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) VH, VxMyH1-y (M = 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(H-H) within homogeneity composition range of bcc V1-xMyHx phase at arbitrary temperature T. Results of the present statistical thermodynamic analysis showed that detected H solubility suppression for the examined V1-xMyHx was consistently interpreted in terms of decrease of available number of 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(H-H) within homogeneity composition range of bcc V1-xMyHx phase at arbitrary temperature T. Results of the present statistical thermodynamic analysis showed that detected H solubility suppression for the examined V1-xMyHx was consistently interpreted in terms of decrease of available number of H\textsubscript{1} for occupation by H atoms per metal atom in the V1-yM\textsubscript{1} lattice from \( \theta = 0.55 \) determined for bcc VH\textsubscript{1} in the earlier work of the author. The extent \( Q \) of stabilization of H atoms in the V1-xM\textsubscript{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 \( \Delta Q(VH\textsubscript{1}) \) with \( M = Fe \) and Co became less negative than \( \Delta Q(VH\textsubscript{1}) \) in pure bcc VH\textsubscript{1}, implying that the extent of stabilization of H atoms in V1-xM\textsubscript{y} lattice with M = Fe or Co increased with reference to that in pure VH\textsubscript{1} in spite of decreased \( \theta \) from that (0.55) in VH\textsubscript{1}. On the other hand, \( \Delta Q(VM\textsubscript{1}) \) with M = Cr and Mo became less negative (that is decreased stability of H) than \( \Delta Q(VH\textsubscript{1}) \) corresponding straightforwardly to the detected decrease of \( \theta \) value from that in VH\textsubscript{1}. Noting the promoted H permeability reported for V1-xFe\textsubscript{1} 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 V1-xM\textsubscript{y} lattice concluded to be a pragmatic guideline for the screening of alloying constituent towards development of V-based H permeation membrane material. [doi:10.2320/matertrans.M2015415]

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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 \( V_{1-x}M_yH_x \)) over a range of temperature \( T \) between 773 K and 673 K by Suzuki et al.\textsuperscript{10} on a recent issue of this journal. The reported isothermal PC relationships for poly-crystalline bcc \( V_{1-x}M_yH_x \) 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.\textsuperscript{2,3} There appears to be no necessity for interpreting reported isothermal PC relations for \( V_{1-x}M_yH_x \) by Suzuki et al.\textsuperscript{10} 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.\textsuperscript{3} for epitaxial V (001) thin films with thickness 50 and 100 nm from that for the bulk bcc V.

Suzuki et al.\textsuperscript{10} evaluated semi-quantitatively the alloying effect of M towards suppression of H solubility to \( V_{1-x}M_y \) lattice using an arbitrary chosen index referring to equilibrium H\textsubscript{2} partial pressure \( p(H\textsubscript{2}) \) to yield ratio \( x \) of H atoms against total metal atoms (V + M) in \( V_{1-x}M_yH_x \) 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\textsubscript{1} and M\textsubscript{2} and single interstitial component X, \( (M_1)_x(M_2)_yX_z \) (X = H, C, N, P or S), and those consisting of single metal component and two interstitial constituents, Z and X, \( MZ_xX_z \) suppressed or enhanced X solubility in \( M_1 \) by alloying with \( M_2 \) by presence of another interstitial constituent Z besides X might be appreciated in terms of modified number \( \theta \) of available interstitial sites for occupation by the interstitial atom X per metal atom from that in \( M_1 \) by substitutional alloying with \( M_2 \) 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 \( \theta \) 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\textsubscript{z} 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\textsuperscript{4–30} were all made by assigning \( \theta \) value to fulfill a simplifying \textit{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.\textsuperscript{31} In the preceding works,\textsuperscript{4–30} values of parameters desirable for the calculation were taken from JANAF\textsuperscript{32} or NIST-JANAF\textsuperscript{33} Thermophysical Tables.

In this work, equilibrium PC isotherms reported for bcc \( V_{1-x}M_yH_x \) (M = Cr, Mo, Fe, Cr) by Suzuki et al.\textsuperscript{10} are analyzed following standardized statistical thermodynamic