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Effect of $LaNi_5H_6$ hydride particles size on desorption kinetics

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Abstract

The H_2 desorption rate of $LaNi_5H_6$ hydride was measured as a function of the size distribution of $LaNi_5$ particles and the number (N) of cyclic hydriding and dehydriding reactions by a volumetric method at 298 K. The measured data showed that the rate of H_2 desorption depends on N, i.e. the particle size. The H_2 desorption rate increased as N increased from $N = 10$, to 30 to 100, and as the particle size decreased. The measured desorption curves were found to be diffusion controlled. By fitting a diffusion equation to the measured curves, apparent diffusion coefficients of 1.8×10^{-9}–2.2×10^{-9} cm^2/s at 298 K were obtained for $LaNi_5H_6$ hydride with a median particle sizes of between $N = 10$ (18 μm) and $N = 100$ (10 μm).

Keywords: Diffusion of hydrogen; $LaNi_5H_6$ hydride; Hydrogen desorption; Pulverization; Cyclic hydriding

1. Introduction

When $LaNi_5$ absorbs H_2, the volume of the $LaNi_5$ lattice expands more than 25%, and this induces pulverization of the alloy or hydride, where the size of the particle becomes drastically reduced depending upon the number of cyclic hydriding and dehydriding reactions and also on the purity of the H_2 gas [1]. In addition, the H solubility changes by more than a factor of 10 depending upon the particle size, where the ease of release of the internal stresses in the particles appears to be responsible for the marked solubility change [2]. Based on these results, in a previous study we reported a significant dependence of the activation energy for H diffusion in $LaNi_5H_x$, $LaNi_{4.5}Al_{0.5}H_x$ and $LaNi_{2.5}Co_{2.5}H_x$ on the H concentration in these hydrides [3]. This study examined the relation between the particle size of the hydride and the H_2 desorption kinetics of $LaNi_5H_6$. Based on our previous study [3], we examined the dependence of the apparent value of the diffusion coefficient (D) on the particle size.

2. Experimental details

The weight of the $LaNi_5$ sample was 0.25 g. This sample was produced by high-frequency melting at Japan Steel Works, Japan. Identification of the structures and compositions of the samples was made by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX), respectively. The analyses yielded the stoichiometric composition $LaNi_{5.02\pm0.05}$. The lattice parameters of the $LaNi_5$ sample with hexagonal structure were determined to be $a = 5.017 \pm 0.002$ and $c = 3.989 \pm 0.002$. These data are consistent with the standard values reported for stoichiometric $LaNi_{5.0}$ [2,4]. The H_2 desorption rate was measured using a Sieverts' type apparatus. Details of the apparatus are reported elsewhere [4]. The purity of the H_2 gas was 7N grade (99.99999%). The vacuum leak rate of the system has a significant effect on the surface conditions of the sample, and the heat conductivities of the reaction tube and inside the alloy powder strongly affect the apparent kinetics. These factors lead to irreproducible kinetic results [5]. In this study, the vacuum leak rate was controlled to maintain a value of 7.56×10^{-9} Pa m^3 s^{-1}. Details of the significant effects of the vacuum leak rate on kinetics are reported elsewhere [6,7].

3. Result and discussion

Fig. 1 shows the change in the H_2 desorption curves of a $LaNi_5H_6$ sample as a function of time t and the number N of cyclic hydriding and dehydriding reactions at 298 K. The H_2 desorption rate increased as N increased from $N = 10$, to 30 to 100. At $N = 10$, at least 50% of the particles are >15 μm and after 100 cycles the particle size is <10 μm. With increasing N, the median particle size decreases from 18 μm at $N = 10$ to 13 μm at $N = 30$, down to 10 μm at $N = 100$. When this reduction of the sample particle size with N is taken into account, the

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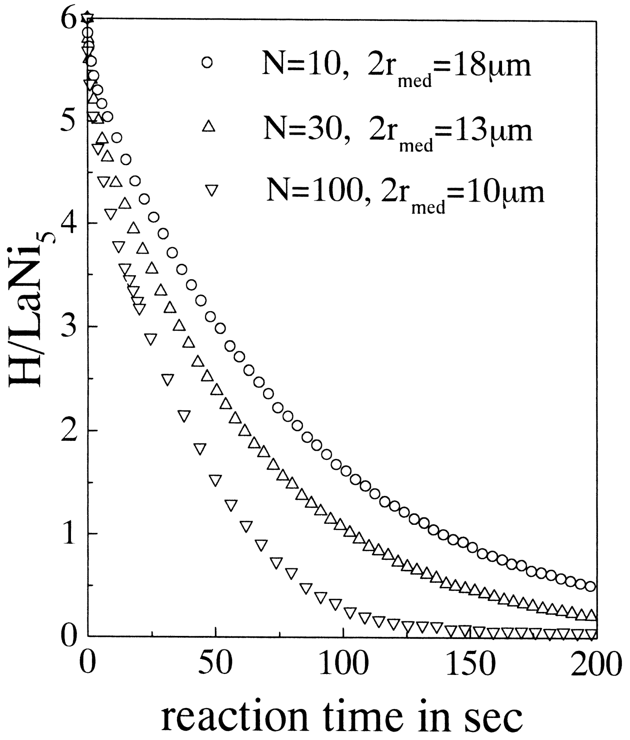

Fig. 1. Changes in the desorption curves for $LaNi_5H_6$ as a function of time t and the number N of cyclic hydriding and dehydriding reactions.

increased desorption rate with increasing N seems to be related to the reduction in particle size.

The measured desorption curves were plotted as a function of the square root of time t, as shown in Fig. 2. The measured desorption curves exhibit a linear relation in a plot of $t^{1/2}$–H concentration for H/$LaNi_5$ atomic ratio. These results are indicative of diffusion controlled kinetics of the measured desorption rates [8].

For a sample with a spherical form of radius r, the rate change by diffusion controlled kinetics can be expressed as

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \qquad (1)$$

From Eq. (1), the following equation can be obtained for the desorption curve of a sample with a spherical form of radius r_0:

$$\frac{\bar{c} - c_0}{c_s - c_0} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2\frac{Dt}{r_0^2}\right) \qquad (2)$$

where $\bar{c}$ is the mean H concentration, c_0 the initial H concentration, c_s the surface H concentration, t the reaction time and D the apparent diffusion coefficient. The samples used in this study consisted of various sizes of alloy particles. Therefore, r_0 was assumed to be the median particle size in this study. As reported previously [3], the measured curves were fitted to Eq. (2) by a mathematical expansion from $n = 1$ to 100, as shown in Fig. 3. The measured and calculated curves are shown by solid and dotted lines, respectively.

From this fitting, the apparent diffusion coefficients of H in $LaNi_5H_6$ were calculated at 298 K as $D = 1.8 \times 10^{-9}$ cm^2/s for a sample with a median particle size of 18 μm, $D = 2.0 \times 10^{-9}$ cm^2/s for a sample with a median particle size of 13 μm, and $D = 2.2 \times 10^{-9}$ cm^2/s for a sample with a median particle size of 10 μm. According to Eq. (2) the diffusion coefficient D should be constant, independent of the sample size. However, the apparent D values obtained from fittings of the equation to the measured curves were found not to be constant. In a previous paper [3], the apparent D values were found to be strongly dependent on the hydrogen concentration.

In Fig. 2, the measured desorption rate can be seen to

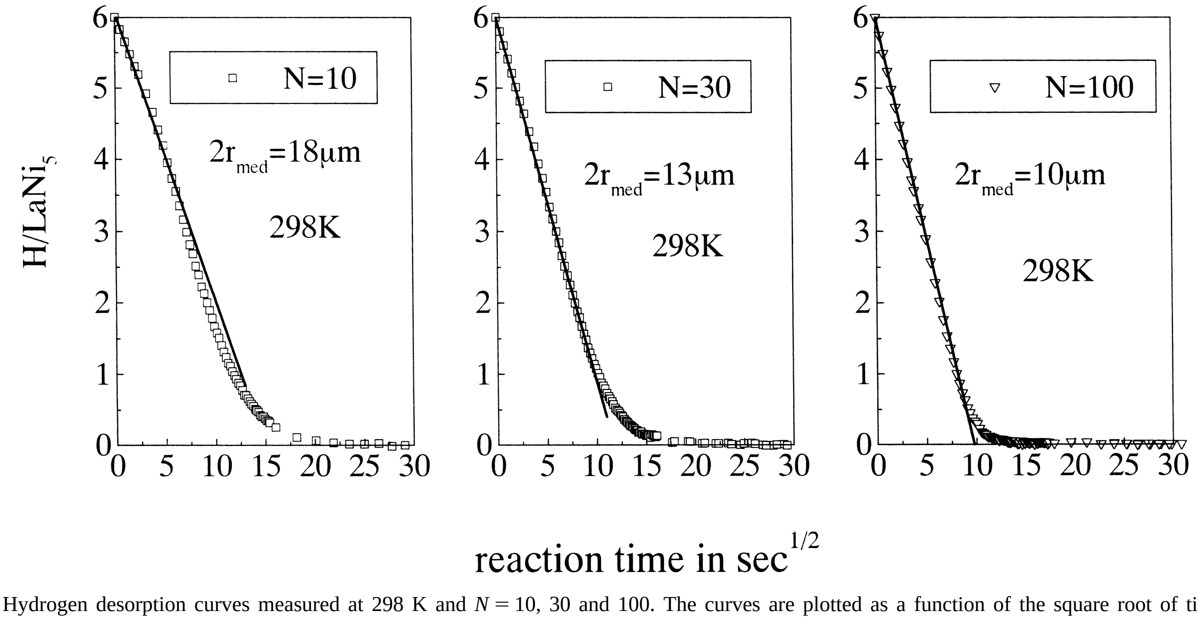

Fig. 2. Hydrogen desorption curves measured at 298 K and $N = 10$, 30 and 100. The curves are plotted as a function of the square root of time, $t^{1/2}$.

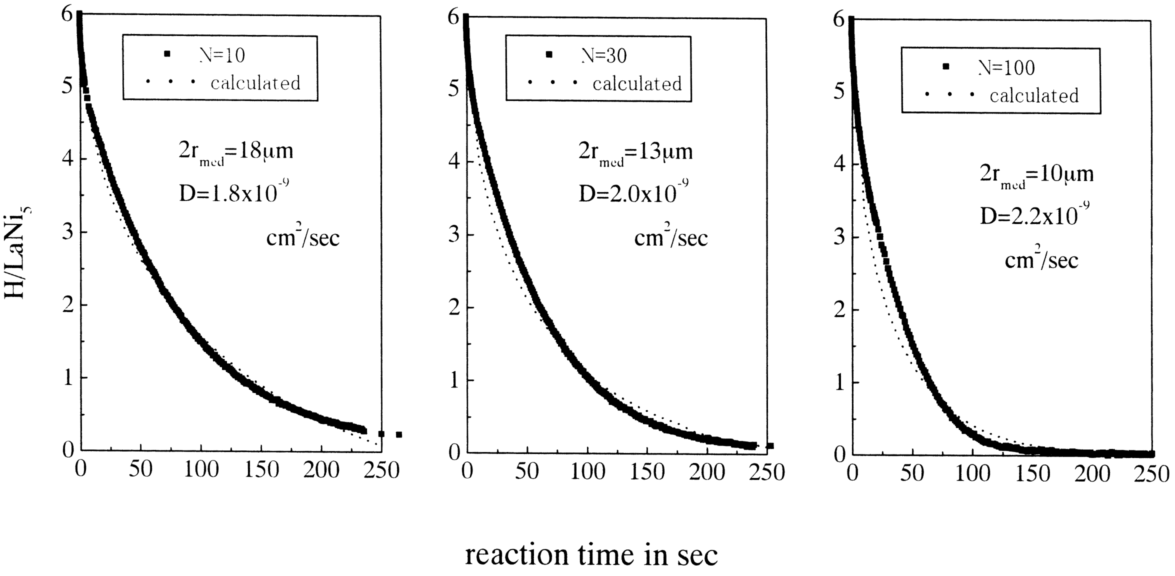

Fig. 3. Fitting of measured desorption curves at $N=10$, 30 and 100 (in Fig. 1) to theoretical curves calculated from a diffusion controlled kinetic model.

increase by about 20% in the $t^{1/2}$ vs. H/LaNi$_5$ plot as the median particle size decreases from 18 to 10 μm. This is in good agreement with the increase in the apparent diffusion coefficient D of about 20% with decreasing particle size.

For the case of samples with larger particle sizes, the volume of the samples expands with hydriding, where high densities of defects such as internal stresses, dislocations and microcracks accumulate inside the sample. The internal stresses may be released by pulverization of alloy particles with large sizes. However, larger particles still have high densities of defects, dislocations and microcracks, which may act as H trap sites and lead to a decrease in the diffusion rate of hydrogen. For the case of samples with a much reduced particle size, the volume change in the particle due to hydriding and dehydriding may become more elastic because the generated dislocations can easily migrate from the surface. Elastic internal stresses may dominate in volume expansion by hydriding and contraction by dehydriding for small particles [2]. Thus, the H trapping effect becomes smaller in diffusion as the particle size becomes smaller. If the overall desorption kinetics is controlled by H diffusion, an enhanced diffusion rate leads to an enhanced desorption rate. Thus, the particle size of the LaNi$_5$H$_6$ hydride sample appears to be a crucial factor in determining the diffusion controlled desorption kinetics.

The obtained results were compared with those reported previously for measurement of the diffusion coefficient of H in LaNi$_5$H$_x$ for $0<x<3.8$ [3]. From Fig. 3a of Ref. [3] the diffusion coefficient at $x=6$ can be assumed (by extrapolation from data at lower H concentration) to be about 2×10^{-9} cm^2/s at 298 K for a LaNi$_5$H$_6$ sample with a median particle size of 17 μm. One can use the median as r_0 in Eq. (2) only for a normal distribution, which is true only for $N>30$. The data obtained in this study are in good agreement with the result reported in Ref. [3]. The significant dependence of the apparent H diffusion coefficient of LaNi$_5$H$_x$ for $0<x<6$ on the H concentration is shown in Fig. 4.

Table 1 lists the reported diffusion coefficients D for H in LaNi$_5$H$_6$. For many studies, the size of sample used is unknown. The inconsistent data reported in Table 1 may be ascribed to differences in sample size, H concentration and the measurement method.

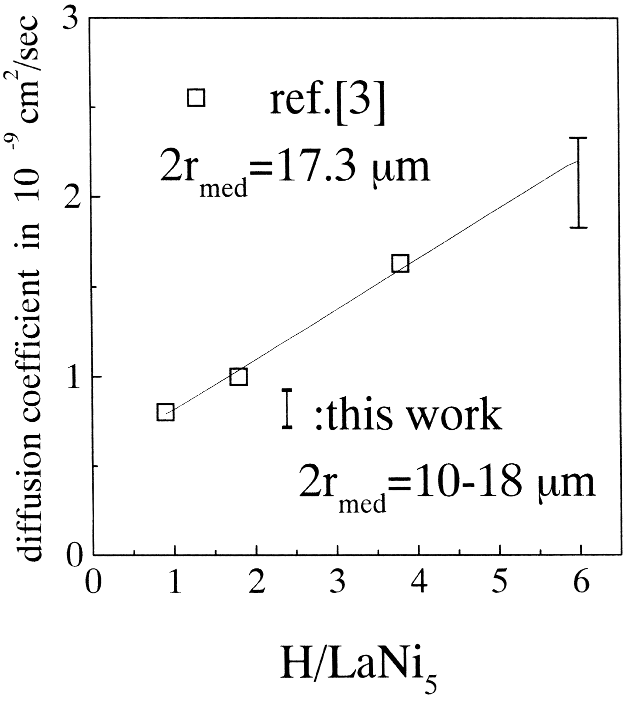

Fig. 4. Dependence of the diffusion coefficient of H in LaNi$_5$H$_x$ hydrides on the hydrogen concentration, x.

Table 1
Diffusion coefficient of hydrogen in $LaNi_5H_x$

D (cm^2/s)	T (K)	Sample state	Sample size	Hydrogen concentration	Ref.
0.8×10^{-9}	298	Powder	17.3 μm (median)	$H/M=0.8$	[3]
1.0×10^{-9}				$H/M=1.8$	
1.7×10^{-9}				$H/M=3.8$	
$2.03–2.70\times10^{-8}$	298	Single crystal	Block	α-Phase	[9]
5×10^{-8}	300	Powder	Unknown	$H/M=6$	[10]
1.3×10^{-8}	298	Unknown	Unknown	$H/M=6.5$	[11]
0.7×10^{-8}	300	Powder	Unknown	$H/M=4.95$	[12]
$1.8–2.2\times10^{-9}$	298	Powder	10–18 μm (median)	$H/M=6$	This study

4. Conclusion

From measurement of the desorption rate of $LaNi_5H_6$ with different particle size distributions at 298 K, diffusion controlled rates were found. The obtained apparent diffusion coefficient of H increases slightly with decreasing sample particle size. This appears to be associated with the density of defects and the ease of internal stress release by the desorption reaction. Together with the previous report of a significant influence of H concentration on the diffusion coefficient [3], the particle size of $LaNi_5H_6$ and other hydrides of hydrogen storage alloys accompanied by large volume changes in hydriding and dehydriding should be taken into account in diffusion kinetic studies.

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