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The confinement of hydrogen in $LaNi_5$ by poisoning of the hydride surface

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Abstract

Surface treatment with CO gas was found to contribute to the confinement of hydrogen in hydrogenated $LaNi_5$. The confinement of hydrogen was enhanced by extension of the CO treatment time and by lowering the temperature at which the sample stood in air. Fourier transform IR spectra suggested that CO molecules chemisorbed on the surface of precipitated Ni which is considered to play the role of recombination center of hydrogen atoms. Since the pathway for hydrogen desorption is sealed by chemisorbed CO molecules, hydrogen appears to be confined in $LaNi_5$. It was found that one chemisorbed CO molecule can confine ca. 10^4 molecules of hydrogen when the average diameter of $LaNi_5$ particles is about 3.6 μm.

Keywords: Hydrogen storage; Hydrides; Carbon monoxide; Adsorption; Poisoning

1. Introduction

$LaNi_5$ is the most widely investigated of all the hydrogen storage alloys, because it exhibits excellent rechargeable hydrogen storage properties at ambient temperature and pressure.

The equilibrium hydrogen pressure of $LaNi_5$ at room temperature is about 2×10^5 Pa, so that hydrogenated $LaNi_5$ must always be handled under a hydrogen atmosphere more than equilibrium pressure. To maintain the hydrogen atmosphere, vessels which are airtight and stable under pressure and heat must be used and, in addition, both the temperature and pressure must be controlled. If it were possible to deal with hydrogenated $LaNi_5$ under atmosphere or inert gases, these inconveniences would be removed and some advantages, for example, hydrogen storage and transport without the need for heavy vessels, would be available.

Sandrock and Goodell investigated the surface poisoning of $LaNi_5$, which occurs as a result of impurities in the hydrogen gas, such as carbon monoxide and some sulfer compounds [1–3]. They reported that the poisoning decreases the rate of hydrogen absorption in $LaNi_5$ and the amount of hydrogen taken up by the alloy. Gualtieri et al. found that $LaNi_5$ hydride can be sealed effectively by the adsorption of the SO_2 gas [4]. Ron et al. also reported that the hydride is poisoned by SO_2 gas to prevent dehydriding [5]. However, it has not been revealed how much hydrogen was confined in $LaNi_5$, and how the amount of hydrogen, and the mechanism of confinement of hydrogen with poisoning gases changes with time.

In the present study, we tried to confine hydrogen in $LaNi_5$ using surface poisoning with CO gas to enable handling of the hydrogenated $LaNi_5$ in air. The hydrogen content in poisoned $LaNi_5$ hydride and its retention time were investigated in detail. To clarify the mechanism of confinement with CO gas, the state of CO molecules adsorbed on the surface of $LaNi_5$ hydride is elucidated.

2. Experimental details

$LaNi_5$ ingots were supplied by Santoku Metal Industry Co., Ltd., Kobe, Japan, and have the following composition: 30 wt.% La, 69 wt.% Ni, 0.25 wt.% Al, 0.076 wt.% Ca. The ingots were crushed and the resulting powders were loaded in a stainless-steel vessel. H_2 gas with a pressure of 9.0×10^5 Pa was applied to the sample, and the temperature increasing–decreasing cycling (363–77 K) was repeated until the sample could adequately absorb and desorb hydrogen. After a sufficient activation process, the sample was maintained

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at 273 K. In this condition, hydrogen is stored in $LaNi_5$. Subsequent to evacuation of the residual hydrogen gas for 0.12 ks, CO gas of 1.0×10^6 Pa was applied immediately to the sample, and the sample was exposed to the CO atmosphere for 43.2 or 129.6 ks at 273 K. After the CO gas treatment, the sample was allowed to stand in air or an atmosphere of argon for a definite time at room temperature (ca. 300 K) or 267 K.

Films of amorphous $LaNi_5$ were deposited using an r.f. magnetron sputtering apparatus. Details of the preparation technique have been described previously [6,7]. The film sample was treated with CO gas in the same manner as the powder sample.

To determine the change with the passage of time in hydrogen concentrations in the samples, X-ray diffraction (XRD) measurements (MAC Science, M18XHF-SRA) were taken of hydrogenated $LaNi_5$ crystalline powders treated and untreated with CO gas. The XRD pattern of each sample obtained involved a mixture of two kinds of peaks, belonging respectively to the hydride ($LaNi_5H_{6.8}$) and unhydrogenated alloy ($LaNi_5$) phases. The peak intensities of the (111) plane for both the hydride and alloy phases were estimated from the peak height (cps) multiplied by the full width at half-maximum (deg), and the ratio of peak intensities ($LaNi_5H_{6.8}$-to-$LaNi_5$) was determined. A change with time of the hydrogen concentrations in the samples was conjectured from the ratios of peak intensities.

The amount of hydrogen in the sample for various ratios of peak intensities was determined using a Sieverts' type apparatus [8]. The relationship between the hydrogen concentrations in the samples ([H]/[$LaNi_5$]) and the ratios of peak intensities is shown in Fig. 1.

For the amorphous $LaNi_{5.0}$ films, the hydrogen content in the sample was measured using a quartz crystal mass monitoring (QCMM) method described previously [7,9].

The adsorbed CO on the surface of $LaNi_5$ hydrides was analyzed using a Fourier transform IR diffuse reflectance spectrometer (Shimadzu, FT-IR 4000) equipped with a vacuum and heating apparatus. The $LaNi_5$ hydride treated with CO gas was measured. The measurement was first performed at room temperature in a stream of nitrogen, and next at elevated temperature (400 K).

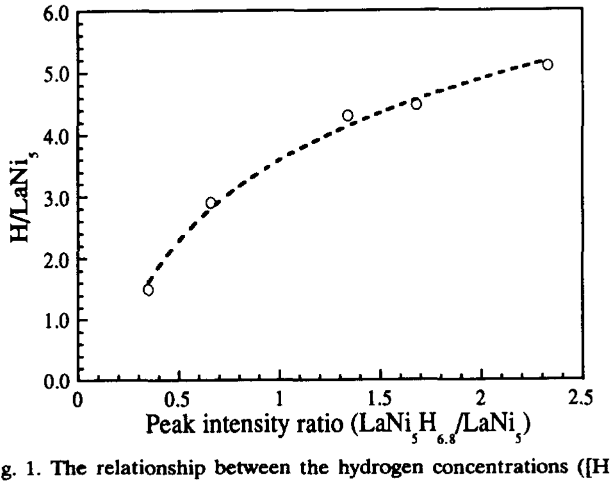

Fig. 1. The relationship between the hydrogen concentrations ([H]/[$LaNi_5$]) and the ratios of peak intensities ($LaNi_5H_{6.8}$-to-$LaNi_5$).

The specific surface area of the activated $LaNi_5$ particles used was determined by a high speed surface area analyzer (Shimadzu, model 2205).

The amount of carbon monoxide chemisorbed on the surface of crystalline $LaNi_5$ powders was determined using a conventional constant volume method. The adsorption measurement was carried out at 297 K. To remove oxygen adsorbed on the sample, reduction treatment with hydrogen was performed at 773 K for 0.36 ks. The cell which contained the resulting sample was evacuated at 573 K to remove the chemisorbed hydrogen until there was no change in pressure at 0.4 Pa. The amount of chemisorbed CO was found by subtracting the amount of physisorbed CO from the total amount of adsorbed CO.

3. Results and discussion

Fig. 2 shows the XRD patterns for various samples of hydrogenated crystalline $LaNi_5$ powders. Immediately after exposure to air, the XRD pattern of the hydrogenated sample with CO gas treatment was obtained (Fig. 2(a)). The sample was a mixture of $LaNi_5H_{6.8}$ and unhydrogenated $LaNi_5$ phases. Although the peaks which belong to unhydrogenated $LaNi_5$ phase remain, a large amount of hydride phase ($LaNi_5H_{6.8}$) was formed in the sample, and the average hydrogen concentration ([H]/[$LaNi_5$]) was 4.8.

When the hydrogenated $LaNi_5$ powder sample without CO gas treatment was allowed to stand in air at room temperature for 129.6 ks, the hydride phase disappeared completely (Fig. 2(b)). As for the samples with CO gas treatment, the hydride phase still remained after exposure to air for 129.6 ks (Fig. 2(c), (d)).

Fig. 3 illustrates the change with time in the hydrogen concentration. The hydrogen concentration in the sample with CO gas treatment for 129.6 ks was constant at ca. 5 until after exposure to air for 46.8 ks (Fig. 2(e)). Furthermore, the time required for disappearance of the hydride peak for this sample was ca. 720 ks, which was more than 20 times longer than for the untreated sample. This indicates that hydrogen in $LaNi_5$ was sealed by CO molecules adsorbed on the surface.

After treatment with CO gas, as shown in Fig. 2(c) and (d), the ratio of peak intensities for the sample with CO gas treatment for 129.6 ks, which is 0.96, is twice as large as the ratio after 43.2 ks. The sealing of hydrogen in $LaNi_5$ by CO treatment was, therefore, found to be enhanced by lengthening the treatment time with CO gas.

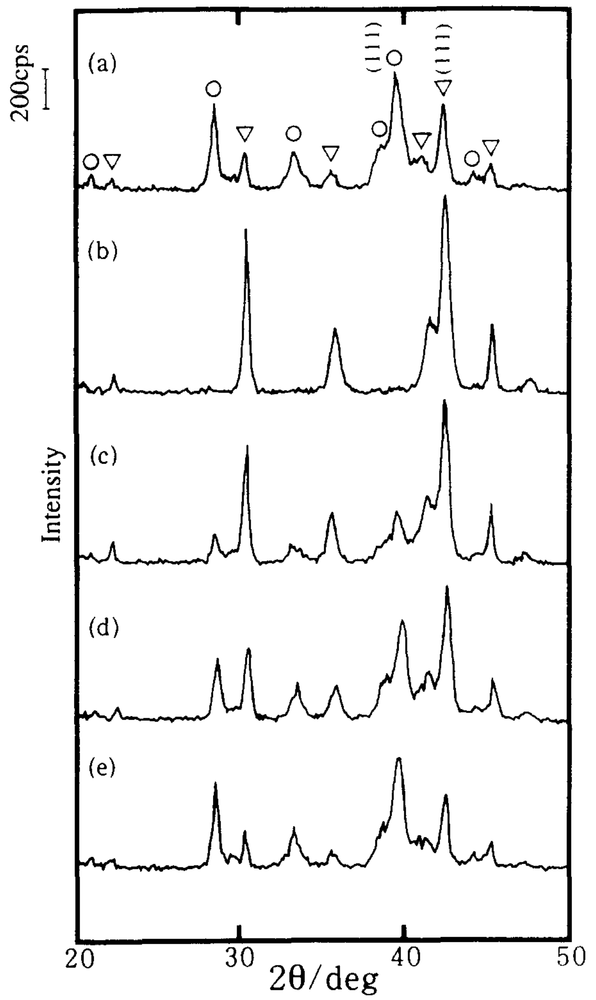

Fig. 2. X-ray diffraction patterns for the hydrogenated $LaNi_5$, of samples allowed to stand in air at room temperature, ○ $LaNi_5H_{6.8}$, ▽ $LaNi_5$:
(a) Immediately after exposure to air ($[H]/[LaNi_5]=4.8$); (b) not treated with CO gas and exposure to air for 129.6 ks; (c) treatment with CO gas for 43.2 ks and exposure to air for 129.6 ks; (d) treatment with CO gas for 129.6 ks and exposure to air for 129.6 ks; (e) treatment with CO gas for 129.6 ks and exposure to air for 46.8 ks.

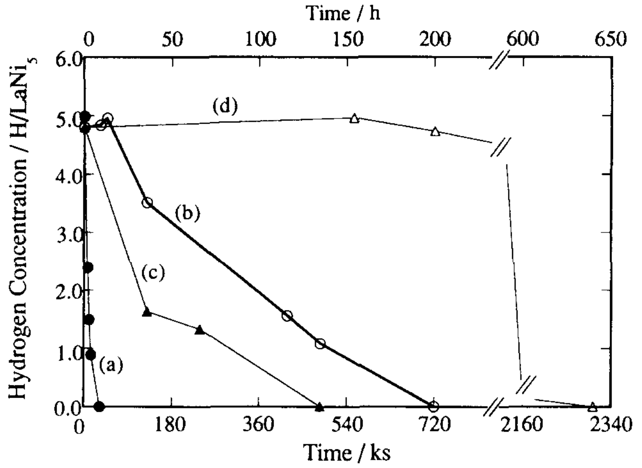

Fig. 3. Change with time of the hydrogen concentration in hydrogenated $LaNi_5$:
(a) ● not treated with CO gas and exposure to air at room temperature; (b) ○ treatment with CO gas and exposure to air at room temperature; (c) ▲ not treated with CO gas and exposure to argon at 267 K; (d) △ treatment with CO gas and exposure to argon at 267 K. Argon gas was used as atmosphere for the experiment at 267 K to avoid contamination with moisture.

To extend the sealing effect of CO, samples with CO gas treatment were allowed to stand at lower temperature (267 K). The retention time for hydrogen storage was found to be extended remarkably in comparison with that at room temperature (Fig. 3(b) and (d)).

The CO gas treatment was also effective for hydrogenated amorphous $LaNi_5$ films. The initial hydrogen content in the film, which was $1.7[H]/[LaNi_5]$, was retained after exposure to air for 18 ks.

The mechanism of the confinement of hydrogen in $LaNi_5$ using CO poisoning was considered as follows. Some mechanisms for the activation of $LaNi_5$ have been proposed. Wallace et al. claimed that the surface of $LaNi_5$ exposed to air consists of a layer with $La(OH)_3$ and precipitated Ni and hydrogen molecules are dissociated into atoms on the Ni sites [10]. Schlapbach et al. reported that segregation occurs on the $LaNi_5$ surface owing to the oxidation of La and the precipitation of Ni clusters, and the Ni clusters act as a catalyst for hydrogenation [11]. However, Uchida and Ozawa investigated the kinetics of hydrogen absorption by $LaNi_5$ with oxide layers [12]. They suggested that the surface of $LaNi_5$ exposed to air is covered with the oxides and hydroxides of both La and Ni, and hydrogen atoms dissociated at the surface diffuse through the coating layers. Although the mechanism of activation is complicated, metallic Ni on the surface appears to play an important role for dissociation and recombination of hydrogen molecules. CO molecules adsorb on metallic Ni precipitated on the surface of hydrogenated $LaNi_5$, and replace chemisorbed hydrogen atoms owing to the high adsorptive activity for CO in comparison with hydrogen. The recombination center of hydrogen atoms, namely an exit for hydrogen molecules, is stopped with the adsorbed CO molecules, so that hydrogen appears to be confined in $LaNi_5$.

It needed a long time to confine hydrogen with CO gas. Hydrogen is supplied continually from the $LaNi_5$ hydride to the surface Ni because $LaNi_5$ prefers to desorb hydrogen during CO gas treatment owing to the absence of hydrogen in the atmosphere. This may influence the chemisorption of CO on the surface Ni.

FTIR absorption spectroscopy was used to study CO adsorbed on the surface of hydrogenated $LaNi_5$ powder. Fig. 4 illustrates IR spectra for hydrogenated $LaNi_5$ powders with CO gas treatment. For spectrum (a) measured at 295 K, a weak broad band is observed at the region of 1900–2200 cm^{-1}. This band disappeared after heating the sample at 400 K (spectrum (b)). The

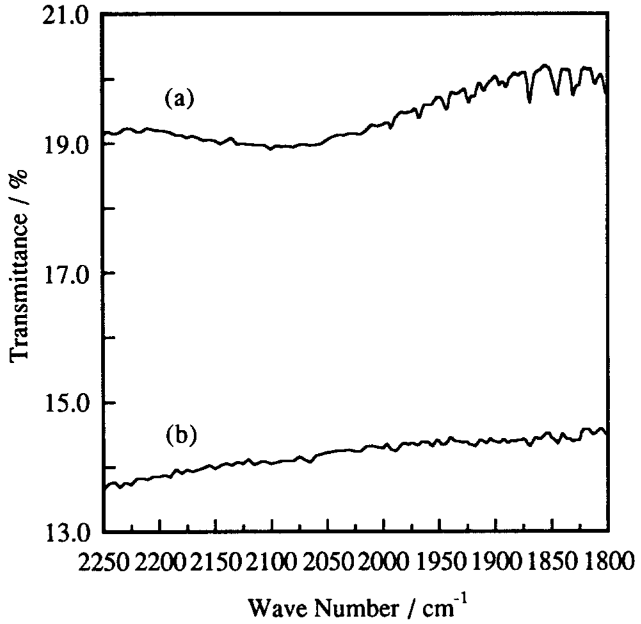

Fig. 4. FTIR absorption spectra for hydrogenated $LaNi_5$ powder with CO gas treatment; measurements were taken in a stream of nitrogen: (a) room temperature (295 K),
(b) 400 K.

absorption band can be assigned to C≡O stretching vibration, because IR absorption peaks for gases which may be in contact with $LaNi_5$, such as H_2O and CO_2 except for CO (gaseous CO stretching vibrations, 2143 cm^{-1}), are absent in the range 1900–2200 cm^{-1}. Furthermore, the disappearance of the peak at elevated temperature suggests the desorption of CO from the surface of the hydrogenated $LaNi_5$. From the FTIR analysis, it is suggested that CO molecules are adsorbed on the precipitated Ni which is the active site for recombination of hydrogen atoms.

Carbon monoxide on the precipitated Ni surface appears to exist in two forms, 'linear' and 'bridged' CO. The IR absorption bands at 1910 and 2020 cm^{-1} are known to be assigned to bridged and linear CO respectively [13,14]. Although the accurate bridged-to-linear ratio cannot be obtained from the broad IR absorption band observed, the linear CO which is the more weakly bound species appears to be dominant since the peak position is close to that of linear CO. Further detailed investigation will be necessary to clarify the state of CO adsorption on the hydrogenated $LaNi_5$.

The retention time for hydrogen storage increased at a lower temperature (267 K). There are two factors which influence the confinement of hydrogen. One is the stabilization of hydrogen in the hydride, and the other is the stabilization of the adsorbed CO on the surface of the hydride. The activation energy for CO desorption from the surface of Ni(100), which is 110 kJ mol^{-1}, has been determined at low CO coverages which are less than a monolayer [15]. The ratio of rate constants, $k(300\ K)/k(267\ K)$, is estimated at about 1.01 from the activation energy. This suggests that CO desorption is little affected by the temperature within this experimental ranges. However, it has been reported that there are differences in the rate of reaction for dehydriding, $R_{0.5}=d([H]/[M])/dt$ at $[H]/[M]=0.5$, between 300 K and 267 K [16]. The ratio of two rates, $R_{0.5}(300\ K)/R_{0.5}(267\ K)$, is calculated at about 9. This value is in agreement with values obtained from samples with CO gas treatment and the untreated samples, which are about 11 and 12 respectively. Therefore, extension of the retention time for hydrogen storage was found to cause stabilization of hydrogen in the hydride.

The specific surface area of sufficiently activated $LaNi_5$ powders was found to be $0.20 \pm 0.01\ m^2\ g\text{-}LaNi_5{}^{-1}$. The average diameter of the $LaNi_5$ particles evaluated from the surface area was about 3.6 μm. The amount of CO chemisorbed at 297 K was evaluated at 3.66×10^{17} CO molecules $g\text{-}LaNi_5{}^{-1}$, indicating that the area occupied by chemisorbed CO was $6.15 \times 10^{-2}\ m^2 g\text{-}LaNi_5{}^{-1}$. A value of $1.68 \times 10^{-19}\ m^2$ was used as the cross-sectional area of a CO molecule adsorbed on Ni in order to evaluate the area occupied by CO molecules [17]. From the surface area and the area of chemisorbed CO for activated $LaNi_5$ powders, the coverage of CO molecules on the surface of $LaNi_5$ particle was estimated at about 30%.

On the basis of the amount of chemisorbed CO, the amount of hydrogen confined in $LaNi_5$ per CO molecule was estimated. As mentioned above, the chemical composition of $LaNi_5$ hydride used was $LaNi_5H_{4.8}$ which corresponds to 6.7×10^{21} H atoms per g-$LaNi_5$. Therefore, it was found that one CO molecule can confine about 10^4 molecules of hydrogen in $LaNi_5$. This value appears to depend on the particle size and the surface condition of $LaNi_5$. It is assumed that more hydrogen molecules can be confined in $LaNi_5$ with larger particle sizes. It remains for the relationship between the distribution of metallic Ni on the $LaNi_5$ surface and the sealing effect to be clarified in detail.

We have performed neutron scattering measurements of hydrogenated $LaNi_5$ using the technique of hydrogen confinement by CO gas treatment. It has been confirmed that the technique is very effective in removing the difficulties of handling this kind of hydride.

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