

***In situ* X-ray and neutron powder diffraction study of LaNi_{5-x}Sn_x-H systems**

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ABSTRACT

We have studied structural change and lattice strain formation during absorption and desorption of hydrogen (deuterium) by high purity LaNi_{5-x}Sn_x alloys ($x = 0.22, 0.25$) using *in situ* X-ray and neutron diffraction along with simultaneously measuring the *P-C* isotherms. From profile analysis of the X-ray diffraction data, lattice parameter and lattice strain in each hydriding state are evaluated. *In situ* neutron diffraction data provided hydrogen occupation changing with hydrogen content. Significant lattice contract and strain formation were observed in the hydride phase in desorption. This behavior was related with decrease in hydrogen occupation in the hydride phase revealed from the neutron diffraction data.

INTRODUCTION

LaNi₅ is a representative intermetallic compound, which has a reversible hydrogen absorbing property under ambient conditions. The alloy phase transforms into hydride phase through two-phase coexistence region. The lattice parameters and the cell volume increase by 7 % and 24 %, respectively, in the transformation from the alloy phase to the hydride phase, respectively. The hydriding reaction with such large lattice expansion in absorption and contraction in desorption could induce various kinds of lattice defects and strain.

Nakamura and Akiba have made an *in situ* X-ray diffraction (XRD) study of LaNi₅ and LaNi_{4.75}Al_{0.25} in the initial absorption-desorption [1]. LaNi₅ showed heavy anisotropic lattice strain in the direction of $\langle hk0 \rangle$. It formed in absorption and did not disappear in the following desorption reaction. LaNi_{4.75}Al_{0.25} did not show such type of strain but showed another type of anisotropic strain in the direction of $\langle 00l \rangle$, which disappeared in the following phase transformation. These results suggest that strain formation strongly depends on the substitution elements.

Hydriding properties of LaNi_{5-x}Sn_x have been reported as a good candidate of heat pump material for space use by one of the present authors [2,3]: these alloys show a wide and flat plateau region and good stability for repeated absorption-desorption cycles. They show little peak broadening in XRD profiles even after hydriding [4,5]. The good stability in repeated hydriding and little peak broadening in XRD profiles are similar to properties of LaNi_{5-x}Al_x [6,7]. From the viewpoint of the relation between strain and stability in repeated cycles, introduction and properties of lattice strain in LaNi_{5-x}Sn_x in absorption-desorption are of much interest.

This paper will present results of *in situ* XRD measurements of $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ during the initial absorption-desorption cycle. These measurements were performed under a similar condition to that for $\text{LaNi}_{4.75}\text{Al}_{0.25}$ previously reported [1]. The data were analyzed by the Rietveld method. Lattice parameter change and strain formation accompanying hydride phase formation and decomposition will be discussed. In addition, results of *in situ* neutron diffraction of $\text{LaNi}_{4.78}\text{Sn}_{0.22}$, focusing on hydrogen occupation in the hydride phase, will be presented.

EXPERIMENTAL DETAILS

Preparation of alloy ingots

Alloy ingots of $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ and $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ were prepared from high purity metals [3] using the arc melting technique. They were annealed at 1223K for ~100h in a purified Ar atmosphere.

XRD measurements

In situ X-ray powder diffraction were measured using a horizontal sample stage type diffractometer (Rigaku, RINT-TTR) with a rotating Cu anode, a high-pressure chamber and temperature controller. Measurements were performed at generator power of 50 kV and 200 mA with 0.5 degree of divergence and scattering slits and 0.15 mm of receiving slit. Alloy powder was filled into a stainless steel holder and covered with a beryllium plate with 0.1 mm thick. The sample was kept at a constant temperature, 323K after evacuation at 373K for 1h. XRD profiles were measured along the P-C isotherms. Hydrogen content in the sample was measured simultaneously by Sieverts' method.

Neutron measurements

Neutron powder diffraction was measured in a TOF diffractometer (Sirius; KENS (KEK), Japan) using two 90° detector banks. A cadmium mask with 3-mm-wide beam windows was used to eliminate diffraction caused by stainless steel from the sample holder [8]. Weak diffraction of γ -Fe was observed, but the maximum peak height of γ -Fe was less than a few percents of that of the strongest peak of the main phase.

Peak profile analysis

The XRD data in the 2θ range between 25° and 90° were analyzed by Rietveld refinement program RIETAN-97beta [9,10]. A pseudo-Voigt function is used for expressing peak profiles, where FWHM of Gaussian part and Lorentzian part, H_{KG} and H_{KL} , are expressed as follows [11]:

$$H_{KG} = [8 \ln 2 (U \tan^2 \theta_K + V \tan \theta_K + W + P \sec^2 \theta_K)]^{1/2} \quad : \text{Gaussian part} \quad (1)$$

$$H_{KL} = (X + X_e \cos \phi_K) \sec \theta_K + (Y + Y_e \cos \phi_K) \tan \theta_K \quad : \text{Lorentzian part} \quad (2)$$

θ_K is the Bragg angle. X and X_e in the Lorentzian part are parameters for crystallite-size effect. U , Y and Y_e are parameters expressing peak broadening caused by strain of the crystal lattice. Strain and crystallite size were calculated from the corresponding parameters using the equation in Ref.11. In this study, the anisotropic strain parameter Y_e in addition to the isotropic strain

parameters U and the crystallite size parameter X were refined.

The neutron diffraction data were analyzed using RIETAN-2001TN for TOF diffractometer [10].

RESULTS AND DISCUSSION

In situ X-ray diffraction of $\text{LaNi}_{4.75}\text{Sn}_{0.25}$

XRD profiles

XRD profiles in absorption and desorption processes were obtained along the P - C isotherms (Figure 1). It should be noted that during desorption the profiles of the hydride peaks became broader and drastically shifted toward higher 2θ in the two-phase region while peaks of the solid solution phase do not either broaden or shift. Such significant peak shift and broadening were not observed in the profiles during absorption.

Lattice parameters

Lattice parameters of each hexagonal phase were determined from the Rietveld analysis. Lattice parameter c of each phase is plotted in Figure 2 for example. Error bars for c are shown but they are smaller than the size of the marks in most points. Lattice parameters of the solid solution phase increased by about 0.001-0.002 nm in the single-phase region, and they were almost at constant in the two-phase region (Figure 2(a)). By comparison, those of the hydride phase showed apparent increase and decrease even in the two-phase region (Figure 2(b)). The decrease during desorption is significant, which appears as large peak shift in XRD profiles shown in Figure 1(b). The decrease over the two-phase region was more than 0.005 nm, which corresponds to more than 1 % of the lattice parameter. Large hysteresis between hydriding and dehydriding should be also noted. However, only modest hysteresis effects have been reported [3] for this system. Such significant changes in the lattice parameters and hysteresis were not observed in hydride phase of LaNi_5 .

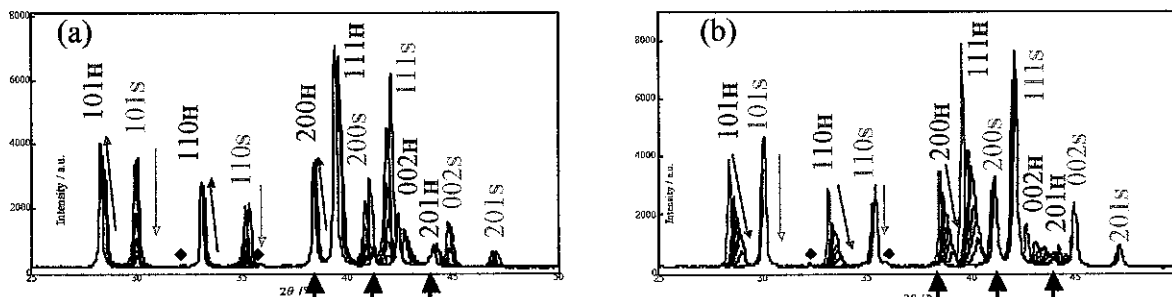


Figure 1. In situ XRD profiles of $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ in absorption (a) and desorption (b).

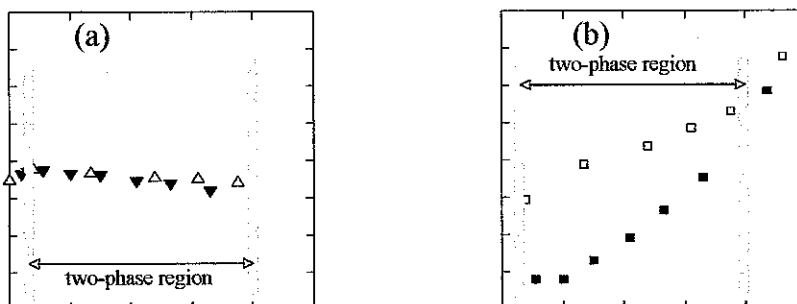


Figure 2. Lattice parameter c of the solid solution phase (a) and the hydride phase (b). Open marks: absorption, closed marks: desorption.

Lattice strain

Lattice strain in the solid solution phase was around 0.5 % over absorption-desorption, and became smaller after complete dehydriding. Strain formation in the hydride phase is remarkably different from that in the solid solution phase. In absorption (Figure 3(a)), isotropic strain was about 0.5 % at the beginning of the reaction, but it decreased down to almost zero with increase of the hydrogen content. In desorption (Figure 3 (b)), anisotropic strain was observed in addition to isotropic strain. The isotropic strain rapidly increased up to 1.7 %, and then gradually decreased. Anisotropic strain did not form in the hydride single-phase region, but was produced during formation of the solid solution phase and reached around 0.5 % just before complete disappearance of the hydride phase.

In summary, substantial strain formation occurs only in the hydride phase during desorption in the two-phase region, and it disappears upon the transformation into the solid solution phase.

In situ neutron diffraction of $\text{LaNi}_{4.78}\text{Sn}_{0.22}$

We investigated hydrogen occupation change in $\text{LaNi}_{4.78}\text{Sn}_{0.22}\text{D}_x$ to understand the quite unusual behavior, lattice contract and strain formation, observed in the hydride phase mentioned

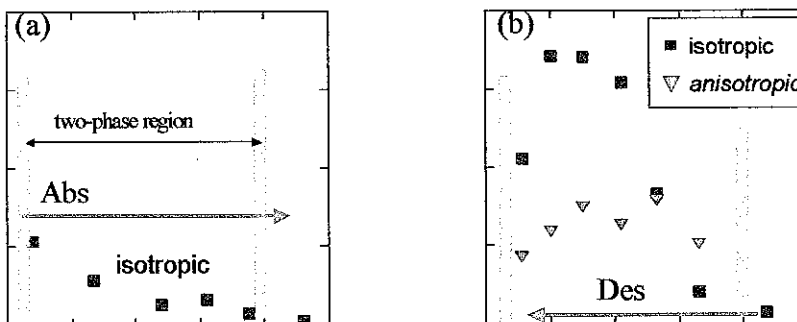


Figure 3. Lattice strain in the hydride phase in absorption (a) and desorption(b).

above.

Structural analysis of the full-hydride

The diffraction data of the full-hydride single phase $\text{LaNi}_{4.78}\text{Sn}_{0.22}\text{D}_{-6}$ were analyzed using a structural model with a $P6mm$ symmetry, containing four hydrogen sites, 3c, 6e₁, 6e₂ and 2b. It provided a good fit as shown in Figure 4. A seven hydrogen sites model with a $P6mm$ symmetry reported by Joubert et al., employed for structural analysis of $\text{LaNi}_{4.8}\text{Sn}_{0.2}\text{D}_{6.1}$ [12], was also tried. Using this model, however, we obtained reasonable values of occupancies only for four sites, 3c(or 6d), 6e₁, 6e₂ and 2b, but negative or negligibly small values for the other sites at the mirror positions of 3c(or 6d), 6e₂ and 2b. In our case, value for the hydrogen content agreed better with the P - C isotherm using the four-site model than any other models with five to seven hydrogen sites.

Hydrogen occupation and hydrogen content in the hydride phase

Hydrogen occupancies obtained for the four D sites during desorption are plotted in Figure 5(a). The D1 site is fully occupied in absorption, but the occupancy slightly decreases in the two-phase region in desorption. Occupancy of the D2 site is almost constant. Occupancies of D3 and D4 decrease in the single-phase region, and slowly decrease even in the two-phase region.

Hydrogen content (total hydrogen occupation) in the hydride phase was calculated from the occupancies of all the hydrogen sites. Figure 5(b) shows calculated hydrogen content in the hydride phase plotted against the *average* hydrogen content measured by the P - C isotherm. The data clearly indicates that the hydrogen content in the hydride phase decreases even in the two-phase region during desorption. This decrease is mainly caused by decrease in occupancies of the D3 and D4 sites as shown in Figure 5(a).

Relation between the lattice contract and the hydrogen content in the hydride phase

From the analysis results of the neutron diffraction, lattice contract of the hydride phase in the two-phase region observed in the *in situ* XRD can be attributed to decrease of hydrogen occupation. However, the fact that the hydrogen content of the hydride phase changes in the two-phase region cannot be explained by the Gibbs' phase rule. It suggests possibility that the hydride phase does not

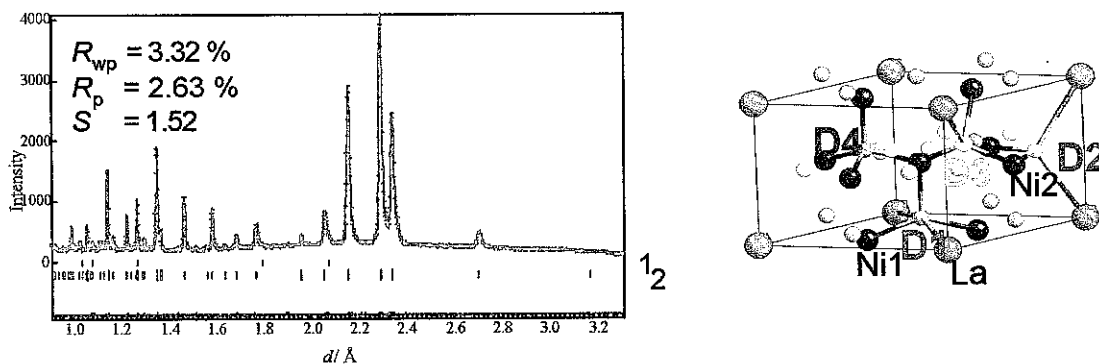


Figure 4. *In situ* neutron diffraction data and the refined crystal structure of the hydride phase $\text{LaNi}_{4.78}\text{Sn}_{0.22}\text{D}_{-6}$.

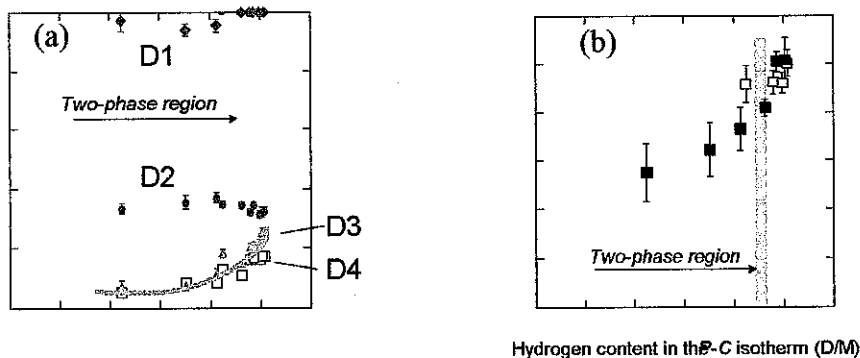


Figure 5. Occupancies of D sites (a) and total hydrogen content (b) in the hydride phase.

have homogenous hydrogen occupation during desorption, for example, consisting of regions containing slightly different hydrogen content. The lattice strain reflects distribution of the lattice dimension and lattice relaxation accompanied by fluctuation of the hydrogen content, and also probably relates with interaction between the coexisting two phases.

SUMMARY

$\text{LaNi}_{5-x}\text{Sn}_x$ alloys ($x = 0.22, 0.25$) were investigated using *in situ* X-ray and neutron diffraction along the *P-C* isotherms. Remarkable lattice contract and strain formation were observed in the hydride phase in the two-phase region during desorption. Results of neutron diffraction revealed decrease in hydrogen occupation in the hydride phase even in the two-phase region. The lattice contract and strain formation can be attributed to the hydrogen occupation change.

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