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Studies of *P–C* isotherms in RNi_5–H (R: La, Pr, Nd, Sm, Gd, Tb and Dy) systems

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Abstract

We have investigated the hydrogenation and dehydrogenation properties of binary RNi_5 (R: La, Pr, Nd, Sm, Gd, Tb and Dy) intermetallic compounds in the pressure range of 0.1–35 MPa and temperature range of 223–298 K. Pressure–composition isotherms demonstrated that as the atomic number of R increased in RNi_5–H systems, the single pressure plateau ($LaNi_5$) split into two plateaux ($PrNi_5$, $NdNi_5$, $SmNi_5$ and $GdNi_5$), and then into three plateaux ($TbNi_5$ and $DyNi_5$), indicating the presence of two hydrides (β_2 and γ_2 phases) and then three hydrides (β_3, γ_3 and δ_3 phases). The β_3–γ_3 and γ_3–δ_3 phase transitions in the $TbNi_5$–H system corresponded, respectively, to the α_2–β_2 and β_2–γ_2 transitions in the RNi_5–H (R: Pr, Nd, Sm and Gd) systems having two plateaux.

Keywords: Hydrogen storage materials; Intermetallics; Gas–solid reactions

1. Introduction

Several types of intermetallic compounds have been proposed as hydrogen storage materials. The pressure–composition (*P–C*) isotherm is an important property in intermetallic compound–hydrogen systems [1]. Some intermetallic compounds can absorb hydrogen with a pressure plateau corresponding to the phase transition between solid solution and hydride.

For a hydrogen supply medium, a reversible hydrogen storage capacity above 0.1 MPa is necessary for intermetallic compounds. An increase in hydrogen pressure improves the capacity because it induces a new phase transition. At approximately 150 MPa, Lakner et al. found the third phase transition between $LaCo_5H_6$ and $LaCo_5H_9$ [2], which shows the largest hydrogen storage capacity for $CaCu_5$-type compounds.

The plateau pressure (P_p) of rare earth (R)-based $CaCu_5$-type compounds is logarithmically related to the unit cell volume (V) of the compounds ($\ln P_p \propto V$) [3]. The V of RNi_5 compounds decreases with increasing atomic number of R due to the lanthanide contraction, suggesting an increase in plateau pressure. However, the $\ln P_p \propto V$ relation is only valid for elements between La and Gd in RNi_5–H systems.

In our previous reports [4–6], we evaluated the *P–C* isotherms in RNi_5–H systems (R: La, Pr, Nd, Sm, Gd, Tb and Dy) and found linear correlation between $\ln P_p$ and V in these systems. Only portions of plateaux on dehydrogenation confirm to the regularity, the relations between plateaux on hydrogenation and dehydrogenation remain uncertain, especially for hydrogenation in the $TbNi_5$–H system. In this study, we investigated the plateaux in the $TbNi_5$–H system and compared the phase transitions in this system with the other RNi_5–H systems.

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2. Experimental details

Processes for preparation of binary RNi_5 intermetallic compounds (R: La, Pr, Nd, Sm, Gd, Tb and Dy) by arc melting have been described previously [4–6]. Prior to measurement of the *P–C* isotherms, the sample ingots were crushed and sieved to obtain particles of 75 μm under Ar atmosphere, and activated several times by cooling to 196 K under H_2 at 35 MPa until the amounts of absorbed and desorbed hydrogen stopped changing. We measured the *P–C* isotherms in RNi_5–H systems in the pressure range of 0.1–35 MPa and temperature range of 223–298 K at least twice using different sample batches to confirm reproducibility of the isotherm.

3. Results and Discussion

Fig. 1 shows the pressure–composition (*P–C*) isotherms in lanthanide (R) series for RNi_5–H systems. One reversible pressure plateau between $LaNi_5$ solid solution (α_1 phase) and $LaNi_5H_6$ hydride (β_1 phase) splits into two plateaux with increasing atomic number of R, indicating the presence of two hydrides having compositions of $RNi_5H_{3–4}$ and $RNi_5H_{6–7}$ (β_2 and γ_2 phases) together with one solid solution (α_2 phase) [4,5]. The first pressure plateau corresponds to the α_2–β_2 phase transition and the second plateau to the β_2–γ_2 transition. Although the second plateau in $SmNi_5$–H and $GdNi_5$–H systems are scarcely distinct at 298 K, these systems at 223 K possess the hydrogenation properties qualitatively similar to those of the $PrNi_5$–H and $NdNi_5$–H systems. Partial measurements of *P–C* isotherms indicate that both α_2–β_2 and β_2–γ_2 transitions allow reversible changes in the hydrogen content with small hysteresis between hydrogenation and dehydrogenation branches.

On going from Gd to Dy in the RNi_5–H systems, three specific dehydrogenation properties can be seen [6]: (1) the pressure of first plateau corresponding to $H/RNi_5 \approx 2.5$ increases; (2) the second plateau tends to disappear; (3) the flat, first plateau splits and gives rise to a new plateau at low hydrogen content. On hydrogenation the pressure of first plateau in $TbNi_5$–H system is highest in the RNi_5–H systems, and the hysteresis at the level of $H/RNi_5 = 2.5$ in the $TbNi_5$–H system is largest in this series. The *P–C* isotherm in this system shows two plateaux upon hydrogenation ($TbNi_5H_{0.5–3.3}$ and $TbNi_5H_{3.6–4.2}$) in contrast to three plateaux on dehydrogenation. These results differ from those in other RNi_5–H systems exhibiting two well-separated plateaux.

On hydrogenation and dehydrogenation, a partial *P–C* isotherm in the $TbNi_5$–H system was obtained. Fig. 2 shows this isotherm together with the original *P–C* isotherm taken from Fig. 1 for comparison. The partial *P–C* isotherm starts at the point $H/TbNi_5 = 3.5$ on the hydrogenation branch of the original *P–C* isotherm. With decreasing hydrogen pressure, the hydrogen content nearly does not decrease until the original dehydrogenation isotherm is reached, suggesting that a reversible phase transition exists above $H/TbNi_5 = 3.5$ (i.e., the second plateau on hydrogenation corresponds to the third plateau on dehydrogenation in the original *P–C* isotherm). As the hydrogen pressure starts increasing after the decrease below the second plateau on dehydrogenation, the hydrogen content $H/TbNi_5 \approx 1.3$ remains nearly unchanged. Subsequently, a dramatic increase in hydrogen content occurs above 2.0 MPa, revealing another plateau. This novel plateau on hydrogenation occurs at all temperatures in the large hysteresis region of the original *P–C* isotherm. Eventually, the partial *P–C* isotherm returns to the starting point on the hydrogenation branch of the original isotherm.

These *P–C* isotherms demonstrate that the $TbNi_5$–H system contains three phase transition steps among one hydrogen solid solution (α_3) and three types of hydride (β_3,

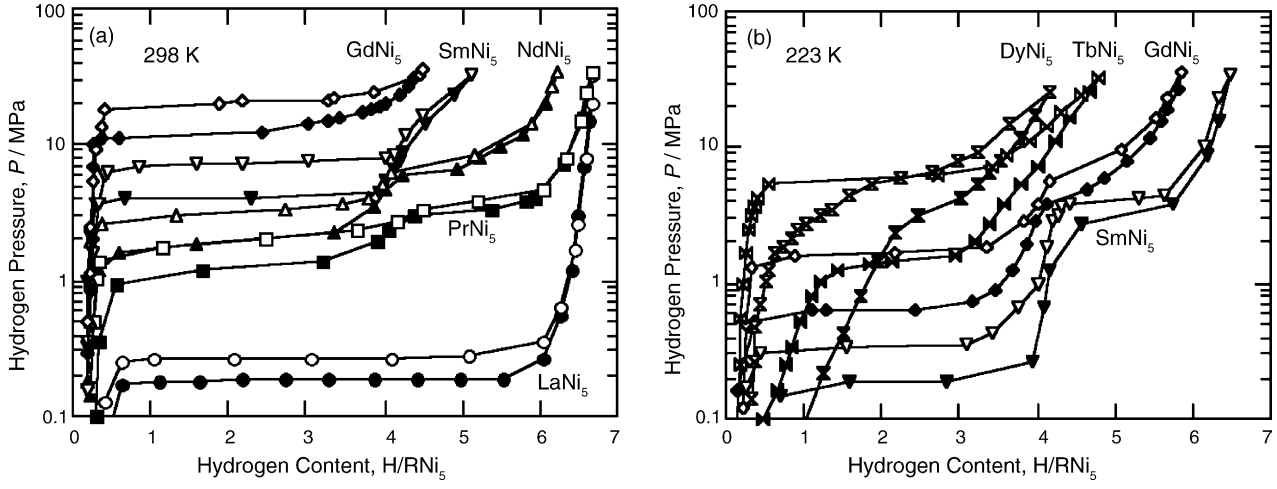

Fig. 1. Pressure–composition isotherms on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi_5–H (R: La, Pr, Nd, Sm, Gd, Tb and Dy) systems at 298 K (a) and 223 K (b).

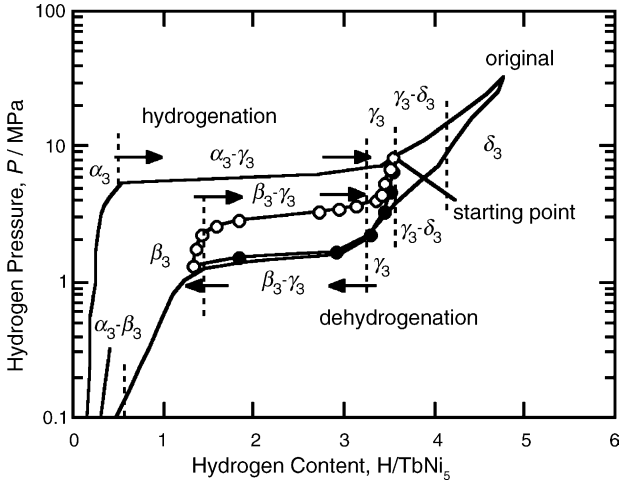

Fig. 2. Partial pressure–composition isotherm on dehydrogenation (filled symbols) and hydrogenation (empty symbols) in $TbNi_5$–H system at 223 K together with the *P–C* isotherm (original) shown in Fig. 1(b).

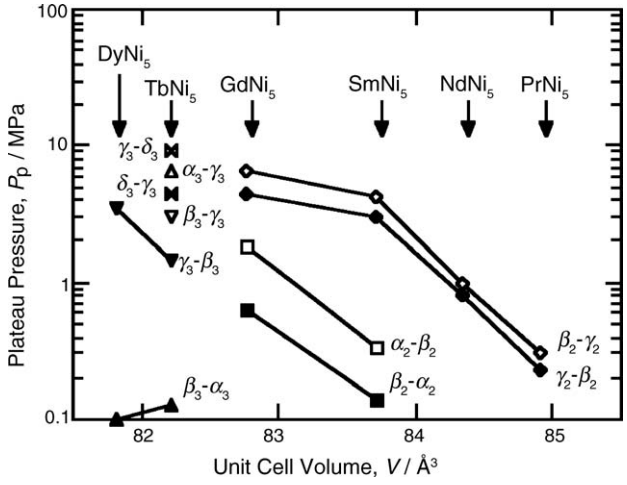

Fig. 3. Plateau pressures at 223 K on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi_5–H (R: Pr, Nd, Sm, Gd, Tb and Dy) systems as a function of unit cell volume of RNi_5 compounds.

γ_3 and δ_3). A schematic representation of phase transitions on the *P–C* isotherm is shown in Fig. 2. On hydrogenation, two plateaux corresponding to the α_3–γ_3 and γ_3–δ_3 phase transitions appear, while three plateaux on dehydrogenation corresponding to the δ_3–γ_3, γ_3–β_3 and β_3–α_3 phase transitions also exist. The β_3–γ_3 phase transition does not appear on the original *P–C* isotherm unless the hydrogen pressure increases starting from the *P–T* region of the β_3 phase formed previously on dehydrogenation. The α_3–γ_3 phase transition on hydrogenation due to overlap of the α_3–β_3 and β_3–γ_3 transitions in this system is similar to that in the $LaNi_5$–H system, in which the α_1–β_1 transition practically contains the α_1–β'_1 and β'_1–β_1 transitions (β'_1: intermediate phase) at room temperature [7,8]. Despite the complex phase transitions on hydrogenation and dehydrogenation, the *P–C* isotherm in the $TbNi_5$–H system is reversible. Analogous phase transitions are also observed in $DyNi_5$–H system [9].

The enthalpy (ΔH) and entropy (ΔS) corresponding to the phase transitions are evaluated from van't Hoff plots of each plateau pressure and summarized in Table 1. The ΔH value to the γ_3–β_3 transition on dehydrogenation is consistent with that estimated by extrapolation of the values in the $TbNi_{5-x}Al_x$–H ($x = 0.5, 1.0$) systems [10] to $x = 0$. For comparison of phase transitions in the $TbNi_5$–H system with those

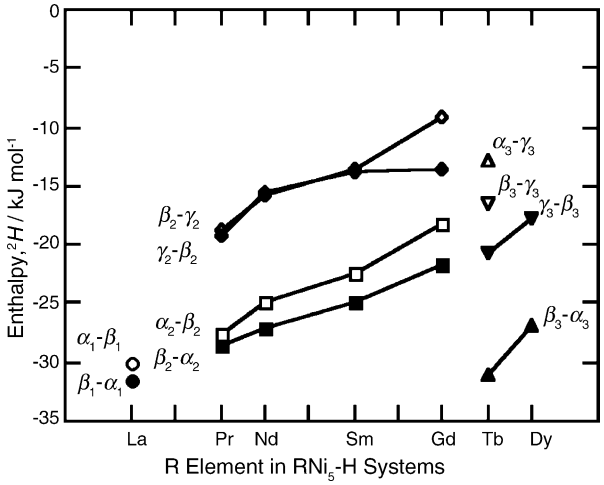

Fig. 4. Enthalpies of phase transitions on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi_5–H (R: La, Pr, Nd, Sm, Gd, Tb and Dy) systems.

in other RNi_5–H systems [4–6,9], the plateau pressures at 223 K determined on both hydrogenation and dehydrogenation are summarized in Fig. 3 and the ΔH values in Fig. 4. As seen from Fig. 3, the points of the γ_3–β_3 and β_2–α_2 transitions form an approximately linear dependence and the

Table 1
Enthalpy (ΔH) and entropy (ΔS) corresponding to phase transitions on hydrogenation and dehydrogenation in $TbNi_5$–H system

Composition		Phase transition	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	
$TbNi_5$	Hydrogenation	α_3–γ_3	-12.8 ± 0.2	-91.8 ± 0.9	This study
		β_3–γ_3	-16.5 ± 0.2	-102.3 ± 0.9	This study
	Dehydrogenation	β_3–α_3	-31.2 ± 0.6	-141.6 ± 2.4	This study
		γ_3–β_3	-20.7 ± 0.1	-115.0 ± 0.4	This study
$TbNi_{4.5}Al_{0.5}$[a]	Dehydrogenation		−27.3	−112.4	Ref. [10]
$TbNi_4Al$[a]	Dehydrogenation		−33.9	113.4	Ref. [10]

[a] The data were estimated at fixed hydrogen content ($H/TbNi_{5-x}Al_x = 1.5$).

point of the β_3–γ_3 transition does not deviate much from the straight line drawn through the α_2–β_2 transition points. This suggests that the β_3–γ_3 and γ_3–β_3 transitions in the $TbNi_5$–H system correspond, respectively, to the α_2–β_2 and β_2–α_2 transitions in the RNi_5–H systems having two plateaux. Similarly, the γ_3–δ_3 and δ_3–γ_3 transitions correspond to the β_2–γ_2 and γ_2–β_2 transitions.

4. Conclusion

We have measured the detailed *P–C* isotherms in $TbNi_5$–H system with RNi_5–H (R: La, Pr, Nd, Sm, Gd and Dy) systems for comparison. The $TbNi_5$–H system contained three phase transition steps among one hydrogen solid solution (α_3) and three types of hydride (β_3, γ_3 and δ_3). The *P–C* isotherm in this system showed two pressure plateaux (α_3–γ_3 and γ_3–δ_3) on hydrogenation, in contrast to three pressure plateaux (δ_3–γ_3, γ_3–β_3 and β_3–α_3) on dehydrogenation. The β_3–γ_3 phase transition appeared on the hydrogenation of the *P–C* isotherm when the hydrogen pressure increased starting from the β_3 phase formed previously on dehydrogenation. Despite the complex phase transitions on hydrogenation and dehydrogenation, the *P–C* isotherm in this system has reversible change in the hydrogen content.

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