded by a factor of 10. The unit cell parameters for the samples investigated are shown in Table 1.

Matsumoto et al [3] obtained the XRD pattern for the γ-phase by subtracting the α and β-phase reflections from a XRD pattern of $LaNi_5H_x$ obtained *in situ* at 353 K, 1.41 MPa PH_2. It had reflections at $2\theta=29.5$, 34.0, 39.4, 41.0 and 44.9 with the 29.5 and 41.0 being the strongest. The latter could be masked in the present patterns by the (200) reflection but, nonetheless, only a trace of the γ-phase could be present in the dehydrided samples because this peak does not appear to have a shoulder or be unusually broad or intense and it does not change before and after cycling. If it is present in the $LaNi_5$ during partial

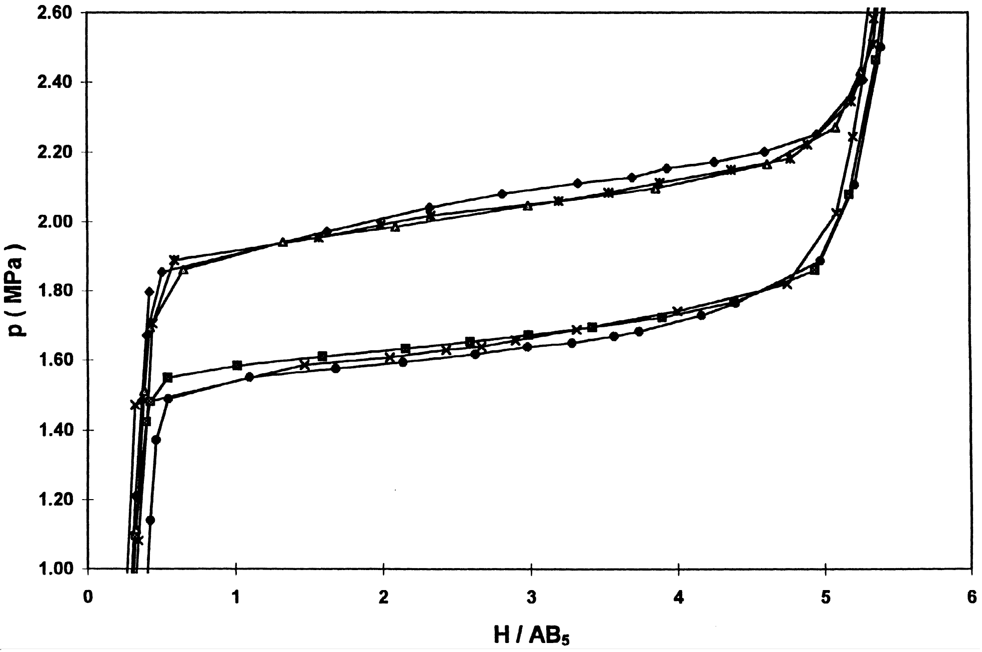

Fig. 5. Hydrogen isotherms at 373 K for the $LaNi_{4.95}Sn_{0.05}$ alloy. There were two isotherms measured between these, at 393 K, and then the sample was returned to 373 K for two more isotherm measurements. There is no indication of splitting. The upper curves are for absorption and the lower ones for desorption.

dehydriding, then it reverts back to the normal pattern after dehydriding.

4. Conclusions

Splitting of the decomposition plateau was first observed at $T \geq 353$ K for $LaNi_5$–H during isotherm measurements and it was subsequently found down to even 273 K after splitting had occurred at higher temperatures. Accompanying the splitting there was a decreased capacity and a sloping of the plateaux. Splitting and a decrease in capacity was enhanced by ‘‘soaking’’ at 373 K at high H contents. Splitting has been attributed to internal stresses which may also be the cause of the sloping plateaux, however, it is not clear why these factors should cause a decreased capacity. Dislocations have also been suggested to be a factor during cycling [7] but it is difficult to reconcile this with the effect of ‘‘soaking’’. The relationship between the appearance of the γ-phase, i.e., splitting, and degradation is apparent but has not been explained. It seems that splitting may be a result of degradation. The analogy between the $LaNi_5$–H and FeTi–H systems has been pointed out [2].

Remarkably no splitting or degradation was observed at 373 K for the $LaNi_{5-x}Sn_x$ alloys even for $x = 0.05$ which is a very small amount of Sn substitution. Again the splitting and degradation appear to accompany each other since neither appear after a few cycles at 373 K.

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Table 1
XRD Data for $LaNi_5$-Sn_x at 298 K

Dehydrided Alloy	Cycles	a/nm	c/nm	V/nm^3	Comments
$LaNi_5$	50×	0.50163(1)	0.39895(4)	0.08694(4)	Split plat.
$LaNi_5$	Several at RT	0.50258(6)	0.39822(1)	0.08711(1)	Greatest FWHM
$LaNi_{4.95}Sn_{0.05}$	0	0.50249(1)	0.39870(3)	0.08718(3)	
$LaN_{4.95}Sn_{0.05}$	11×	0.50263(8)	0.39904(1)	0.08731(2)	
$LaN_{4.90}Sn_{0.10}$	0	0.50345(5)	0.40027(3)	0.08786(5)	
$LaNi_{4.90}Sn_{0.10}$	11×	0.50371(3)	0.39992(3)	0.087887(3)	
$LaNi_{4.80}Sn_{0.20}$	0	0.50516(2)	0.40098(9)	0.08862(3)	
$LaN_{4.80}Sn_{0.20}$	38×	0.50598(4)	0.40242(6)	0.08923(2)	
$LaN_{4.80}Sn_{0.20}$	1330×	0.50558(3)	0.40181(3)	0.08895(4)	

Some of these cycled samples have small amounts of hydrogen which were not removed by evacuation but generally these amounts are small.
The numbers in parentheses indicate the uncertainty in the last figure. V is the unit all dimension.

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