한국수소 및 신에너지 학회 논문집(2003.12), 제14권 제4호
Trans. of the Korean Hydrogen and New Energy Society (2003.12), Vol. 14, No. 4, pp. 327~334

수소 동위체의 분리농축을 위한 수소저장합금의 수소 동위체 효과

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Hydrogen Isotope Effects in Hydrogen Storage Alloy for Separation and Concentration of Hydrogen Isotopes

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ABSTRACT

경수소와 중수소를 사용하여 Ti1.0Mn0.9V1.1합금의 경우 313K와 353 K에서, $Ti_{1.0}Cr1.5V_{1.7}$합금의 경우 313 K와 338K에서 각각 수소 동위체 효과를 조사하였다. 합금의 결정구조, 각 상의 존재량, 격자상수 등은 Rietveld method에 의해 결정되었다. 두 합금 모두 온도에 관계 없이 중수소의 흡장량이 경수소에 비하여 많았고, 이들 합금의 수소 동위체 효과는 $LaNi_5$합금에 비하여 대단히 크게 나타났다. 실험 온도 범위에서 $Ti_{1.0}Mn_{0.9}V_{1.1}$합금의 경수소화물은 중수소화물에 비하여 안정하였고, Ti1.0Cr1.5V1.7합금에 있어서는 중수소화물이 더욱 안정하였다. 또한 $Ti_{1.0}Cr_{1.5}V_{1.7}$합금이 $Ti_{1.0}Mn_{0.9}V_{1.1}$합금보다 많은 량의 경수소와 중수소를 흡장하였다.

주요기술용어 : Hydrogen isotope effect(수소 동위체 효과), Hydrogen storage alloy(수소저장합금), BCC allov(BCC합금)

1. Introduction

Metal hydrides which have hydrogen isotope effects can be applicable for the recovery, storage and concentration of deuterium and tritium which are the fuel of a nuclear fusion reactor. Many articles[1-4] have reported on the hydrogen isotope effect of metals and/or binary alloys. The majority of them showed that metal deuterides are less stable than the corresponding metal hydrides. Wiswall and Reilly[5], however, found an inverse behaviour that the replacement of protium by deuterium and tritium results in more stable compounds in some metal hydrides such as VH_2, NbH_2, (V, Nb)H_2 and $LaNi_5H_6$. Also, titanium has been known to

show little isotope effect. Haag and Shipko[6] found a zero isotope effect in titanium at 500℃. Ueda[7] reported that the deuterides with D/M=1 of Ti-V alloys are more stable than the corresponding protides without regard to the alloy composition by comparing the composition dependence of the activation energy for the diffusion of protium and deuterium.

Akiba and Iba reported a new generation alloy, "Laves phase related BCC solid solution alloy", which has a large hydrogen capacity of >2 mass%[8]. The $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ alloys, in particular, were found to have high hydrogenation rate as well as large hydrogen capacity[8~9]. Thus, it is expected that if these BCC alloys show large hydrogen isotope effects they can be used for separation of hydrogen isotopes.

With this point of view, in this study, the hydrogen isotope effects in $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ alloys have been investigated at 313K and 353K, and at 313K and 338K respectively by using protium and deuterium.

2. Experimental Procedure

The alloys of $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ were made in massive production(1kg lot) by a vacuum high-frequency induction furnace to ensure the reproducibility of the experimental results and used without heat treatment. Table 1 shows the chemical compositions of the alloys, which were analyzedby ICP emission spectrometer. The ingots were mechanically crushed into powder in air. The powders under 500μm were taken for the experiments. The activation treatment was carried out as follows. In the case of alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$, the sample powders of about 10g were placed in the reactor and evacuated for 1 h by a diffusion pump at 773K, and then the hydrogen gas with the pressure of 5MPa was introduced into the reactor at room temperature. It was repeated three times. Thereafter, in order to desorb the hydrogen, the reactor was evacuated for 1 h by a diffusion pump at 773K. In the case of alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$, the reactor was evacuated for 2h by a rotary pump at 313K, which was carried out only once.

The P-C isotherms of the alloys $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ were measured at 313K and 353K, and at 313K and 338K, respectively, up to a hydrogen pressure of 5MPa by a volumetric method.

Table 1. Chemical compositions of the alloys analyzed by ICP (at%)

Sample	Ti	Mn(Cr)	V	Chemical Formula
alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$	33.3	30.7	36.0	$Ti_{1.0}Mn_{0.9}V_{1.1}$
alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$	24.0	36.0	40.0	$Ti_{1.0}Cr_{1.5}V_{1.7}$

Table 2. Parameters of the alloys refined by the X-ray Rietveld analysis

Sample	Phase	Lattice	RI	a (Å)	c (Å)	Phase abundance(%)
$Ti_{1.0}$ $Mn_{0.9}V_{1.1}$ R_{wp}=19.0 S=2.47	Matrix	BCC	4.38	3.0183 (1)	-	57.1
	Ti-rich	FCC	13.9	11.293 (1)	-	39.0
	Ti-conc.	HCP	17.6	2.9669 (9)	4.784 (2)	3.9
$Ti_{1.0}Cr_{1.5}V_{1.7}$ R_{wp}=11.0 S=1.97	Matrix	BCC	1.28	3.0212 (9)	-	96.1
	Ti-conc.	HCP	10.2	2.9602 (7)	4.789 (1)	3.9

Since purity and pressure of commercially available deuterium(99.5% min., 3MPa) are not sufficient, deuterium was absorbed by $MmNi_5$ to increase the pressure, to purify it, and to recover the used one.

The phases, crystal structures, phase abundance, and lattice parameters of the alloys were determined by using XRD and the Rietveld analysis method. The sample powders under 30μm were used for the XRD measurements.

3. Results and Discussion

RIETAN 97[10] was used for the Rietveld analysis. Alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$ was assumed to be composed of three phases, as derived from the XRD qualitative analysis: The matrix with BCC structure, a phase with FCC structure, and α-Ti with

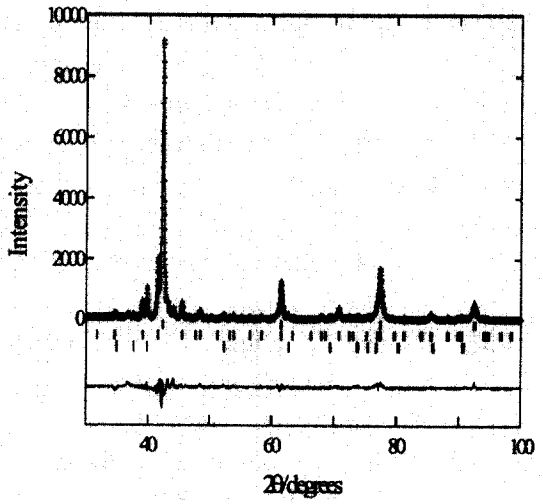

Fig.1. Rietveld refinement for alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$.

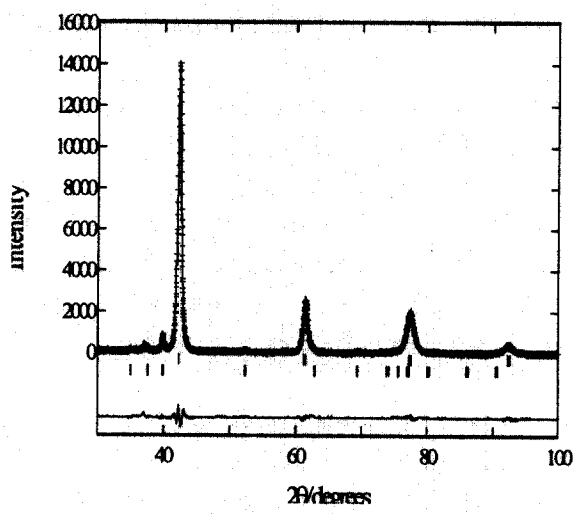

Fig. 2. Rietveld refinement for alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$.

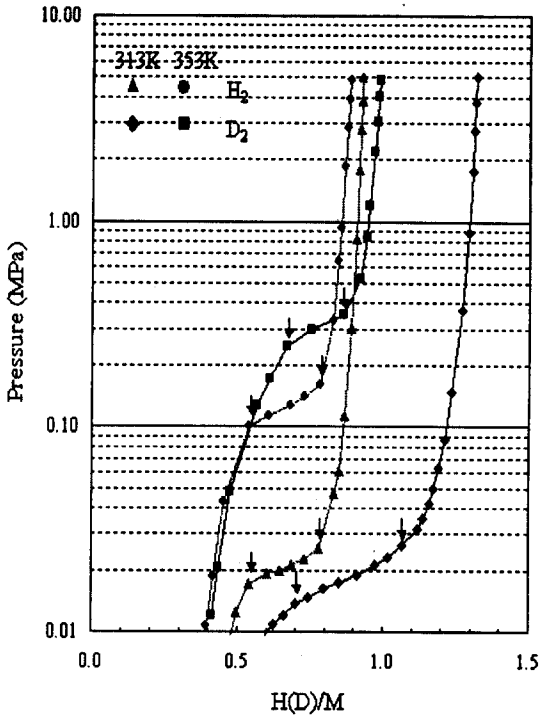

Fig. 3. Desorption isotherms of deuterium and protium for alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$.

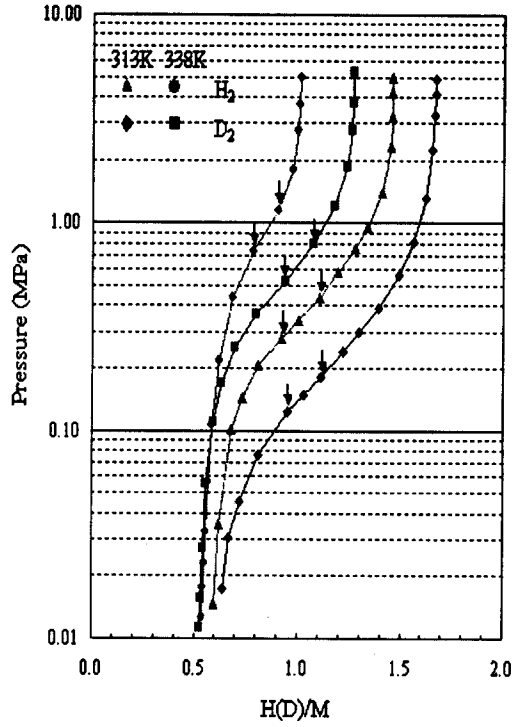

Fig. 4. Desorption isotherms of deuterium and protium for alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$.

HCP structure. Fig. 1 shows the result of the Rietveld analysis for this alloy. In this figure, the diffraction pattern calculated from the model, which is represented by the full curve, agreed well with the measured data represented by the plus marks. The phase abundance of the matrix, the phase with FCC structure, and α-Ti calculated from the parameters refined by the X-ray Rietveld analysis were 57.1%, 39.0% and 3.9%, respectively. The parameters refined are summarized in Table 2.

Alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$ was assumed from the XRD qualitative analysis to consist of two phases: The matrix with BCC structure and α-Ti with HCP structure. The result of the X-ray Rietveld analysis for this alloy is shown in Fig. 2. As shown in this figure, the diffraction pattern calculated from the model is in good agreement with that measured. The phase abundance of the matrix and the α-Ti calculated from the parameters refined by the Rietveld analysis were respectively 96.1% and 3.9%. The parameters refined for this alloy are also summarized in Table 2.

Figs. 3 and 4 show the desorption isotherms of deuterium and protium for the alloys $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ respectively. It was found that both alloys, except the data for $Ti_{1.0}Mn_{0.9}V_{1.1}$ measured at 313K, show marked hydrogen isotope

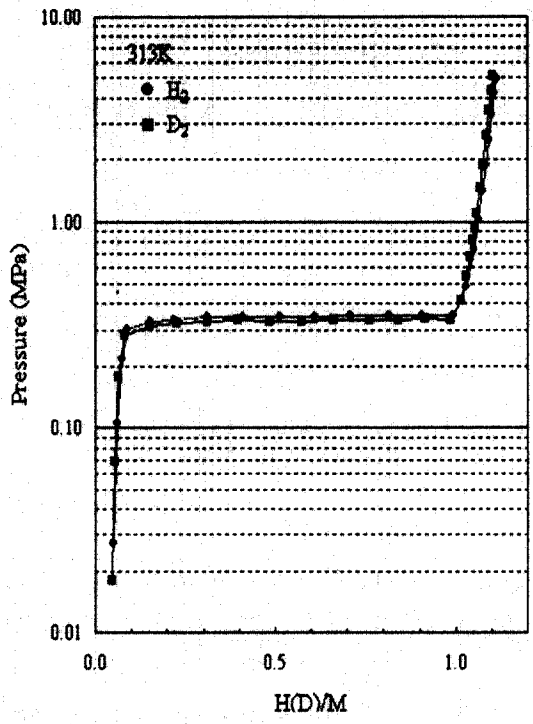

Fig. 5. Desorption isotherms of deuterium and protium for $LaNi_5$

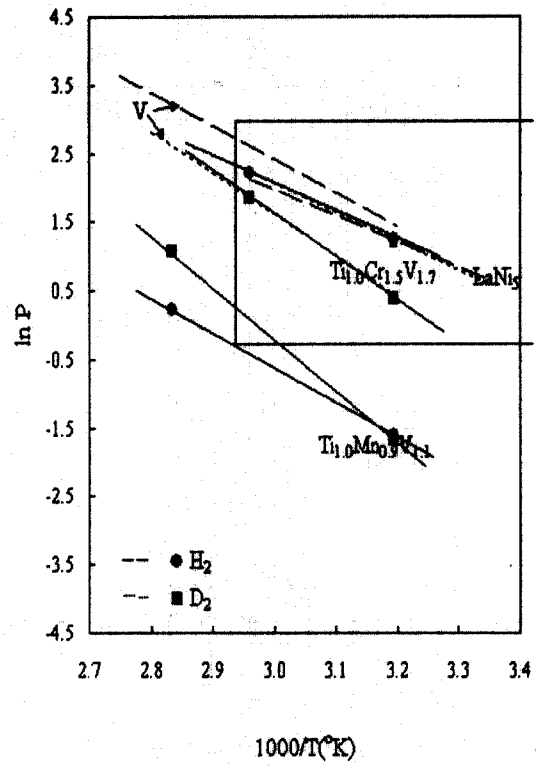

Fig. 6. Van' t Hoffplots of the studied alloys:(--V - H[5],·····V - D[5],●$LaNi_5$ - H in this work ■$LaNi_5$ - D in this work — - $LaNi_5$ - H[4], ·····$LaNi_5$ - D[4])

effects. As a reference, data for $LaNi_5$measured at 313K are shown in Fig. 5. In the latter material the hydrogen isotope effect was hardly observed. Also, from Figs. 3 and 4, differences in the absorbed amounts were found between deuterium and protium. In both alloys and regardless of temperature, the absorbed amount of deuterium was larger than that of protium. Alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$ absorbed more deuterium and protium than alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$. This is because the content of the BCC phase of the alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$ was larger than that of the alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$, which is represented in Table 2.

Fig. 6 shows a plot of ln P vs. 1/T obtained in this study, in which the respective plateau pressure was obtained from the middle point between two points indicated by the arrow marks in Figs. 3 and 4, assuming a straight line between the two points. Data for the zone-refined vanadium obtained by Wiswall and Reilly[5] are also represented by the dotted line in this figure. Results for $LaNi_5$ obtained by Biris et al.[4] as well as results obtained in this study are also shown. Alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$ showed an inverse behaviour without regard to the measured temperature, which were different to those for alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$ the plateau

Table 3. Standard formation enthalpies and entropies of hydrides

Sample	H(D)	ΔH°(kJ/mol H_2)	ΔS°(J/mol H_2 K)
$Ti_{1.0}$ $Mn_{0.9}V_{1.1}$	H	-42	-120
	D	-63	-187
$Ti_{1.0}Cr_{1.5}V_{1.7}$	H	-34	-119
	D	-52	-168
V[a]	H	-40	-141
	D	-50	-164
$LaNi_5$[b]	H	-31	-109
	D	-35	-123

pressures of deuterium were lower than those of protium in alloy $Ti_{1.0}Cr_{1.5}V_{1.7}$ and vise versa in alloy $Ti_{1.0}Mn_{0.9}V_{1.1}$.

This difference can be explained by the differences in the formation enthalpies and entropies between protide and deuteride in each alloy. Fig. 7 shows a schematic drawing of the van't Hoff equation. The formation enthalpies and entropies of the hydrides are correlated with the slopes and the intercepts on the y-axis of the van't Hoff plot, respectively. Also, the temperature of the crossing point (T_{cross}) can be expressed as

$$T_{cross} = (\Delta H^{\circ}_D - \Delta H^{\circ}_H) / (\Delta S^{\circ}_D - \Delta S^{\circ}_H) \quad (1)$$

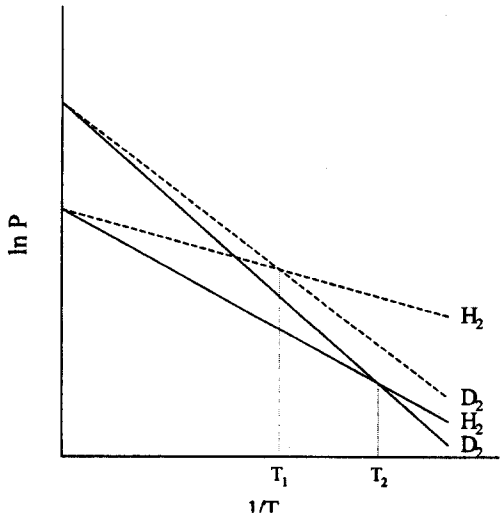

Fig. 7. Schenatic drawing of the van' t Hoff equation

where ΔH°_D, ΔH°_H, ΔS°_D, and ΔS°_H are the standard formation enthalpies and entropies of the deuteride and the corresponding protide. The standard formation entropy of the hydride is mainly determined by the loss of the absolute entropy of hydrogen gas (S°_{D2} = 144.8, S°_{H2} = 130.5 J/mol H_2 K at 298K). It means that ΔS°_D and ΔS°_H can be assumed to be constants and do not depend on the nature of each alloy[11]. Therefore, equation (1) can be rewritten as

$$T_{cross} = (\Delta H^{\circ}_D - \Delta H^{\circ}_H) / C \quad (2)$$

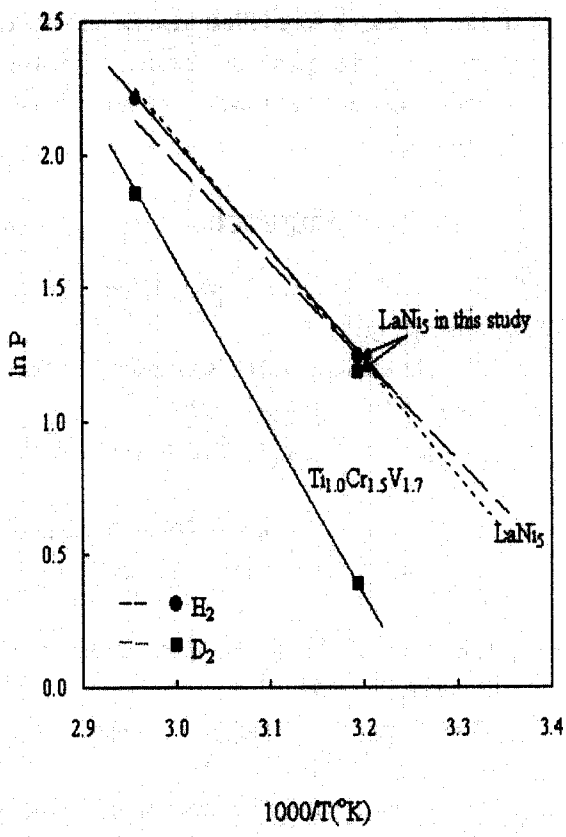

Fig. 8. Enlarged representation of the framed part shown in fig. 9(- ● - $Ti_{1.0}$ $Cr_{1.5}$ $V_{1.7}$ —H, - ■ - $Ti_{1.0}$ $Cr_{1.5}$ $V_{1.7}$ —D, - - $LaNi_5$ —H[4], - - $LaNi_5$ —D[4], ●$LaNi_5$ —H in this work ■$LaNi_5$ —D in this work)

where C is the constant ($\Delta S^\circ_D - \Delta S^\circ_H$). Here, it should be pointed out that the C value is negative because ΔS°_D is more negative. Thus, only when the deuteride's formation enthalpy is more negative than that of the corresponding protide ($\Delta H^\circ_D - \Delta H^\circ_H < 0$), can inverse behaviour occurr. In such a case, when the value of ($\Delta H^\circ_D - \Delta H^\circ_H$) becomes more negative, the temperature of the crossing point increases. Fig. 7 shows such a case. In which, the absolute value of the difference in standard formation enthalpies between the deuteride and protide shown by dotted lines is larger than that shown by the solid lines. Therefore, T_{cross} of the dotted lines (T_1) is higher than that of the solid lines (T_2). Consequently, it can be said that if the difference in standard formation entropies between isotope hydrides is constant, T_{cross} depends only on the difference in ΔH°. The "inverse isotope effect"[5] can be explained in the same way.

Table 3 shows the standard formation enthalpies and entropies of hydrides obtained in this work together with those reported for V[5] and $LaNi_5$[4]. The values of ΔS° in Table 3 show a dispersed behaviour; in particular, the absolute values of ΔS°_D measured for the BCC alloys and V are larger than the absolute entropy of deuterium (144.8 J/mol H_2 K at 298K). There are several reasons for this. One is the difficulty in determining the equilibrium pressures from the P-C isotherms obtained. It is not easy to define them from sloping isotherms. Figs. 3 and 4 are typical examples. Also, the errors in measuring temperature and pressure are not negligible. Another difficulty is the difference in standard formation entropies between monohydride and dihydride in BCC alloys. In addition, deuterium in V occupies different interstitial sites than protium.

Because the ΔS°_D values obtained for $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ differ from each other, the order of the magnitude of ($\Delta H^\circ_D - \Delta H^\circ_H$) of these alloys does not correlate with that of T_{cross}. However, it is clear that ΔH° and ΔS° can describe the

hydrogen isotope effect of metal-hydrogen systems.

Fig. 8 shows the framed part of Fig. 6. It should be noted that the hydrogen isotope effect of $LaNi_5$ is very small and those of the alloys $Ti_{1.0}Mn_{0.9}V_{1.1}$ and $Ti_{1.0}Cr_{1.5}V_{1.7}$ are fairly large. In the case of $LaNi_5$, the differences in ΔH° and ΔS° between protide and deuteride are small, which makes the hydrogen isotope effect of $LaNi_5$ small.

4. Conclusions

The hydrogen isotope effects in Ti1.0Mn0.9V1.1 and Ti1.0Cr1.5V1.7 alloys have been investigated at 313K and 353K, and at 313K and 338K, respectively, by using protium and deuterium. The conclusions of this study are summarized as follows.

1) In both alloys and regardless of temperature, the absorbed amounts of deuterium are larger than those of protium.
2) While the hydrogen isotope effect of LaNi5 is very small, those of the alloys Ti1.0Mn0.9V1.1 and Ti1.0Cr1.5V1.7 are fairly large.
3) The plateau pressure of deuterium is higher than that of protium in the Ti1.0Mn0.9V1.1 alloy, although at 313K it shows the opposite behaviour. In the Ti1.0Cr1.5V1.7 alloy the plateau pressure of deuterium is always lower than that of protium in the experimental temperature range.
4) The inverse isotope effect can be explained by the differences in standard formation enthalpies and entropies between isotope hydrides.

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