Surface Observation of LaNi₅ under Deuterium Atmosphere Using Small-Angle Neutron Scattering

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We developed a new sample holder for small-angle neutron scattering (SANS) experiments under controlled atmospheres. Using this new sample holder, SANS profiles of conventional hydrogen-absorbing alloy LaNi₅ under a deuterium atmosphere were measured. Changes in the SANS profile of LaNi₅ were clearly observed during absorption and desorption. It was found that there is reversibility in the surface morphology of LaNi₅; it changed from being markedly rough (fractal dimension of particle surface $D_s = 2.8$, before deuteration) to smoother ($D_s = 2.5$ at 1.05 D/M, i.e., LaNi₅D_{6.3}) during absorption (up to 1 MPa), and then reverted to being rough ($D_s = 2.8$) during desorption (under vacuum <5 Pa), where D/M is the deuterium-to-metal ratio. [doi:10.2320/matertrans.M2014009]

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1. Introduction

Hydrogen-absorbing alloys are key materials for modern industrial applications; La₂Ni₇-based intermetallic alloys are used as cathodes in Ni/metal-hydride batteries, and Ti-Cr-V-based solid-solution alloys are promising candidates for application in high-pressure metal-hydride tanks in fuel-cell vehicles.^{1–3} The hydrogenation properties are characterized by the hydrogen storage capacities (i.e., hydrogen-to-metal ratio, H/M), residual hydrogen contents, rates of hydrogen absorption and desorption, and reliabilities of such alloys. For further improvement of the hydrogenation properties, it is very important to understand the morphology of the surface of alloy particles, in addition to the crystal structures and the hydrogen absorption-desorption cycles.

LaNi₅, which has a hexagonal crystal system (space group: $P6_3/mmm$), is one of the most popular hydrogen-absorbing alloys. The P (pressure)– C (composition) isotherm for LaNi₅ shows that the absorption pressure drastically decreases for the first absorption-desorption cycle and then remains stable during further absorption-desorption cycles.⁴ The morphology of the surface of LaNi₅ has previously been studied by transmission electron microscopy (TEM).^{4–7} In TEM images, numerous dislocations are observed in LaNi₅ after the first hydrogenation. Additionally, X-ray diffraction (XRD) for LaNi₅ after the first hydrogenation demonstrates anisotropic peak broadening (i.e., lattice strain).⁸ The XRD patterns for further absorption-desorption cycles are almost the same as that for the first hydrogenation, with the expectation that there is reversibility in the surface morphology of LaNi₅ particles with the numerous dislocations during the absorption-desorption cycles. However, there is insufficient information on the surfaces of LaNi₅ particles under a hydrogen atmosphere. Small-angle neutron scattering (SANS) has attracted much attention as a powerful tool for observing the particle surfaces of materials. The fractal dimension of the particle surface, D_s , can be extracted from the slope of a SANS profile, $I(q)$, in the Porod region, that is,

$$I(q) \propto q^{-(6-D_s)}, \quad (1)$$

where q is the magnitude of a scattering vector ($= 4\pi \sin \theta / \lambda$, where θ is half of the scattering angle, 2θ , and λ is the neutron wavelength).⁹ It is a smooth surface as D_s is close to 2, whereas a rough surface as D_s is close to 3. SANS technique is surely applicable to hydrogen-absorbing alloys, although almost all of them (e.g., LaNi₅) require a controlled hydrogen atmosphere during SANS experiments to prevent hydrogen desorption.

The aim of this study is to clarify the changes in the morphology of the surface of LaNi₅ particles under a hydrogen atmosphere. In our SANS experiments, however, we used deuterium (D) instead of light hydrogen (H) to suppress the background level in SANS data due to the large incoherent scattering, σ_{inc} , from H. Because the incoherent scattering cross-section of the D nucleus ($\sigma_{\text{inc}}(\text{D}) = 2.0 \text{ b}$, where a barn (units of b) is defined as 10^{-28} m^2) is considerably lower than that of the H nucleus ($\sigma_{\text{inc}}(\text{H}) = 80.2 \text{ b}$), using D enables us to clearly observe SANS profiles, even in the high- q region. Furthermore, we developed a new sample holder for SANS experiments under controlled atmospheres (controlled atmosphere sample (CAS) holder, hereafter). The P - C isotherm for LaNi₅ under a deuterium atmosphere and XRD data for LaNi₅ before deuteration and after deuteration were also collected.

2. Experimental Procedure

Prior to the SANS experiments for LaNi₅ under a deuterium atmosphere, the P (pressure)– C (composition) isotherm for LaNi₅ were measured under a deuterium atmosphere. A LaNi₅ ingot, which was synthesized by Ar-arc-melting a mixture consisting of La (99.9%, Furuuchi Chem.) and Ni (99.9%, Furuuchi Chem.) in appropriate molar proportions, was crushed into a powder; then, the LaNi₅ powder sample was sealed in a cylindrical stainless-steel container and was subsequently kept at 413 K under vacuum for 1 h. After the sample was activated with high-purity D₂ gas (99.995%), the P - C isotherm for activated LaNi₅ was

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Fig. 1 Sample holder developed for SANS experiments on hydrogen-absorbing alloys under controlled atmospheres (CAS holder).

measured using Sieverts' method at RT (~ 298 K) during the absorption-desorption cycle. The crystal structures of LaNi_5 before deuteration (i.e., no activation) and after deuteration were characterized using XRD with $\text{Cu-K}\alpha$ radiation (SmartLab, Rigaku). The XRD data were measured in air at RT and analyzed with a Rietveld-refinement program, RIETAN-FP.¹⁰⁾

As shown in Fig. 1, the CAS holder was composed of a rectangular parallelepiped stainless-steel body (SS304, $25 \text{ mm} \times 25 \text{ mm} \times 55 \text{ mm}$), a stainless-steel flange (SS304, $25 \text{ mm} \times 25 \text{ mm}$), and two 3-mm-thick, 20-mm-diameter disk-shaped quartz windows. A 1-mm-diameter indium wire was used between the stainless-steel body and the quartz window (side wall), and an O-ring was used between the stainless-steel body and the stainless-steel flange (upper part) to seal the CAS holder. Additionally, the CAS holder was equipped with an inlet and outlet gas pipeline (SS304, 6.35 mm (0.25 in) in diameter), a stainless-steel in-line filter ($< 0.5 \mu\text{m}$, Swagelok®), high-pressure diaphragm valves (Swagelok®), and a pressure gauge for constantly monitoring the gas pressure. A 0.5-mm-thick cadmium plate was used as a neutron-shielding material and was placed on the front wall to redirect the incident neutron beam to reduce the intensity of the background signals during SANS.

SANS experiments for LaNi_5 under a deuterium atmosphere were performed using a SANS spectrometer installed at the CN-2 beam line of the Research Reactor Institute, Kyoto University (KUR-SANS).¹¹⁾ LaNi_5 powder was placed in a commercial quartz cell ($10 \text{ mm} \times 45 \text{ mm} \times 2 \text{ mm}$). The sample was 2-mm thick along the direction of the incident neutron beam. The quartz cell containing the LaNi_5 powder was subsequently put into the CAS holder and was kept at ~ 393 K for 9 h under vacuum (< 5 Pa). After the sample was activated twice with high-purity D_2 gas (99.995%), SANS data were measured at RT (~ 299 K) for 5 h for each deuterium-to-metal ratio (D/M): (1) D/M = 0 (before deuteration, that is, no activation), (2) D/M = 1.05 at 1 MPa during absorption, and (3) D/M ≈ 0 during desorption (under vacuum < 5 Pa). Note that the gas pressure in the CAS holder is displayed by the pressure gauge, and D/M is

Fig. 2 P (pressure)- C (composition) isotherm for LaNi_5 under a deuterium atmosphere during the absorption-desorption cycle at room temperature (~ 298 K) after the activation process. The solid line is drawn to guide the eye.

estimated from the deuterium storage capacity according to Sieverts' method. The incident neutron beam was $5 \times 5 \text{ mm}^2$ at the sample position. The neutron wavelength, λ , which was monochromatized using a double-reflection Ni-Ti multilayer monochromator,¹²⁾ was 0.46 nm (long-wavelength mode). Scattered neutrons were detected using a two-dimensional position-sensitive ^3He gas detector installed at a small-angle scattering bank, and $I(q)$ profiles were collected in the q range 0.16 – 1.6 nm^{-1} .

3. Results and Discussion

Figure 2 shows the P - C isotherm for LaNi_5 under a deuterium atmosphere during the absorption-desorption cycle at RT (~ 298 K) after the activation process. A plateau appeared at ~ 0.4 MPa in the range 0.1 – 1.0 D/M during absorption. The maximum hydrogen storage capacity was 1.05 D/M at 1 MPa; therefore, the composition of the deuteride phase was $\text{LaNi}_5\text{D}_{6.3}$. The plateau appeared at 0.14 MPa in the range 0.1 – 0.9 D/M during desorption. D/M abruptly decreased to zero below 0.1 MPa, meaning that virtually no residual hydrogen existed in vacuum (i.e., D/M ≈ 0). Thus, our LaNi_5 sample showed excellent deuteration property.

The XRD patterns for LaNi_5 before deuteration (i.e., no activation) and after deuteration are shown in Figs. 3(a) and 3(b), respectively. The XRD data for LaNi_5 after deuteration were collected immediately after the SANS experiments for LaNi_5 under a deuterium atmosphere. In Rietveld analyses, the atomic positions La(1) (0, 0, 0), Ni(1) ($1/3, 2/3, 0$), and Ni(2) ($1/2, 0, 1/2$) were used to refine the crystal structures on the basis of the $P6/mmm$ space group. The lattice parameters of LaNi_5 before deuteration were determined to be $a = 0.50177(4) \text{ nm}$ and $c = 0.39816(2) \text{ nm}$ ($R_{\text{wp}} = 7.95\%$ and $S = 2.18$), and those of LaNi_5 after deuteration were determined to be $a = 0.5012(2) \text{ nm}$ and $c = 0.3988(1) \text{ nm}$ ($R_{\text{wp}} = 9.96\%$ and $S = 2.76$), where R_{wp} is the R -factor and S is the goodness-of-fit. The lattice parameters did not significantly change, although the ($hk0$) Bragg reflections of LaNi_5 after the deuteration were somewhat broad. Such an

Fig. 3 Full Rietveld refinement patterns for LaNi₅ (a) before deuteration (i.e., no activation) and (b) after deuteration. The plus marks indicate data for observed XRD intensities, and the solid lines indicate data for calculated intensities. The vertical marks below the XRD data denote the positions of Bragg reflections. The gray curves at bottom indicate the difference between observed and calculated intensities.

anisotropic peak broadening in XRD patterns due to the numerous hydrogenation-induced dislocations has also been reported in the literature.⁸⁾

Figure 4 exhibits the SANS data for the CAS holder and LaNi₅ before deuteration. Note that q is defined on a logarithmic scale, whereas the SANS intensities are defined on a linear scale. The SANS intensities for the CAS holder were significantly weaker than those for LaNi₅ before deuteration in the low- q region. Furthermore, the obtained transmission rates for the neutron beams were 83% and 73% for the CAS holder and LaNi₅ before deuteration, respectively. It is sufficient to say that the CAS holder does not significantly affect the SANS intensities for the LaNi₅.

Next, activated LaNi₅ was deuterated at 1 MPa in the CAS holder; D/M was estimated to be 1.05 (i.e., LaNi₅D_{6.3}), taking into account the deuterium storage capacity obtained from the pressure gauge in the CAS holder, which was in good agreement with that for the P - C isotherm (see Fig. 2). Figure 5 shows the SANS profiles, $I(q)$, for LaNi₅D_{6.3} measured at 1 MPa during absorption and LaNi₅ (D/M $\approx$ 0) during desorption (under vacuum <5 Pa). The intensities attributed to the CAS holder have already been subtracted from the SANS intensities for the samples. With eq. (1), the surface morphology of LaNi₅D_{6.3} was first assessed through D_s , which was obtained from the least-

Fig. 4 SANS intensities measured for the developed CAS holder (filled circles) and LaNi₅ before deuteration (open circles) at room temperature (~ 299 K).

Fig. 5 SANS profiles, $I(q)$, for LaNi₅D_{6.3} (D/M = 1.05) measured at 1 MPa at room temperature (~ 299 K) during absorption (open circles), LaNi₅ (D/M $\approx$ 0) during desorption (open triangles). The solid lines represent least-squares fits obtained using the equation: $I(q) \propto q^{-k}$, where q represents the magnitude of the scattering vector and k represents the slope of the SANS profile. The scattering appeared in the q range between ~ 0.6 to ~ 1.6 nm⁻¹ for LaNi₅D_{6.3} during absorption is described by the dashed line.

squares fit in the q range 0.17–0.45 nm⁻¹. As a result, D_s for LaNi₅D_{6.3} was estimated to be 2.5 ($k = 3.5$). The SANS profile obviously changed during desorption; that is, $I(q)$ for LaNi₅ was smaller than that for LaNi₅D_{6.3}, suggesting that the marked decrease in $I(q)$ during desorption was solely due to neutron scattering from D. The slope of the SANS profile decreased to $k = 3.2$ ($D_s = 2.8$) in the q range 0.17–1.45 nm⁻¹, indicating that the surface morphology changes from being significantly smoother ($D_s = 2.5$) to rough ($D_s = 2.8$). Furthermore, a scattering due to the formation of nanostructure after deuterium absorption appeared in the q range between ~ 0.6 to ~ 1.6 nm⁻¹ for LaNi₅D_{6.3}, which completely disappeared in $I(q)$ for LaNi₅. This result suggests that the observed change in $I(q)$ is strongly associated with the density fluctuations of deuterium.

Fig. 6 SANS profiles, $I(q)$, for LaNi_5 ($D/M \approx 0$) during desorption (open triangles) and LaNi_5 before deuteration (open squares). The solid lines represent least-squares fits obtained using the equation: $I(q) \propto q^{-k}$, where q represents the magnitude of the scattering vector and k represents the slope of the SANS profile.

Additionally, we compared $I(q)$ for LaNi_5 during desorption with that for LaNi_5 before deuteration (i.e., no activation). As shown in Fig. 6, $I(q)$ for LaNi_5 during desorption was consistent with that for LaNi_5 before deuteration, of which D_S was estimated to be 2.8 ($k = 3.2$) in the q range $0.17\text{--}1.45\text{ nm}^{-1}$. The anisotropic strain remained in the lattice after deuteration (see Fig. 3), although there was reversibility in the surface morphology of LaNi_5 particles, even in the first deuteration. Here, we point out that the surface morphology of LaNi_5 changed from being significantly rough ($D_S = 2.8$, before deuteration, that is, no activation) to smoother ($D_S = 2.5$ at 1.05 D/M , i.e., $\text{LaNi}_5\text{D}_{6.3}$) during absorption and reverted to being rough ($D_S = 2.8$) during desorption, regardless of the anisotropic strain in the lattice due to numerous deuteration-induced dislocations. In fact, such reversibility in the surface morphology during absorption-desorption cycles has also been observed in SANS experiments on $\text{Ti}_{0.31}\text{Cr}_{0.33}\text{V}_{0.36}$ alloy.¹³⁾ Further SANS investigations are now in progress to clarify the relationship between the surface morphology and the anisotropic strain in the lattice due to the numerous deuteration-induced dislocations.

4. Conclusions

We developed a new sample holder for SANS experiments under controlled atmospheres. Using this new sample holder, SANS profiles of conventional hydrogen-absorbing alloy LaNi_5 under a deuterium atmosphere were measured. Addi-

tionally, $P\text{--}C$ isotherms for activated LaNi_5 were measured under a deuterium atmosphere, and the crystal structures of LaNi_5 before deuteration (i.e., no activation) and after deuteration were characterized by Rietveld analyses with XRD data. The surface morphology of LaNi_5 changed from being significantly rough ($D_S = 2.8$, before deuteration, that is, no activation) to smoother ($D_S = 2.5$ at 1.05 D/M , i.e., $\text{LaNi}_5\text{D}_{6.3}$) during absorption and reverted to being rough ($D_S = 2.8$) during desorption (under vacuum $<5\text{ Pa}$). Such reversibility in the surface morphology of LaNi_5 during absorption-desorption cycles was observed despite the introduction of deuteration-induced anisotropic strain in the lattice of LaNi_5 observed in the XRD experiments. Furthermore, a scattering due to the formation of nanostructure after deuterium absorption appeared in the q range between ~ 0.6 to $\sim 1.6\text{ nm}^{-1}$ for $\text{LaNi}_5\text{D}_{6.3}$ during absorption, which completely disappeared during desorption. The result suggests that the scattering in $I(q)$ for $\text{LaNi}_5\text{D}_{6.3}$ is strongly associated with the density fluctuations of deuterium.

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