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PROPOSING DESIGN GUIDELINE FOR HYDROGEN PERMEATION MEMBRANE ALLOY BASED ON Va-GROUP METALS (V, Nb AND Ta) TAKING INTO ACCOUNT ATOMIC INTERACTION ENERGY PARAMETER EVALUATED BY STATISTICAL THERMODYNAMICS

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Abstract

Yukawa and his collaborators at Nagoya University investigated systematically hydrogen (H) absorption and permeation behaviors of membranes of alloys based on Va-group metals (V, Nb and Ta) possessing body centered cubic (*bcc*) lattice structure. They aimed at developing Va-group alloy $A_{1-y}M_y$ with suppressed susceptibility to hydrogen embrittlement (HE) without sacrificing H permeation performance by alloying Va-group metal A (= V, Nb or Ta) with another metallic constituent M (= Cr, Mo, W, Ru, Fe or Co) possessing affinity to H weaker than that of Va-group metal to H. Yukawa and his co-workers identified some $A_{1-y}M_y$ alloys as

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favorable H permeation membrane materials. The author carried out statistical thermodynamic analysis for the reported equilibrium pressure-temperature-composition (*PCT*) relationships for *bcc* $A_{1-y}M_yH_x$ by Yukawa and co-workers and evaluated parameter Q referring to extent of stabilization of H in $A_{1-y}M_y$ alloy lattice. In this work, the author reviewed correlation between the Q parameter values estimated by statistical thermodynamic analysis and the reported H permeation performances with hope of proposing simple pragmatic guideline for screening *bcc* $A_{1-y}M_y$ alloy membrane possessing favorable H permeation performance among candidate materials. The review result indicated that alloying element M that leads to suppressed H solubility in *bcc* $A_{1-y}M_y$ lattice but realizes increased extent of stability for H in $A_{1-y}M_yH_x$ lattice (i.e. $Q(A_{1-y}M_yH_x) < Q(AH_x)$) must be considered as the preferred alloying element in view of improved H permeation performance. Then, susceptibility to HE must be evaluated experimentally for thus-screened group of $A_{1-y}M_y$ alloy membranes by H permeation test. Such primary screening process of $A_{1-y}M_y$ on the basis of equilibrium *PCT* data would contribute towards reducing number of desired kinetic H permeation experimental test runs on selection of favorable $A_{1-y}M_y$ alloy membrane material from candidate alloys.

1. Introduction

Towards realization of sustainable global community with minimized CO_2 emission, use of hydrogen (H) as the energy source besides more extensive integration of renewable energy sources (e.g., solar, wind, wave, geothermal, etc.) in commercial electric power grid is considered as one of possible solutions. To run H-based energy generation systems smoothly, steady feed of high purity H_2 gas must be somehow guaranteed. For this, reliable membrane materials must be made available for H_2 separation and purification processes. With such potential applications in mind, Yukawa and collaborators [1-3] invested intensive efforts to evaluate systematically H

permeation behavior as well as H absorption capacity for Va-group metals A (V [3], Nb [1] and Ta [2]) alloyed with another metallic constituent M that tended to suppress H absorption in $A_{1-y}M_yH_x$ with body centered cubic (*bcc*) lattice structure from that in *bcc* AH_x under comparable conditions of temperature *T* and H_2 gas partial pressure $p(H_2)$. Principal aim of alloying A with M to form $A_{1-y}M_y$ alloy was to enhance H permeation performance of the $A_{1-y}M_y$ membrane but it was also intended to suppress susceptibility of $A_{1-y}M_y$ to hydrogen embrittlement (HE) to elongate service life of $A_{1-y}M_y$ membrane in H_2 gas environment.

The author was intrigued by the quality of equilibrium pressure-temperature-composition (*PCT*) relationships for $A_{1-y}M_yH_x$ reported by Yukawa and co-workers [1-3] that were seamlessly consistent with the *PTC* data reported for binary A-H systems (A = V, Nb and Ta) earlier by Veleckis and Edwards [4]. So, the author decided to analyze the reported *PCT* data by Yukawa and collaborators [1-3] on the basis of statistical thermodynamics [5, 6].

When the acquired statistical thermodynamic analysis results for $A_{1-y}M_yH_x$ (A = V, Nb or Ta; M = Cr, Mo, W, Ru, Fe or Co) [5, 6] were compared with the reported H permeation data by Yukawa and co-workers [1-3], it seemed probable to propose a simplifying guideline based on estimated values of statistical thermodynamic parameters for the purpose of screening alloy composition adequate to gain favorable H permeation performance characteristics although prediction of mechanical properties including HE-resistance cannot be made on the basis of statistical thermodynamic analysis results.

In this report, design guideline for H permeation membrane alloy composition $A_{1-y}M_y$ with reference to evaluated values of statistical thermodynamic parameters through analysis of equilibrium *PTC* relationships for $A_{1-y}M_yH_x$ is proposed. Plausible qualitative reasoning to

justify this criterion is also presented by taking into account prevailing mechanisms of H entry at the H-charging side of the membrane and of H release at the H-discharging side of the membrane.

2. Statistical Thermodynamic Analysis Results for *bcc* $A_{1-y}M_yH_x$ Alloy Membranes

Statistical thermodynamic analysis procedure is not so well known as conventional thermodynamic analysis procedure. Thus, characteristic features of statistical thermodynamic analysis procedure developed for characterizing interstitial non-stoichiometric compound MX_x are given in Appendix for convenience of the readers who are not familiar with the statistical thermodynamic analysis procedure [5-32]. Basics of standard statistical thermodynamic analysis procedure might be referred to a classical textbook authored by Fowler and Guggenheim [33]. In the preceding works [5-32], values of parameters desirable for the calculation were taken from JANAF [34] or NIST-JANAF [35] Thermochemical Tables.

In the statistical thermodynamic analysis for interstitial non-stoichiometric compound MX_x the author proposed [5-32], number θ of available interstitial sites per occupation by interstitial atoms X per metal atom M is determined at the onset of the analysis to fulfill an *a prior* assumption of constant nearest neighbour interaction energy $E(\text{X-X})$ among interstitial atoms X within a given homogeneity composition range at arbitrary temperature *T*. $E(\text{X-X})$ might vary at different *T*. Then, parameter Q $(\text{kJ}\cdot\text{mol}^{-1})$ referring to extent of stabilization of X atoms in MX_x and contribution of electronic term $R\ln Zf_{\text{X}}$ $(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ (corresponding to electronic entropy term of localized electrons in conventional thermodynamic sense) are evaluated through analysis of experimentally determined *PCT* relationships for MX_x in equilibrium with ideal diatomic X_2 gas at temperature *T* under X_2 gas partial pressure $p(X_2)$.

The analysis results for *bcc* $A_{1-y}M_yH_x$ [5, 6] obtained through analysis of equilibrium *PCT* data reported by Yukawa and co-workers [1-3] are reproduced in Table 1 together with previous analysis results for $Nb_{1-y}M_yH_x$ (M = Mo, Al, Cu, Sn, Ni or Pd) [8, 9, 17].

It is noticed in Table 1 that, in general, corresponding to decreased θ in $A_{1-y}M_yH_x$ from that in AH_x as the consequence of alloying with M, Q became less negative (i.e., decreased extent of stability of H in the *bcc* $A_{1-y}M_y$ lattice) for most of $A_{1-y}M_yH_x$ but with some exceptions, $V_{0.95}Fe_{0.05}H_x$, $V_{0.948}Co_{0.052}H_x$ and $Nb_{0.95}W_{0.05}H_x$ for which $Q(A_{1-y}M_yH_x)$ became more negative than $Q(AH_x)$ (i.e., H atoms being more stable in these $A_{1-y}M_y$ alloy lattices than in pure A) in spite of decreased $\theta(A_{1-y}M_yH_x)$ from $\theta(AH_x)$ although such situation appeared somewhat strange.

3. Hydrogen Permeation Measurement Results by Yukawa and Collaborators [1-3]

Rigorous quantitative evaluation of H permeability of alloy membrane does not seem to be very easy. Steady state H flux $J \cdot L\,(\mathrm{mol\,H \cdot m^{-1} \cdot s^{-1}})$ of membrane of thickness $L(\mathrm{m})$ would vary depending on $p(H_2)^{in}$ at H-charging side of the membrane surface and on $p(H_2)^{out}$ at H-discharging side of the membrane as well as on *T*. For example, in Figure 5 in [3], Suzuki et al. demonstrated that $J \cdot L$ for $V_{0.95}Fe_{0.05}$ membrane at 773 K under condition of $p(H_2)^{in}/p(H_2)^{out} = 0.80(\mathrm{MPa})/0.01(\mathrm{MPa}) = 80$ was by about factor 6 higher than that for pure Pd membrane under the same conditions of *T* and $p(H_2)$. Likewise, Yukawa et al. showed in Figure 3 in [2] that, when compared at 773 K under $p(H_2)^{in}/p(H_2)^{out} = 0.15(\mathrm{MPa})/0.01(\mathrm{MPa}) = 15$, $J \cdot L$ for $Ta_{0.95}W_{0.05}$ was by 5 times higher than that for

$Pd_{0.73}Ag_{0.27}$. Similarly, Yukawa et al. showed in Figure 9 in [1] that, at 773 K, $J \cdot L$ of $Nb_{0.95}Ru_{0.05}$ and that of $Nb_{0.95}W_{0.05}$ was higher than that of Nb membrane showing trend of increasing $J \cdot L$ with increasing $\Delta p(H_2)$ $(= p(H_2)^{in} - p(H_2)^{out})$ reporting that no sign of HE damage was detected for $Nb_{0.95}Ru_{0.05}$ and $Nb_{0.95}W_{0.05}$ after the H permeation test at 773 K.

4. Proposing Guideline for Designing Hydrogen Permeation Membrane Alloy

It is intriguing to note that *Q* values for most of $A_{1-y}M_yH_x$ membranes that were identified as favorable hydrogen permeation alloy ($V_{0.95}Fe_{0.05}$ [3]; $Nb_{0.95}Ru_{0.05}$ and $Nb_{0.95}W_{0.05}$ [1]; $Ta_{0.95}W_{0.05}$ [2]) were evaluated to be more negative than for AH_x (i.e., H atoms being more stable in $A_{1-y}M_yH_x$ lattice than in pure AH_x) as seen in Table 1 despite $\theta(A_{1-y}M_yH_x) < \theta(AH_x)$ implying suppressed extent of H solubility in $A_{1-y}M_y$ compared with that in A.

Thence, the condition

$$Q(A_{1-y}M_yH_x) < Q(AH_x) \tag{1}$$

might be accepted as a rough guideline for screening of H permeation alloy membrane material among candidate materials for $A_{1-y}M_yH_x$ alloys fulfilling the condition

$$\theta(A_{1-y}M_yH_x) < \theta(AH_x). \tag{2}$$

Rational explanation for the validity of this criterion represented by equation (1) might be as follows. For H penetration to commence on the H-charging side of the membrane, H_2 molecules adsorbed over the $A_{1-y}M_y$ membrane surface must be dissociated into atomic H over the surface

$$H_2^{ads} \rightarrow 2H^{ads}. \tag{3}$$

Then, H^{ads} must enter into the interstitial sites in the $A_{1-y}M_y$ alloy matrix

$$H^{ads} \rightarrow H^{abs}. \quad (4)$$

Rate of entry of adsorbed atomic H^{ads} into $A_{1-y}M_y$ lattice as absorbed H^{abs} must be faster than that of H^{ads} into pure A under the condition represented by equation (1) being due to energetic (enthalpy in conventional thermodynamic term) merit. However, in the $A_{1-y}M_yH_x$ fulfilling the condition

$$\theta(A_{1-y}M_yH_x) < \theta(AH_x) \quad (2)$$

proportion *x* of H atoms against total number of metals $[(1-y)A + yM]$ must be smaller in $A_{1-y}M_y$ lattice than in pure A. Accordingly, under comparable $p(H_2)^{in}/p(H_2)^{out}$ condition, rate of expulsion of H out of the H-discharging side surface must become higher for $A_{1-y}M_y$ than for pure A to result in greater rate $J \cdot L$ of permeation of H through $A_{1-y}M_y$ than through pure A.

On the other hand, for $A_{1-y}M_y$ alloy membrane fulfilling the condition represented by equation (2) but a condition contrary to the one defined by equation (1) is fulfilled

$$Q(A_{1-y}M_yH_x) > Q(AH_x) \quad (5)$$

rate of H absorption reaction represented by equation (4) over H-charging side of the membrane surface would become slower for $A_{1-y}M_y$ than for pure A and, as the consequence, rate $J \cdot L$ of H permeation through $A_{1-y}M_y$ would become lower than that through pure A.

This is quite crude qualitative explanation but, if the criterion represented by equation (1) is proved valid for $A_{1-y}M_y$ alloy fulfilling the condition represented by equation (2), the proposed criterion determined from statistical thermodynamic analysis for equilibrium *PCT* relationships might

be employed as pragmatic criterion for primary screening of $A_{1-y}M_y$ alloys to be used as H permeation membrane material among a number of candidate materials to contribute towards minimizing number of somewhat tedious H permeation measurement experimental runs.

Anyway, one thing seems certain that, when A is alloyed with M that possesses chemical affinity to H stronger than the affinity of A to H, such $A_{1-y}M_y$ alloy membrane would not exert favorable H permeation performance compared with that of pure A membrane. Example of this category of alloy is $Nb_{1-y}Ti_yH_x$. As listed in Table 2, statistical thermodynamic estimation results [5, 8, 9, 12] for $Nb_{1-y}Ti_yH_x$ showed that $\theta(Nb_{1-y}Ti_yH_x)$ increases and $Q(Nb_{1-y}Ti_yH_x)$ value become increasingly more negative with increasing *y* implying increased extent of stability of H atoms in $Nb_{1-y}Ti_y$ lattice with increasing *y*. As seen in Table 2, at $y = 0.50$ and 0.75, $Q(Nb_{1-y}Ti_yH_x)$ was estimated to be even more negative than $Q(TiH_x)$. Thus, for $Nb_{1-y}Ti_y$ alloy membrane, it is anticipated that entry of H atoms to the membrane from the H-charging side of the surface might be easier than that for pure Nb membrane in view of both $\theta(Nb_{1-y}Ti_yH_x)$ and $Q(Nb_{1-y}Nb_yH_x)$ but release of H atoms from the H-discharging side of the membrane surface must be more difficult due to higher stability of H atoms in the $Nb_{1-y}Ti_xH_x$ lattice than that in Nb (in fact, H atoms in $Nb_{1-y}Ti_yH_x$ appear to be even more stable than in the TiH_x lattice at $y = 0.50$ and 0.75 (cf. Table 2)).

Thence, alloying of Va-group metal (V, Nb or Ta) with IV-group metal (Ti, Zr or Hf) or other metal that possesses affinity to H stronger than that of Va-group metal must be definitely an unfavorable option in view of H permeation acceleration as well as of rise of susceptibility to HE by increased H solubility in Nb due to alloying with Ti or other IVa-group metals.

It is also noticed in Table 1 for $V_{1-y}Cr_yH_x$, $Nb_{1-y}Mo_yH_x$ and

$Nb_{1-y}Pd_yH_x$ (group of alloying elements M that lead to decreased $\theta(A_{1-y}M_yH_x)$ form $\theta(AH_x)$) as well as in Table 2 for $Nb_{1-y}Ti_yH_x$ (affinity of Ti to H is appreciably stronger than affinity of Nb to H) that $Q(A_{1-y}M_yH_x)$ would vary depending on composition *y* as well as on alloying element M and, accordingly, on the concerned alloy designing, not only the choice of alloying constituent M but also the optimization of composition *y* for given alloying constituent M is of pragmatic significance.

5. Concluding Remarks

Looking at values of parameter *Q* referring to extent of stabilization of H atoms in the alloy lattice for *bcc* $A_{1-y}M_yH_x$ estimated from statistical thermodynamics [5, 6, 8, 9, 17] for the list of alloys defined as possessing favorable H permeation performances of *bcc* $A_{1-y}M_y$ membrane by Yukawa and collaborators [1-3], it seems allowable to accept condition

$$Q(A_{1-y}M_yH_x) < Q(AH_x) \tag{1}$$

as the pragmatic criterion for screening purpose among candidate materials that fulfill condition represented by equation (4),

$$\theta(A_{1-y}M_yH_x) < \theta(AH_x). \tag{2}$$

There remain still some dubious points to accept the above criterion straightforwardly as pointed out below:

(i) $V_{0.948}Co_{0.052}$ was not identified explicitly as favorable hydrogen permeation membrane alloy by Suzuki et al. [3] in spite of fulfillment of the proposed criterion.

(ii) Yukawa et al. [1] identified $Nb_{0.95}Ru_{0.05}$ besides $Nb_{0.95}W_{0.05}$ as favorable hydrogen permeation membrane materials in spite of the failed fulfillment of the proposed criterion equation (1) by $Nb_{0.95}Ru_{0.05}$.

(iii) $Ta_{0.95}W_{0.05}$ was identified as favorable hydrogen permeation

membrane material in spite of failed fulfillment of the proposed criterion equation (1). For $Ta_{0.95}W_{0.05}H_x$, $\theta = 0.55$ of TaH_x was also maintained unchanged in spite of certain extent of H solubility suppression in $Ta_{0.95}W_{0.05}H_x$ from that in TaH_x.

Whether the proposed criterion for screening of H permeation alloy membrane materials is really acceptable as the universal criterion or not must be decided by further compilation of relevant experimental data.

Anyway, considering tediousness of the kinetic H permeation measurement experiment, it would be of pragmatic convenience if preliminary screening for H permeation membrane alloy composition is made through equilibrium *PCT* measurement for H solubility in $A_{1-y}M_yH_x$.

Appendix: Standard Statistical Thermodynamic Analysis Procedure

Generalized fundamental formulae proposed for this line of analysis of interstitial non-stoichiometric condensed phase MX_x are as follows [5-32]:

$$A \equiv RT \ln\{[(\theta - x)/x][p(X_2)]^{1/2}\} = g(T) + \beta x E(\text{X-X}), \tag{A.1}$$

$$K(T) = g(T) - [D(X_2)/2 - RTC(T)] = Q - RT \ln Zf_X(T), \tag{A.2}$$

$$C(T) = -(1/2)\ln\{[(4\pi m_x)^{3/2}/h^3][(T^{7/2}/\Theta_r)(1 + \Theta_r/(3T))][\rho^2 \upsilon_0^*/2]\}$$
$$+ \Theta_v/(4T) + (1/2)\ln[1 - \exp(-\Theta_v/T)], \tag{A.3}$$

$$\ln f_X(T) = -\int_0^\infty g(\nu)\ln[1 - \exp(-h\nu/(kT))]d\nu + \ln \rho\upsilon_0, \tag{A.4}$$

$$Q + \beta x E(\text{X-X}) = \partial E(MX_x)/\partial n_x. \tag{A.5}$$

Symbols used in the above formulae are classified as follows: universal constants, known materials constants, experimentally measured parameter values and parameters evaluated from the statistical thermodynamic analysis.

<universal constants>

R : universal gas constant $(= 8.31451\,\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$,

h : Planck constant $(= 6.6260755\times10^{-34}\,\mathrm{J}\cdot\mathrm{s})$,

k : Boltzmann constant $(= 1.380658\times10^{-23}\,\mathrm{J}\cdot\mathrm{K}^{-1})$,

<known materials constants>

m_{X} : mass of X atom

ρ : nuclear spin weight

Θ_r : characteristic temperature for rotation of X_2 $(\Theta_r(\mathrm{H}) = 85.4\,\mathrm{K})$

Θ_v : characteristic temperature for vibration of X_2 $(\Theta_v(\mathrm{H}) = 6100\,\mathrm{K})$

υ_0^* : electronic state of normal state of X_2 molecule

$D(\mathrm{X}_2)$: dissociation energy of X_2 molecule per mole

β : factor determined from crystal structure consideration

θ_0 : geometrically available number of interstitial site per M in MX_x

υ_0 : statistical weight of tightly bound electrons around X in MX_x

ν : vibrational frequency of X atom in MX_x lattice

$g(\nu)$: distribution function

<experimentally measurable parameters>

$p(\mathrm{X}_2)$: equilibrium pressure of ideal gas X_2

T : absolute temperature (K)

x : composition (X/M atom ratio) in MX_x

n_X : number of X atoms in MX_x

n_M : number of M atoms in MX_x

<parameters to be evaluated>

Q : degree of stabilisation of X atom in MX_x lattice with reference to isolated X and M atoms in vacuum

$E(i\text{-}j)$: interaction energy between i and j atoms in MX_x lattice

$E(MX_x)$: lattice energy

$f_X(T)$: partition function of X atom in MX_x

$f_M(T)$: partition function of M atom in MX_x

K and g : parameters determined by equations (A.1) and (A.2) from the experimental *PTC* (pressure-temperature-composition) data

<a factor to be assigned *a priori*>

θ : number of the interstitial sites per M atom available for occupation by X atoms in MX_x

<a resultant model parameter referring to extent of blocking of interstitial sites>

Z : extent of blocking of interstitial sites by X in MX_x $(= \theta_0/\theta)$; that is, when one interstitial site in MX_x is occupied by an X atom, $(Z-1)$ neighbouring interstitial sites are blocked from occupation by other X atoms

For example, in case that X atoms in MX_x occupy octahedral interstitial sites (O-sites) expression for Q in close packed lattices like *fcc* (face centered

cubic) and *hcp* (hexagonal close packed) is simply

$$Q(fcc/hcp) = 6E(\text{X-M}) \tag{A.6}$$

but that for *bcc* lattice is expressed as

$$Q(bcc) = 2E(\text{X-M}) + 4E(\text{X-M})^{II} - E(\text{X-X})^{II} \tag{A.7}$$

taking into account second nearest neighbour interactions, $E(\text{X-M})^{II}$ and $E(\text{X-X})^{II}$, besides nearest neighbour X-M interaction $E(\text{X-M})$ due to openness of the atom packing in the *bcc* crystal lattice [7, 9, 16].

On the other hand, geometrical factor β to $E(\text{X-X})$ in equation (A.1) is $4/3$ if X atoms are distributed over O-sites in *bcc* lattice [7, 9, 16].

At the onset of the analysis, isothermal A vs. *x* plots must be prepared from available isothermal *PC* relationship at arbitrary *T* using equation (A.1) by varying θ. As understood from equation (A.1), slope of isothermal A vs. *x* plot would represent nearest neighbour X-X interaction $E(\text{X-X})$. To fulfill the *a priori* assumption of constant $E(\text{X-X})$ within homogeneity composition range of MX_x at arbitrary *T*, θ yielding linear A vs. *x* relationship must be chosen for the subsequent calculations.

Then, from the intercept $g(T)$ calculated using equation (A.1), $K(T)$ vs. *T* relationship must be drawn using equation (2). Term *Q* on the right hand side in equation (A.2) refers to extent of stabilization of atom X in the MX_x lattice due to formation of X-M bonds in the MX_x lattice while the coefficient $R\ln[Zf_{\text{X}}(T)]$ to *T* refers to electronic contribution to entropy term in thermodynamic sense. In fact, partition function $f_{\text{X}}(T)$ of X atom in the MX_x lattice is a *T*-dependent function as represented by equation (A.4) but, as the *T* range of statistical thermodynamic analysis for MX_x is typically no wider than 500 K, it has been a common practice to approximate $f_{\text{X}}(T)$ as a *T*-independent term [5-32].

As represented by equation (A.5), term $[Q + \beta xE(\text{X-X})]$ refers to the net extent of stabilization of X atom in the MX_x lattice $\partial E(MX_x)/\partial n_x$ taking into account the contribution of the X-X interaction besides Q which represents contribution of the X-M interaction alone where $E(MX_x)$ refers to lattice energy of compound MX_x taking into account all nearest neighbour pairwise atomic interactions $E(i\text{-}j)$.

For pragmatic convenience of calculating $K(T)$ using equation (A.2), $[D(X_2)/2 - RTC(T)]$ values for X = H and N are presented in tabulated form in [7, 28] at 100 K interval up to 3000 K so that $[D(X_2)/2 - RTC(T)]$ value at arbitrary T is evaluated readily by interpolation. In Table 1, the values for $[D(X_2)/2 - RTC(T)]$ calculated with $\rho(H)$ being taken as 2 are listed for calculation of data with $p(H_2)$ given in bar unit.

Table 1. Available statistical thermodynamic parameter values estimated for *bcc* $A_{1-y}M_yH_x$ that showed suppressed H solubility compared to that in *bcc* AH_x, where A refers to Va-group metals (V, Nb or Ta) (Reproduced principally from [5, 6] with supplements taken from [8, 9, 17].)

bcc $A_{1-y}M_yH_x$	θ	Q** ($kJ \cdot mol^{-1}$)	$R \ln Zf_H$ ($J \cdot K^{-1} \cdot mol^{-1}$)	Reference (analysis)	*PTC* data source
VH_x	0.55	–223.6	64.7	6, 8, 9	4
$V_{0.96}Cr_{0.04}H_x$	0.525	–220.0	26.9	6	3
$V_{0.916}Cr_{0.084}H_x$	0.475	–207.2	54.5	6	3
$V_{0.949}Mo_{0.051}H_x$	0.525	–207.3	37.5	6	3
$V_{0.95}Fe_{0.05}H_x$	0.45	**–229.4**	23.7	6	3
$V_{0.948}Co_{0.052}H_x$	0.45	**–230.1**	21.5	6	3
NbH_x	0.75	–229.6 –229.5	61.8 61.7	8, 9 9	4 36
$Nb_{0.95}Ru_{0.05}H_x$	0.55	–221.8	41.2	5	1
$Nb_{0.95}W_{0.05}H_x$	0.725	**–243.1**	14.1	5	1
$Nb_{0.90}Mo_{0.10}H_x$	0.45	–225.5	65.4	9	36
$Nb_{0.80}Mo_{0.20}H_x$	0.30	–228.2	61.3	9	36
$Nb_{0.70}Mo_{0.30}H_x$	0.20	–220.8	67.7	9	36
$Nb_{0.95}Al_{0.05}H_x$	0.60	–225.8	36.9	17*	37

$Nb_{0.95}Cu_{0.05}H_x$	0.60	–223.5	41.2	17*	37
$Nb_{0.95}Sn_{0.05}H_x$	0.60	**–231.8**	30.6	17*	37
$Nb_{0.95}Ni_{0.05}H_x$	0.60	–219.2	45.0	17*	37
$Nb_{0.95}Pd_{0.05}H_x$	0.60	**–231.8**	26.1	17*	37
$Nb_{0.90}Pd_{0.10}H_x$	0.45	–213.9	45.5	17*	37
TaH_x	0.55	–229.4	62.4	8, 9	4
$Ta_{0.95}W_{0.05}H_x$	0.55	–228.6	32.1	5	2

*Values of Q and R ln Zf_H for these $A_{1-y}M_yH_x$ were presented in graphical form and not given as numerals in [17] but the listed values in this table are taken from the filed record of raw calculation results.

**Q values for $A_{1-y}M_yH_x$ that were evaluated to be more negative than that for AH_x are displayed with bold letter.

Table 2. Available statistical thermodynamic parameter values estimated for *bcc* $Nb_{1-y}Ti_yH_x$ that showed enhanced H solubility compared to that in *bcc* NbH_x (Reproduced principally from [5] with supplements taken from [12].)

bcc $Nb_{1-y}Ti_yH_x$	θ	Q (kJ · mol^{-1})	R ln Zf_H (J · K^{-1} · mol^{-1})	Reference (analysis)	*PTC* data source
NbH_x	0.75	–229.6 –229.5	61.8 61.7	5, 8, 9 5, 9	4 36
$Nb_{0.75}Ti_{0.25}H_x$	0.75	**–233.4**	35.4	5, 12*	36
$Nb_{0.50}Ti_{0.50}H_x$	0.80	**–253.6**	26.5	5, 12*	36
$Nb_{0.25}Ti_{0.75}H_x$	1.025	**–257.3**	29.7	5, 12*	36
TiH_x	1.25	–251.1	35.2	5, 12*	36

*Values of Q and R ln Zf_H for these $Nb_{1-y}Ti_yH_x$ were presented in graphical form and not given as numerals in [12] but the listed values in this table are taken from the filed record of raw calculation results.

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