



# Hydrogen desorption kinetics of hydrides of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ , $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ and $\text{LaNi}_{2.5}\text{Co}_{2.5}$

T. Haraki\*, N. Inomata, H. Uchida

*Department of Applied Physics, School of Engineering, Tokai University, 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan*

## Abstract

The  $\text{H}_2$  desorption rates of the hydrides of the H storage alloys  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ ,  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  and  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  were measured as a function of H concentration by a volumetric method in the range of temperatures from 298 to 348 K and of  $\text{H}_2$  pressures between 0.01 and 0.6 MPa. The measured data showed that the desorption rates are controlled by the diffusion of H in the hydrides of the alloys. The obtained diffusion coefficient ranged from  $3 \times 10^{-10}$  to  $5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for the alloy hydrides at these temperatures. The activation energy for H diffusion tended to increase with increasing H concentration in the hydrides of the alloys. However, the activation energy was found to decrease on partial substitution of Ni in  $\text{LaNi}_5$  with Al, Mn and Co. © 1999 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Desorption kinetics of  $\text{H}_2$ ; Diffusion of H;  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ ;  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ ;  $\text{LaNi}_{2.5}\text{Co}_{2.5}$

## 1. Introduction

The features of the high rates of reversible  $\text{H}_2$  absorption and desorption of H storage alloys are well known. Extensive studies have been made of the thermodynamic and kinetic properties of the alloys [1–3]. Generally, the rate of the initial activation or hydriding of the alloys is controlled by surface processes such as  $\text{H}_2$  dissociation and H permeation through surface oxide layers [1,4–7]. In these surface processes, the exchange of electrons between  $\text{H}_2$  molecules and the metal or oxide surface is crucial for  $\text{H}_2$  dissociation [8].

Compared with the many reports on investigations of the reaction mechanisms of  $\text{H}_2$  absorption and hydriding of alloys, little work has been carried out on  $\text{H}_2$  desorption kinetics. This study aimed at investigating the mechanism of the  $\text{H}_2$  desorption kinetics of the hydrides of H storage alloys such as  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ ,  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  and  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  to examine the effect of substitutional elements such as Al, Mn and Co on the desorption kinetics.

## 2. Experimental procedures

Block samples of the alloys,  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ ,  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  and  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  were prepared by arc melting. Sub-

sequently, the samples were annealed at 1023 K in a vacuum of  $1 \times 10^{-5} \text{ Pa}$  for 8 h. The structure and composition of the prepared samples were determined with standard data using X-ray diffraction (XRD) and inductively coupled plasma (ICP), respectively [7]. The block samples were pulverized by cyclic hydriding and dehydriding reactions, which resulted in median particle sizes of 17  $\mu\text{m}$  for  $\text{LaNi}_5$ , 13  $\mu\text{m}$  for  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ , 15  $\mu\text{m}$  for  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  and 27  $\mu\text{m}$  for  $\text{LaNi}_{2.5}\text{Co}_{2.5}$ .

The rate of  $\text{H}_2$  desorption of the samples was measured volumetrically as the rate of increase of  $\text{H}_2$  pressure per second in a vacuum cell of known volume using a Sieverts-type apparatus [4]. The cell was evacuated to a vacuum of  $7 \times 10^{-1} \text{ Pa}$  before measurement of the desorption rate. The vacuum leak rate was  $2 \times 10^{-6} \text{ Pa m}^3 \text{ s}^{-1}$ , which was low enough to measure the increase in  $\text{H}_2$  pressures desorbed from the alloy samples. The measurement was made using hydrided samples with H concentrations ranging from  $x = 0.4$  to 4, where  $x = [\text{H}]/[\text{M}]$  (M: alloy) is the atomic ratio, at temperatures between 298 and 348 K and  $\text{H}_2$  pressures from 0.01 to 0.6 MPa. This range of H concentration corresponds to the region where the hydride phase ( $\beta$ ) decomposes into  $\text{H}_2$  gas and H solid solution ( $\alpha$ ) in the measurement of the  $\text{H}_2$  desorption rate. Hydrogen gas of purity 99.99999% (7N grade) was used for the hydriding of samples. Details of the apparatus used and experimental factors such as heat conductivity, cell materials, vacuum leak rate and  $\text{H}_2$  gas purity, which

\*Corresponding author.

should strictly be taken into account in kinetic measurements, are reported elsewhere [1,4].

### 3. Results and discussion

Typical hydrogen desorption curves are shown as solid lines in Fig. 1a for  $\text{LaNi}_5\text{H}_x$ , Fig. 1b for  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$ ,

Fig. 1c for  $\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$  and Fig. 1d for  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$ . The initial  $\text{H}_2$  desorption rate increases with increasing H content in the hydrides (Fig. 1a,d) and with increasing temperature (Fig. 1b,c). The measured curves were examined in a  $t^{0.5}$  vs.  $[\text{H}]/[\text{M}]$  plot which resulted in the linear relations shown in Fig. 2. This suggests that the measured rates are controlled by the diffusion of H atoms in the hydrides.

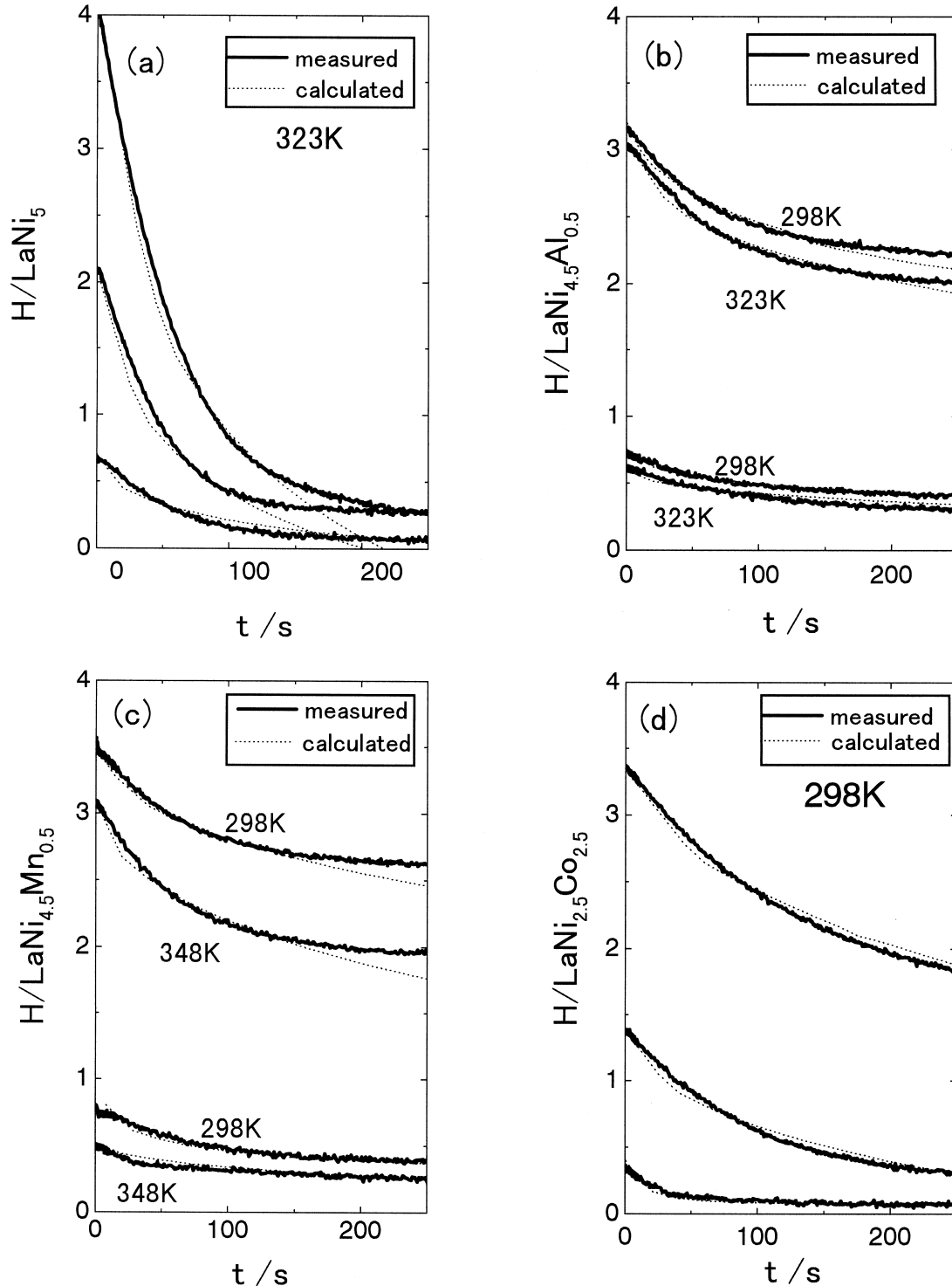


Fig. 1. Dehydrogenating curves for (a)  $\text{LaNi}_5\text{H}_x$ , (b)  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$ , (c)  $\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$  and (d)  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$ .

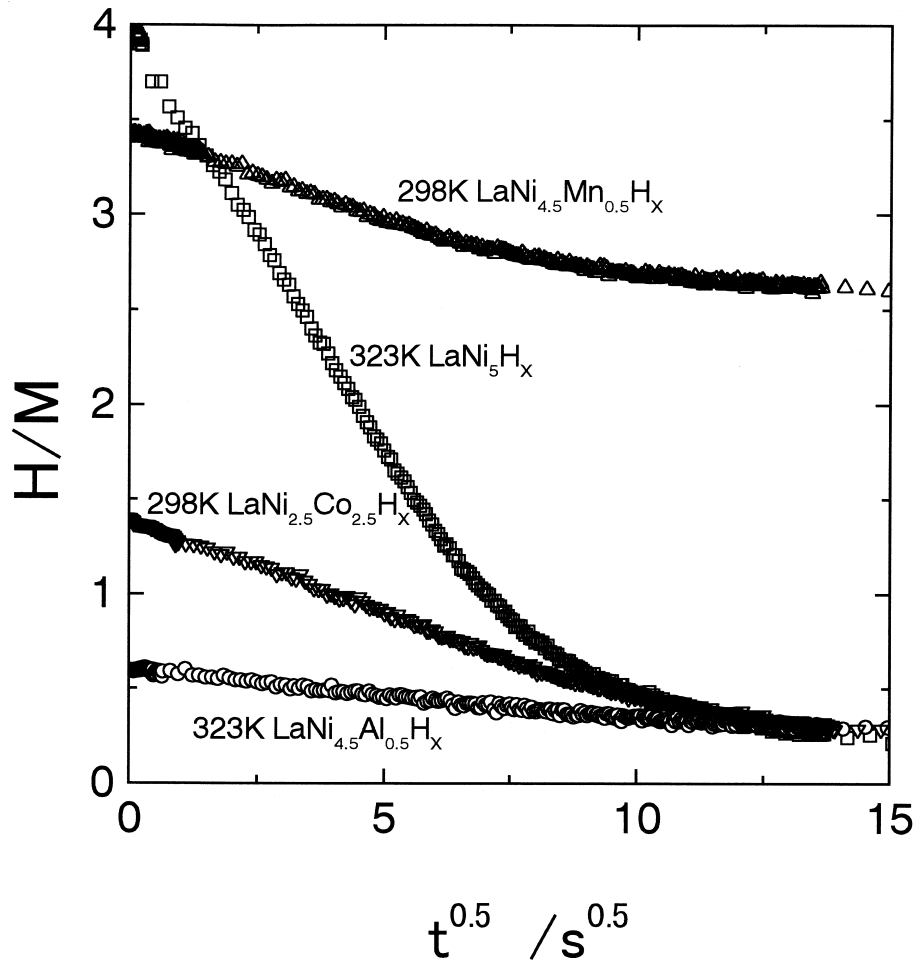


Fig. 2. H/M vs.  $t^{0.5}$  plots of the dehydrating curves.

The decrease in H concentration in a hydride particle with radius  $r_0$  can be expressed by [9]:

$$\frac{c}{c_s} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{Dt}{r_0^2}\right) \quad (1)$$

where  $t$  is the reaction time,  $c$  the H concentration,  $c_s$  the H concentration of the hydride sample at  $t=0$ , and  $D$  the diffusion coefficient.

The measured curves were fitted to this equation by mathematical expansion from  $n=1$  to 100. The fitted curves are shown as dotted lines in Fig. 1a–d. With decreasing H concentration, the deviation of the calculated curves from the measured curves becomes large. This may be caused by our experimental conditions. The  $H_2$  gas was desorbed into a vacuum cell. However, as the desorption proceeded, the  $H_2$  pressure in the cell increased, which depressed the desorption rate in the final stage of the reaction.

The diffusion coefficient  $D$  was calculated from the fitting. The temperature dependence of  $D$  is shown in Fig. 3a for  $LaNi_5$ , Fig. 3b for  $LaNi_{4.5}Al_{0.5}$ , Fig. 3c for  $LaNi_{4.5}Mn_{0.5}$  and Fig. 3d for  $LaNi_{2.5}Co_{2.5}$ . In fact, the mechanism of H diffusion in these alloys seems very

complex, where more than one jump process takes place in the diffusion [11]. Therefore, the obtained  $D$  in this study should be considered as approximate values.

The obtained  $D$  increases with increasing temperature and increasing H concentration. This H concentration dependence of  $D$  agrees with the result reported by Zuechner et al. [11]. They reported that the value of  $D$  for  $LaNi_5H_6$  exhibits a wide range from  $4 \times 10^{-9}$  to  $1.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at 298 K [11]. When the fact that  $D$  increases with increasing H content is taken into account, our result of  $D = 1.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for  $LaNi_5H_{3.5}$  at 298 K (Fig. 1a) seems to be in good agreement with the reported values.

From the linear relation in the  $\ln D$  vs.  $1/T$  plot for each alloy, the apparent activation energy  $A$  for H diffusion was calculated for each alloy:

$$\ln D \propto -A/RT \quad (2)$$

where  $R$  is the gas constant and  $T$  is temperature (K).

The calculated activation energies are summarized in Table 1 for different hydride compositions  $x$ . Values of  $A$  increase with increasing H concentration for each alloy. Extrapolation of  $A$  with increasing H concentration yields an activation energy of  $A = 21.6 \text{ kJ mol H}^{-1}$  for  $LaNi_5H_6$ , which coincides with the value reported by Kohdosov et al.

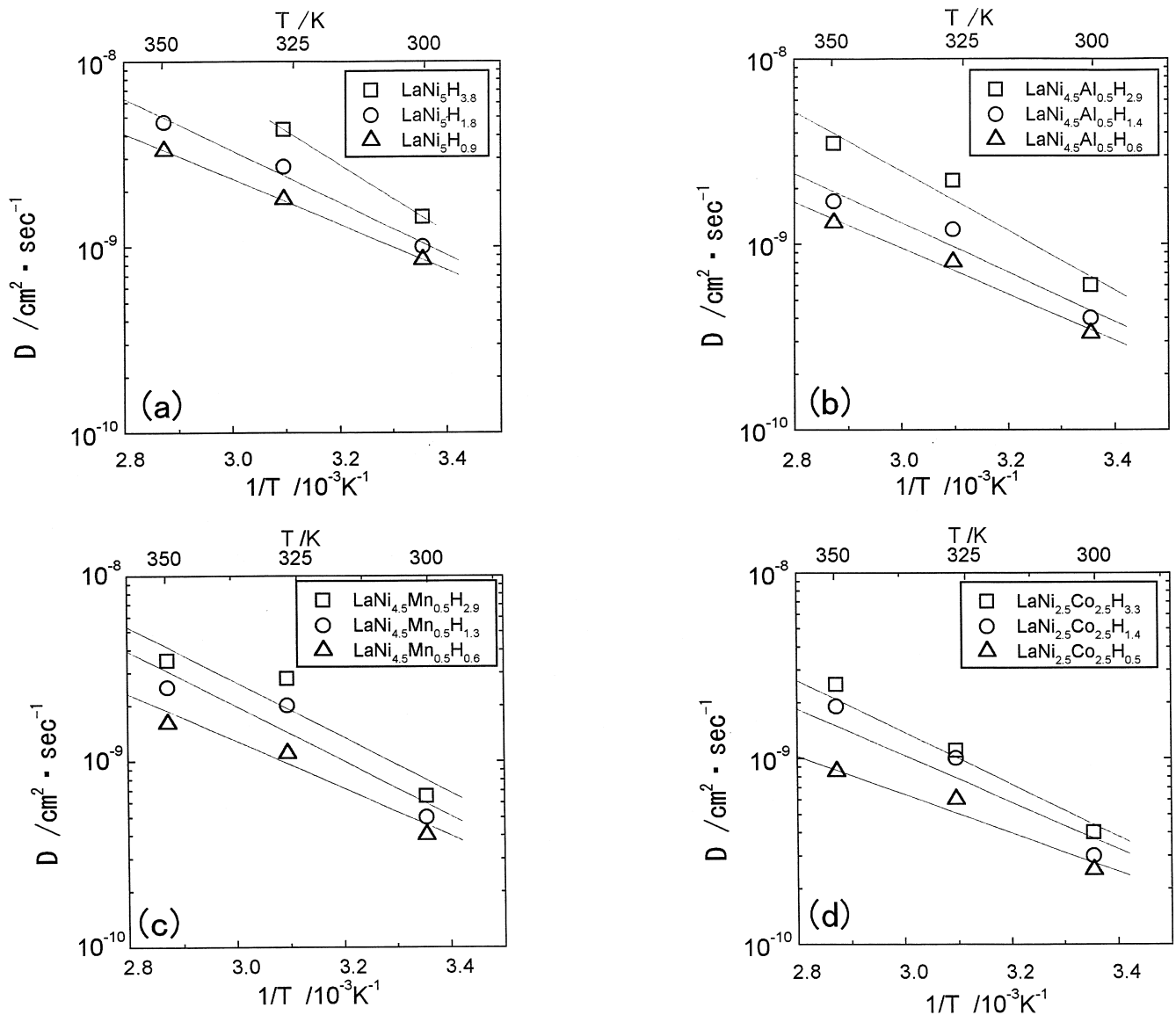


Fig. 3.  $\ln D$  vs.  $1/T$  plots for (a)  $\text{LaNi}_5\text{H}_x$ , (b)  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$ , (c)  $\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$  and (d)  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$ .

[10] (Fig. 4). The activation energies reported for H diffusion in  $\text{LaNi}_5\text{H}_6$  are markedly scattered [10–15]. Table 1 lists the values of  $A$  for  $\text{LaNi}_5\text{H}_6$  from Refs. [10–15].

$\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$  exhibits much lower apparent diffusivities and lower activation energies than  $\text{LaNi}_5\text{H}_x$ ,  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$  and  $\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$ . The small volume expansion of the  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$  hydride might be respon-

Table 1

Apparent activation energies ( $\text{kJ mol}^{-1}$ ) for the diffusion of H in  $\text{LaNi}_5\text{H}_x$ ,  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$ ,  $\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$  and  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$

$x$	$\text{LaNi}_5\text{H}_x$	$\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$	$\text{LaNi}_{4.5}\text{Mn}_{0.5}\text{H}_x$	$\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$
0.4–1	$10.2 \pm 1.0$	$10.3 \pm 1.0$	$10.5 \pm 1.1$	$8.58 \pm 0.9$
1–2	$11.6 \pm 1.2$	$11.1 \pm 1.1$	$12.2 \pm 1.2$	$10.4 \pm 1.0$
3–4	$15.8 \pm 1.6$	$13.3 \pm 1.3$	$12.3 \pm 1.2$	$11.6 \pm 1.2$
6	$21.6 \text{ kJ mol}^{-1}$ (10.6–39.6; Refs. [10–15])			

sible for the low diffusivity, as argued by Zhang et al. based on results from a kinetic measurement of  $\text{H}_2$  absorption by  $\text{LaNi}_{4.25}\text{Co}_{0.5}\text{Sn}_{0.25}$  [13]. In fact, the reduction in particle size by the cyclic hydriding and dehydriding treatment of Co-containing alloys is less than the alloys without Co addition. The lattice parameters of rare-earth-based hydrogen storage alloys expand anisotropically, and the volume change is over 24% for  $\text{LaNi}_5$  and  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ , 18.5% for  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ , and 14.6% for  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  [12], where the change in the  $c$ -axis ( $\Delta c/c = 1.3\%$ ) in the hydriding or dehydriding of  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  is much less than for the other alloys ( $\Delta c/c = 5.0$ – $7.9\%$  for  $\text{LaNi}_5$ ,  $\text{LaNi}_{4.5}\text{Al}_{0.5}$  and  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  [12]). These facts imply that the diffusion process of H atoms in  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  is different from that in the other alloys. When the anisotropic diffusion process of H atoms in  $\text{LaNi}_5\text{H}_x$  [11] and  $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_x$  [15] is taken into

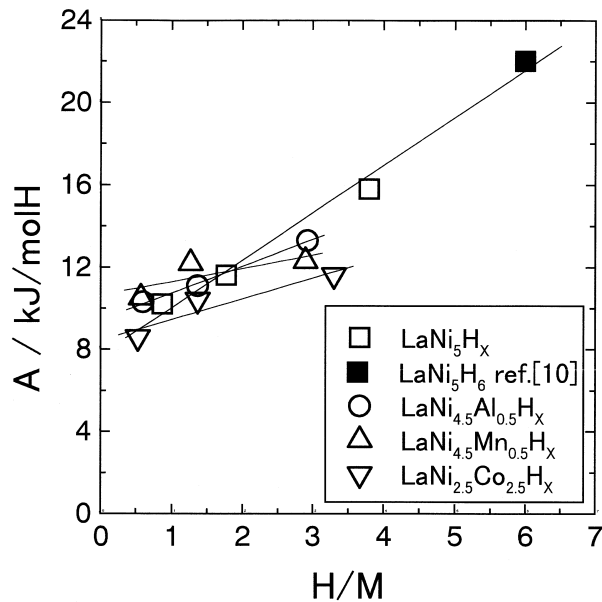


Fig. 4. Change in the apparent activation energy  $A$  for diffusion of H as a function of the H concentration  $H/M$ .

account, the obtained lower diffusivity and activation energy for H diffusion in  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$  suggest the presence of rather complicated diffusion processes in  $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_x$  in the dehydriding process.

As can be seen from Fig. 3 and Table 1, the substitution of Ni in  $\text{LaNi}_5$  with Al or Mn also decreases the value of  $D$ . This is in good agreement with the results of Osumi et al. [14] and Bowman et al. [15]. However, as mentioned before, when the complex diffusion mechanisms in these alloys are taken into account, more precise studies are required to determine the dependence of the diffusivity and the activation energy on the substitution of Ni in  $\text{LaNi}_5$  with other metal elements such as Al, Mn and Co.

#### 4. Conclusions

The desorption rates of the hydrides of  $\text{LaNi}_{4.5}\text{Al}_{0.5}$ ,  $\text{LaNi}_{4.5}\text{Mn}_{0.5}$  and  $\text{LaNi}_{2.5}\text{Co}_{2.5}$  were measured. The results indicate that the desorption rate is controlled by H diffusion in the hydrides. The apparent diffusion coefficient  $D$

becomes larger with increasing H concentration and temperature. The substitution of Ni in  $\text{LaNi}_5$  with Al, Mn and Co results in a decrease in the value of  $D$ . Substitution with Co was found to be most profound in the decrease of the apparent diffusivity and the activation energy for H diffusion. More precise investigations are necessary to understand substituent effects on the diffusion mechanism of H in these alloy hydrides.

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#### References

- [1] H. Uchida, K. Terao, Y.C. Huang, Z. Phys. Chem. N.F. 164 (1989) 1275.
- [2] L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds, Vol. I, Topics in Applied Physics, Vol. 63.
- [3] L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds, Vol. II, Topics in Applied Physics, Vol. 67.
- [4] H. Uchida, M. Ozawa, Z. Phys. Chem. N.F. 147 (1986) 77.
- [5] Y. Ohtani, S. Hashimoto, H. Uchida, J. Less-Common Met. 172–174 (1991) 841.
- [6] H. Uchida, S. Hashimoto, Z. Phys. Chem. 181 (1993) 417.
- [7] H. Uchida, S. Seki, S. Seta, J. Alloys Comp. 231 (1995) 403.
- [8] H. Uchida, Y. Ohtani, M. Ozawa, T. Kawahata, T. Suzuki, J. Less-Common Met. 172–174 (1991) 983.
- [9] G. Hoerz, in: E. Fromm, E. Gebhardt (Eds.), Kinetik und Mechanismen in Gase und Kolenstoff in Metallen, Springer, Berlin, 1976, p. 128.
- [10] E.F. Kohdosov, A.I. Linnik, G.F. Kobsenko, V.G. Evanchenko, Phys. Met. Metall. 44 (1977) 187.
- [11] H. Zuechner, T. Rauf, R. Hempelmann, J. Less-Common Met. 172–174 (1991) 611.
- [12] T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa, J. Less-Common Met. 161 (1990) 193.
- [13] W. Zhang, M.P.S. Kumar, A. Visintin, S. Srinivasan, H.J. Ploehn, J. Alloys Comp. 242 (1996) 143.
- [14] Y. Osumi, H. Suzuki, K. Oguro, M. Nakane, J. Chem. Soc. Jpn. 9 (1981) 1493.
- [15] R.C. Bowman Jr., B.D. Craft, A. Attalla, M.H. Mendelssohn, D.M. Gruen, J. Less-Common Met. 73 (1980) 227.