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Statistical Thermodynamic Analysis for Isothermal Hydrogenation Performances of $Mg_{2-y}Pr_yNi_4$ Intermetallics (y = 0.6, 0.8, 1.0)

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Abstract Isothermal hydrogenation performances of intermetallic $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 reported by Terashita *et al.* were analyzed on the basis of statistical thermodynamics under a simplifying *a priori* assumption of constant nearest neighbour H-H interaction E(H-H) in a given phase at arbitrary T aiming at characterizing basic aspects of state of H atoms in the interstitial sites in H-storage alloy. To fulfill this *a priori* assumption, number θ of available interstitial sites per metal atom was chosen by preliminary search attempt at the onset of the statistical thermodynamic analysis. Primary H solution in $Mg_{2-y}Pr_yNi_4$ was analyzed by the model with θ = 0.15. The chosen θ value 0.15 for the model analysis was close to be 1/6 (≈ 0.167) which was half of 1/3 (=[Mg + Pr]/[Mg + Pr + Ni]) implying that about half of the (Mg + Pr)-related interstitial sites were provided as the available sites for occupation by H atoms in the primary H solution of $Mg_{2-y}Pr_yNi_4$. On the other hand, hypo-stoichiometric M_4H_3 type hydride of $Mg_{2-y}Pr_yNi_4$ was analyzed by the model with θ = 0.75 and θ' = 0.333 where θ' refers to the lower limiting composition of the phase. This model yielded situation with E(H-H) = 0 for any $Mg_{2-y}Pr_yNi_4$ examined. Chosen value of θ' = 0.333 appeared to imply that the filling of Ni-related interstitial sites by H atoms started after preferential full occupation of the (Mg + Pr)-related interstitial sites by H atoms in the two-phase equilibrium range at invariable $p(H_2)$ plateau during H-charging.

Keywords $(Mg,Pr)_2Ni_4$ intermetallics, Hydrogenation, Non-Stoichiometry, Interstitial Solid Solution, Statistical Thermodynamics

1. Introduction

Hydrogen (H) storage alloys are of strategic importance towards development of H-based energy systems with zero-CO_2 emission. In this context, many researchers have been investing efforts to discover adequate alloy composition to allow high H-storage capacity with favorable absorption/desorption performances.

In a recent publication, Terashita *et al.*[1] reported isothermal hydrogenation performances of ternary intermetallic compounds $Mg_{2-y}Pr_yNi_4$ ($0.6 \leq y \leq 1.4$) that is considered as one of candidate H-storage alloys. In their publication, pressure-temperature-composition (*PTC*) relationships on H-charging/discharging cycle is presented as isotherms on *P-C* coordinate (log $p(H_2)$ vs. x = H/M; M = $Mg_{2-y}Pr_yNi_4$; $p(H_2)$: partial pressure of H_2 gas) for alloys with y = 0.6, 0.8 and 1.0 that maintained crystalline lattice structures during H-charging/discharging cycle (cf. Table 2 in Ref.[1]). For the $Mg_{2-y}Pr_yNi_4$ alloys with y = 1.2 and 1.4, amorphization progressed during H-charging and thence alloys with these compositions had to be disregarded as reversible H-storage alloy and, as such, *PC* isotherm for the alloys with y = 1.2 and 1.4 was not reported in Ref.[1].

In metal-hydrogen (M-H) systems, hysteretic performance is a commonplace rather than exception in H-absorption/desorption cycle. In simplifying model for hysteresis of M-H system, hysteresis is presented for plateau levels of $p(H_2)$ representing transition between primary solid solution phase of H in M and higher hydride phase designating the equilibrium H_2 gas pressure $p(H_2)^f$ for the hydride formation during ascending $p(H_2)$ and the equilibrium H_2 gas pressure $p(H_2)^d$ for dissociation of the hydride during descending $p(H_2)$ where $p(H_2)^f > p(H_2)^d$[2]. In such simplifying model for hysteresis of M-H system, *PC* isotherm in single-phase region on H-charging and that on H-discharging are considered to be comparable to one another assuming reversible nature of the H-absorption/desorption processes in single-phase regions (e.g., Fig. 1 and Fig. A1 in Ref.[2]).

Nevertheless, all the *PC* isotherms reported for the $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 by Terashita *et*

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al.[1] show clearly the hysteretic performance in the single-phase regions as well as in the two-phase region yielding plateaus for distinguishable$p(H_2)^f$ and $p(H_2)^d$. Thus, in the present work, *PTC* relationships reported forthe single-phase regions of the $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 by Terashita*et al.*[1] were analyzed by statistical thermodynamics for the absorption process and for the desorption process separately for respective isotherms aiming at identifying the possible causes leading to hysteretic performance forH dissolution in the $Mg_{2-y}Pr_yNi_4$ alloy lattice.

Basic principles for statistical thermodynamic analysis are provided in a classical textbook authored by Fowler and Guggenheim[3] and desired thermodynamic parameter values of the calculation might be retrieved from NIST-JANAF Thermochemical Tables[4]. In statistical thermodynamic approach, *PTC* relationships in single-phase region are analyzed to derive atomistic interaction parameter values in a given phase while range of composition where two phases are co-existing (i.e., plateau $p(H_2)$ regime in isothermal plot of *PC* relationship) cannot be handled by statistical thermodynamics unlike by conventional thermodynamics.

Statistical thermodynamic analyses were made for extensive range of MH_x and MZ_zH_x under standardized *a priori* assumption of constant nearest neighbor (*n.n.*)H-H interaction energy E(H-H) within a phase at respective temperature T where M might be pure metal or substitutional alloy of type $A_{1-y}B_y$ and Z refers to another interstitial element besides H[5-23]. At the onset of the statistical thermodynamic analysis, number θ of interstitial sites available for occupation by H atoms per M atom is chosen to fulfill the *a priori* assumption of constant E(H-H) within a phase by trial-and-error plotting of$A(x,T) \equiv RT \ln \{[p(H_2)]^{1/2} (\theta - x)/x\}$ against $x$at an arbitrary $T$to find θ value yielding linear $A(x,T)$ vs. x relationship in which slope of the plot refers to E(H-H) as explained in some detail later in Chapter 2.

There is no firstprinciple-based justification for validity of the *a priori* assumption of constancy of E(H-H) within a phase at arbitrary$T$ on the statistical thermodynamic modelling. In fact, in some earlier statistical thermodynamic analyses made for interstitial non-stoichiometric compounds MX_x by other authors, θ was assumed arbitrarily on the basis of crystal lattice structure consideration and, when slope change of $A(x,T)$ vs. x plot with composition x was detected, it was accepted as the inherent variation of E(X-X) with respect to composition x.Normally, E(X-X) tended to become less attractive on going from dilute range of X to higher X concentration range in the same phase MX_xin such evaluation and this trend was appreciated as the consequence of rising elastic strain in the lattice with increasing x in the same phase. However, noting the reality that phase change even between liquid and solid is involved with enthalpy difference of up to mere 20 kJ mol^{-1}(e.g., Ref.[4] and Fig. 1 in Ref.[24]), it would be more natural and straightforward to accept that change in E(X-X) of non-stoichiometric interstitial compound with x at a given Twould end up with phase transformation rather than being maintained in a specified crystal lattice structure. Further, set of statistical thermodynamic interaction parameter values estimated on the basis of the simplifying *a priori* assumption of constant E(H-H) for extensive range of metals and alloys appear to be self-consistent among themselves[5-24].

Thus, in this work, *PC* isotherms reported for the $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 by Terashita*et al.*[1] are analyzed on the basis of statistical thermodynamics with the*a priori* assumption of constant E(H-H) within a phase at arbitrary$T$.

2. Statistical Thermodynamic Analysis

Noting the realitythat the statistical thermodynamic analysis procedure is not so widely known as the conventional thermodynamic analysis procedure among materials researchers, essence of the statistical thermodynamic analysis procedure is reviewed briefly in the following.

In the statistical thermodynamics, partition function *PF* for condensed phase (either solid or liquid) under consideration is composed taking into account pairwise nearest neighbor atomic interactions $E(i\text{-}j)$ between the constituents, i and j. Then, chemical potential $\mu(i)^c$ of the constituent element i in the condensed phase is derived through partial differentiation of *PF* with respect to the number n_i of the constituent element i. Subsequently, $\mu(i)^c$ in the condensed phase is put equal to $\mu(i)^g$ of the same element i in the gas phase.

The expression for $\mu(X)^g$of ideal diatomic gas X_2 is readily made available in the classical textbook authored by Fowler and Guggenheim[3]. The detailed derivation procedure of $\mu(X)^c$ for the condensed phase MX_x might be referred to elsewhere[7,11].Anyway, the statistical thermodynamic equilibrium condition is eventually reduced to the following Eq.(1) for the purpose of analyzing H solution under consideration[5-23]

$$A(x,T) \equiv RT \ln \{[p(H_2)]^{1/2} (\theta - x)/x\} = g + \beta x E(H\text{-}H) \quad (1)$$

$$K = g - [D(H_2) / 2 - RTC(T)] = Q - RT \ln f_H(T) \quad (2)$$

$$C(T) = -(1/2) \ln \{[(4\pi m_H)^{3/2} k^{5/2}/h^3] [(T^{7/2}/\Theta_r) (1 + \Theta_r/3T)] \cdot [\rho^2 \upsilon_0{}^*/2]\} + \Theta_v/4T + (1/2) \ln[1 - \exp(-\Theta_v/T)] \quad (3)$$

$$\ln f_H(T) = -\int_0^\infty g(\nu) \ln[1 - \exp(-h\nu/kT)] d\nu + \ln \rho\upsilon_0 \quad (4)$$

$$Q + \beta x E(H\text{-}H) = \partial E/\partial n_H \quad (5)$$

wherevalues for the dissociation energy $D(H_2)$ (kJ·mol^{-1}) of H_2 molecule per mole, characteristic temperature Θ_r (= 85.4 K) for rotation of H_2 molecule and characteristic temperature Θ_v (= 6100 K) for vibration of H_2 molecule might be taken from available thermodynamic table[4]. Definitions of symbols used throughout the text are listed in the APPENDIX.

To start the statistical thermodynamic analysis using Eq.(1), the value for the parameter θ must be chosen adequately to yield linear $A(T)$ *vs.* x isotherms. This is to fulfill the *a priori* assumption of constant *E*(H-H) over a range of homogeneity composition *x* at a given *T* for MH_x.

3. General Features of the *PC* Isotherms for H Solutions in $Mg_{2-y}Pr_yNi_4$ Alloy Lattice (*y* = 0.6, 0.8 and 1.0)

To carry out statistical thermodynamic analysis for the MH_x lattice, it was desirable to convert the graphically presented *PC* isotherms for the $Mg_{2-y}Pr_yNi_4$ alloys by Terashita *et al.*[1] into numerical tables as summarized in Tables 1 (for *y* = 0.6), 2 (for *y* = 0.8) and 3 (for *y* = 1). The data were read from magnified *PC* isotherms presented in Ref.[1] as Figs. 3-5 by cutting the mesh of *x* (= H/M) with interval 0.025 to read $p(H_2)$ value while finer mesh interval 0.0125 was taken partially for primary H solution range in $MgPrNi_4$ to acquire sufficient number of data points for the analysis. With this procedure, introduction of certain extent of error in reading the experimental data presented in graphical form is inevitable but, as $p(H_2)$ enters in the calculation formula of Eq.(1) in form of $\log[p(H_2)]^{1/2}$, the error margin introduced by the graphical data reading into the calculation results must remain relatively small being held in acceptable level.

Table 1. Isothermal *PC* relationships for $Mg_{2-y}Pr_yNi_4$ alloy with *y* = 0.6 on H-charging and on H-discharging read from Fig. 3 in the publication by Terashita *et al.*[1]. The $p(H_2)$ values are indicated with **bold** letters where there was no distinction between the H-charging process and the H-discharging process. Shaded data were not used for the analysis

x = H/M	$p(H_2)$ (atm)					
	323 K		313 K		293 K	
	absorption	desorption	absorption	desorption	absorption	desorption
0.010	**0.30**	**0.30**	-----	-----	-----	-----
0.025	**0.90**	**0.90**	0.21	-----	0.10	-----
0.050	**1.8**	**1.8**	0.95	0.36	0.45	-----
0.075	3.0	2.2	1.7	1.0	0.75	-----
0.100	3.8	2.8	1.9	1.3	0.90	0.22
0.125	4.5	3.3	2.2	1.8	1.1	0.31
0.150	5.2	3.9	2.9	2.0	1.2	0.55
0.175	5.5	4.0	3.5	2.4	-----	0.65
0.450	7.5	6.5	-----	-----	-----	-----
0.475	8.5	7.5	-----	-----	-----	-----
0.500	**12**	**12**	4.2	-----	-----	-----
0.525	**19**	**19**	5.2	3.2	1.9	-----
0.550	**29**	**29**	7.5	4.8	2.4	1.2
0.575	**51**	**51**	12	6.8	3.6	1.9
0.600	-----	-----	22	12	6.0	3.2
0.625	-----	-----	55	40	13	7.0
0.650	-----	-----	-----	-----	30	20

M = $Mg_{1.4}Pr_{0.6}Ni_4$

Table 2. Isothermal *PC* relationships for $Mg_{2-y}Pr_yNi_4$ alloy with *y* = 0.8 on H-charging and on H-discharging read from Fig. 4 in the publication by Terashita *et al.*[1]. Shaded data were not used for the analysis with θ = 0.15

x = H/M	$p(H_2)$ (atm)					
	353 K		333 K		313 K	
	absorption	desorption	absorption	desorption	absorption	desorption
0.075	1.9	-----	0.75	0.33	-----	0.10
0.100	3.5	1.8	1.8	0.80	-----	0.30
0.125	5.6	2.7	2.7	1.3	-----	0.48
0.150	7.5	3.9	3.9	1.7	-----	0.65
0.175	-----	4.8	4.8	2.1	-----	0.80
0.550	12	-----	4.9	3.0	3.2	-----
0.575	17	7.5	7.5	3.8	4.8	1.6
0.600	29	14	14	7.0	6.8	2.6
0.625	48	35	25	14	12	4.5
0.650	-----	-----	36	27	19	10
0.675	-----	-----	80	75	29	20
0.700	-----	-----	-----	-----	52	45

M = $Mg_{1.2}Pr_{0.8}Ni_4$

Table 3. IsothermalPC relationships for $Mg_{2-y}Pr_yNi_4$ alloy with *y* = 1.0 onH-charging and on H-discharging read from Fig. 5 in the publication by Terashita*et al*[1].Shaded data were not used for the analysis with θ = 0.15

x = H/M	*p*(H_2) (atm)					
	373 K		353 K		323 K	
	absorption	desorption	absorption	desorption	absorption	desorption
0.050	0.85	-----	0.40	-----	-----	-----
0.075	1.9	-----	0.82	-----	0.28	-----
0.0875	2.7	0.8	1.3	0.45	0.40	-----
0.100	3.2	1.2	1.8	0.60	0.60	-----
0.1125	4.0	1.6	2.4	0.90	0.85	-----
0.125	6.0	2.4	3.2	1.2	1.1	-----
0.150	7.0	3.3	3.5	1.8	-----	-----
0.175	7.8	-----	-----	2.0	-----	-----
0.600	-----	-----	6.2	-----	1.7	0.68
0.625	11	5.8	8.0	4.5	2.2	0.85
0.650	18	11	15	10	4.0	2.2
0.675	33	28	32	28	18	16

M = $Mg_{1.0}Pr_{1.0}Ni_4$

Although Terashita*et al.*[1]carried outthe isothermal hydrogenation experiments for the $Mg_{2-y}Pr_yNi_4$ alloys with *y* = 1.2 and 1.4 as well, they did not report *PC*isotherms for the alloys with these compositions because of amorphization of the alloy lattice during the H-charging process and, as the consequence, reversible cyclic H-charging/discharging was not possible.

Following features are noticeableregarding isothermal hydrogenation performances for the $Mg_{2-y}Pr_yNi_4$ alloys with *y* = 0.6, 0.8 and 1.0 in Tables 1 - 3;

i) primary solid solubility of H into these M lattices extended up to $x \approx 0.2$,

ii) hydride phase is with the composition range extending between $x \approx 0.5$ and $x \approx 0.75$,

iii) *PC* isotherms showed hysteretic performances on H-charging and on H-discharging as well as for two-phase region ($p(H_2)^f > p(H_2)^d$).

Although not analyzed in the present work, Terashita*et al.*[1] reported *PC* isotherms for the $Mg_{2-y}Pr_yNi_4$ alloys with *y* = 1.0 at *T* = 298 K and 273 K (Fig. 6 in Ref.[1]) demonstrating presence of even higher hydride phase with *x* around 1(mono-hydride MH) besides the hydride phase with the composition range extending between $x \approx 0.5$ and $x \approx 0.75$ (hypo-stoichiometric M_4H_3).

Noting these features of the isothermal hydrogenation performances of the $Mg_{2-y}Pr_yNi_4$ alloys with *y* = 0.6, 0.8 and 1.0, following statistical thermodynamic analysis shall be made individually for the primary solid solubility range up to $x \approx 0.2$ and for the M_4H_3type hydride phase with composition range between $x \approx 0.5$ and $x \approx 0.75$ distinguishing the absorption isotherm and the desorption isotherm.

4. Analysis for Primary H Solution in $Mg_{2-y}Pr_yNi_4$Lattice ($x < 0.2$; y = 0.6, 0.8 and 1.0)

To commence statistical thermodynamic analysis process, adequate value for θ must be chosen first of all. A trial-and-error test for evaluating *A* vs. *x* relationships defined by Eq.(1) was done using sets of data for $Mg_{1.4}Pr_{0.6}Ni_4$ at *T* = 323 K in the range of$x < 0.2$ listed in Table 1. This set of data showed the smallest extent of hysteresis between the H absorption and the H desorption processes.

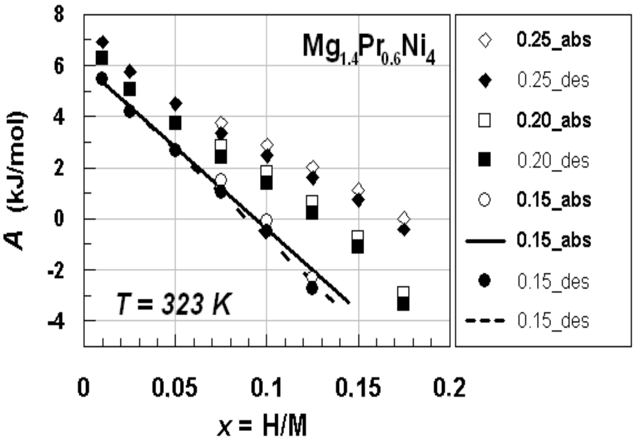

Figure 1. *A* vs. *x* relationships estimated for isothermal*PC* data at *T* = 323 K forprimary H solution in $Mg_{1.4}Pr_{0.6}Ni_4$ alloy lattice on H-absorption and on H-desorption (Table 1) with different choices of θ parameter value.Best-fit linear relationships were calculated using all the data points plotted herein

Search for θ yielding linear *A* vs. *x* isothermal relationship was started from θ = 0.25 noting that the reported *PC* isotherms in Fig. 3 in Ref.[1]reached a plateau at around *x* =

0.2. As shown in Fig. 1, slope referring to E(H-H) varied with x with the choice of θ = 0.25 and 0.20 implying that such value of θ could not be accepted for the analysis.However, when θ was taken to be 0.15, linear$A$ vs. x relationship was established for both the absorption and for the desorption. By least-mean-squares liner fitting procedure, expression for A vs. x relationship for $Mg_{1.4}Pr_{0.6}Ni_4$ at T = 323 K for absorption and that for desorption, respectively, are determined to be

$$A(Mg_{1.4}Pr_{0.6}Ni_4;\ x, 323\ K;\ abs.;\ \theta = 0.15) = 6.000 - 63.884x(kJ\ mol^{-1}) \tag{6}$$

$$A(Mg_{1.4}Pr_{0.6}Ni_4;\ x, 323\ K;\ des.;\ \theta = 0.15) = 6.086 - 68.442x(kJ\ mol^{-1}) \tag{7}$$

As might be understood from the above attempt for determining θ value for the primaryH solution the $Mg_{1.4}Pr_{0.6}Ni_4$ lattice, θ for the absorption process and θ for the desorption process were equally 0.15 and$E$(H-H) on the desorption and that on the absorption were comparable to one another showing only slight difference between them. E(H-H) in the desorption process (Eq.(7)) was slightly more attractive than that in the absorption process (Eq.(6)). This order of E(H-H) on the absorption and on the desorption at a given Tappears rational suggesting that the*n.n.* H-H interaction was more attractive in the M lattice during H-discharging than in the M lattice during H-charging not being in contradiction to the fact that $p(H_2)^f > p(H_2)^d$.

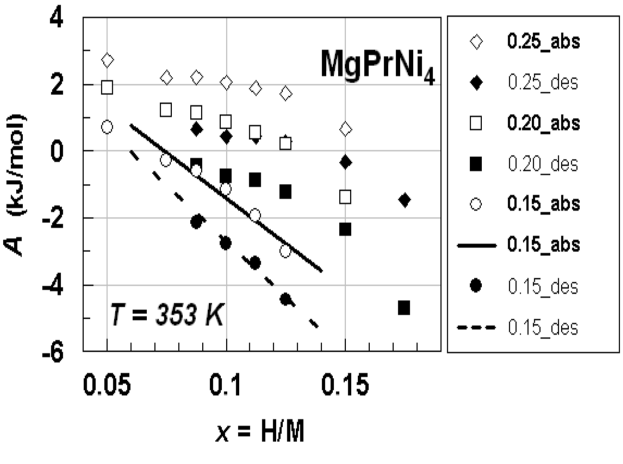

Figure 2. A vs. x relationships estimated for isothermal PC data at T = 353 K forprimary H solution in $MgPrNi_4$ alloy lattice on H-absorption and on H-desorption (Table 3) with different choices of θ parameter value, Best-fit linear relationships were calculated excluding the data points at x = 0.05

Similar attempt of search for θ parameter value was made for primary H solution in $MgPrNi_4$ lattice using PC isotherm at T = 353 K. As plotted in Fig. 2, θ = 0.15 appears to be the adequate choice for the θ value like for H solution in $Mg_{1.4}Pr_{0.6}Ni_4$ to yield linear$A$ vs. x relationships

$$A(MgPrNi_4;\ x, 353\ K;\ abs.;\ \theta = 0.15) = 4.026 - 54.306x(kJ\ mol^{-1}) \tag{8}$$

$$A(MgPrNi_4;\ x, 353\ K;\ des.;\ \theta = 0.15) = 3.985 - 66.885x(kJ\ mol^{-1}) \tag{9}$$

Like for the $Mg_{1.4}Pr_{0.6}Ni_4$ lattice, E(H-H) during H-discharging (Eq.(9)) was more attractive than that during H-charging (Eq.(8)) for the $MgPrNi_4$.

It is somewhat surprising to know that θ = 0.15 appeared to be valid for analysis of primary H solution in $MgPrNi_4$ as well as that for $Mg_{1.4}Pr_{0.6}Ni_4$noting that, in the earlier statistical thermodynamic analyses for $A_{1-y}B_yX_x$ type non-stoichiometric interstitial solutions[9-12,16,19,20,22], θ varied with y. As such, in the present cases for H solutions in $Mg_{1.4}Pr_{0.6}Ni_4$ and $MgPrNi_4$, θ = 0.15 was evaluated to yield equally the linear$A$ vs. x relationships for y = 0.6 and 1.0. Thus, the analysis for the primary H solution in $Mg_{1.2}Pr_{0.8}Ni_4$ was decided to be done also withθ = 0.15. Reason for why θ for primary H solution in $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 held constant with y is not clear. The reason for this might be speculated with reference to the outer shell electronic configurations of elemental states of Mg, Pr and Ni which are $2p^63S^2$, $\mathbf{4f^3}5p^26s^2$ and $3p^6\mathbf{3d^8}4s^2$, respectively, where incompletely filled electron shell, **4f** in Pr and **3d** in Ni, are presented with **bold** letters to distinguish from completely filled outermost p and s electron shells. That is, Mg and Pr distributed over the same metal sub-lattice positions on account of similarity of the outermost electron shells although with scarcely populated **4f** shell of Pr. On the other hand, Ni distributed over the other group of metal sub-lattice positions on account of existence of nearly filled**3d** shell. The above cited electron configurations for Mg, Pr and Ni are the electron configurations in the elemental state and thence they must be certainly modified in the $Mg_{2-y}Pr_yNi_4$ intermetallic alloy lattice. Thus, reason for why theθ parameter value for the analysis of the primary H solution in $Mg_{2-y}Pr_yNi_4$ alloys with varying y in the range between 0.6 and 1.0 was estimated to hold constant at 0.15 must be elucidated somehow by further investigation.

Table 4 summarizes the thus-evaluated A vs. x relationships for primary H solutions in $Mg_{2-y}Pr_yNi_4$ alloys with y = 0.6, 0.8 and 1.0 under assumption of θ = 0.15.The analysis was made for absorption and for desorption separately for H solutions in $Mg_{2-y}Pr_yNi_4$ alloys at respective T. The A vs. x relationships given in parentheses in Table 4 were derived with mere two data points and thence they are not used for the further analysis in evaluating K vs. T relationship. The A vs. x relationship was not evaluated for the H-charging in $Mg_{1.2}Pr_{0.8}Ni_4$ at T = 313 K and for H desorption in $MgPrNi_4$ at T = 323 K on account of unavailability of the PTC data.

Corresponding graphical presentations of A vs. x relationships are given in Figs. 3-5. Looking at Table 4, it was judged that $A(x,T;\theta = 0.15)$ vs. x relationships acquired during the H-discharging process for the primary H solutions in any examined $Mg_{2-y}Pr_yNi_4$ were insufficient for further analysis to evaluate the K vs. T relationships. Thus, further analysis for the primary H solution in $Mg_{2-y}Pr_yNi_4$was done for the H-charging data for y = 0.6 and y = 1.0 alone but not for y = 0.8.

Table 4. Calculated *A* as a function of *x* at given *T* for primary H solution in $Mg_{2-y}Pr_yNi_4$ lattice with *y* = 0.6, 0.8 and 1.0 for absorption and desorption processes of H reported by Terashita *et al*[1]

T	***D*(H₂)/2 - *RTC*(*T*)**		***A*(*x*,*T*;θ= 0.15)**(kJ/mol)		
(K)	(kJ/mol)		**$Mg_{1.4}Pr_{0.6}Ni_4$**	**$Mg_{1.2}Pr_{0.8}Ni_4$**	**$MgPrNi_4$**
373	535.829	**abs.**			**6.072 - 65.365x**
		des.			4.020 - 60.354x
353	517.429	**abs.**		**5.792 - 62.749x**	**4.026 - 54.306x**
		des.		(7.205 - 83.772x)	3.985 - 66.885x
333	499.029	**abs.**		**3.837 - 53.656x**	
		des.		2.498 - 51.161x	
323	489.829	**abs.**	**6.000 - 63.884x**		**2.053 - 48.037x**
		des.	6.086 - 68.442x		--------
313	480.629	**abs.**	**5.299 - 65.431x**	--------	
		des.	(3.204 - 29.082x)	0.458 - 42.946x	
293	462.229	**abs.**	**3.946 - 60.116x**		
		des.	(3.725 - 72.581x)		

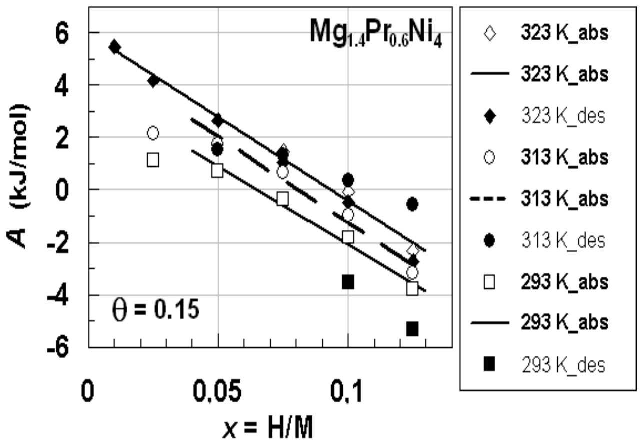

Figure 3. *A* vs. *x* relationships estimated for isothermal *PC* data at different *T* for primary H solution in $Mg_{1.4}Pr_{0.6}Ni_4$ alloy lattice on H-absorption and on H-desorption (Table 1) with θ = 0.15. Best-fit linear relationship at *T* = 323 K on H-absorption was calculated using the all data points plotted herein whereas best-fit linear relationships at *T* = 313 K and 293 K on H-absorption were calculated excluding the data points at *x* = 0.05

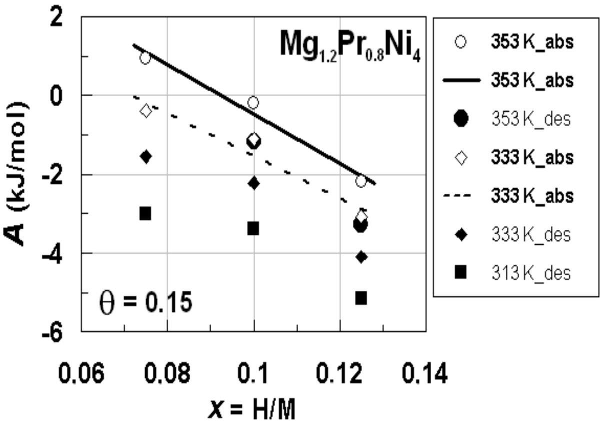

Figure 4. *A* vs. *x* relationships estimated for isothermal *PC* data at different *T* for primary H solution in $Mg_{1.2}Pr_{0.8}Ni_4$ alloy lattice on H-absorption and on H-desorption (Table 2) with θ = 0.15. Best-fit linear relationships at *T* = 353 K and 333 K on H-absorption were calculated using the all data points plotted herein

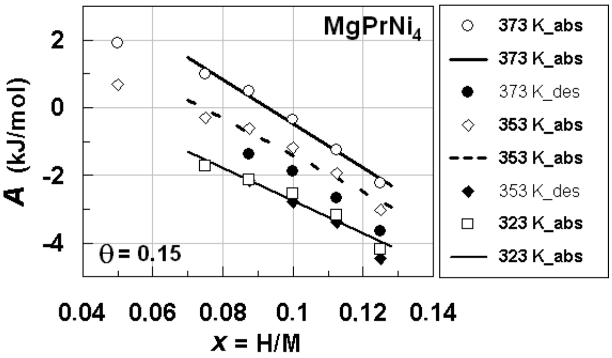

Figure 5. *A* vs. *x* relationships estimated for isothermal *PC* data at different *T* for primary H solution in $MgPrNi_4$ alloy lattice on H-absorption and on H-desorption (Table 3) with θ = 0.15. Best-fit linear relationships at *T* = 373 K and 353 K on H-absorption were calculated excluding the data points at $x < 0.05$

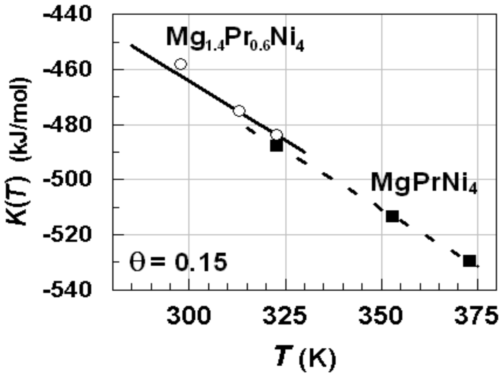

Figure 6. *K* vs. *T* relationships estimated for primary H solutions in $Mg_{1.4}Pr_{0.6}Ni_4$ and $MgPrNi_4$ alloy lattices on H-absorption with θ = 0.15

From these estimation results, *K* vs. *T* relationships were determined as exhibited in Fig. 6 and, as such, values of *Q* and $R \ln f_H$ are evaluated to be

$$Q(Mg_{1.4}Pr_{0.6}Ni_4) = -208.753\ (kJ\ mol^{-1}) \tag{10}$$

$$R \ln f_H(Mg_{1.4}Pr_{0.6}Ni_4) = +852\ (J\ K^{-1}\ mol^{-1}) \tag{11}$$

$$Q(MgPrNi_4) = -216.321\ (kJ\ mol^{-1}) \tag{12}$$

$$R \ln f_H(MgPrNi_4) = +841\ (J\ K^{-1}\ mol^{-1}) \tag{13}$$

As such, Q value was ca. -210 kJ mol^{-1} and R ln f_H was around +850 J K^{-1} mol^{-1} for either $Mg_{1.4}Pr_{0.6}Ni_4$ or $MgPrNi_4$. Thus, although values of Q and R ln f_H for $Mg_{1.2}Pr_{0.8}Ni_4$ were not estimated on account of scarcity of data points, they must be comparable to those estimated for $Mg_{1.4}Pr_{0.6}Ni_4$ and $MgPrNi_4$ (i.e., $Q \approx$ -210 kJ mol^{-1} and R ln $f_H \approx$ +850 J K^{-1} mol^{-1}).

The virtual constancy of values of Q and R ln f_H for the primary H solutions in $Mg_{2-y}Pr_yNi_4$ with respect to y in the range of y between 0.6 and 1.0 does not seem to be incompatible with the constancy of the chosen value of θ to be 0.15 for these alloy lattices with varying y in the range between 0.6 and 1.0.

5. Analysis for Hypo-stoichiometric M_4H_3 Type Hydride of $Mg_{2-y}Pr_yNi_4$ (0.45 < x < 0.75; y = 0.6, 0.8 and 1.0)

Search of θ for analysis of hypo-stoichiometric M_4H_3 type hydride of $Mg_{2-y}Pr_yNi_4$ (0.45 < x < 0.75; y = 0.6, 0.8 and 1.0) was done in the same fashion as that for the primary H solutions described above in Chapter 4. For this, the analysis was done for the *PC* isotherms for H-absorption and H-desorption at T = 323 K for $Mg_{1.4}Pr_{0.6}Ni_4$ and at T = 353 K for $MgPrNi_4$.

As plotted in Fig. 7, A vs. x relationships for these isotherms were calculated with θ = 0.75 and with θ = 1.0 for the sake of comparison. It looks that the data point for x = 0.45 for $Mg_{1.4}Pr_{0.6}Ni_4$ at T = 323 K was out of contention and thence it was discarded for evaluation of the A vs. x relationships for $Mg_{1.4}Pr_{0.6}Ni_4$.

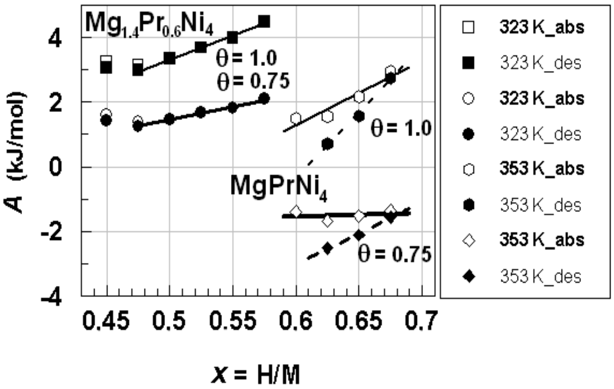

Figure 7. A vs. x relationships estimated for isothermal *PC* data for hypo-stoichiometric M_4H_3 alloy lattice with M = $Mg_{1.4}Pr_{0.6}Ni_4$(Table 1) and M = $MgPrNi_4$(Table 3) with choices of θ = 0.75 and 1.0. Best-fit linear relationships for $Mg_{1.4}Pr_{0.6}Ni_4$ on H-absorption and on H-desorption were calculated excluding the data points at x < 0.50 while those for $MgPrNi_4$ on H-absorption and on H-desorption were calculated using all the data points plotted herein

At either choice of θ = 0.75 or 1.0, linear A vs. x relationships were drawn for the H solutions in hypo-stoichiometric M_4H_3 type hydride of $Mg_{2-y}Pr_yNi_4$ yielding positive E(H-H) (repulsive *n.n.* H-H interaction) in contrast to negative E(H-H) for the primary H solutions in $Mg_{2-y}Pr_yNi_4$ (Figs. 1 and 2). Thus, it was felt difficult to decide which θ value had to be chosen for further analysis. Noting that MH type mono-hydride phase would exist at least at T = 273 K and at T = 298 K for $MgPrNi_4$ (Fig. 6 in Ref.[1]) to which θ = 1.0 might be assigned for the analysis, we decided to undertake analysis for the M_4H_3 type hypo-stoichiometric hydride of $Mg_{2-y}Pr_yNi_4$ with the choice of θ = 0.75.

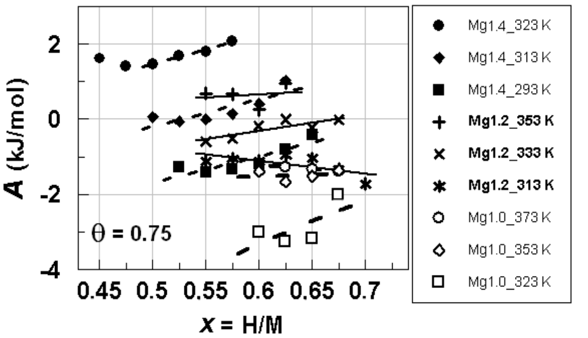

Figure 8. A vs. x relationships estimated for isothermal *PC* data at different T for hypo-stoichiometric M_4H_3 alloy lattices with M = $Mg_{1.4}Pr_{0.6}Ni_4$ and $MgPrNi_4$ on H-absorption with θ = 0.75

Figure 8 plots the calculated A vs. x relationships for M_4H_3 type hypo-stoichiometric hydrides of $Mg_{2-y}Pr_yNi_4$ at y = 0.6, 0.8 and 1.0 with the choice of θ = 0.75. In most cases, E(H-H) appears to be positive (repulsive) while E(H-H) for $Mg_{1.2}Pr_{0.8}Ni_4$ at T = 313 K was estimated to be slightly negative (attractive).

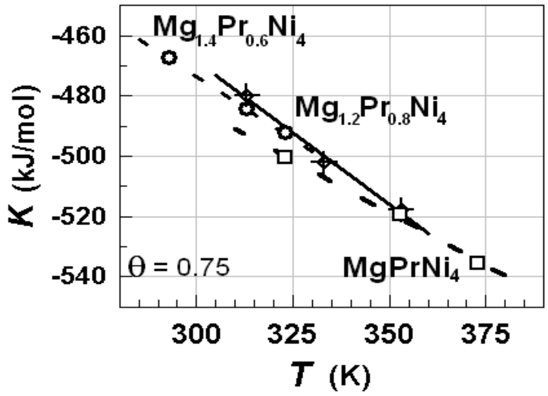

Figure 9. K vs. T relationships estimated for hypo-stoichiometric M_4H_3 alloy lattice with M = $Mg_{1.4}Pr_{0.6}Ni_4$, $Mg_{1.2}Pr_{0.2}Ni_4$ and $MgPrNi_4$ with θ = 0.75

Extent of scatter of calculated A values from the least-mean-squares lines for the M_4H_3 type hypo-stoichiometric hydrides of $Mg_{2-y}Pr_yNi_4$(Fig. 8) appears to be greater than that of the calculated A values for the primary H solutions in $Mg_{2-y}Pr_yNi_4$ (Figs. 3-5). Thence, the error margin for the estimated K vs. T relationships for the M_4H_3 type hypo-stoichiometric hydrides of $Mg_{2-y}Pr_yNi_4$ (Fig. 9) and that for the estimated values for Q and R ln f_H for the M_4H_3 type hypo-stoichiometric hydrides (Table 5) must be greater than the corresponding error margins for the primary H solutions in $Mg_{2-y}Pr_yNi_4$.

Table 5. Estimated values for the statistical thermodynamic parameters, Q (kJ mol^{-1}) and R ln f_H (J K^{-1} mol^{-1}), for primary solid solution MH_x with θ = 0.15 and for hypo-stoichiometric hydride M_4H_3 with θ = 0.75 using the *PTC* data reported for absorption process for M = $Mg_{2-y}Pr_yNi_4$ by Terashita *et al*[1]

M	T (K)	primary solid solution MH_x (θ= 0.15)		hypo-stoichiometric hydride M_4H_3 (θ = 0.75)	
		Q (kJ/mol)	R ln f_H (J/K/mol)	Q (kJ/mol)	R ln f_H (J/K/mol)
$Mg_{1.4}Pr_{0.6}Ni_4$	293-323	-208.753	+852	-224.842	+829
$Mg_{1.2}Pr_{0.8}Ni_4$	313-353	------	------	-183.232	+951
$MgPrNi_4$	323-373	-216.321	+841	-275.092	+696

Table 6. Valuesof statistical thermodynamic parameters, Q and R ln f_H, estimated for $LnCo_3H_{4x}$ type intermetallic hydride (reproduced from Table 5 in Ref.[16])

$LnCo_3H_{4x}$	x	θ	θ'	Q (kJ/mol)	R ln f_H (J/K/mol)
$DyCo_3H_{4x}$	1.1-0.75	1.05	0.725	-230.4	-70.2
$ErCo_3H_{4x}$	1.1-0.75	1.05	0.775	-266.5	-174.4
$DyCo_3H_{4x}$	0.5-0.25	0.475	0.25	-215.2	+22.3
$ErCo_3H_{4x}$	0.5-0.25	0.475	0.275	-212.8	+16.6

θ: number of interstitial sites per M atom available for occupation of H atoms referring to the upper composition limit of the phase,
θ': number of interstitial sites per M atom available for occupation of H atoms referring to the lower composition limit of the phase.

The data set for the M_4H_3 type hypo-stoichiometric hydrides of $Mg_{2-y}Pr_yNi_4$ listed in Table 5 appeared to be with lacking regularity.Graphical presentation of K-T relationships for M_4H_3 type hypo-stoichiometric hydrides of $Mg_{2-y}Pr_yNi_4$ in Fig. 9 also does not seem to show any realistic regularity with respect to variation of y. Thence, re-consideration for the statistical modelling for the M_4H_3 type hypo-stoichiometric hydride of $Mg_{2-y}Pr_yNi_4$ was felt desirable.

When comparing values of Q and R ln f_H for $Mg_{1.4}Pr_{0.6}Ni_4$ between the primary H solution and the M_4H_3 type hypo-stoichiometric hydride (Table 5), Q was more negative (i.e. E(H-M) was more attractive) in the M_4H_3 than in the primary H solution and R ln f_H was positive in both the primary H solution and the M_4H_3 hydride.

Table 6 reproduces the statistical thermodynamic analysis results for $LnCo_3H_{4x}$ reported earlier in Ref.[16]. The analysis for $LnCo_3H_{4x}$ was done using modified basic formula as below in place of Eq.(1)

$$A'(x,T) \equiv RT \ln \{[p(H_2)]^{1/2} (\theta - x)/(x - \theta')\} = g + \beta x\ E(\text{H-H}) \quad (14)$$

whereθ representsthe number of interstitial sites per M atom available for occupation of H atoms referring to the upper composition limit of the phase while θ' representsthe number of interstitial sites per M atom available for occupation of H atoms referring to the lower composition limit of the phase[9,12,16].

One of remarkable aspects noticeable in Table 6 is that R ln f_H for $LnCo_3H_{4x}$ in the higher hydride phase ($0.75 < x < 1.1$) was negative while that in the lower hydride phase ($0.25 < x < 0.5$) was positive. This was interpreted as suggesting drastic modification of electronic surroundings around H atom from the former to the latter. It might be that, in the higher hydride phase with $x > 0.75$, filling of Ln-related sites ([Ln]/[Ln + Co] = 1/4]) might have proceeded with Co-related sites ([Co]/[Ln + Co] = 3/4) being fully occupied preferentially during isothermal increase of $p(H_2)$ judging from the values of θ and θ' chosenfor the model(θ = 1.05 and θ' ≈ 0.75±0.025; Table 6) whereas, in the lower hydride phase of $LnCo_3$, partial (probably, in regular fashion) filling of the Co-related sites with H atoms have been in progress (θ ≈ 0.5 and θ' ≈ 0.25).

Remembering composition procedures for the modified statistical model for the H solutions in $LnCo_3$ intermetallic lattice by specifying θ' referring to the lower limiting H solubility of the phase besides θ referring to the higher limiting H solubility of the phase[9,12,16], introduction of θ' parameter for the statistical model for the M_4H_3 type hypo-stoichiometric hydride of $Mg_{2-y}Pr_yNi_4$ besides θ = 0.75 was sought.

Noting that lattice parameter of the $Mg_{2-y}Pr_yNi_4$ Laves phase increased linearly with the composition y following the Vegard's rule (Fig. 2 in Ref.[1]), Mg and Pr substituted one type of metal sub-lattice positions randomly while Ni occupied another type of metal sub-lattice positions. Ratio of[Mg + Pr]/[Mg + Pr + Ni] in the $Mg_{2-y}Pr_yNi_4$lattice was 1/3 (≈ 0.333). Thus, modified model calculation was attempted with the choice ofθ = 0.75 and θ' = 0.333.

Table 7. Estimated values of $A'(x,T;\ \theta= 0.75,\ \theta' = 0.333)$ using Eq.(14) for hypo-stoichiometric M_4H_3 type hydride of $Mg_{1.4}Pr_{0.6}Ni_4$and calculated values of $g$by simple arithmetic averagingof A' values under assumption of E(H-H) = 0

x	$A'(x,T;\ \theta = 0.75,\ \theta' = 0.333)$ for $Mg_{1.4}Pr_{0.6}Ni_4$(kJ/mol)					
	323 Kabs	323 K des	**313 Kabs**	313 Kdes	**293 Kabs**	293 Kdes
0.45	**5.234**	5.042	-----	-----	-----	-----
0.475	**4.649**	4.481	-----	-----	-----	-----
0.50	**4.420**	4.420	**2.917**	-----	-----	-----
0.525	**4.380**	4.380	**2.558**	1.926	**1.168**	-----
0.55	**4.303**	4.303	**2.409**	1.829	**0.868**	0.023
0.575	**4.409**	4.409	**2.390**	1.651	**0.771**	-0.008
0.60	-----	-----	**2.521**	1.733	**0.778**	0.012
0.625	-----	-----	**3.006**	2.592	**1.057**	0.303
0.65	-----	-----	-----	-----	**1.332**	0.838
g(kJ/mol)	**4.566**	4.506	**2.634**	1.946	**0.996**	0.234

Table 8. Calculatedvalues of *g*and *K* for thehypo-stoichiometric M_4H_3 type hydrides ofMg$_{2-y}$Pr$_y$Ni$_4$ with $y = 0.6$, 0.8 and 1.0 for absorption and desorption processes of H reported by Terashita*et al*[1]according to a modified statistical model with the choice ofθ= 0.75 and θ'= 0.333 that led to *E*(H-H) = 0

T	**$D(H_2)/2 - RTC(T)$**			***g*** **/ *K***(kJ/mol)	
(K)	(kJ/mol)		**$Mg_{1.4}Pr_{0.6}Ni_4$**	**$Mg_{1.2}Pr_{0.8}Ni_4$**	**$MgPrNi_4$**
373	535.829	**abs.**			**0.902 / -534.927**
		des.			0.232 / -535.597
353	517.429	**abs.**		**3.108 / -514.321**	**0.692 / -516.737**
		des.		2.304 / -515.125	0.049 / -517.380
333	499.029	**abs.**		**1.944 / -497.085**	
		des.		1.299 / -497.730	
323	489.829	**abs.**	**4.566 / -485.263**		**-0.872 / -490.701**
		des.	4.506 / -485.323		-1.739 / -491.568
313	480.629	**abs.**	**2.634 / -477.995**	**0.819 / -479.810**	
		des.	1.946 / -478.683	-0.172 / -480.801	
293	462.229	**abs.**	**0.996 / -461.233**		
		des.	0.234 / -461.995		
***K*(*T*)(kJ/mol)**		**abs.**	**-225.146 - 0.806*T***	**-209.768 - 0.863*T***	**-205.294 - 0.883*T***
		des.	-232.024 - 0.786*T*	-212.138 - 0.858*T*	-207.496 - 0.879 *T*

The model calculation results made for the non-stoichiometric M_4H_3 type hydride of $Mg_{1.4}Pr_{0.6}Ni_4$with θ = 0.75 and θ' = 0.333 are summarized in Table 7. It looked that, with this modified model with θ = 0.75 and θ' = 0.333, slope of *A*' vs. *x* at any given *T* became practically 0 (i.e., *E*(H-H) = 0). At the bottom row in Table 7, averaged values of *A*' at given *T* were listed as the values of *g* defined in Eq.(2).The values of *g* calculated in the similar fashion for Mg$_{2-y}$Pr$_y$Ni$_4$ at $y = 0.8$ and 1.0 as well as at $y = 0.6$ are summarized in Table 8 together with *K* values. At the bottom of Table 8, calculated *K* vs. *T* relationships are given separately for the H-absorption process and for the H-desorption process.

As seen in Table 8, the modified model with θ = 0.75 and θ' = 0.333 appeared to yield *K* vs. *T* relationships showing certain regularity with respect to variation of y in Mg$_{2-y}$Pr$_y$Ni$_4$. Graphical presentation of the drawn *K* vs. *T* relationships on the basis of this model (Fig. 10) also seem to be in better order than that drawn on the basis of a simplifying model with θ = 0.75 presented in Fig. 9.

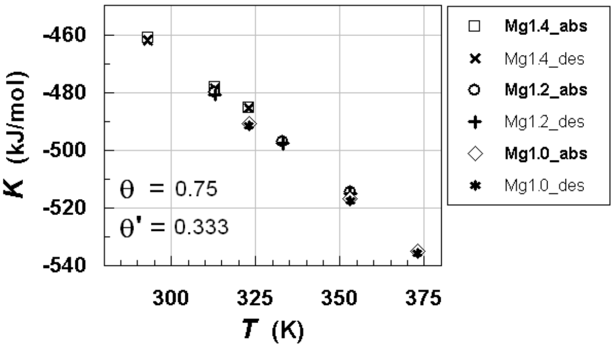

Figure 10. *K*vs. *T* relationships estimated for hypo-stoichiometric M_4H_3 alloy lattice with M =$Mg_{1.4}Pr_{0.6}Ni_4$, $Mg_{1.2}Pr_{0.2}Ni_4$ and $MgPrNi_4$with θ = 0.75 and θ' = 0.333

Following trends are noticeable for the M_4H_3 type hypo-stoichiometric hydrides of Mg$_{2-y}$Pr$_y$Ni$_4$ in Table 8.

i) *Q* value tended to become more negative (that is, increasing extent of stabilization of H atoms in the Mg$_{2-y}$Pr$_y$Ni$_4$ lattice) with the increasing *y* suggesting positive contribution of Pr alloying to substitute Mg towards stabilization of H in the Mg$_{2-y}$Pr$_y$Ni$_4$ lattice.

ii) For Mg$_{2-y}$Pr$_y$Ni$_4$with a given *y*, *Q* value for the H-discharging process was slightly more negative than that for the H-charging process.

The latter feature appears rational and acceptable noting that, on H-absorption process, H atoms are desired to be forcibly inserted into certain interstitial sites while, on H-desorption process, H atoms in certain interstitial sites have to be pulled out of the site.

6. Concluding Remarks

Isothermal hydrogenation performances of Mg$_{2-y}$Pr$_y$Ni$_4$ alloys with $y = 0.6$, 0.2 and 1.0 reported by Terashita*et al.*[1] were analyzed on the basis of statistical thermodynamics under an *a priori* assumptionof constant *E*(H-H) in a given phase at arbitrary *T*.

Primary H solution in Mg$_{2-y}$Pr$_y$Ni$_4$was analyzed by the model with θ = 0.15 to yield $Q \approx -210$ kJ mol^{-1} and $R \ln f_H = +850$ J K^{-1} mol^{-1}. The chosen θ value 0.15 for the model was close to 1/6 (≈ 0.167) which was half of 1/3 (=[Mg + Pr]/[Mg + Pr + Ni]) implying that about half of the (Mg + Pr)-related interstitial sites were provided as the available sites for occupation by H atoms in the primary H solution of Mg$_{2-y}$Pr$_y$Ni$_4$.

On the other hand, hypo-stoichiometric M_4H_3 type hydride of Mg$_{2-y}$Pr$_y$Ni$_4$ was analyzed by the model with θ = 0.75 and θ' = 0.333. This model yielded situation with *E*(H-H) = 0. Chosen value of θ' = 0.333 appeared to imply that the filling of Ni-related interstitial sites by H atoms started after preliminary full occupation of the (Mg + Pr)-related interstitial sites by H atoms in the two-phase equilibrium range at invariable $p(H_2)$ plateauduring H-charging.

APPENDIX / List of Symbols

$A(x,T)$: ≡ $RT \ln \{[p(H_2)]^{1/2} (\theta - x)/x\}$ (kJ·mol^{-1}); calculated from experimentally determinedvalues of $p(H_2)$, T and x for specified value of θ using Eq.(1)

$C(T)$: defined by eqn.(3) to represent contributions of translational, rotational andvibrational motions of H_2 molecule

$D(H_2)$: dissociation energy of H_2 molecule per mole (kJ·mol^{-1})

E: lattice energy (kJ·mol^{-1})

$E(i\text{-}j)$: nearest neighbor pair-wise interaction energy between $i$and j atoms in MH_x lattice

$f_H(T)$: partition function of H in MH_x lattice at temperature T

g: parameter determined as the intercept of the $A(T)$ *vs.* x plot at $x = 0$ using Eq.(1)

$g(\nu)$: distribution function as a function of vibrational frequency ν of H atom in MH_x lattice

h: Planck constant

k: Boltzmann constant

K: parameter calculated from g using Eq.(2)

m_H: mass of H atom

n_H: number of H atoms in the MH_x lattice

n_V: number of M atoms in the MH_x lattice

$p(H_2)$: partial pressure of ideal H_2 gas molecule (atm)

P-T-C: pressure-temperature-composition

Q: degree of stabilization of H atom in MH_x lattice with reference to isolated H atom in vacuum

R: universal gasconstant (= 0.0083145 kJ·mol^{-1} K^{-1})

T: absolute temperature (K)

x: atom fraction of H against M in MH_x

β: geometrical factor determined from crystal structure consideration

θ: number of available interstitial sites for occupation by H atom per metal atom in MH_x

Θ_r: characteristic temperature for rotation of H_2 molecule (= 85.4 K)

Θ_v: characteristic temperature for vibration of H_2 molecule (= 6100 K)

$\mu(H)^c$: chemical potential of H atom in the condensed phase MH_x

$\mu(H)^g$: chemical potential of H atom in the ideal diatomic H_2 gas molecule

ν:vibrational frequency of H atom in MH_x lattice

ρ: nuclear spin weight (= 2 for H while 3 for D)

υ_0: statistical weight of tightly bound electrons around H in MH_x lattice

υ_0*: statistical weight of electrons in H_2 molecule in normal state (= 1)

REFERENCES

[1] N. Terashita, K. Sakai, S. Tsunokake, Y. Nakamura and E. Akiba: Mater. Trans., 53 (2012) 513-517.DOI: 10.2320/matertrans.M2011334."Hydrogenation properties of ternary intermetallic compounds $Mg_{2-x}Pr_xNi_4$".

[2] T. B. Flanagan and J. D. Clewley: J. Less-Common Met., 83 (1982) 127-141."Hysteresis in metal hydrides".

[3] R.H. Fowler and E.A. Guggenheim: Statistical Thermodynamics, Cambridge University Press (1949).

[4] M.W. Chase, Jr. (Ed.): NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph No. 9, Amer. Chem. Soc. and Amer. Inst. Phys., 1998.

[5] N. Shohoji: J. Less-Common Met., 90 (1983) L5-L6."Comments on 'Hysteresis in metal hydrides'".

[6] N. Shohoji: J. Less-Common Met., 90 (1983) L27-L29."On the construction of a statistical model for primary solid solutions of hydrogen in the group Va transition metals (vanadium, niobium and tantalum)".

[7] N. Shohoji: Phys. Stat. Sol. (b), 118 (1983) 811-822. "Statistical thermodynamic approach to some hyperstoichiometric-dihydrides of lanthanides (La, Ce, Pr, Nd, Sm) and actinides (Np, Pu, Am)".

[8] N. Shohoji: Phys. Stat. Sol. (b), 119 (1983) K87-K90."Statistical thermodynamics of hydrogen solution in some lanthanides".

[9] N. Shohoji: J. Less-Common Met., 102 (1984) 53-65."Statistical thermodynamics of metal-hydrogen systems".

[10] N. Shohoji: Mater. Lett.,3 (1985) 206-208."Statistical model for the hydrogen solution in bcc $Nb_{1-y}M_y$ alloys (M = Al, Cu, Sn, Ni, Pd)".

[11] N. Shohoji: Z. Metallkde., 76 (1985) 192-197."Statistical thermodynamics of the very dilute interstitial solid solutions".

[12] N. Shohoji: J. Less-Common Met., 114 (1985) 249-256."The application of statistical thermodynamics to interstitial solid solutions".

[13] N. Shohoji: J. Nucl. Mater.,127 (1985) 88-96."Statistical thermodynamic study of the ternary compounds ThX_yH_x (X = C, Ni; $y< 1$; $x< 2$)".

[14] N. Shohoji: J. Mater. Sci. Lett., 5 (1986) 522-524."Interaction between hydrogen atoms in metals".

[15] N. Shohoji: J. Mater. Sci., 21 (1986) 2147-2152."Comparative study of solubilities of hydrogen, nitrogen and carbon in □ -iron".

[16] N. Shohoji: Surface Coatings Technol., 28 (1986) 365-382."Statistical thermodynamic aspects of hydrogen in metals".

[17] N. Shohoji and T. Marcelo: J. Mater. Sci. Lett., 6 (1987) 1251-1253."Tetragonality in crystal lattice of zirconium dihydride".

[18] M. C. Monteiro Dias and N. Shohoji: J. Mater. Sci., 27 (1992) 5154-5158." Stability of hydrogen and nitrogen in group VIa metals (Cr, Mo, W) and iron-group metals (Fe, Co, Ni) evaluated by statistical thermodynamics".

[19] M. C. Monteiro Dias and N. Shohoji: Mater. Chem. Phys.,39 (1995) 193-199."Atomic configuration in hexagon-

al-close-packed TiC_zH_x phase estimated by statistical thermodynamics".

[20] N. Shohoji: Mater. Trans., JIM, 42 (2001) 2225-2231. "Statistical thermodynamics as a tool for evaluating atom clustering around interstitial atom".

[21] N. Shohoji: Thin Solid Films, 518 (2010) 7167-7173.DOI: 10.1016/j.tsf.2010.06.052. "Hydrogen absorption in epitaxial *bcc* V (001) thin films analysed by statistical thermodynamics".

[22] N. Shohoji: Internat. J. Mater. Eng. Technol., 7 (2012) 33-54."Suppressed hydrogen solubility in body centred cubic Va-group metal (Nb and Ta) by alloying with W or Ru analysed on the basis of statistical thermodynamics".

[23] N. Shohoji: Mater. Trans., 53 (2012) 1273-1277.DOI: 10.2320/matertrans.M2012071."Statistical thermodynamic analysis for hydrogen absorption behaviour in a four monolayers (4 ML) thick *bcc* vanadium (110) superlattice being in contact with molybdenum layer".

[24] N. Shohoji: Mater. Chem. Phys., 17 (1987) 391-398."Estimation of carbon-metal interaction in the carbides of d-transition metals".