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

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Pressure-composition (P-C) isotherms of RNi$_5$-H (R = Pr, Nd, 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; RNi$_5$H$_{0.3}$) and two hydrides (β phase; RNi$_5$H$_{2.0}$ and γ phase; RNi$_5$H$_{2.7}$). To explore the mechanism of the phase transitions, we investigated the structural changes in RNi$_5$-H systems with ex-situ XRD. During hydrogen desorption, the ex-situ XRD profiles show that the crystal structures in RNi$_5$-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 RNi$_5$-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 RNi$_5$-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 LaNi$_5$-H system shows three phases during hydrogen absorption and desorption: LaNi$_5$, hydrogen solid solution (α phase), LaNi$_5$H$_{3-4}$ hydride (β phase) and LaNi$_5$H$_{6-7}$ hydride (γ phase). The pressure-composition (P-C) isotherm of the LaNi$_5$-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 diffractionmetry (XRD), but with different lattice parameters. In the PrNi$_5$-H system two well-separated pressure plateaux are present due to two different hydrides, with compositions of PrNi$_5$H$_4$ (β phase) and PrNi$_5$H$_6$ (γ phase). Although the γ phase with hexagonal structure in the PrNi$_5$-H system is similar to that in the LaNi$_5$-H system, the structure of the β phase in the PrNi$_5$-H system is classified as C-centered monoclinic lattice. In the other RNi$_5$-H system (R = Nd, Sm, and Gd) with two plateaux on the P-C isotherm, 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 known 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 RNi$_5$-H (R = Pr, Nd, 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$_5$ (R = Pr, Nd, Sm and Gd) alloys by arc melting has been described previously. 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 Cu Kα 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 NdNi$_5$-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...
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 disappear 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.⁶ 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 P6₃mc. This space group is identical to that of the LaNi₅ full hydride.⁷ 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.⁸ 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).⁹

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.¹⁰ 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,⁵ 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 (θₐ) 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 aₓ, cₓ and Vₓ 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 (P6₃mc) is twice that of the alloy, the expansions between the γ phase and the alloy, normalized as P6₃mc, are shown in Fig. 2(b). In the case of the β phase shown in Fig. 2(a), the lattice expansion of the aₓ axis is the same as that of the cₓ axis, which is twice as large as that of bₓ axis. Although the lattice expansion is almost constant regardless of R in RNi₅-H systems, the volume expansion (∆Vᵧ) decreases gradually with the increasing atomic number of R due to the increase of angle θᵧ. This is related to the unit cell volume of the alloys (Vₓ). For the γ phase (Fig. 2(b)), both lattice expansions (especially the ∆cᵧ value) in the SmNi₅-H and GdNi₅-H systems are much smaller than those in PrNi₅-H and NdNi₅-H systems, indicating a small ∆Vᵧ. 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.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Space group</th>
<th>a/nm</th>
<th>b/nm</th>
<th>c/nm</th>
<th>θₓ/°</th>
<th>V/nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrNi₅ (β)</td>
<td>C2/m</td>
<td>1.0362(9)</td>
<td>0.8117(4)</td>
<td>0.9029(9)</td>
<td>149.37(3)</td>
<td>0.3868(4)</td>
</tr>
<tr>
<td>NdNi₅ (β)</td>
<td>C2/m</td>
<td>1.0329(8)</td>
<td>0.8111(1)</td>
<td>0.8997(7)</td>
<td>149.42(3)</td>
<td>0.3835(3)</td>
</tr>
<tr>
<td>SmNi₅ (β)</td>
<td>C2/m</td>
<td>1.0273(6)</td>
<td>0.8101(2)</td>
<td>0.8944(9)</td>
<td>149.52(4)</td>
<td>0.3776(5)</td>
</tr>
<tr>
<td>GdNi₅ (β)</td>
<td>C2/m</td>
<td>1.0248(3)</td>
<td>0.8089(3)</td>
<td>0.8912(9)</td>
<td>149.64(8)</td>
<td>0.3733(9)</td>
</tr>
<tr>
<td>PrNi₅ (γ)</td>
<td>P6₃mc</td>
<td>0.5359(1)</td>
<td>—</td>
<td>0.8475(2)</td>
<td>—</td>
<td>0.2108(1)</td>
</tr>
<tr>
<td>NdNi₅ (γ)</td>
<td>P6₃mc</td>
<td>0.5337(1)</td>
<td>—</td>
<td>0.8471(4)</td>
<td>—</td>
<td>0.2089(1)</td>
</tr>
<tr>
<td>SmNi₅ (γ)</td>
<td>P6₃mc</td>
<td>0.5245(1)</td>
<td>—</td>
<td>0.8196(3)</td>
<td>—</td>
<td>0.1952(1)</td>
</tr>
<tr>
<td>GdNi₅ (γ)</td>
<td>P6₃mc</td>
<td>0.5217(2)</td>
<td>—</td>
<td>0.8214(4)</td>
<td>—</td>
<td>0.1936(2)</td>
</tr>
</tbody>
</table>
Figure 3 shows the relationship between the hydrogen plateau pressures observed on the hydrogen desorption of P-C isotherms in RNi$_5$-H systems$^7$ and the unit cell volumes of the RNi$_5$ alloys and $\beta$ 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 $\alpha$ phase) is well known.$^8$ This is attributed to the correlation between the hydrogen stability and the hydrogen radius in the interstitial 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 $\beta$ 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 $\beta$ 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:

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

As mentioned above, the P-C isotherms in RNi$_5$-H systems show two pressure plateaux corresponding to three phases ($\alpha$, $\beta$, and $\gamma$) with hexagonal, monoclinic and hexagonal structures, respectively. During hydrogen absorption and desorption, only the $\beta$ 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 researchers$^{12-14}$ 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 $\beta$ phase is RNi$_5$H$_x$, 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, 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 $\theta_2$ 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 $\gamma$ phase may be stable in RNi$_5$-H systems. In the case of the LaNi$_5$-H system, the unit cell is larger than those of the RNi$_5$-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 $\beta$ phase in the LaNi$_5$-H system.

4. Conclusion

Structural changes in RNi$_5$-H ($R = \text{Pr, Nd, Sm and Gd}$) systems were investigated by ex-situ XRD measurement. Regardless of which R is present in RNi$_5$-H systems, three phases ($\alpha$, $\beta$, and $\gamma$) with hexagonal, monoclinic and hexagonal structures, respectively, were found during hydrogen desorption. The $\alpha$-$\beta$, $\beta$-$\gamma$ 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 $\beta$ 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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REFERENCES