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Letter

Reversible hydrogen absorption and desorption achieved by irreversible phase transition

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Abstract

Phase relations in the Zr_7Ni_{10}-H system were examined with a conventional Sieverts'-type apparatus. The hydrogen pressure–composition–temperature (*PCT*) relations obtained under the conditions such as a temperature of 410 K and a pressure range of 0.01–3 MPa demonstrated the existence of two hydride phases (β, γ) in the system and indicated the following unprecedented hydrogenation behavior of the Zr_7Ni_{10} compound: (1) the β-hydride phase, which has lower hydrogen content than the other (γ), appears only in hydrogen desorption but not in hydrogen absorption; (2) the hydrogen capacity of the continuous solid solution phase (α) is 0.56H/M (H/M; the atomic ratio of hydrogen to metal) in hydrogen absorption and only 0.40H/M in hydrogen desorption; (3) The Zr_7Ni_{10} compound absorbs hydrogen accompanied by the phase transition from α to γ (α→γ transition) and desorbs hydrogen accompanied by the γ→β and β→α transitions, however, the reverse of these three transitions, i.e. γ→α, β→γ and α→β transitions are not observed in the *PCT* relations under the conditions mentioned above. From the fact about the irreversibility of the phase transitions, the Zr_7Ni_{10} compound can reversibly absorb and desorb hydrogen by the irreversible phase transition.

Keywords: Hydrogen storage materials; Casting; X-ray diffraction; Phase transitions; Thermal analysis

1. Introduction

Zr_7Ni_{10}, which possesses an orthorhombic structure (space group symmetry, $C_{2v}^{17} = Aba2$) [1], is one of the intermetallic compounds in the binary Zr–Ni system. Some pieces of information are available for the hydrogenation of the Zr_7Ni_{10} compound [2–5]. Tannenbaum et al. reported that the hydrogen-absorbing capacity of this compound ranged from 0.9 to 1.1 in an atomic hydrogen to metal ratio (H/M) [2]. Spit et al. reported the pressure–composition–temperature (*PCT*) relations at 333, 433 and 533 K for the Zr_7Ni_{10} compound and the heat of formation of the corresponding hydride [3]. More recently Joubert et al. reported the *PCT* relations at 298 and 353 K for this compound and its hydrogen absorption kinetics [5]. The latter authors described that the compound exhibited a pressure plateau under the pressure of 0.03 MPa at 353 K and a very large hysteresis during hydrogen desorption [5].

In the *PCT* relations reported by Joubert et al., it is observed that the slope of the hydrogen pressure plateau is larger for hydrogen desorption than for hydrogen absorption [5]. This disagrees with the general experimental observation that the slope of the plateau for hydrogen absorption is greater than that for hydrogen desorption [6]. No explanation has been given for the mechanism of this unusual hydrogenation behavior observed in the Zr_7Ni_{10} hydride.

The present objective was to give the explanation for the unusual hydrogenation behavior of the Zr_7Ni_{10} compound. Re-measurements of the *PCT* relations of this compound gave us many pieces of new information for its unprecedented hydrogenation behavior as a result.

2. Experimental details

The alloy sample was obtained by arc melting of the pure elements of Zr and Ni on a water-cooled copper hearth under an Ar atmosphere. The Ar gas was purified in advance by melting a Zr getter. The alloy sample was turned over and remelted three times in order to improve their homogeneity. The alloy ingot was annealed for 259.2

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ks (=3 days) at a temperature of 1273 K in a high vacuum furnace.

The alloy ingot thus obtained was mechanically pulverized to be supplied to analyses. The grain size of the pulverized powder was less than 75 μm for X-ray diffraction (XRD) analysis and about 1 mm for measurements of *PCT* relations.

The constituent phases in the sample before and after hydrogenation were examined by XRD analysis using Cu-Kα radiation. The XRD analysis exhibited that the constituent phase in the sample was only Zr_7Ni_{10} and that no disproportionation occurred in the sample during hydrogenation and dehydrogenation.

The measurements of the *PCT* relations at temperatures in the range from 343 to 478 K were conducted with an automatic Sieverts'-type apparatus equipped with a diffusion pump. Before starting the measurement, the sample was initially hydrogenated at a temperature of 423 K under a hydrogen pressure of 3 MPa and degassed at 573 K under high vacuum for 10.8 ks. In most cases, the hydrogen pressure became stable within 0.6 ks after starting the reaction of the sample with hydrogen gas. The measurement of each equilibrium pressure was done when at least 1.8 ks passed from starting the reaction.

We examined the enthalpy change (ΔH_{H_2}) and entropy change (ΔS_{H_2}) of hydriding by using the van't Hoff equation,

$$\ln P_{H_2} = \frac{\Delta H_{H_2}}{R} \cdot T^{-1} - \frac{\Delta S_{H_2}}{R},$$

where R and T mean the gas constant and absolute temperature, respectively. The pressure corresponding to the midpoint of each hydrogen pressure plateau (plateau pressure) was used for the calculation of these thermodynamic values.

3. Results and discussion

The *PCT* relations at 410 and 453 K for the Zr_7Ni_{10} sample are shown in Fig. 1. A large hysteresis loop was observed in the *PCT* curve, which was pointed out before [5]. Only in the direction of hydrogen desorption, small two hydrogen pressure plateaus were clearly observed at the hydrogen contents ranging from 0.40 to 0.57 in the atomic ratio of hydrogen to metal (H/M) and from 0.71H/M to 0.89H/M, respectively. On the other hand, only one plateau was observed from 0.56H/M to 0.89H/M in the absorption direction. The *PCT* relations at the high temperatures up to 478 K showed that no other plateau appeared in the *PCT* relations in the hydrogen content range from 0.2H/M to 1.0H/M for the sample.

In general, a hydrogen pressure plateau observed in a *PCT* relation means that two hydrogen occlusion phases with low and high hydrogen contents coexist in the hydrogenated sample. On the other hand the *PCT* curve with a large slope indicates that only one hydrogen occlusion phase exists. When the *PCT* relation shown in Fig. 1 was analyzed based on these rules, the phase relations in the Zr_7Ni_{10}–H system can be indexed as shown in Fig. 2. The Zr_7Ni_{10}–H system shows at least three hydrogen occlusion phases, α, β and γ. The α-phase is a continuous hydrogen solid solution of the compound, and the β and γ phases are hydrides with the low and high hydrogen contents, respectively.

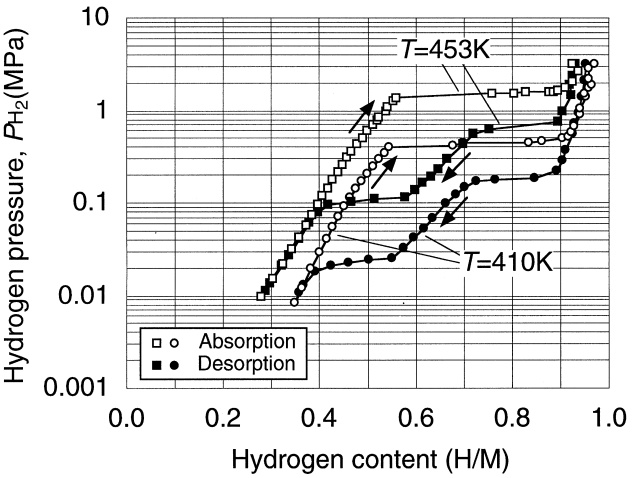

Fig. 1. Hydrogen pressure–temperature–composition (*PCT*) relations at 410 and 453 K for Zr_7Ni_{10} compound.

We characterize the *PCT* relation of the Zr_7Ni_{10} compound as follows:

1. the β-hydride phase appears only in hydrogen desorption but not in hydrogen absorption;
2. the hydrogen solubility of the α-phase in hydrogen absorption is quite different from that in hydrogen desorption; the value is 0.56H/M for hydrogen absorp-

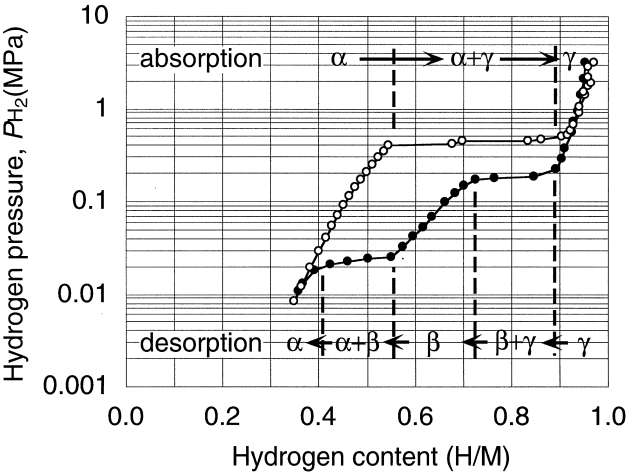

Fig. 2. Phase relations in hydrogen absorption and desorption for Zr_7Ni_{10} compound.

tion, whereas it is only 0.40H/M for hydrogen desorption. The maximum hydrogen content of the α-phase in hydrogen absorption (0.56H/M) is almost equal to the minimum hydrogen content (0.57H/M) of the β-phase.

Fig. 2 also indicates that in hydrogen absorption, the phase transition from α to γ (α→γ transition) occurs, whereas the γ→β and β→α transitions occur in hydrogen desorption, respectively. Surprisingly, these coexisting phases which undertake the three phase transitions are different each other and the phase transitions in the opposite direction (γ→α, β→γ and α→β) do not occur. We refer to these phase transitions with the hydrogenation direction dependence as the 'irreversible' phase transitions in the present paper. Conventional hydrogen storage alloys absorb and desorb hydrogen by the reversible phase transitions; however, the Zr_7Ni_{10} compound can absorb and desorb hydrogen reversibly by the irreversible phase transitions under the present conditions.

The *PCT* relations with the same characteristics as mentioned above were obtained in the temperature range from 408 to 453 K. From these *PCT* relations at the different temperatures, the enthalpy and entropy changes of hydriding were calculated by using the van't Hoff equation. The calculated thermodynamic values are listed in Table 1.

It is supposed that, because the β-phase is not formed in hydrogen absorption, the Zr_7Ni_{10} compound exhibits the unusual hydrogen absorption behavior shown in Fig. 1. In order to confirm the characteristics of the phase transitions, we performed the additional measurements of the *PCT* relations of the Zr_7Ni_{10} compound. Fig. 3 shows the *PCT* relations which were obtained by performing hydrogen desorption down to the limited content of 0.57H/M followed by hydrogen absorption. The β-hydride phase, which was formed by the phase transition from γ in hydrogen desorption, absorbed hydrogen to change to the γ-hydride one. Therefore the phase transition between β and γ is reversible in fact, unless the α-phase is formed by hydrogen desorption.

Many measurements were performed in order to confirm the reversibility of the other two α→γ and β→α transitions. In the measurements, the waiting time to judge the equilibrium in the measurements of *PCT* relations was prolonged from 1.8 to 604.8 ks (=1 week). Also, the

Table 1
Enthalpy and entropy changes of hydriding for phase transitions from α to γ, β to α and γ to β in the Zr_7Ni_{10}–H system: these thermodynamic values are calculated by using van't Hoff equation

	Phase transition		
	From α to γ	From β to α	From γ to β
Correlation coefficient	−0.997	−0.998	−0.987
ΔH_{H_2} (kJ mol H_2^{-1})	−49	−61	−52
ΔS_{H_2} (J K^{-1} mol H_2^{-1})	−132	−136	−129

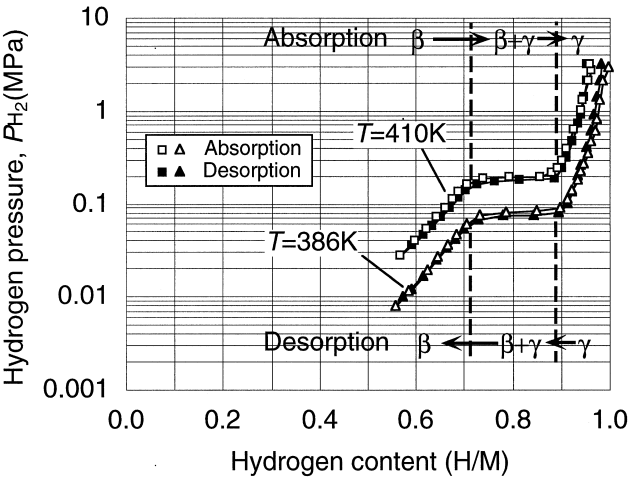

Fig. 3. *PCT* relations measured in limited range over 0.57H/M in hydrogen content for Zr_7Ni_{10} compound.

measurements were conducted at the various temperatures and in the limited hydrogen pressure and content ranges. Moreover they were performed by increasing the cycle numbers of hydrogen absorption and desorption up to 30 cycles. These trials indicated that neither γ→α transition in hydrogen desorption nor α→β transition in hydrogen absorption occurred. Therefore we could not obtain any proof that the phase transitions between α and β and between α and γ were reversible.

In order to know the cause of the difference in hydrogen solubility of the α-phase between in hydrogen absorption and desorption, we conducted hydrogen desorption from the α-phase with the hydrogen content more than 0.5H/M. Fig. 4 shows the *PCT* relations which were obtained by performing hydrogen absorption up to the limited content of 0.55H/M followed by hydrogen desorption. The *PCT* relations in hydrogen desorption did not show any plateau. This fact indicates that the Zr_7Ni_{10} compound desorbs

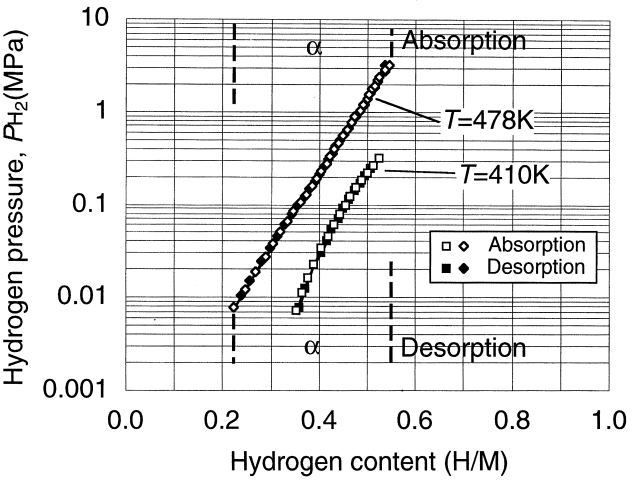

Fig. 4. *PCT* relations measured in limited range below 0.55H/M in hydrogen content for Zr_7Ni_{10} compound.

hydrogen in the range from 0.55H/M to 0.40H/M as an α-phase unless the β-phase was formed.

The *PCT* relations at 410 K for hydrogen absorption in Figs. 1 and 3 are redrawn in Fig. 5, and the relations at 410 K for hydrogen desorption in Figs. 1 and 4 are redrawn in Fig. 6. When we compare the hydrogen pressures at any hydrogen content ranging from 0.57H/M to 0.89H/M each other for the *PCT* relations in Fig. 5, the plateau pressure of the α→γ transition is higher than not only the hydrogen absorption pressure of the β-phase but also the plateau pressure of β→γ transition. The same comparison as described above shows that, at any hydrogen content in the range from 0.40H/M to 0.52H/M in Fig. 6, the hydrogen desorption pressure of the α-phase is higher than the plateau pressure of the β→α transition. That is to say, at any hydrogen content ranging from 0.4H/M to 0.9H/M, the hydrogen pressures of the reactions involving the β-phase are lower than those of the reactions without the β-phase. The fact implies that, due to the difficulty of the formation of the β-phase in hydrogen absorption, the Zr_7Ni_{10} compound absorbs hydrogen from 0.4H/M to 0.9H/M with holding the α-phase as a metastable phase.

It can be expected that the comparison of the crystal structures of these hydrogen occlusion phases will give us information to understand the mechanism of the unprecedented hydrogenation behavior of the Zr_7Ni_{10} compound. The XRD profiles of the hydride phases were complicated and the diffraction peaks were diffused. We are making an effort to determine the crystal structures and atomic positions of these hydrogen occlusion phases. The results will be reported in other papers.

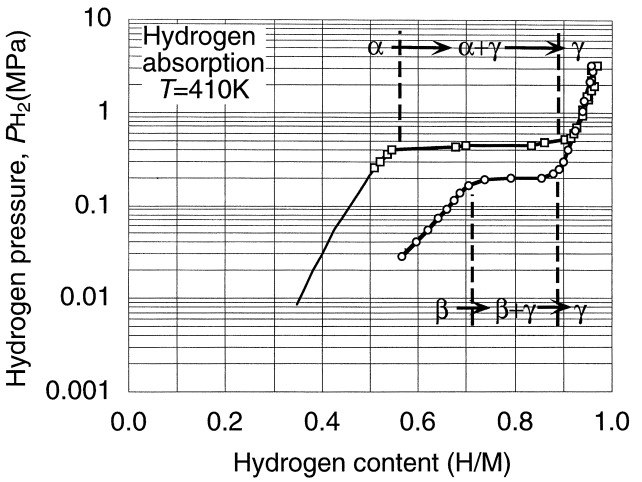

Fig. 5. Comparison of *PCT* relation in hydrogen absorption which was measured in limited range over 0.57H/M in hydrogen content (Fig. 3) with that measured without limitation (Fig. 1) for Zr_7Ni_{10} compound.

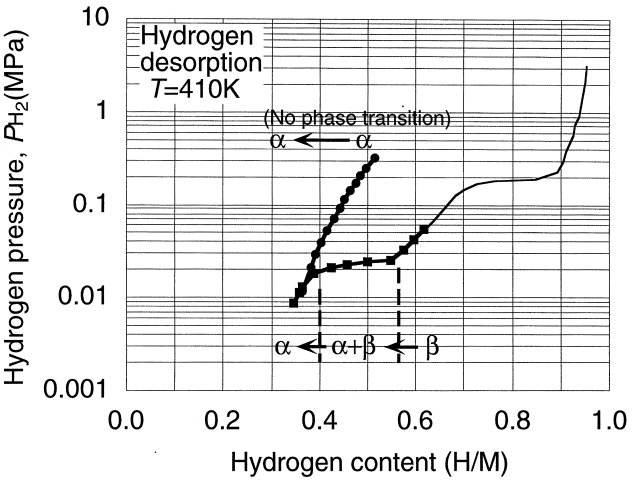

Fig. 6. Comparison of *PCT* relation in hydrogen desorption, which was measured in limited range below 0.55H/M in hydrogen content (Fig. 4) with that measured without limitation (Fig. 1) for Zr_7Ni_{10} compound.

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