A relation between the vacancy concentration and hydrogen concentration in the Ni–H, Co–H and Pd–H systems

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Abstract

The formation of superabundant vacancies (Vac-H clusters) has been observed in many M–H alloys, but the factors that determine the equilibrium concentration of vacancies have not been identified yet. To identify these factors, the equilibrium concentration of vacancies was estimated from lattice contraction measurements on Ni, Co and Pd having a fcc structure, at high temperatures (930–1350 K) and high hydrogen pressures (2.4–7.4 GPa). The results show that the vacancy concentration is not so much dependent on temperature and hydrogen pressure as the hydrogen concentration. In Ni and Co, the vacancy concentration (x_{cl}) increases linearly with the hydrogen concentration (x_H) for the whole concentration range, reaching $x_{cl} \sim 0.3$ at $x_H \sim 1.0$. In Pd, the vacancy concentration is very small up to $x_H \sim 0.6$ and increases linearly thereafter with nearly the same slope as in Ni and Co. The maximum vacancy concentration reached in Pd is $x_{cl} \sim 0.12$. It is noted that the observed difference in the x_H–x_{cl} relation correlates with the magnitude of the formation energy of Vac-H clusters, which is very small in Ni and Co and relatively large in Pd.
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1. Introduction

Although the vacancy concentration (x_v) in pure metals amounts to only $x_v = 10^{-4}$ to 10^{-3} at temperatures around the melting point, concentrations as high as 0.3 were observed when Ni and Co specimens were held under high temperatures and high hydrogen pressures. This phenomenon called superabundant vacancy (SAV) formation has been substantiated by the observation of lattice contraction [1–5], density reduction [6], enhancement of diffusion [7,8], etc. The mechanism of SAV formation is now understood as being primarily due to the reduction of the formation energy in the presence of interstitial H atoms. If a vacancy traps H atoms and forms a vacancy-hydrogen (Vac-H) cluster, the formation energy of this cluster (e_f^{cl}) should be smaller than the formation energy of a vacancy (e_f^v) by the sum of binding energies (e_b), viz. [9]:

$$e_f^{cl} = e_f^v - \Sigma_i e_{bi} \tag{1}$$

As H atoms trapped by a vacancy in fcc metals are known to occupy positions slightly displaced from nearest-neighbor O-sites [10], and the number of H atoms trapped by a vacancy (r) can be assumed to be $r \leq 6$, substituting the known values of e_f^v and e_b, we readily find that the formation energy of a Vac-H cluster can be reduced nearly to zero or even to a negative value.

At low concentrations of the constituents (x_v, x_H, $x_{cl} \ll 1$), an application of Boltzmann statistics to the equilibrium Vac + rH $\leftrightarrow$ VacH$_r$ leads to the relation [5,9]:

$$x_{cl} \propto x_H^r \exp\left(-e_f^{cl}/kT\right) \tag{2}$$

in which x_H is implicitly dependent on the temperature, T, and hydrogen pressure, p_H. This expression has not been checked experimentally, however.

The purpose of this paper is to experimentally clarify the dependence of the Vac-H concentration on temperature, hydrogen pressure and hydrogen concentration. For this purpose, the lattice contraction caused by SAV formation was measured in fcc Ni, Co and Pd at high temperatures ($T = 930$–1350 K) and high hydrogen pressures
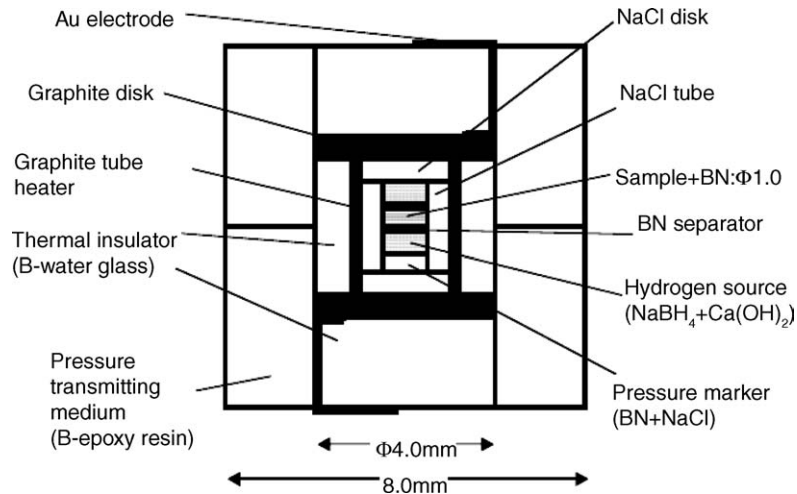
Fig. 1. A cross sectional view of the sample cell assembly used for Ni and Co experiments. For Pd experiments, the hydrogen source is replaced by a stack of Pd foils having the same hydrogen concentration as the sample. Collimated X-rays are passed horizontally through the sample.

($p_H = 2.4$–7.4 GPa) in the range of hydrogen concentrations $x_H = 0$–1.

2. Experimental techniques

The lattice contraction was measured by in situ energy-dispersive XRD under high temperature (<1350 K) and high hydrogen pressure (<7.4 GPa), using a cubic anvil press MAX80 at a synchrotron radiation source in Tsukuba (KEK).

The MAX80 compresses a sample placed in a solid pressure-transmitting medium (amorphous boron-epoxy resin composite, a cube of 8 mm in edge length) simultaneously from six perpendicular directions.

The sample is mixed with BN powder to avoid X-ray absorption and grain growth, encased in a hydrogen-sealing capsule made by compression forming of NaCl powder, and placed at the center of the pressure-transmitting medium. The heating was performed by passing an electric current in a graphite tube heater surrounding the capsule. A cross-sectional view of the sample cell assembly is shown in Fig. 1. A well-collimated X-ray beam of $\sim 0.05 \times 0.3$ mm was passed horizontally through the sample. In the case of Ni and Co, which require high hydrogen pressures for hydrogenation, the internal hydrogen source ($NaBH_4 + Ca(OH)_2$) was placed inside the capsule. Thermal decomposition of this material is completed at ~ 500 K and produces hydrogen atmosphere around the sample. In the case of Pd, the sample was prepared in advance, and the hydrogen source in the sample cell was replaced with the stack of Pd foils hydrogenated to the same concentration as the sample. The Pd foils served as a buffer and kept the hydrogen concentration of the sample very nearly constant.[1] The pressure in the
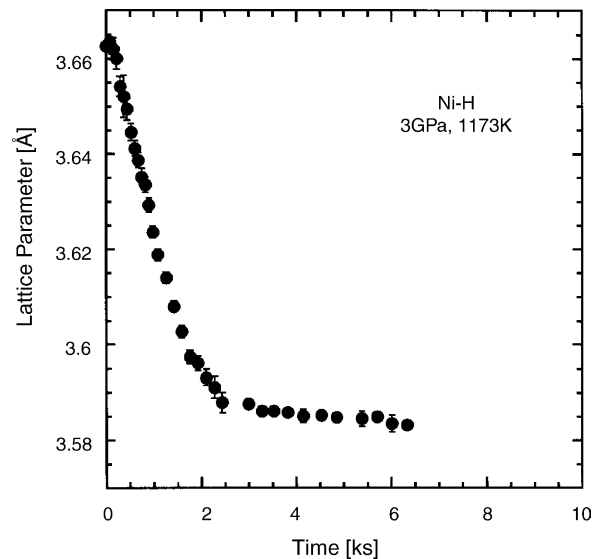

Fig. 2. A representative dependence of the lattice parameter of Ni measured as a function of time under a hydrogen pressure of 3 GPa at 1173 K.

cell was determined from the lattice parameter of NaCl using a Decker scale [11].

An example of the lattice contraction measurements is shown in Fig. 2. After compression to 3 GPa and subsequent heating to 1173 K, the lattice parameter was measured as a function of time. Since the diffusion of hydrogen is sufficiently fast, hydrogen reaches the equilibrium concentration in Ni immediately after heating. The difference between the initial atomic volume of hydrogenated Ni and the standard atomic volume of Ni under the same p, T condition without hydrogen was regarded as an expansion caused by

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[1] It was recognized that a pure Pd sample, after high-pressure heat treatment without internal hydrogen source, contained a small amount of hydro-

gen (of concentration H/Pd ~ 0.1). As this effect was suppressed by inserting Pd of larger volume in the capsule, we inferred that the limited supply of hydrogen came from water in the grain boundaries of compressed NaCl powder.

hydrogen, and the hydrogen concentration was estimated from this difference divided by the hydrogen-induced volume $v_H = 2.2 \, \text{Å}^3$/H-atom in Ni [12]. The Vac-H concentration, on the other hand, was estimated from the relation:

$$x_{cl} = (3\Delta a/a)/(v_R^{cl}/\Omega) \qquad (3)$$

where $\Delta a/a$ is the lattice contraction and v_R^{cl}/Ω is the relaxation volume, i.e. the lattice contraction caused by a unit concentration of Vac-H clusters. In the absence of reliable data, here we assume the relaxation volume $v_R^{cl}/\Omega = -0.36$, which is the average of calculated values for vacancies in a number of fcc metals [13]. Measurements of the lattice parameter of the pure metals performed in the relevant range of pressure and temperature will be reported separately.

3. Results and discussion

The measured lattice contraction, $\Delta a/a$, in Ni, Co and Pd as a function of the hydrogen concentration, x_H, is shown in Fig. 3a–c. The Vac-H cluster concentration, x_{cl}, estimated from Eq. (3) is also given on the right-hand scale.

Fig. 3a shows the result obtained for Ni at $T = 940$–1200 K, $p_H = 2.4$–5.5 GPa. The H concentration varies in a wide range ($x_H = 0.1$–0.8) and the maximum Vac-H cluster concentration attained is extremely high ($x_{cl} \approx 0.3$). This result suggests that the Vac-H cluster concentration is primarily determined by the H concentration, to be expressed by an empirical formula $x_{cl} = 0.42x_H$.

Fig. 3b shows the result for Co at $T = 930$–1350 K, $p_H = 2.0$–7.4 GPa. The H concentration was estimated using $v_H = 1.9 \, \text{Å}^3$/H-atom in Co [14]. The x_H–x_{cl} relation is closely the same as for Ni: $x_{cl} = 0.38x_H$. A similar dependence $x_{cl} = 0.29x_H$ is reported for Fe–H [15].

Fig. 3c shows the result for Pd–H at $T = 920$–1120 K, $p_H = 3.0$–5.0 GPa. The H concentration was estimated using $v_H = 2.7 \, \text{Å}^3$/H-atom in Pd. At $x_H < 0.6$, the Vac-H cluster concentration is too small to be measured by lattice contraction, but it increases linearly at $x_H > 0.6$ with a slope similar to the case of Ni and Co. The maximum cluster concentration $x_{cl} \approx 0.12$ reached in Pd is smaller than in Ni and Co.

The result obtained for a bcc metal Nb can be quoted for comparison [16]. Unlike the method used in the present work, the Vac-H cluster concentration in Nb was estimated by electrical resistivity measurements. For H concentrations of $x_H \le 0.5$, the equilibrium concentration of vacancies was an order of magnitude smaller, $x_{cl} \le 0.01$. The Vac-H cluster concentration was nearly proportional to the H concentration; $x_{cl} = 0.022x_H$, but it was also dependent on the temperature and hydrogen pressure.

The above results show that, in the fcc phase of Fe, Co, Ni and Pd, the Vac-H cluster concentration is determined by the H concentration rather than the temperature and hydrogen pressure. We note that a distinctive difference in the x_H–x_{cl} relation for Fe, Co, Ni on the one hand and
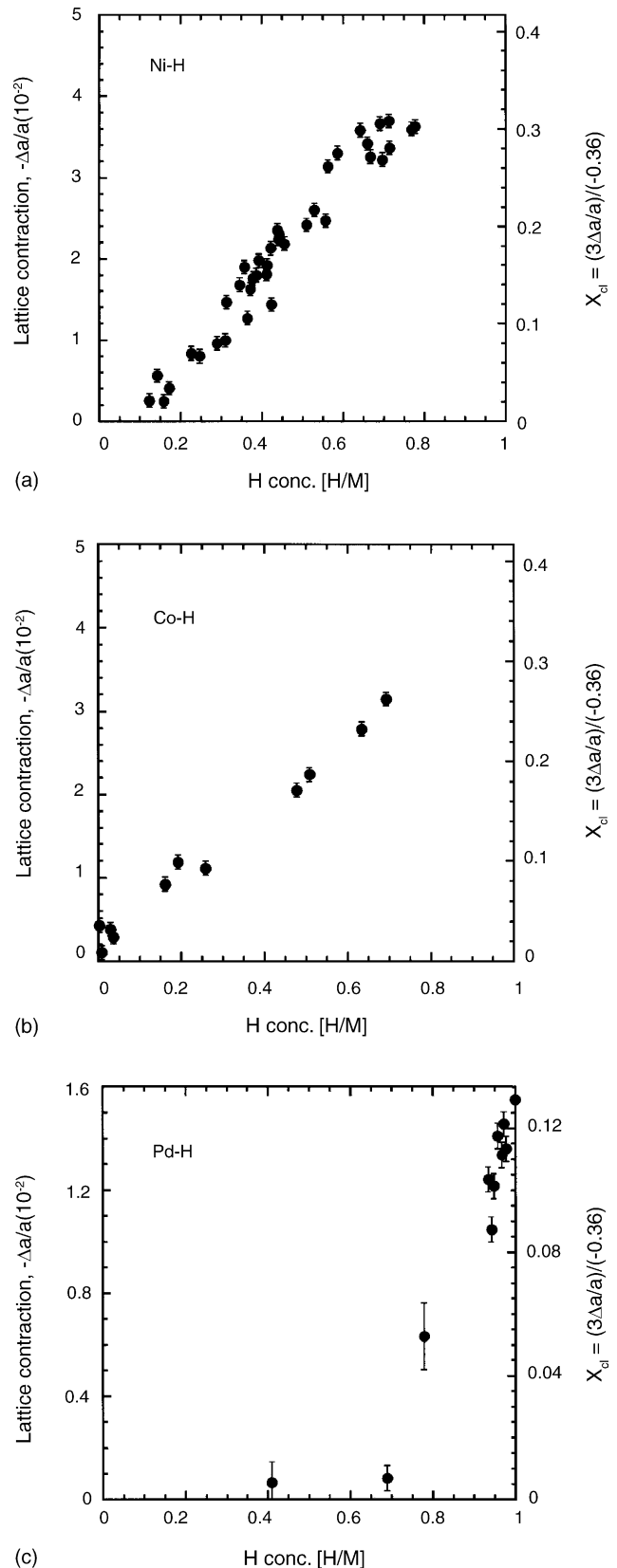

Fig. 3. The lattice contraction of the Ni–H (a), Co–H (b) and Pd–H (c) alloys as a function of H concentration. The Vac-H concentration estimated as $x_{cl} = (3\Delta a/a)/(-0.36)$ is indicated on the right axis.

Pd on the other may be correlated with the magnitude of the formation energy of Vac-H clusters.[2] For Ni, substituting $e_f^v = 1.67$–1.78 eV [13] and $e_b = 0.28$ eV [17] into Eq. (1), we obtain $e_f^{cl} = -0.01$ to 0.10 eV. For Fe, $e_f^v = 2.65$ eV [13] and $e_b = 0.43$ eV [18] lead to $e_f^{cl} = 0.07$ eV. For Co, $e_f^v = 2.18$ eV [13] and $e_b \approx 0.35$ eV give $e_f^{cl} \sim 0.08$ eV. In Pd, on the other hand, substitution of $e_f^v = 1.70$ eV [19] and $e_b = 0.15$ eV [20] into Eq. (1) gives $e_f^{cl} = 0.80$ eV, which is in reasonable agreement with the value deduced from previous experiments $e_f^{cl} = 0.72$ eV [5]). It can be added that the cluster formation energy $e_f^{cl} = 0.30$ eV for Nb is also relatively large, and the observed x_H–x_{cl} relation is consistent with the result for Pd in the sense that the cluster concentration remains very small up to $x_H \sim 0.5$.

These results indicate that the correlation between the x_H–x_{cl} relation and the magnitude of the cluster formation energy is quite general, being valid for both fcc and bcc structures.

A simple physical explanation of the observed x_H–x_{cl} relation is not available at present. It is no surprise that Eq. (2), valid only at low cluster concentrations, fails at high hydrogen and cluster concentrations. At best, it can be applied to the low-concentration region of the Pd–H system and to the Nb–H system. A clue for understanding the high-concentration behavior of the SAV formation is provided by the formation of a vacancy-ordered structure in fcc hydrides (Ni_3VacH_4, Pd_3VacH_4), which is likely to be a $L1_2$-type structure. In practice, superlattice lines manifesting this structure were observed only in few cases [6], probably because the temperature was too high for the ordering of vacancies and/or the concentration of vacancies was too low to stabilize the ordered structure. The SAV formation data shown in Fig. 3a–c indicate that the limiting concentration $x_{cl} = 1/3$ of Vac-H clusters is the concentration characteristic of this ordered structure. The repulsive interaction between vacancies, which gives rise to the vacancy-ordered structure, should be a limiting factor for the maximum vacancy concentration. The origin of this repulsive interaction has not been identified, however.

Recently, Ono and Sugimoto [21] performed a preliminary calculation by the Monte-Carlo method for the case of a large cluster formation energy in the fcc lattice, and succeeded in reproducing the x_H–x_{cl} relation observed for the Pd–H system. It was shown that x_{cl} is nearly zero for $x_H < 0.5$ and increases linearly at $x_H > 0.5$ and reaches $x_{cl} \sim 0.1$ at $x_H = 1$. Qualitatively this is believed to be a combined effect of the configurational entropies of interstitial hydrogen atoms and M-atom vacancies. As their calculation is in progress, it is expected that the physical understanding of the x_H–x_{cl} relation should be attained in the near future.

Finally, one supplementary remark about the analysis of the experimental data. In the present experiment, the sample in contact with fluid H_2 constitutes an open system. Vacancies should be introduced together with H atoms, and in consequence both vacancy and H concentrations will increase with time. We therefore regard the SAV formation process as a process of a gradual approach to the ultimate structure M_3VacH_4, the intermediate state being a fine-scale fluctuating mixture of the original hydride MH_x and a short-range ordered phase $M_{3/4}Vac_{1/4}H$ in the ratio $(1 - \alpha)$: α. Thus, the average composition should be $M_{1-\alpha/4}Vac_{\alpha/4}H_{(1-\alpha)x+\alpha}$. In terms of the Vac-H cluster concentration, this can be rewritten as $MVac_{x_{cl}}H_{(1-3x_{cl})x+4x_{cl}}$, and the concomitant change of the atomic volume as $\Delta v = x_{cl}[v_R^{cl} + (4 - 3x)v_H]$. The significance of this expression can be assessed in the Nb–H alloys. Substituting $v_R^{cl}/\Omega = 0.18 - 1.0 = -0.82$ and $v_H/\Omega = 2.8/20 = 0.14$ [14], we obtain $\Delta v/\Omega = -(0.26 + 0.42x)x_{cl}$, with the proportionality coefficient ranging between -0.26 and -0.47 for $x = 0$–0.5. The average value -0.36 of the coefficient in this range of H concentrations is very close to the average for a vacancy in various metals [13]. Thus, our estimation of the Vac-H concentration from the lattice contraction data proved to be appropriate numerically, although its physical basis was different.

4. Conclusion

In this study the equilibrium concentration of vacancies was estimated from the lattice contraction experiments on Ni, Co and Pd having the fcc structure at $T = 930$–1350 K, $p_H = 2.4$–7.4 GPa. The results show that the Vac-H cluster concentration is determined by H concentration rather than the temperature and hydrogen pressure. We note that a distinctive difference in the x_H–x_{cl} relation for Fe, Co, Ni on the one hand and Pd on the other can be correlated with the magnitude of the formation energy of Vac-H clusters. A physical explanation of the observed x_H–x_{cl} relation is not available at present. As the calculation of the x_H–x_{cl} relation is in progress, it is expected that the physical understanding of this relation should be attained in the near future.

Note added in proof

A tentative interpretation of the x_H–x_{cl} relation (Fig. 3) has since been re-examined, and a fairly complete understanding of the overall feature has been attained [22].

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[2] In the paucity of reliable experimental data, here we adopt calculated values of the vacancy formation energy [13]. For the binding energy, the value for Fe is determined in the bcc phase, and the one for Co is approximated by the average for Fe and Ni.

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