

Suppressed Hydrogen (H) Solubility in Body Centered Cubic Vanadium (V) by Alloying with Molybdenum (Mo), Chromium (Cr), Iron (Fe) or Cobalt (Co) Appreciated in Terms of Statistical Thermodynamics

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Equilibrium isothermal pressure-composition relationships reported for H solubility in body centered cubic (bcc) $V_{1-y}M_yH_x$ ($M = \text{Cr, Mo, Fe or Co}$) by Suzuki *et al.* recently on this journal were analyzed with statistical thermodynamics under *a priori* assumption of constant H-H interatomic interaction energy $E(\text{H-H})$ within homogeneity composition range of bcc $V_{1-y}M_yH_x$ phase at arbitrary temperature T . Results of the present statistical thermodynamic analysis showed that detected H solubility suppression for the examined $V_{1-y}M_yH_x$ was consistently interpreted in terms of decrease of available number θ for occupation by H atoms per metal atom in the $V_{1-y}M_y$ lattice from $\theta = 0.55$ determined for bcc VH_x in the earlier work of the author. The extent Q of stabilization of H atoms in the $V_{1-y}M_y$ lattice through formation of H-V and H-M bonds was one of principal parameters determined by the statistical thermodynamic analysis. It was intriguing to note that $Q(V_{1-y}M_yH_x)$ with $M = \text{Fe and Co}$ became less negative than $Q(VH_x)$ in pure bcc VH_x implying that the extent of stabilization of H atoms in $V_{1-y}M_y$ lattice with $M = \text{Fe or Co}$ increased with reference to that in pure VH_x in spite of decreased θ from that (0.55) in VH_x . On the other hand, $Q(V_{1-y}M_yH_x)$ with $M = \text{Cr and Mo}$ became less negative (that is decreased stability of H) than $Q(VH_x)$ corresponding straightforwardly to the detected decrease of θ value from that in VH_x . Noting the promoted H permeability reported for $V_{1-y}\text{Fe}_y$ membrane by Suzuki *et al.*, search for alloying element M that induced H solubility drop form that in the bcc V but with effect of enhancing stability of H in the $V_{1-y}M_y$ lattice was concluded to be a pragmatic guideline for the screening of alloying constituent towards development of V-based H permeation membrane material.

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1. Introduction

Equilibrium isothermal pressure-composition (PC) relationships were recently reported for hydrogen (H) solubility in membranes of body centered cubic (bcc) vanadium (V) alloyed with Mo, Cr, Fe or Co (in the following, simply referred to as $V_{1-y}M_yH_x$) over a range of temperature T between 773 K and 673 K by Suzuki *et al.*¹⁾ on a recent issue of this journal. The reported isothermal PC relationships for poly-crystalline bcc $V_{1-y}M_yH_x$ membranes appear to be interpreted straightforwardly in terms of H solubility suppression due to alloying with M to bulk V for which isothermal PC relationships were reported by Veleckis and Edwards.²⁾ There appears to be no necessity for interpreting reported isothermal PC relations for $V_{1-y}M_yH_x$ by Suzuki *et al.*¹⁾ to take into account contributions of other factors (such as extremely small thickness of the V film or preferential crystal orientation of the thin film) as was done on statistical thermodynamic analysis for significant modulation of H absorption behavior reported by Andersson *et al.*³⁾ for epitaxial V (001) thin films with thickness 50 and 100 nm from that for the bulk bcc V.

Suzuki *et al.*¹⁾ evaluated semi-quantitatively the alloying effect of M towards suppression of H solubility to $V_{1-y}M_y$ lattice using an arbitrary chosen index referring to equilibrium H_2 partial pressure $p(\text{H}_2)$ to yield ratio x of H atoms against total metal atoms ($V + M$) in $V_{1-y}M_yH_x$ to be equal to 0.2 (cf. Figs. 2–4 in Ref. 1)). However, as demonstrated by series of statistical thermodynamics analyses for extensive range of ternary non-stoichiometric interstitial compounds consisting of two metallic constituents, M_I and M_{II} and single interstitial component X, $(M_I)_{1-y}(M_{II})_yX_x$ ($X = \text{H, C, N, P or S}$), and those consisting of single metal component and two

interstitial constituents, Z and X, MZ_xX_x ,^{4–30)} suppressed or enhanced X solubility in M_I by alloying with M_{II} or by presence of another interstitial constituent Z besides X might be appreciated in terms of modified number θ of available interstitial sites for occupation by the interstitial atom X per metal atom from that in M_I by substitutional alloying with M_{II} or by additional presence of another interstitial constituent Z besides X in M and, using the sub-lattice model with the designated value of the θ parameter, nearest neighbour interaction energy terms $E(i-j)$ were evaluated ($i, j = M, X$). By such statistical thermodynamic approach, nature of X-M bonding among different non-stoichiometric MX_x compounds was demonstrated to be compared quantitatively with common base of zero energy level taken at infinite separation of constituent atoms in vacuum.

The series of statistical thermodynamic analyses published along this line^{4–30)} were all made by assigning θ value to fulfill a simplifying *a priori* assumption of constant $E(X-X)$ within a homogeneity composition range at any given temperature T . $E(X-X)$ might vary with T but, at a given T , $E(X-X)$ was assumed to hold a constant value within an entire composition range. If $E(X-X)$ varied with composition x at a given T , phase transition was considered to take place inevitably instead of maintaining the same crystal structure.

Basics of standard statistical thermodynamic analysis procedure might be referred to a classical textbook co-authored by Fowler and Guggenheim.³¹⁾ In the preceding works,^{4–30)} values of parameters desirable for the calculation were taken from JANAF³²⁾ or NIST-JANAF³³⁾ Thermochemical Tables.

In this work, equilibrium PC isotherms reported for bcc $V_{1-y}M_yH_x$ ($M = \text{Cr, Mo, Fe, Cr}$) by Suzuki *et al.*¹⁾ are analyzed following standardized statistical thermodynamic