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Journal of Alloys and Compounds 293–295 (1999) 270–274

Journal of
ALLOYS
AND COMPOUNDS

Protium diffusion in La–Ni alloys

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Abstract

The effect of microstructure on the diffusion of protium (hydrogen) in La–Ni alloys was studied by the desorption method. Five alloys were prepared; one was the well known protium absorbing alloy LaNi_5 with the stoichiometric composition, and the others were the two phase alloys LaNi_x ($x=5.5\text{--}8.1$) consisting of the LaNi_5 phase and the Ni phase. By the analysis of the desorption curves for the temperature range 353–573 K, the diffusion coefficient of protium in the alloys was determined under the assumption that the sample particles were spheres. The Arrhenius plots of the diffusion coefficients, D , for all the alloys show linear relationships. The value of D in LaNi_x ($x=6.0, 6.5, 8.1$) increases with increasing the value of x , and they are larger than that in LaNi_5 , although the value of D in $\text{LaNi}_{5.5}$ is the smallest in the temperature range examined. The literature value of D in LaNi_5 obtained by the quasielastic neutron scattering (QNS) method is in the middle of the coefficients of the five alloys. This suggests that the effective surface area of the LaNi_5 specimen for the desorption is reduced by the formation of oxide layer and that in the two phase alloys the protium diffusion is enhanced via a network of the Ni phase deformed by the expansion of the LaNi_5 phase due to the absorption of protium, although the Ni phase in $\text{LaNi}_{5.5}$ is insufficient to form the network. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Protium; Diffusion; La–Ni alloy; Desorption; Microstructure

1. Introduction

Metal hydride LaNi_5H_x ($0 \leq x \leq 6$) possesses very high content of protium. This family of alloys has been used as negative electrode materials of hydride batteries. Although the formation and characteristic of La–Ni hydride have been well studied, research on the diffusional behavior of protium in the hydride is still insufficient. For the technical applications of these alloys, fundamental research on the kinetics of absorption and desorption processes in the alloys with different microstructures is very important. Martin et al. [1] have tried to elucidate the reaction mechanism of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ with protium and pointed out that the rate of absorption process is controlled by surface reactions, whereas a diffusion model explains the rate of desorption data much better. This suggests that the important factor acting on the desorption kinetics in the La–Ni alloy is the protium diffusion. In recent years [2–4], it has been reported that by choosing an appropriate composition and microstructure of heterogeneous alloys,

new materials with excellent absorption and desorption kinetics and with desirable working temperatures can be realized. In particular, the hydrogenation kinetics of these materials largely depends on the characteristics of the grain boundary [2–4]. Therefore, the investigation of the effect of grain boundary on the desorption behavior of protium in the storage materials is also important.

The diffusion of protium in the storage materials has been reviewed by Hempelmann [5]. According to Hempelmann, most of the experiments are on the measurements of short range diffusion by employing QNS and NMR techniques and the like, while the effect of microstructure which involves grain boundaries, vacancies and impurities on the protium diffusion has been scarcely studied. The diffusion coefficient determined by QNS and NMR methods is not influenced by the oxide layer on the surface of the specimen, because these methods are concerned with the short range diffusion of protium. However, the experimental data on the long range diffusion in the samples with different microstructures are vital to the development of the practical protium storage systems.

In the present work, the effect of the composition and microstructure of La–Ni alloys on the protium diffusion has been investigated by a desorption technique.

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2. Experimental

2.1. Sample preparation and characterization

Buttons of LaNi_x ($x=5.5, 6.0, 6.5, 8.1$) alloys were prepared by arc melting pellets of pure metals (La 99.9 at.%, Ni 99.95 at.%) in an argon atmosphere. The buttons were annealed at 1473 K for 48 h in an argon atmosphere and then crushed into small particles with the mean diameter of 300 μm or less. As shown in Fig. 1, optical microscopic observation showed that all samples consisted of the two phases, which were determined to be the LaNi_5 phase and the Ni phase by SEM-EDX measurements. Further, X-ray diffraction measurements showed the characteristic peaks of a hexagonal AB_5 phase and a fcc Ni phase. Additionally, LaNi_5 stoichiometric compound was also prepared for the comparison with these alloys.

2.2. Protium charge and desorption method

Protium was charged into these samples in a protium atmosphere of 0.7MPa at 313 K. During hydrogenation, as well known, a bulk LaNi_5 changes into a fine powder owing to the large strain by the volume expansion by about 25%. After the protium absorption, the mean particle sizes of LaNi_x ($x=5.5, 6.0, 6.5, 8.1$) were 80, 146, 166 and 166 μm , respectively, while that of LaNi_5 was 120 μm .

A schematic diagram of the present experimental apparatus for the protium desorption is shown in Fig. 2. After the protium charge, the sample was set in a tube and evacuated under the pressure of 1×10^{-5} MPa. Then, the samples were heated at a constant temperature in the range of 353–573 K and the pressure of protium gas desorped from the sample was measured by a baratron gauge. A cold

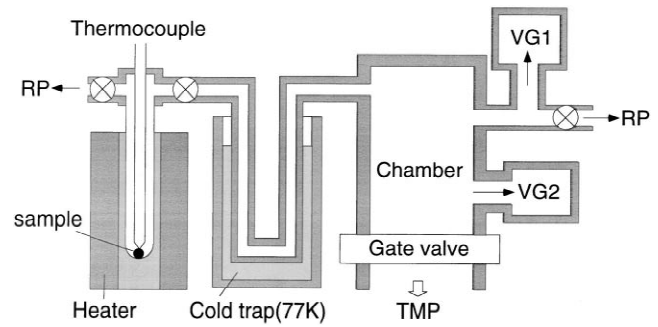


Fig. 2. A schematic diagram of the present experimental apparatus for the protium desorption. VG 1: Vacuum gauge for high pressure (Baratron), VG 2: Vacuum gauge for low pressure (B–A gauge), TMP: Turbomolecular pump, RP: Rotary pump.

trap kept at 77K, which was placed before the vacuum gauge, was used to freeze out additional gases such as N_2 , O_2 , or H_2O , which would be attributed to the total pressure. By the analysis of the desorption curve, the diffusion coefficient of protium in the alloys was determined under the assumption that the sample particles were spheres.

In the present experiment, a steady state diffusion condition was not realized, and the diffusion coefficient for gas into, or out of, a solid was thus obtained under the conditions that the flux was time dependent rather than in the steady state [6]. The appropriate solution to the equation for the gas diffused out of a sphere with the radius r is

$$\frac{\bar{C} - C_i}{C_f - C_i} = 1 - \frac{6}{\pi^2} \sum_{\nu=1}^{\infty} \frac{1}{\nu^2} \exp\left(\frac{-\nu^2 \pi^2}{r^2} Dt\right) \quad (1)$$

where \bar{C} , C_i , and C_f are the average, initial, and final

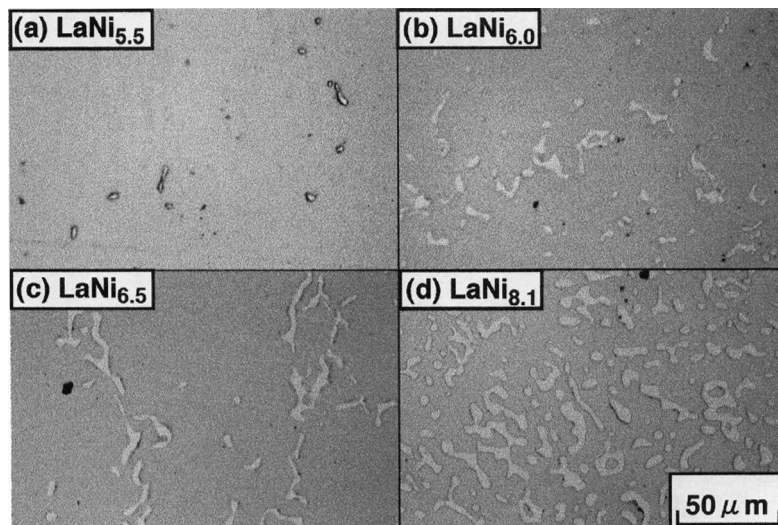


Fig. 1. Optical micrographs of two phase La–Ni alloys annealed at 1473 K for 48 h. The bright area corresponds to the Ni phase and the dark to the LaNi_5 phase.: (a) $\text{LaNi}_{5.5}$ (b) $\text{LaNi}_{6.0}$ (c) $\text{LaNi}_{6.5}$ and (d) $\text{LaNi}_{8.1}$

concentrations within the sphere, respectively. With sufficiently long time, all the terms with $\nu > 1$ can be neglected, and thus the approximate solution is

$$\frac{\bar{C} - C_i}{C_f - C_i} \cong 1 - \frac{6}{\pi^2} e^{-t/\tau} \quad (2)$$

where $\tau = r^2/\pi^2 D$ [7]. Applying the Eq. (2) to the desorption curve, the protium diffusion coefficient in the alloy can be determined.

3. Results

Typical desorption curves for the single phase LaNi_5 and the two phase $\text{LaNi}_{8.1}$ alloys at 423 K are represented in Fig. 3. The vertical axis of this plot, $(1 - \bar{C})$, shows the pressure change in a vacuum tube which is previously evacuated under 1×10^{-5} Pa. The protium desorption curves are normalized, considering C_i to be unity and C_f to be zero. The resulting curves are shown in Fig. 4. Each curve has a straight region, and the slope gives the value of $-\pi^2 D/r^2$. From the slope the diffusion coefficient of protium was calculated.

Fig. 5 shows the temperature dependence of the protium diffusivity in the LaNi_5 stoichiometric compound determined by the present work in comparison with those by the

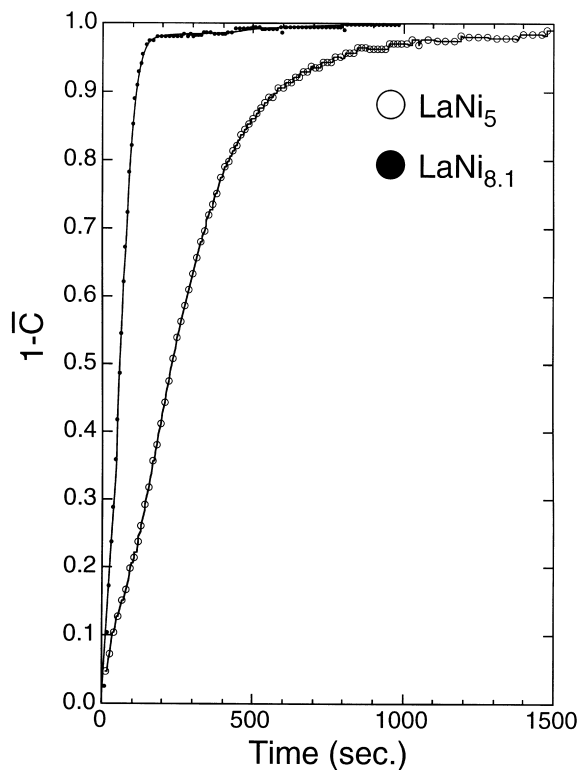


Fig. 3. Typical desorption curves of protium at 423 K in LaNi_5 single phase and in $\text{LaNi}_{8.1}$ two phase alloys. \bar{C} is the average concentration of protium in the sample.

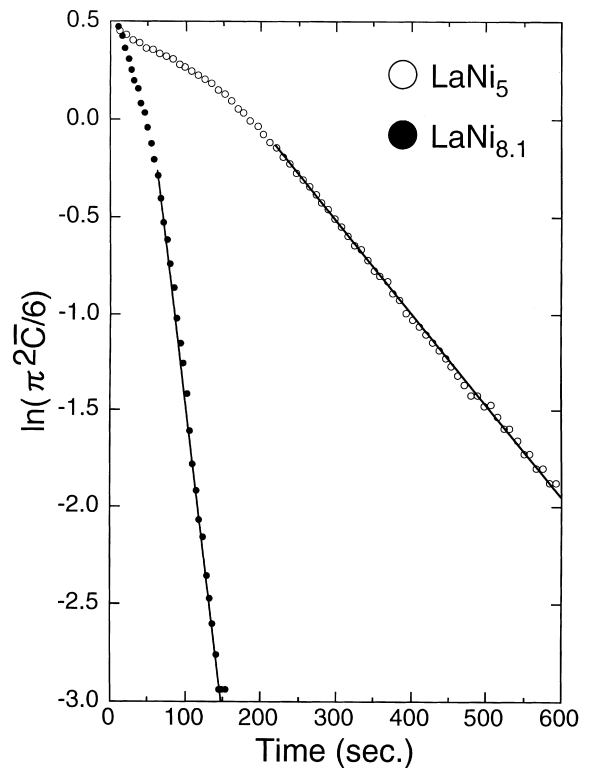


Fig. 4. Plot of $\ln(\pi^2 \bar{C}/6)$ vs. time for the curves in Fig. 3. The data represent the rate of outgassing of protium from LaNi_5 and $\text{LaNi}_{8.1}$ alloys at 423 K.

previous authors by means of the quasi-elastic neutron scattering (QNS) method [8–10] and the nuclear magnetic resonance (NMR) method [11–15]. The activation energies determined by the QNS measurements [8–10] are in the range from 10.6 kJ mol^{-1} to 26.5 kJ mol^{-1} , while the diffusion coefficients by these measurements [8–10] at room temperature are scattered in a broad band between $0.8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $1.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. On the other hand, the NMR experiments [11–15] yield the activation energies between 19.9 kJ mol^{-1} and 39.8 kJ mol^{-1} and the diffusion coefficients at room temperature have a wide band between $1.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $1.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The value of the activation energy obtained by the present desorption measurement in the LaNi_5 stoichiometric compound is $Q = 27 \text{ kJ mol}^{-1}$, which is in agreement with the results of the quasi-elastic neutron scattering ($Q = 26.5 \text{ kJ mol}^{-1}$) in single-phase LaNi_5H_6 [9] and the nuclear magnetic resonance ($Q = 24 \text{ kJ mol}^{-1}$) in LaNi_5H_6 [15]. However, the diffusion coefficients determined by the present work are about one order of magnitude smaller than those of the previous work.

Fig. 6 shows the temperature dependence of protium diffusivities in the LaNi_5 stoichiometric compound and in the LaNi_x ($x = 5.5, 6.0, 6.5, 8.1$) alloys determined by the present desorption measurements. The Arrhenius line for each composition can be recognized as being linear, although the experimental points show some scatter. The

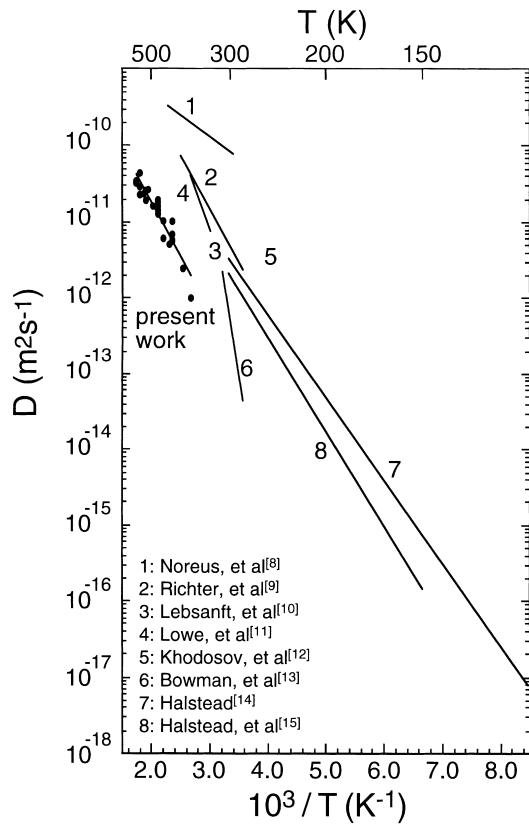


Fig. 5. Arrhenius plot of protium diffusivity in LaNi_5 determined by the present work in comparison with those by the quasi-elastic neutron scattering (QNS) and the nuclear magnetic resonance (NMR) method.

activation energy Q and the pre-exponential factor D_0 for the protium diffusion in the La–Ni alloys are summarized in Table 1. Except for $\text{LaNi}_{5.5}$, the protium diffusion coefficient increases with increase in x ; the composition shifts to the Ni-rich side from the stoichiometric composition. In particular, for the $\text{LaNi}_{8.1}$ alloy, the activation energy is 15 kJ mol^{-1} , which is only one half of that for the LaNi_5 alloy. These results suggest that the diffusion coefficients determined by the long-range diffusion measurements such as the desorption method are seriously affected by the surface condition of samples, and that the increase of Ni amounts has an enhancement effect on the protium diffusion in these alloys.

4. Discussion

The activation energy obtained by the present desorption measurements are fairly in agreement with those of QNS and NMR. Therefore, the present experimental method can be recognized as reasonable. However, as shown in Fig. 5, the diffusion coefficients of protium in LaNi_5 by the present experiments are about one order of magnitude smaller than those of the previous studies. Richter et al. [9] have found that the diffusion coefficient increases with

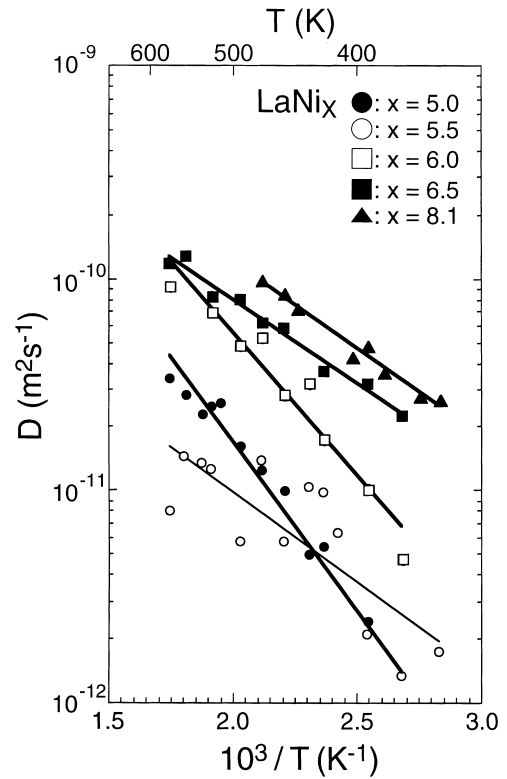


Fig. 6. Arrhenius plot of protium diffusivity in LaNi_5 compound and in LaNi_x ($x = 5.5, 6.0, 6.5, 8.1$): ● LaNi_5 , ○ $\text{LaNi}_{5.5}$, □ $\text{LaNi}_{6.0}$, ■ $\text{LaNi}_{6.5}$, ▲ $\text{LaNi}_{8.1}$.

increasing protium content. In the present experiment, after the protium charge, samples are set into a tube, and then the tube is evacuated under the pressure of $1 \times 10^{-5} \text{ MPa}$. According to the protium pressure–composition isotherms of LaNi_5 [16], at this pressure the samples are dehydrided substantially, so we measure the protium diffusion process in the $\alpha\text{-LaNi}_5\text{H}_x$. Since lanthanum is easily oxidized, a part of the surface of the samples may be covered with La-oxide, which acts as a barrier for the protium diffusion. The oxide layer formed on the surface of the sample results in the apparent decrease of the radius of the sample. Therefore, the radius r in the Eq. (2) is decreases, and the diffusion coefficient becomes small.

The desorption kinetics, however, is not only controlled by the surface oxide layer but also by the microstructure of the sample. As shown in Fig. 6, the diffusion coefficient increases with the increase of Ni content. The addition of Ni over the stoichiometric composition LaNi_5 makes the

Table 1
Protium diffusion parameters for LaNi_x ($x = 5.0\text{--}8.1$) alloys

Sample (LaNi_x)	Q (kJ mol^{-1})	D_0 ($\text{m}^2 \text{s}^{-1}$)
$x = 5.0$	30	2.5×10^{-8}
$x = 5.5$	15	4.8×10^{-10}
$x = 6.0$	26	2.7×10^{-8}
$x = 6.5$	15	2.9×10^{-9}
$x = 8.1$	16	5.1×10^{-9}

two phase alloys consisting the LaNi_5 phase and the Ni phase. The latter precipitates along grain boundaries of the LaNi_5 phase, as shown in Fig. 1. During the hydriding, the Ni phase is heavily deformed by the expansion of the LaNi_5 phase and a high density of dislocations is induced in the Ni phase. The interface between the Ni phase and the LaNi_5 phase acts as the high diffusivity path for protium. Furthermore, increase of the Ni content produces the net work of the Ni phase, as shown in Fig. 1(d). Therefore, the protium diffusion coefficient increases with increase in x of LaNi_x . However, in the $\text{LaNi}_{5.5}$ alloy, as shown in Fig. 1(a), the small amount of the Ni phase is insufficient to form the network. As a result, the Ni phase in the $\text{LaNi}_{5.5}$ alloy does not contribute to the increase of the diffusion coefficient but act as trapping sites for protium.

In conclusion, to improve the protium desorption rate the addition of Ni to the stoichiometric compound LaNi_5 is effective.

Acknowledgements

We would like to thank Dr. H. Enoki, National Institute of Materials and Chemical Research, for supply of LaNi_5 samples. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area A of 'New Protium Function' from the Ministry of Education, Science, Sports and Culture.

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