

# HYDROGEN STORAGE BY RARE EARTH METAL BASED ALLOYS

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## Introduction

Among various  $AB_5$ -H systems, where A is a rare earth and B is Co or Ni, the  $LaNi_5$ -H system is the best-known system, and an important prospective compound for the hydrogen storage media in stationary applications, or where weight is not a limiting consideration.

The  $LaNi_5$ -H system was found by VAN VUCHT et al. [1—5], and more extensive work has been done by J. J. REILLY et al. [6—12], at Brookhaven. This system has the unique feature of readily absorbing and desorbing a large quantity of hydrogen at modest pressures and room temperatures. Also considerable research from various aspects has been done on this system which can be found in literature elsewhere. [13—16]

The aim of the present paper is focussed on the assessment of the influence of La/Ni atomic ratio to the absorption limit and the equilibrium pressure of hydrogen at the plateau, through the measurement of  $La-Ni_x$ , where x stands for 0, 1.0, 1.4, 2.0, 3.0, 4.0 and 5.0 atoms of Ni, and Misch metal- $Ni_5$  alloys. The Pressure-Composition isotherms at different temperatures for these alloys were measured at the hydrogen pressure ranging from  $10^{-5}$  to 40 kg/cm<sup>2</sup>, and at that temperature ranges mostly from 20 °C to 90 °C, and 550° to 750 °C for some cases. The influence of Ce, which is commonly found in Misch metal, and Co, on the equilibria in La-Ni-H alloys were also discussed through the results of P-C-T measurements.

## Thermodynamics

There are many thermodynamic properties to be considered for Metal-Hydrogen Systems, and they can be derived from the equilibrium pressure of hydrogen to the composition, at different temperatures of the samples. Procedures for deriving those properties can be seen in literature elsewhere, [17—19] and so only the properties calculated from P-C isotherms will be considered in this paper.

## Experimental

The samples were prepared by arc-melting under purified argon from starting materials of 3N purity of La, Ce, Ni, and 2N of Co. The chemical composition of Misch metal produced in Japan was shown in Table 1. To improve homogeneity, the button samples were repeatedly remelted for several

**Table 1**  
Chemical Composition of Misch Metal

Element	wt%		
	A	B	C
La	74.38	62.61	49.45
Ce	14.62	25.00	15.24
Nd	7.00	8.39	31.87
Pr	2.73	3.96	8.00
Sm	0.67	0.5	0.5
Others		0.95	0.95
Fe	1.03	1.18	1.00
T.R.E.	98.0	97.87	98.05

T.R.E.: Total Rare Earth

times and no further annealing treatment was performed. Samples of about 5 gr. of 1 mm in diameter were taken from the crushed particles of button ingot for the high pressure measurement. A 0.5 mm thick sample was sliced from the button, and was used for the low pressure measurement. Hydrogen gas used for high pressure measurement was 7N purity of Nippon Oxygen Gas Co, and that for low pressure measurement was obtained from desorption of  $TiH_2$ , and purified by Pd tubing permeation method. The experimental apparatus was separated in two parts; one for a high pressure reactor and the other for a low pressure reactor. However, the principle of measurement was fundamentally not different for both.

A diagram of manifold and reactor assembly is shown in Fig. 1. The high pressure tubing and reactor were made of stainless steel tubing bellow-sealed valves which are capable of sustaining up to  $200 \text{ kg/cm}^2$  of hydrogen. The pressure was measured by the transducer or pressure gauges. On the other hand, the low pressure part was made of pyrex glass and quartz tubing for the reactor. Pressure was measured by mercury manometers or the McLeod gauge, which is capable of reading up to  $1 \times 10^{-6}$  Torr or hydrogen. Both reactors were heated by means of electrical resistance furnaces.

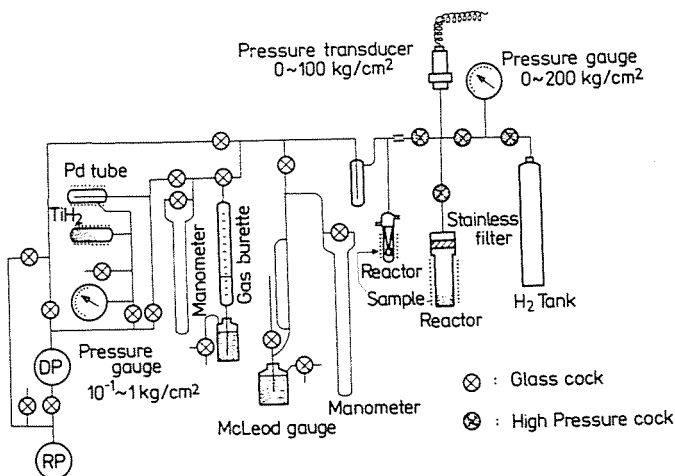


Fig. 1. Apparatus for Pressure-Temperature-Composition Measurement

The volume of the entire system and each individual subsection were calibrated to a known amount of hydrogen. The operation of the equipment is fundamentally the same as that of Siverts' apparatus.

After introducing the sample into the reactor, the sample was outgassed at  $700^{\circ}\text{C}$  to  $750^{\circ}\text{C}$  for several days to reach the low pressure measurement. For the high pressure, the sample was outgassed at  $1 \times 10^{-3}$  Torr, and then we introduced  $100 \text{ kg/cm}^2$  of hydrogen into the reactor for activating the samples. Activation of the samples was easily achieved by absorption-desorption cycles for more than 10 times. The stainless steel filter inserted in the reactor was essential for a voiding sample loss in the reactor. Pressure-Composition isotherms were obtained by the addition of a known amount of hydrogen to the reaction system, and by withdrawing a known amount of hydrogen from the reaction system. The change of composition of hydride was calculated from PVT measurements. The time for equilibration much depended on their composition, temperature and samples, and varied from a few minutes to several hours. Blank runs showed the loss of hydrogen by diffusion through the wall of the reactor and tubing; it was negligible at the experimental temperatures and pressures.

## Results and Discussion

### [1] Effect of Activation

The sample was evacuated at  $1 \times 10^{-6}$  Torr level until the leakage rate could reach  $8 \times 10^{-10} \text{ l} \cdot \text{Torr/sec}$ , at  $700^{\circ}\text{C}$  for the low pressure measurements. However, high vacuum evacuation technique was not the effective method of

measuring P—C isotherms for La—Ni—H alloys. The better process for these alloys is to expose them to hydrogen at a pressure of 50 to 150 kg/cm<sup>2</sup>, at ambient temperatures. In general, it takes only a few minutes for the alloy to absorb hydrogen even for the first time. This activation process is always accompanied by the sample breaking into small particles, thus forming a highly active powder with a large uncontaminated surface. Figure 2 shows the effect of the activation cycle to the equilibration even at the temperature of 0 °C. The

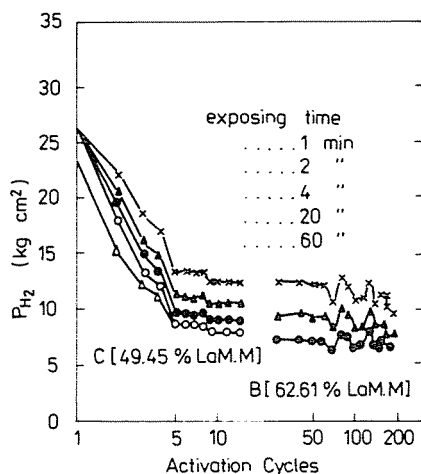


Fig. 2. Relation of activation cycles vs. dissociation pressure. Activation cycles

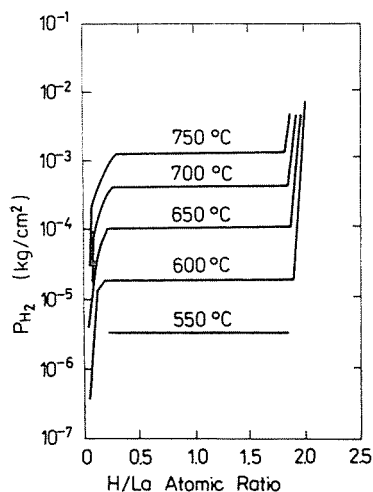


Fig. 3. Isotherms for La—H system H/La Atomic Ratio

pressure of the introduced hydrogen was 56.2 kg/cm<sup>2</sup>, and exposing time was 1 to 60 min. It shows that equilibria could be achieved in less than 10 cycles, and absorption time could be shortened by raising the temperature 20 °C to 50 °C. The absorption capacity of this alloy for hydrogen was not much changed after 200 cycles. The sample was broken to 20 to 50 μ at the first exposition to hydrogen, and it was broken up to 1 to 5 μ. No further effect on rate of absorption or breaking down was seen after 10 cycles of activation.

## [2] La—H, and Ce—H systems

The phase diagrams of La—H, and Ce—H systems were established by measuring P—C—T relationships. Figure 3 is the P—C—T diagram of La—H system, and in the case of Ce—H system, it is almost the same as that of La—H. Some of their thermodynamical functions were shown in Table 2.

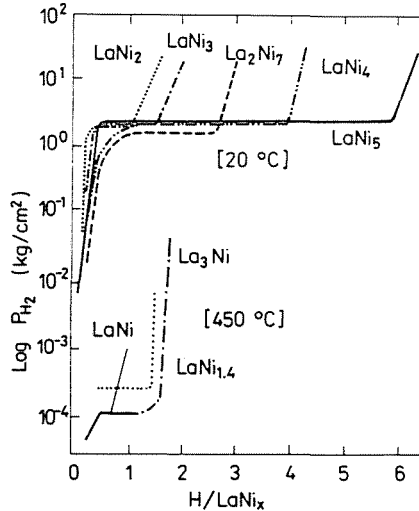
Table 2

Comparison of  $P_{H_2}$  and  $\Delta H_f$  for  $LaNi_x-H$  system

	$P_{H_2}$ (kg/cm <sup>2</sup> ) Absorption	$\Delta H_f$ (-kcal/mol)
La H <sub>2</sub>	$3.5 \times 10^{-6}$	$51.2 \pm 1.40$
Ce H <sub>2</sub>	$8.0 \times 10^{-6}$	$52.0 \pm 1.60$
La <sub>3</sub> Ni H <sub>1.6</sub>	$1.2 \times 10^{-4}$	$35.0 \pm 1.05$
La Ni H <sub>1.4</sub>	$2.8 \times 10^{-4}$	$21.8 \pm 0.65$
La Ni <sub>1.4</sub> H <sub>0.7</sub>	$1.2 \times 10^{-4}$	$18.6 \pm 0.56$
La Ni <sub>2</sub> H <sub>1.1</sub>	2.0	$7.0 \pm 0.21$
LaNi <sub>3</sub> H <sub>1.5</sub>	1.9	$6.4 \pm 0.19$
La <sub>2</sub> Ni <sub>7</sub> H <sub>2.7</sub>	1.65	$6.2 \pm 0.19$
La Ni <sub>4</sub> H <sub>4</sub>	1.95	$5.7 \pm 0.17$
La Ni <sub>5</sub> H <sub>6</sub>	2.3	$5.94 \pm 0.46$

## [3] Effect of Ni on La—H alloys

An addition of Ni to La—H alloy will effect the absorption of hydrogen and the equilibrium pressure, and therefore, the energy of formation of hydrides will differ with their Ni content. The P—C isotherms were shown in Fig. 4. Alloys poor in Ni (La<sub>1.4</sub> to La<sub>3</sub>Ni) were compared at 450 °C, and alloys rich in Ni (LaNi<sub>2</sub> to LaNi<sub>5</sub>) were compared at 20 °C. The equilibrium pressure of hydrogen was about 2 kg/cm<sup>2</sup> at 20 °C for the later alloys, and among them

Fig. 4. Isotherms for  $LaNi_x-H$  system [20°, 450 °C]  $H/LaNi_x$

LaNi<sub>5</sub> alloys absorb the largest quantity of hydrogen. The energy of formation of hydride changes with Ni content as shown in Table 2. An increase in Ni makes a decrease of H<sub>f</sub> of hydrides in La—Ni—H alloys. No further comment can be made on this result at present.

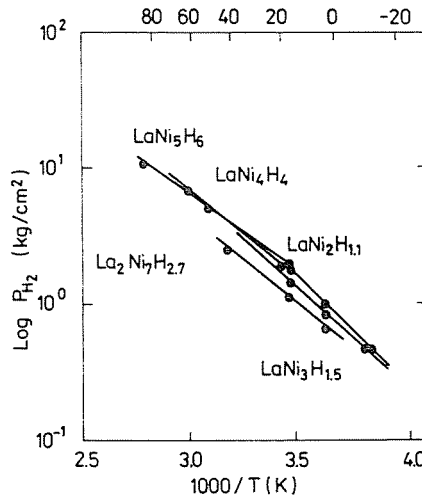


Fig. 5. Log P<sub>H<sub>2</sub></sub> vs 1/T for La—Ni—H alloys 1000/T (K)

#### [4] Misch metal-Ni<sub>5</sub>—H system

Hydride of LaNi<sub>5</sub> is the most prospective compound up to date. However, La is an expensive metal. Misch metal containing La and Ce, as can be seen in Table 1, is a relatively inexpensive mixture. The P—C isotherms of LaNi<sub>5</sub> have been plotted in for comparing with their plateau of hydrogen equilibrium pressure. The equilibrium pressures of hydrogen for these Misch metal-Ni alloys were higher than that of LaNi<sub>5</sub>, but the quantity of absorbed hydrogen was the same as that of LaNi<sub>5</sub> alloys.

#### [5] La<sub>1-x</sub>Ce<sub>x</sub>·Ni<sub>5</sub>—H system

Among the constituents of Misch metal, La and Ce are in the majority. Therefore a number of alloys in La<sub>1-x</sub>Ce<sub>x</sub>Ni<sub>5</sub>—H system were measured on P—C isotherms as a function  $x$ , where  $x$  stands for 0.1, 0.2, 0.3, 0.4, 0.5, 0.6. A partial replacement of La by Ce increases the absorption capacity somehow, for example, the alloy of La<sub>0.7</sub>Ce<sub>0.3</sub>Ni<sub>5</sub> can absorb nearly 7 atoms of hydrogen per formula unit. The increment of Ce in LaNi<sub>5</sub> alloy will affect the lattice parameter of the compound as investigated by K. H. J. BUSCHOW et al. [3] The change in the slope of the curve near  $x = 0.5$ , may be attributed to a change in the valency of the atoms. Since sample of  $x$  is more than 0.5, activation of the

samples became difficult and alloys of up to  $x = 0.6$  could be measured by P—C isotherms in this experiment. The effect of Ce on  $P_{H_2}$  in  $La_{1-x}Ce_xNi_5$  hydrides was shown in Fig. 8, and the plateau pressures were 50 kg/cm<sup>2</sup> for absorption and 15 kg/cm<sup>2</sup> for desorption. Comparison has been made on  $P_{H_2}$  in various La—Ce—Ni<sub>5</sub> alloys as shown in Table 3. Alloys with  $x$  beyond 0.8 were difficult to prepare and it was difficult to determine the P—C isotherms.

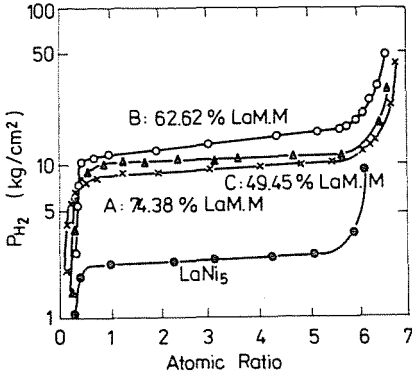


Fig. 6. Absorption isotherm for Misch metal—Ni<sub>5</sub> alloys at 25°C Atomic Ratio

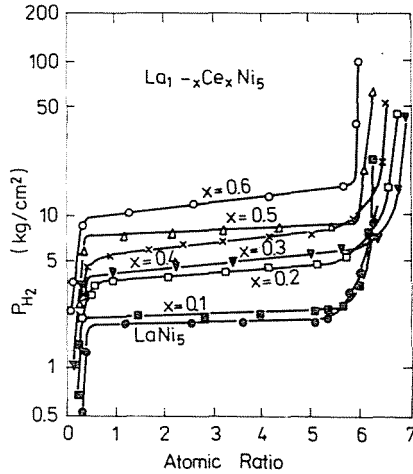


Fig. 7. Absorption isotherms for  $La_{1-x}Ce_xNi_5$ —H system at 20°C Atomic Ratio

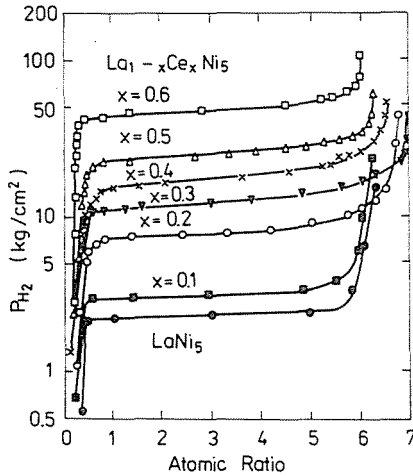


Fig. 8. Desorption isotherms for  $La_{1-x}Ce_xNi_5$ —H system at 20°C Atomic Ratio

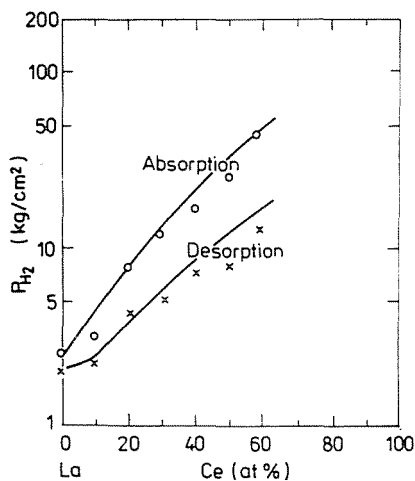
Table 3

Comparison of  $P_{H_2}$  and  $H_f$  for  $La_{1-x}Ce_xNi_5$  alloys

	$P_{H_2}$ (kg/cm <sup>2</sup> , at 20 °C)		$\Delta H_f$ (-kcal/mol)
	Absorption	Desorption	
La Ni <sub>5</sub> H <sub>6</sub>	2.45	2.0	5.94 ± 0.46
La <sub>0.9</sub> Ce <sub>0.1</sub> Ni <sub>5</sub> H <sub>5.8</sub>	3.10	2.25	6.20 ± 0.15
La <sub>0.8</sub> Ce <sub>0.2</sub> Ni <sub>5</sub> H <sub>6.5</sub>	8.20	4.33	6.05 ± 0.23
La <sub>0.7</sub> Ce <sub>0.3</sub> Ni <sub>5</sub> H <sub>6.7</sub>	12.40	5.0	5.80 ± 0.4
La <sub>0.6</sub> Ce <sub>0.4</sub> Ni <sub>5</sub> H <sub>6.3</sub>	17.50	7.33	5.52 ± 0.15
La <sub>0.5</sub> Ce <sub>0.5</sub> Ni <sub>5</sub> H <sub>6.2</sub>	25.50	8.20	5.28 ± 0.51
La <sub>0.4</sub> Ce <sub>0.6</sub> Ni <sub>5</sub> H <sub>6</sub>	46.50	13.0	5.06 ± 0.07

[6] Effects of Co on P—C isotherms of La—Ce—Ni<sub>5</sub> alloy

An addition of Co will effect the P—C isotherms of La—Ce—Ni<sub>5</sub> alloys. For instance, the  $P_{H_2}$  of plateau for La<sub>0.4</sub>Ce<sub>0.6</sub>Ni<sub>5</sub> was 15 kg/cm<sup>2</sup> at 20 °C, and it would be decreased to 0.5 kg/cm<sup>2</sup> by replacing 3 atoms of Co in Ni. Thus the

Fig. 9.  $La_{1-x}Ce_xNi_5$ :  $P_{H_2}$  as a function of  $x$  at 20 °C Ce (at%)

composition would be La<sub>0.4</sub>—Ce<sub>0.6</sub>—Ni<sub>2</sub>Co<sub>3</sub>, and it would slightly reduce the energy of formation of hydride. It did not change hydrogen absorption capacity. Therefore, by engaging the composition of AB<sub>5</sub> compound, where A



stood for La or Ce and B stood for Ni or Co, it was possible to obtain some kinds of alloys which could be suitable compounds with hydrogen for proper service and cost.

### Conclusion

The present paper dealt with the Pressure-Composition-Temperature measurement for alloys of  $\text{LaNi}_x$ , Misch metal— $\text{Ni}_5$ , and  $\text{La}_{1-x}\text{—Ce}_x\text{—Ni}_5$ , and the effect of Ni on La—H, Ce and Co on  $\text{LaNi}_5\text{—H}$  has been confirmed.

Ni will increase the absorption capacity of hydrogen, and an atomic ratio at  $\text{Ni/La} = 5$ , is the largest capacity, to take pressure of hydrogen at plateau will increase remarkably, and meantime, the  $\Delta H_f$ , energy of formation of hydride will decrease from  $-51.2$  kcal/mol for  $\text{LaH}_2$  to  $-5.94$  kcal/mol for  $\text{LaNi}_5\text{H}_6$ . In Misch metal— $\text{Ni}_5\text{H}_{6.7}$ , the  $\Delta H_f$  is  $-6.4$  kcal/mol for absorption, and  $-6.8$  kcal/mol for desorption.

In the studies of hydrogen energy systems, among many hydrides  $\text{LaNi}_5$  alloy is best known for its unique feature and the most convenient for further studies: such as the application of desorbed hydrogen from hydride. The expensive La metal can be replaced by an inexpensive Misch metal.

### Summary

An assessment on the influence of Ni, Ce, and Co to the solubility and equilibrium pressure of hydrogen, in the systems for La—Ni, and Misch metal—Ni alloys have been made by means of measuring Pressure-Temperature-Composition relationships. The hydrogen pressure at plateau, which indicates two-phase coexistence, was shown almost at the same value, above Ni/REM ratio is more than 2 to 5, and the plateau region of isotherms was increased with increasing Ni content. Ce would increase the plateau pressure of hydrogen in La—Ni alloys, and the experiment was carried out up to the  $\text{La}_{0.4}\text{Ce}_{0.6}\text{Ni}_5$  alloy. However, an addition of Co would decrease the plateau of hydrogen pressure remarkably for La—Ce—Ni<sub>5</sub> alloy.

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