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Hydrogen absorption and desorption isotherms in the solid solution regions of the $LaNi_5$–H system

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Abstract

The isotherms of the $LaNi_5$–H system were measured using powder and block samples in H solid solution regions by the H_2 absorption and desorption processes. Marked deviations of the desorption isotherms from the absorption isotherms were measured. The different behaviours of the desorption isotherms between powder and block samples may be associated with the different densities of defects which can be generated in the samples by the H_2 absorption and/or desorption or annihilated during the course of the long-term desorption measurement.

Keywords: $LaNi_5$; Hydrogen solubility; Hydrogen absorption isotherm; Hydrogen desorption isotherm; Hydrogen trapping

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1. Introduction

In previous studies for the H solubility in stoichiometric $LaNi_5$ block and powder samples [1,2], we found a marked dependence of the H solubility and relevant thermodynamic properties upon the sample size in the range from particles of 50–64 μm in diameter to a 9 mm cube. This effect may be attributed to the difference in the readiness of stress relaxation in H uptake by samples rather than to any surface effect [3], because no enhancement in the solubility could be found in particles of below 50–64 μm in diameter. In addition, the volume expansion of a powder sample, $\Delta V/V=0.4\%$ was about twice as large as for a block sample, $\Delta V/V=0.2\%$ at $[H]/[LaNi_5]=1\times10^{-2}$ [2]. Such stress sensitive characteristics may be attributed to the fact that $LaNi_5$ is an intermetallic compound which absorbs large amounts of H with a large volume expansion over 20% and tends to generate a high density of defects by complex dislocation reactions. In the very dilute region $1\times10^{-3}<[H]/[LaNi_5]<7\times10^{-2}$, high reproducibility in equilibrium data can be obtained only with well annealed particles smaller than about 50–60 μm [2,4]. In this study, the effect of these sensitive structural characteristics on the desorption isotherms was examined with stoichiometric $LaNi_{5.0}$ powder and block samples.

2. Experimental

The analyses of the structure and composition of stoichiometric $LaNi_x$ ($x=5.02\pm0.05$) manufactured by Japan Steel Works are reported in Ref. [2]. In this study, a 9 mm cube block sample with grain sizes 3–5 mm and a powder sample with 53–63 μm diameters were used. Before H_2 gas(99.99999% purity) exposure, a Sieverts' type apparatus [1,2] was evacuated in a vacuum 5×10^{-5} Pa at 400 K for pipelines and at 1200 K for the reaction cell until the vacuum leak rate of the whole system became less than 5×10^{-7} $\mathrm{Pa\,l\,s^{-1}}$. This low vacuum leak rate was of great importance for the long-term measurement of the isotherms at low equilibrium pressures. The time needed to reach an equilibrium state in each measured point was 8–12 h in absorption processes and 1–2 days in desorption processes with block samples, and 4–6 h in absorption processes and 10–12 h in desorption processes with powder samples. The judgement of an equilibrium state was made when the pressure change became within 10^{-2} kPa. In this study, annealing treatment of each sample before H_2 exposure was more carefully made at 1173 K in He atmosphere for 24 h in comparison with previous studies [1,2]. The measurements of the absorption and desorption isotherms were made in the ranges of temperature between 573 and 773 K and H_2 pressure from 10^2–10^5 Pa. The precise measurement meth-

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ods for the hydrogen absorption and desorption isotherms are described in Ref. [1].

3. Results and discussion

Fig. 1 shows the isotherms measured at 573 K for the block and powder samples by absorption and desorption processes. The absorption isotherms obey the Sieverts' law at H concentrations lower than $[H]/[LaNi_5]=3.5\times10^{-2}$ for the block sample and $[H]/[LaNi_5]=7.0\times10^{-2}$ for the powder sample. However, the reversibility of the Sieverts' law in the measurements of the absorption and subsequent desorption isotherms can be obtained only for very dilute regions such as H concentrations of $[H]/[LaNi_5]=5\times10^{-3}$ or less [1]. In the measurement of the isotherms, marked deviations from the absorption isotherms were observed for both block and powder samples. More detailed deviations are displayed in Fig. 2 for the block and Fig. 3 for the powder sample, respectively. The deviations become smaller with increasing temperature. This result indicates that defects can be generated even in these H solid solution regions, and that more effective defect generation may take place rather in the desorption process after the prior absorption process obeying the apparent Sieverts' law [1,2]. Recently, using transmission electron microscopy, Kim et al. [5,6] revealed the actual generation of a high density of dislocations in $LaNi_5$ in H solid solution regions and the formation of hydride precipitates at these defects. These results show that the generated defects act as H trapping sites.

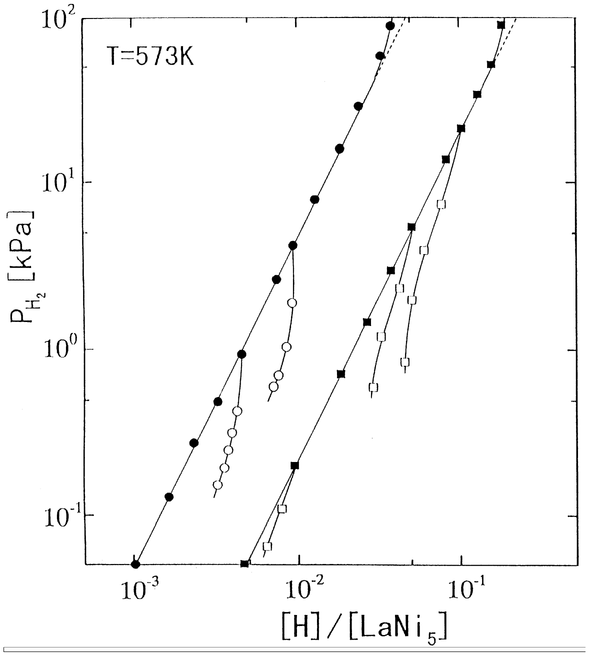

Fig. 1. The H_2 absorption and desorption isotherms at 573 K of the $LaNi_5$–H system in H solid solution regions for a 9 mm cube block sample: (●) absorption, (○) desorption; and a powder sample with 53–63 μm diameters: (■) absorption, (□) desorption.

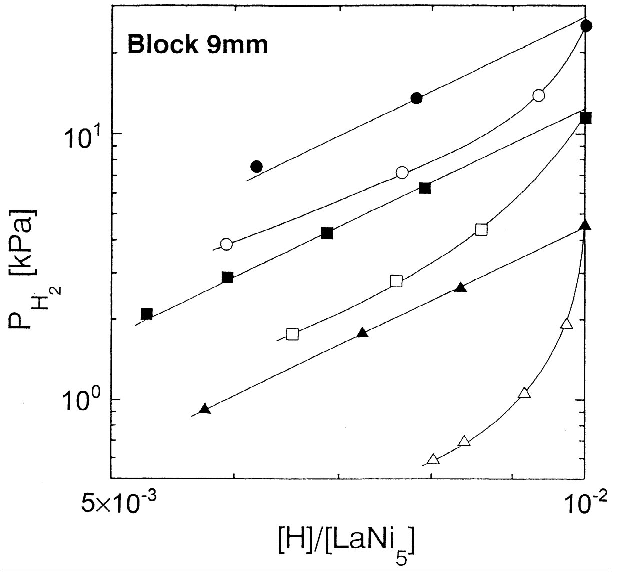

Fig. 2. Temperature dependence of the deviation of the H_2 desorption isotherms: (○) 773 K, (□) 673 K, (△) 573 K; and the absorption isotherms: (●) 773 K, (■) 673 K, (▲) 573 K of the $LaNi_5$–H system for a 9 mm cube block sample.

With decreasing H concentration from $[H]/[LaNi_5]=1\times10^{-2}$ to 5×10^{-3}, the desorption isotherm for the block deviates more markedly to lower equilibrium pressures than for the powder (Fig. 1). From the deviations of the desorption isotherms from the absorption isotherms, the difference in the chemical potentials of H was calculated for both block and powder samples at a H concentration

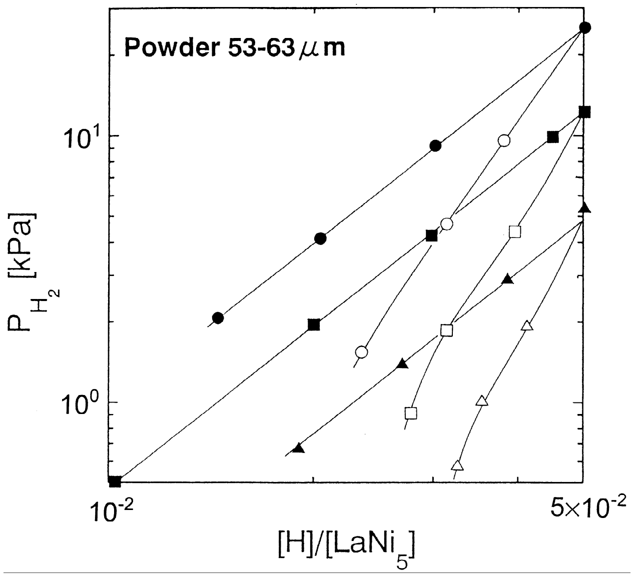

Fig. 3. Temperature dependence of the deviation of the H_2 desorption isotherms: (○) 773 K, (□) 673 K, (△) 573 K; and the absorption isotherms: (●) 773 K, (■) 673 K, (▲) 573 K of the $LaNi_5$–H system for a powder sample with 53–63 μm diameters.

$[H]/[LaNi_5]=6.0\times10^{-3}$ (Fig. 1), and which yielded 3.7 kJ/mol H for the block and 0.5 kJ/mol H for the powder, respectively. For the block sample, the more marked deviation and the more negative H chemical potentials suggest the formation of a higher density of defects and stronger H trapping at the generated defects with deeper potential wells. Whether or not the generation of defects in the sample takes place more in the desorption process is still a question.

For the block sample, the drop of the desorption isotherms with decreasing H concentration deviates slightly to higher pressures from those expected from the linear drop (Fig. 2). Because of the limited volume expansibility, the H atoms in the block sample may be under higher compressive stresses than in smaller crystallites.

For the powder sample, in contrast, the desorption isotherms exhibit rather negative deviation from the linear drop, indicating the presence of the more negative H chemical potentials in the lattice of the powder sample. The larger volume expansion of smaller crystallites leads to the more ready stress relaxation and higher H solubility, and the H atoms in the powder may be under far less compressive stresses. One absorption–desorption cycle up to $[H]/[LaNi_5]=5\times10^{-2}$ induces higher anisotropic residual strains in the basal plane of hexagonal $LaNi_5$ [1]. For the powder sample, the deviations to more negative chemical potentials suggest the more effective role of the inelastically enlarged sites under tensile stresses in the desorption process for the powder sample. This may be connected with the fact that the volume expansibility of the powder sample is twice as high as the block [2].

In addition, we would like to point out the possible contribution of the time dependent reduction of defect density by the release of stress and strains or partial annihilation of dislocations to the desorption isotherms during the extended measurement of the desorption isotherms where about 10 days and two days were needed for a desorption isotherm measurement for the block and powder samples, respectively. For intermetallics such as $LaNi_5$ which generate a high density of defects in the H uptake, the time dependent change in the defect density during an equilibrium measurement should be taken into account. Dantzer et al. pointed out the necessity of the consideration of time dependent change in defect density during the course of an equilibrium measurement to obtain reproducible data [7,8].

4. Conclusion

The different behaviours of the desorption isotherms between the block and powder samples may be associated with the different densities of defects such as stress, strains and dislocations generated, accumulated or annihilated in the measurements. The change in defect density in the H uptake or release induces the redistribution of stresses and H atoms in the samples, resulting in the change in the H chemical potentials. Further investigation using X-ray diffraction is being undertaken to give more precise explanation for the desorption isotherms deviating from the absorption isotherms.

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