Structural Changes in $\text{RNi}_5\text{-H}$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) Systems with Two Hydrogen Pressure Plateaux*

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Pressure-composition (P-C) isotherms of $\text{RNi}_5\text{-H}$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) systems show two hydrogen pressure plateaux during hydrogen absorption and desorption. These correspond to the transitions among three phases: one hydrogen solid solution (α phase; $\text{RNi}_5\text{H}_{\sim 0.5}$) and two hydrides (β phase; $\text{RNi}_5\text{H}_{3\sim 4}$ and γ phase; $\text{RNi}_5\text{H}_{5\sim 7}$). To explore the mechanism of the phase transitions, we investigated the structural changes in $\text{RNi}_5\text{-H}$ systems with *ex-situ* XRD. During hydrogen desorption, the *ex-situ* XRD profiles show that the crystal structures in $\text{RNi}_5\text{-H}$ systems change from hexagonal (γ phase) through monoclinic (β phase) to hexagonal (α phase). The temporary decrease in structural symmetry may be due to hydrogen occupation except in the basal plane of the crystal structure. Lattice expansion between the α and β phases normalized in the monoclinic structure decreases slightly with the increasing atomic number of R in $\text{RNi}_5\text{-H}$ systems. Similarly to the correlation between the first plateau pressure and the unit cell volume of the α phase, the second plateau pressure is logarithmically related to the unit cell volume of the β phase. As far as the $\text{RNi}_5\text{-H}$ (R : from La to Gd except Ce) system is concerned, we can empirically predict the second plateau pressure as well as the first plateau pressure from the unit cell volume of the alloys.

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1. Introduction

The $\text{LaNi}_5\text{-H}$ system shows three phases during hydrogen absorption and desorption;^{1,2)} LaNi_5 hydrogen solid solution (α phase), $\text{LaNi}_5\text{H}_{3\sim 4}$ hydride (β phase) and $\text{LaNi}_5\text{H}_{6\sim 7}$ hydride (γ phase). The pressure-composition (P-C) isotherm of the $\text{LaNi}_5\text{-H}$ system shows two pressure plateaux above 313 K, corresponding to the α - β and β - γ phase transitions, in contact with one pressure plateau at 298 K between the α and γ phases. The crystal structures of these phases are hexagonal, as shown by *in-situ* X-ray diffractometry (XRD), but with different lattice parameters.^{3,4)}

In the $\text{PrNi}_5\text{-H}$ system⁵⁾ two well-separated pressure plateaux are present due to two different hydrides, with compositions of PrNi_5H_4 (β phase) and PrNi_5H_6 (γ phase). Although the γ phase with hexagonal structure in the $\text{PrNi}_5\text{-H}$ system is similar to that in the $\text{LaNi}_5\text{-H}$ system, the structure of the β phase in the $\text{PrNi}_5\text{-H}$ system is classified as C-centered monoclinic lattice. In the other $\text{RNi}_5\text{-H}$ system ($\text{R} = \text{Nd}, \text{Sm}$, and Gd) with two plateaux on the P-C isotherm^{6,7)} the structure of the hydrides, especially of the β phase, remains unknown due to high plateau pressures.

With respect to the first (lower pressure) plateau, it is well known⁸⁾ that the plateau pressure is logarithmically related to the unit cell volume of the α phase or alloy. However, the correlation between the second plateau and the structure of the β phase is not clear. To clarify the appearance of multiple pressure plateaux on the P-C isotherm, it is important to understand the structural changes of the hydrogen storage materials during hydrogen absorption and desorption.

In this work, we investigated the structures of hydrides in $\text{RNi}_5\text{-H}$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$, and Gd) systems. From the analysis of the *ex-situ* X-ray diffraction profiles, we discovered the

mechanism of the phase transitions and clarified the correlation between the plateau pressure of the second plateau and the structure of the β phase.

2. Experimental Details

The preparation of RNi_5 ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) alloys by arc melting has been described previously.^{6,7)} The sample ingots were sieved down to 75 μm and mixed with 10 mass% Si fine powder to calibrate the X-ray diffraction angle. The mixtures were then activated several times under 9.5 MPa of hydrogen and cooled down to 196 K. Prior to the XRD measurement, the fully hydrided samples were exposed to acetone at the same temperature. The crystal structure of each hydrided sample was identified with an X-ray powder diffractometer (RINT2000, Rigaku Co., Ltd.) using $\text{Cu K}\alpha$ radiation in the fixed time mode under air at room temperature (*ca.* 298 K). The *ex-situ* XRD profiles were continuously recorded until the hydride decomposed and changed to the original alloy.

3. Results and Discussion

The partial pressure of hydrogen is so low in air that the full hydrides decompose gradually with hydrogen desorption. Temperature increase from 196 K to room temperature also promotes the decomposition of the hydrides, which returns to their original alloys with phase transition. When exposed to acetone at low temperature, the surface coating inhibits hydrogen desorption. In practice the decomposition of hydrides in acetone at low temperature is slower than in air.

The most informative profiles for the $\text{NdNi}_5\text{-H}$ system are shown in Fig. 1. The *ex-situ* XRD measurement, which requires 3 h for the diffraction range from 10° to 100° , was repeated 20 times. After 60 h, the NdNi_5 hydride decomposes completely; the original NdNi_5 alloy is recovered under these

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Fig. 1 *Ex-situ* XRD profiles of NdNi₅-H system during hydrogen desorption. The crystallographic parameters of each phase are calculated from the XRD profiles (α : $\circ$, β : $\square$, and γ : $\triangle$).

conditions. As there are no obvious peaks below 18.5° , the diffraction angle between 18.5° and 88.5° is used for calculation.

Over the time-course of hydrogen desorption, the diffraction peaks of *ex-situ* XRD profiles can be classified into three sets: those that disappears in a short time, temporary peaks in the middle, and then newly appearing peaks. Taking into account the hydrogen desorption on the P-C isotherm in this system, these sets of diffraction peaks are attributed to the γ , β and α phases, respectively. For the γ phase in the NdNi₅-H system, Che *et al.*⁹⁾ reported that the space group of NdNi₅ full hydride is $P6/mmm$. However, our XRD profiles for this system show that some peaks, such as 21.9° and 37.3° , correspond not to $P6/mmm$ but to $P6_3mc$. This space group is identical to that of the LaNi₅ full hydride.¹⁰⁾ In the middle sets, there are some specific peaks, especially at lower angles such as 19.4° , 19.7° , 34.1° , and 34.7° . All diffraction peaks of the β phase are indexed according not to orthorhombic but to monoclinic structure ($C2/m$), which is the same as that of the β phase in the PrNi₅-H system.⁵⁾ The structure of the β phase in the NdNi₅-H system was also identified by *in-situ* XRD under 5 MPa of hydrogen pressure at 298 K. The final set of α phase peaks shows a hexagonal structure (space group: $P6/mmm$) with the lattice parameters ($a = 0.49550(2)$ nm, $c = 0.39790(3)$ nm) similar to the original NdNi₅ alloy ($a = 0.4950$ nm, $c = 0.3975$ cm).⁶⁾

Other *ex-situ* XRD profiles in the SmNi₅-H and GdNi₅-H systems were also observed under similar conditions, except for shorter measurement times (SmNi₅-H: 24 h, GdNi₅-H: 3 h as total time). The diffraction peaks indicated that the

structural changes in these systems are identical to that in the NdNi₅-H system, that is, the γ , β and α phases have hexagonal, monoclinic and hexagonal structures, respectively. Considering the reversibility of the P-C isotherm in these systems, the structural changes during hydrogen absorption must be reversed during hydrogen desorption.

In the two-phase coexistence region, the proportion of each phase varies with hydrogen desorption. As hydrogen desorption proceeds, the relative intensities of the γ phase peaks decrease while those of the β phase simultaneously increase. Subsequently, an exchange of diffraction peaks between β and α phases occurs. In contrast with the intensity ratio, the angles of diffraction peaks are almost constant because the structure of each phase is practically unchanged over two-phase region.¹¹⁾ So the crystallographic parameters in these systems can be calculated from the diffraction angles of each set of peaks using the least-squares method and summarized in Table 1. As with the original RNi₅ alloy,⁶⁾ the lattice parameters of both β and γ phases decrease gradually with the increasing atomic number of R, probably due to the lanthanide contraction. In contrast, the angle between the a and c axes of monoclinic structure (θ_β) increases slightly.

When the a and b axes of the monoclinic structure ($C2/m$) correspond to the a and c axes of the hexagonal structure ($P6/mmm$), the c axis of the monoclinic is in the $z = 0$ plane of the hexagonal (same as the a axis). Considering a_a , c_a and V_a as the crystallographic parameters of the original hexagonal RNi₅ alloys, the lattice and volume expansions between alloy and β phase, normalized as monoclinic structures, are calculated and summarized in Fig. 2(a). As the unit cell of the γ phase ($P6_3mc$) is twice that of the alloy, the expansions between the γ phase and the alloy, normalized as $P6_3mc$, are shown in Fig. 2(b). In the case of the β phase shown in Fig. 2(a), the lattice expansion of the a_β axis is the same as that of the c_β axis, which is twice as large as that of b_β axis. Although the lattice expansion is almost constant regardless of R in RNi₅-H systems, the volume expansion (ΔV_β) decreases gradually with the increasing atomic number of R due to the increase of angle θ_β . This is related to the unit cell volume of the alloys (V_a). For the γ phase (Fig. 2(b)), both lattice expansions (especially the Δc_γ value) in the SmNi₅-H and GdNi₅-H systems are much smaller than those in PrNi₅-H and NdNi₅-H systems, indicating a small ΔV_γ . This may be related to the disappearance of the second plateau in the SmNi₅-H and GdNi₅-H systems at high temperature.^{6,7)}

Table 1 Crystallographic parameters of RNi₅ (R = Pr, Nd, Sm, and Gd) hydrides. Numbers in parentheses are the estimated standard deviations referring to the last digits.

Hydride	Space group	a/nm	b/nm	c/nm	$\theta_\beta/^\circ$	V/nm^3
PrNi ₅ (β)	$C2/m$	1.0362(9)	0.8117(4)	0.9029(9)	149.37(3)	0.3868(4)
NdNi ₅ (β)	$C2/m$	1.0329(8)	0.8111(1)	0.8997(7)	149.42(3)	0.3835(3)
SmNi ₅ (β)	$C2/m$	1.0273(6)	0.8101(2)	0.8944(9)	149.52(4)	0.3776(5)
GdNi ₅ (β)	$C2/m$	1.0248(3)	0.8089(3)	0.8912(9)	149.64(8)	0.3733(9)
PrNi ₅ (γ)	$P6_3mc$	0.5359(1)	—	0.8475(2)	—	0.2108(1)
NdNi ₅ (γ)	$P6_3mc$	0.5337(1)	—	0.8471(4)	—	0.2089(1)
SmNi ₅ (γ)	$P6_3mc$	0.5245(1)	—	0.8196(3)	—	0.1952(1)
GdNi ₅ (γ)	$P6_3mc$	0.5217(2)	—	0.8214(4)	—	0.1936(2)

Fig. 2 Normalized lattice and volume expansions between RNi_5 (R = Pr, Nd, Sm, and Gd) alloys and hydrides: (a) β hydride, (b) γ hydride.

Fig. 3 Relationship between plateau pressures at 298 K and unit cell volumes of RNi_5 (R = Pr, Nd, Sm, and Gd) alloys⁷⁾ and β hydrides. The data for LaNi_5 β hydride⁴⁾ is normalized to the monoclinic structure.

Figure 3 shows the relationship between the hydrogen plateau pressures observed on the hydrogen desorption of P-C isotherm in RNi_5 -H systems⁷⁾ and the unit cell volumes of the RNi_5 alloys and β phases. The fact that the logarithmic pressure of the first plateau is empirically proportional to the unit cell volume of the alloy (or of the α phase) is well known.⁸⁾ This is attributed to the correlation between the hydrogen stability and the hydrogen radius in the interstitial

Fig. 4 Schematic representation of interstitial positions for hydrogen occupation in the hexagonal structure ($P6/mmm$) projected to basal x - y plane ($z = 0$). Dotted parallelogram is x - z plane of the monoclinic structure ($C2/m$).

space on the $z = 0$ plane of the hexagonal structure. Similar to the first plateau, the second plateau pressure is logarithmically related to the unit cell volume of the β phase. This is probably due to the hydrogen radius in the interstitial space of the $y = 1/4$ plane of the monoclinic structure (or the $z = 1/2$ plane of the hexagonal). Detailed neutron diffraction study of the hydrogen position in the β phase is now under way.

The correlations between the plateau pressures and unit cell volumes suggest that a plateau pressure is determined by the crystal structure of the lower-hydrogen-content phase on the plateau, or the structure before hydrogen absorption. As far as the RNi_5 -H (R: from La to Gd except Ce) system is concerned, alloys with the same crystal structure show similar structural changes and lattice expansions. Therefore we can empirically predict not only the first plateau pressure but also the second plateau pressure (P_{P2}/MPa) from the unit cell volume of the alloys (V_a/nm^3) as follows:

$$\log(P_{P2}) = -5.8949 \times 10^4 \times V_a^2 + 9.4456 \times 10^3 \times V_a - 3.7647 \times 10^2 \quad (1)$$

As mentioned above, the P-C isotherms in RNi_5 -H systems show two pressure plateaux corresponding to three phases (α , β , and γ) with hexagonal, monoclinic and hexagonal structures, respectively. During hydrogen absorption and desorption, only the β phase shows a temporary decrease in structural symmetry due to hydrogen occupation of the structure. For the hexagonal CaCu_5 -type structure with space group $P6/mmm$, Fig. 4 shows two possible positions for a hydrogen atom (D1 and D2) together with the a axis, where the D1 and D2 positions are projected to the basal $z = 0$ plane. The D1 positions are in a tetrahedral environment situated in the basal plane containing R atoms. The tetrahedral D2 positions are situated in the $z = 1/2$ plane.

Based on neutron diffraction analysis, several researchers¹²⁻¹⁴⁾ have proposed that on initial hydrogen absorption 75% of deuterium atoms occupy the D1 positions while 25% occupy the D2 positions. Assuming that the composition of the β phase is RNi_5H_4 , the D1 and D2 positions have three and one hydrogen atoms in the unit cell, respectively. The population of the former is unity, leading to isotropic lattice expansion. In contrast, the population of the latter is far from unity.

According to the Westlake criterion,¹⁵⁾ the minimum hydrogen distance is 0.21 nm. If one hydrogen atom occupies a D2 position, occupation of alternative D2 positions by hydrogen becomes difficult, as shown in Fig. 4. This suggests an anisotropic lattice expansion or a lower θ_β value than 150°. Further increase of hydrogen pressure leads to the occupation of D2 positions by additional hydrogen. If three hydrogen atoms occupy the D2 positions, the distribution of hydrogen atoms is isotropic. In this case, the hexagonal structure of the γ phase may be stable in RNi₅-H systems. In the case of the LaNi₅-H system, the unit cell is larger than those of the RNi₅-H systems, or the distance between D2 positions is somewhat large. This suggests that hydrogen atoms can occupy the D2 positions isotropically, indicating that the hexagonal structure is stable for the β phase in the LaNi₅-H system.

4. Conclusion

Structural changes in RNi₅-H (R = Pr, Nd, Sm and Gd) systems were investigated by *ex-situ* XRD measurement. Regardless of which R is present in RNi₅-H systems, three phases (α , β , and γ) with hexagonal, monoclinic and hexagonal structures, respectively, were found during hydrogen desorption. The α - β , β - γ phase transitions correspond to the two well-separated plateaux on the P-C isotherms. Due to the lanthanide contraction, the unit cell volumes of the β phases as well as the alloys decrease with the increasing atomic number of R, suggesting an increase of both plateau pressures.

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