

Hydrogen Permeation Characteristics of Vanadium-Nickel Alloys

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Hydrogen permeation characteristics of palladium-plated vanadium and vanadium-nickel alloy membranes have been investigated using gas permeation technique in the temperature range 423–673 K and in the hydrogen pressure range 1×10^4 – 3×10^5 Pa. Hydrogen solubilities of vanadium-nickel alloys have been determined using a volumetric method in the temperature range 473–673 K and in the hydrogen pressure range 1×10^2 – 3×10^6 Pa. The vanadium membranes shows a typical hydrogen embrittlement; cracking occurred during a hydrogen permeation at 473 K under an upstream hydrogen pressure of 1×10^4 Pa. The membranes of V-10 at% Ni and V-15 at% Ni alloys showed six to fifteen times and two to five times as high hydrogen permeabilities as the palladium membranes, respectively. The membranes of these alloys showed much stronger resistance to hydrogen embrittlement than that of the vanadium membrane. The membranes of V-10 at% Ni and V-15 at% Ni alloys did not show cracking during hydrogen permeation at 473 K under upstream hydrogen pressures of up to 6×10^4 Pa and 2×10^5 Pa, respectively. The number of the interstitial sites blocked by one solute nickel atom was estimated to be 1.8 at 673 K and under a hydrogen pressure of 1×10^5 Pa. The strong resistance of the alloys to the hydrogen embrittlement is attributed to the moderate decrease in the hydrogen solubility and the depression of the miscibility gap toward lower temperatures by adding nickel.

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I. Introduction

The vanadium-hydrogen system is one of the most extensively studied systems of all metal-hydrogen systems. Numerous basic investigations on hydrogen behavior and hydrogen-induced property changes in vanadium have been performed.

Through such a variety of investigations, vanadium can be characterized by high hydrogen solubility^{(1)–(3)} and high hydrogen diffusivity^{(4)–(6)}. Vanadium shows the highest diffusivity of all the metals in the temperature range around 300 to 700 K except for iron⁽⁷⁾. As a consequence of the two characteristics, vanadium intrinsically possesses a much higher hydrogen permeability than that in a palladium-silver alloy⁽⁸⁾, which has been commercially used for hydrogen purification.

Nevertheless, vanadium has not been recognized as a possible membrane material for hydrogen purification because of its surface oxidation problem and its hydrogen embrittlement. The first problem can be minimized by coating a palladium overlayer. However the second problem is more serious to use vanadium as a membrane material. Cracking occurs easily in the vanadium membrane at low hydrogen pressures even at temperatures where hydride phase does not exist. So the hydrogen pressure to be applied must be kept low to prevent cracking during permeation, and hence it is difficult to attain a high hydrogen permeation flux in spite of its high hydrogen permeability.

The purpose of the present research is to suppress

the hydrogen embrittlement of vanadium by alloying, and to examine the feasibility of applying vanadium-based alloys to hydrogen purification membranes. In this paper, hydrogen permeation characteristics of vanadium-nickel alloy membranes are demonstrated.

II. Experimental

1. Specimen preparation

As raw materials, 99.9 at% vanadium and 99.95 at% nickel were used. Vanadium, V-10 at% Ni, V-15 at% Ni and V-25 at% Ni alloys were prepared by argon arc-melting. Plates 2 mm thick were sliced from each alloy ingot, and the plates were cold rolled to 1.2 mm in thickness. Then disks 12 mm in diameter and rods $1 \times 1 \times 15$ mm were cut from the plates for hydrogen permeation and solubility measurements, respectively. In order to obtain a homogeneous solid solution, most of the disks and rods were annealed at 1523 K for 14.4 ks in a vacuum of 10^{-4} Pa, subsequently cooled rapidly by argon gas. The disks of V-25 at% Ni alloy were used for an experiment without a heat treatment. Some disks of the V-15 at% Ni alloy were aged at 1273 K for 518 ks to attain complete precipitation of the higher nickel phase.

Electron probe microanalysis (EPMA) was carried out for the alloy specimens and the following results were obtained. The V-25 at% Ni alloy consisted of V_3Ni phase having a composition of $VNi_{0.282}$ and a small amount of σ or σ' phase having a composition range of $VNi_{0.587}$ to $VNi_{0.754}$. Solution treated alloys were confirmed to be homogeneous solid solutions. The aged V-15 at% Ni alloy consisted of a solid solution phase having a composition of $VNi_{0.136}$ and σ or σ' phase having a composi-

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tion of VNi_{0.351}.

2. Hydrogen permeation

(1) Measurement

Each disk was mechanically polished by emery paper and finished by 0.05 μm alumina abrasive. Palladium overlayer was electroplated on both sides of the disk. Scanning electron microscopy (SEM) revealed the thickness of the overlayer to be approximately 0.1 μm.

Hydrogen permeabilities and diffusion coefficients of the specimens were determined in the temperature range 423 to 673 K and in the hydrogen pressure range 1×10^4 to 3×10^5 Pa, using hydrogen gas of seven-nine purity. The steady state hydrogen permeation rate was measured by means of a mass flow meter with the Hastings model ST-10 flow transducer used in the previous work⁽⁹⁾⁽¹⁰⁾. The diffusion coefficient of hydrogen was determined by the time-lag method⁽¹¹⁾. The measurement was carried out in a sequence of decreasing temperature. Before each run, the specimen was fully dehydrogenated and then a baking treatment⁽¹²⁾ was carried out in air at 573 K for 600 s in order to activate the surface of the palladium overlayer.

(2) Theoretical consideration

The steady state hydrogen flux through a single layered membrane can be expressed as follows:

$$J = Q/A = D(C_u - C_d)/L \quad (1)$$

$$J = \Phi(P_u^{1/2} - P_d^{1/2})/L \quad (2)$$

where

J = steady state hydrogen flux (mol of H₂/m²·s)

Q = steady state hydrogen permeation rate (mol of H₂/s)

A = membrane area (m²)

D = diffusion coefficient of hydrogen (m²/s)

L = membrane thickness (m)

Φ = hydrogen permeability (mol of H₂/m·s·Pa^{1/2})

C_u, C_d = hydrogen concentrations at the upstream side and the downstream side, respectively (mol of H₂/m³)

P_u, P_d = hydrogen pressures at the upstream side and the downstream side, respectively (Pa).

Equation (2) holds when the solution of hydrogen obeys the following equation, i.e., the Sieverts' law,

$$C = KP^{1/2} \quad (3)$$

where

K = solution constant (mol of H₂/m³·Pa^{1/2}).

And then, the hydrogen permeability Φ is defined by

$$\Phi = DK. \quad (4)$$

In this study P_d is negligibly small compared with P_u , so that eqs. (1) and (2) can be simplified as follows:

$$J = DC_u/L \quad (5)$$

$$J = \Phi P_u^{1/2}/L. \quad (6)$$

Time-lag t_l , is related to the hydrogen diffusion coefficient as follows,

$$t_l = L^2/6D \quad (7)$$

provided that the initial hydrogen concentration in the membrane is zero, and the hydrogen concentration is kept zero at the downstream surface⁽¹¹⁾.

From the formula of Ash *et al.*⁽¹³⁾, the time-lag for the hydrogen permeation through the metal membrane with an overlayer on both sides is given by

$$t_l = \frac{\frac{L_1^2}{D_1} \cdot \frac{4L_1}{3D_1K_1} + \frac{L_2}{D_2K_2} + \frac{L_2^2}{D_2} \cdot \frac{L_1}{D_1K_1} + \frac{L_2}{6D_2K_2} + \frac{L_1^2L_2K_2}{D_1^2K_1^2}}{\frac{2L_1}{D_1K_1} + \frac{L_2}{D_2K_2}} \quad (8)$$

where subscripts 1 and 2 denote the overlayer and the bulk material, respectively.

From the formula of Barrie *et al.*⁽¹⁴⁾, the appropriate equation for hydrogen permeation through that type of composite membrane is given by

$$\frac{1}{\Phi_T} = \frac{2L_1}{(2L_1 + L_2)D_1K_1} + \frac{L_2}{D_2K_2} \quad (9)$$

where Φ_T is the permeability through the composite membrane.

For the thinnest sample examined in this study $L_2 = 0.565$ mm and $L_1 = 0.1$ μm. The ratio of solution constants (K_1/K_2) is approximately 0.1 in the examined temperature range. Diffusion coefficients obtained by substituting these values, the measured time-lag and the value of D in palladium⁽¹⁵⁾ into eq. (8) agreed with those obtained by eq. (7) within the relative error of 0.5%. In the same way the hydrogen permeabilities obtained by eq. (9) agreed with those obtained by eq. (2) within the relative error of 0.2%. Thus, the palladium overlayer functions just to prevent the membrane from oxidation. Consequently eqs. (6) and (7) can be used to determine the permeability and the diffusion coefficient of the alloy membranes, respectively.

3. Hydrogen solubility

Hydrogen absorption isotherms were determined for the V-10 at% Ni and V-15 at% Ni alloys using a conventional Sieverts' type apparatus, in the temperature range 473 to 673 K and in the pressure range 1×10^2 to 3×10^6 Pa. Specimens were mechanically polished and plated with palladium. Before the measurement, the specimens were activated by three hydriding-dehydriding cycles at 673 K and up to 3×10^6 Pa and then dehydrided at 723 K for 10.8 ks. Pressure was considered to be at equilibrium when no change occurred over 1.2 ks.

III. Results

1. Hydrogen permeation through vanadium

Figure 1 shows the hydrogen permeability in vanadium with palladium overlayer determined in this study together with typical literature data⁽¹⁶⁾⁽¹⁷⁾. Namba *et al.*⁽¹⁸⁾

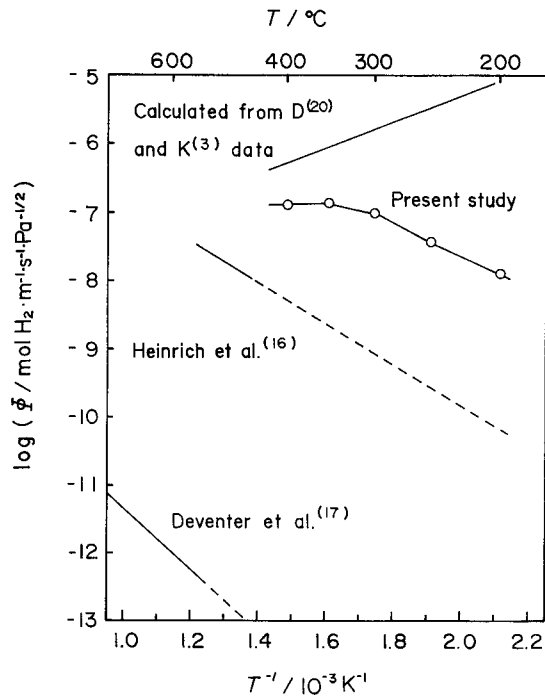


Fig. 1 Temperature dependence of hydrogen permeability in vanadium.

and Katsuta *et al.*⁽¹⁹⁾ have also reported the hydrogen permeability in vanadium. Figure 1 also contains the line obtained by using the data on $D^{(20)}$ and $K^{(3)}$, which is considered to be the ideal hydrogen permeability in vanadium.

The hydrogen permeability in vanadium determined in this study is one or two orders higher than the extrapolated line of Heinrich's data. This result suggests that the surface effect could be significantly reduced by electroplating palladium. However, the problem generally encountered in permeation experiments is its hydrogen embrittlement. During the permeation experiment at 473 K, cracking occurred even under an upstream hydrogen pressure of about 1×10^4 Pa. As is clear from eq. (6), higher hydrogen pressure as well as higher permeability is necessary for attaining higher hydrogen flux. From a practical point of view, a membrane with a stronger resistance to hydrogen embrittlement is required.

In the following, the effects of high nickel alloying to vanadium on hydrogen permeation is discussed.

2. Hydrogen permeation through vanadium-nickel alloys

The effect of palladium overlayer on the hydrogen permeability and diffusivity in the alloy membrane is very small as previously mentioned. However, the general problem in a permeation experiment is the contamination at the surface or at the bulk-overlayer interface. The main reason for the scatter in the reported hydrogen permeabilities in vanadium⁽¹⁶⁾⁻⁽¹⁹⁾ is considered to be the surface contamination.

Figure 2 shows the relations between the square of membrane thickness and the measured time-lag for V-15

at% Ni alloy membranes at 673 K and 573 K. The relations for both temperatures can be described well by the straight lines passing through the origin: the slope of the lines corresponds to $6D$. Figure 2 suggests that the rate determining step in the whole process of the permeation is hydrogen diffusion in bulk alloys.

Figure 3 shows the relations between the product of steady state hydrogen flux and membrane thickness (JL) and the square root of the upstream hydrogen pressure for V-15 at% Ni alloy membranes at 573 K and 448 K. The data points for both temperatures fall quite well on straight lines passing through the origin: the slope of the lines corresponds to Φ . For more precise treatment the value of n in the equation $J = BP^n$, where B is a constant, was determined from plots of $\log J - \log P$. The values of n for 573 and 448 K were 0.51 and 0.43, respectively. The fact that n has the value around 0.5 implies that the solution process of hydrogen obeys the Sieverts' law. The closed circle in Fig. 3 denotes the data at 573 K for a membrane 0.565 mm in thickness. The closed circle falls close to the line for the membrane of 1.814 mm thickness, i.e., the hydrogen permeability has no thickness dependence in the thickness range examined.

Figure 4 shows the temperature dependence of the hydrogen permeability in the membranes of vanadium-nickel alloys and palladium⁽¹⁰⁾. Hydrogen permeability in V-25 at% Ni alloy membrane could not be determined; the membrane showed a lower hydrogen permeation rate than the sensitivity of the mass flow meter (1×10^{-10} mol of H_2/s). On the other hand, the membrane of the solution treated V-10 at% Ni alloy shows hydrogen permeability six to fifteen times as high as palladium membrane. Hydrogen embrittlement was suppressed

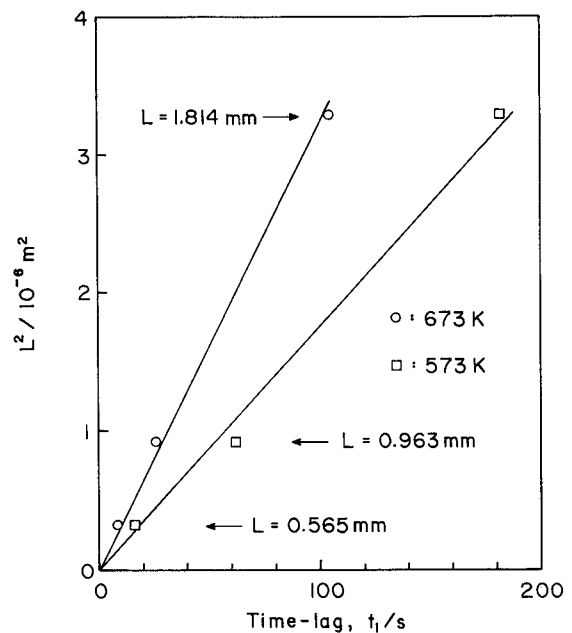


Fig. 2 Relations between the square of the membrane thickness and the measured time-lag for the solution treated V-15 at% Ni alloy membranes at 673 K and 573 K. The slope of the lines corresponds to $6D$.

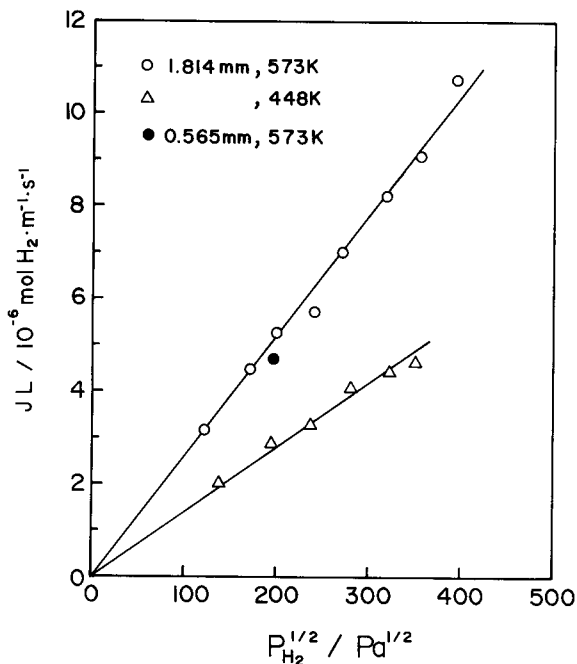


Fig. 3 Relations between the product of the steady state hydrogen flux and the membrane thickness (JL) and the square root of the upstream hydrogen pressure at 573 K and 448 K. The slope of the lines corresponds to Φ .

compared with vanadium: no cracking was observed in the membrane during a hydrogen permeation at 473 K and under an upstream hydrogen pressure up to 6×10^4 Pa. The hydrogen permeability of the solution treated V-15 at% Ni alloy is two to five times as high as that of palladium membrane. It is noteworthy that the membrane of the solution treated V-15 at% Ni showed a strong resistance for cracking. Cracking was not observed during hydrogen permeation even at the upstream hydrogen pressure up to 2×10^5 Pa at 473 K.

The membrane of the aged V-15 at% Ni alloy, which consists of $\text{VNi}_{0.136}$ phase and $\text{VNi}_{0.351}$ phase, shows higher permeability than the membrane of the solution treated alloy. The result for the V-25 at% Ni alloy membrane suggests that the $\text{VNi}_{0.351}$ phase has an extremely low hydrogen permeability. Therefore, the high permeability of the aged alloy membrane is considered to be caused by the $\text{VNi}_{0.136}$ phase. The membrane of the aged V-15 at% Ni alloy, however, showed a weaker resistance to hydrogen embrittlement than the membrane of the solution treated alloy. Cracking occurred at 413 K and under an upstream hydrogen pressure of 1×10^5 Pa.

Figure 5 shows the temperature dependence of hydrogen diffusion coefficients in vanadium-nickel alloys. The

Table 1 Hydrogen diffusion parameters in vanadium-nickel alloys.

	D_0 (m^2/s)	E_D (kJ/mol of H)
V-10Ni	2.3×10^{-7}	20
V-15Ni	1.3×10^{-6}	30
V-15Ni (aged)	8.2×10^{-7}	27

results show the good linearity over the examined temperature range, which can be expressed well by the following equation:

$$D = D_0 \exp(-E_D/RT). \quad (10)$$

Table 1 lists the D_0 and E_D of vanadium-nickel alloys. No reported data are available for high nickel alloyed vanadium. Regarding the other high alloyed vanadium systems, some data are available⁽⁶⁾⁽²¹⁾⁽²²⁾. It should be noted that the diffusion coefficient determined in this study is not the intrinsic (or tracer) diffusion coefficient but the apparent diffusion coefficient. Therefore it seems inappropriate to make a direct comparison between the data listed in Table 1 and the reported data. From Table 1, however, the increase in the activation energy is clearly observed with the increase in the nickel content.

3. Hydrogen solubility of vanadium-nickel alloys

Figures 6 and 7 show the hydrogen pressure-composition isotherms (P-C isotherms) for solution treated V-10 at% Ni alloy and V-15 at% Ni alloy, respectively. The P-C isotherms for both alloys exhibit no plateaux. This suggests these alloys do not form brittle hydride phases over the hydrogen pressure range and temperature range examined, i.e., the miscibility gap (or solvus line) exists at a lower temperature range than examined.

Gahr and Birnbaum⁽²³⁾ found that the stress-induced hydride precipitation and hence the hydrogen embrittlement occurs even at higher temperatures than that of the miscibility gap in niobium-hydrogen system. They also found that niobium-hydrogen alloys exhibit more ductility when the temperature is higher. The same thing is con-

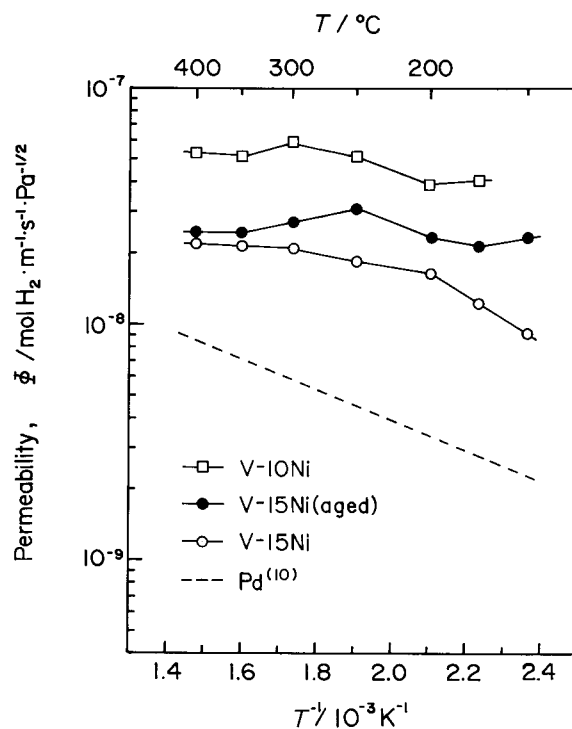


Fig. 4 Temperature dependence of hydrogen permeability in the membranes of vanadium-nickel alloys and palladium⁽¹⁰⁾.

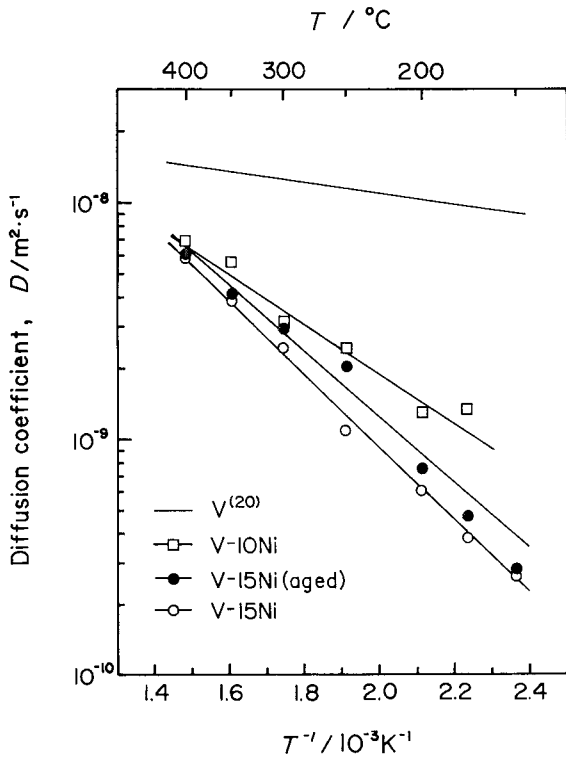


Fig. 5 Temperature dependence of hydrogen diffusion coefficients in vanadium-nickel alloys and vanadium⁽²⁰⁾.

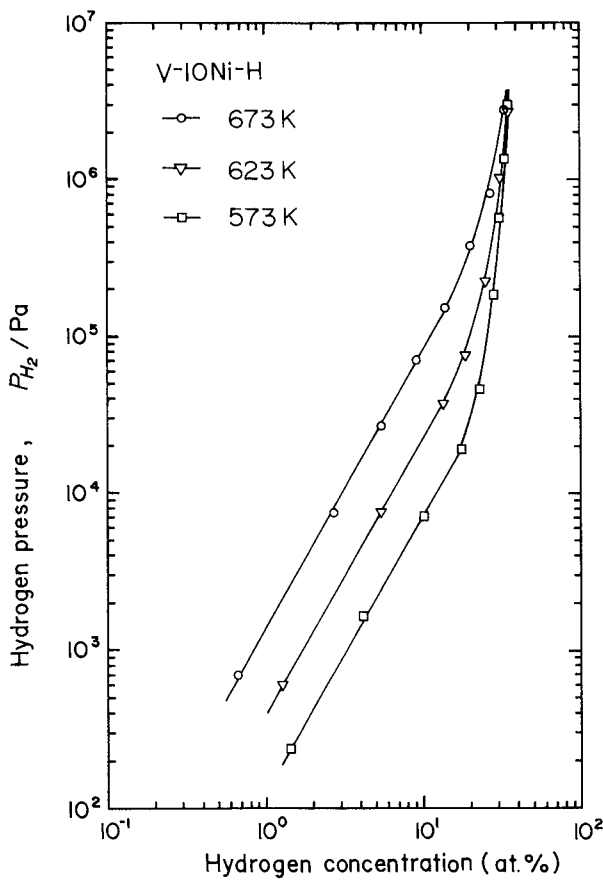


Fig. 6 Hydrogen pressure-composition isotherms for V-10 at% Ni alloy.

considered to hold for vanadium-hydrogen system.

The P-C isotherms for vanadium in the literatures⁽³⁾⁽²⁴⁾ show an inflection point at 473 K in the pressure range 10²-10³ Pa; it is caused by the miscibility gap located in a lower temperature range. On the other hand, as shown in Fig. 7, the P-C isotherms for V-15 at% Ni alloy at 473 K appear to exhibit no inflection point in such a hydrogen pressure range. Comparison of the two P-C isotherms suggests that the miscibility gap is depressed by nickel addition, which is in good agreement with the model proposed by Kirchheim *et al.*⁽²⁵⁾ Saito and Fukai⁽²⁶⁾ showed similar results by alloying iron, chromium, titanium, molybdenum, niobium or zirconium to vanadium. The vanadium-nickel alloy is therefore considered to exhibit a stronger resistance to hydrogen embrittlement than vanadium.

Figure 8 shows the temperature dependence of hydrogen solution constant *K* for vanadium-nickel alloys. Closed marks were obtained directly from the P-C isotherms shown in Figs. 6 and 7. Open marks were calculated from the data shown in Figs. 4 and 5 using eq. (4). Figure 8 also shows the temperature dependence of *K* for vanadium⁽³⁾. The decrease in hydrogen solubility by nickel addition is clearly shown. This is also considered to be an important factor for the improved resistance of vanadium-nickel alloys to cracking during

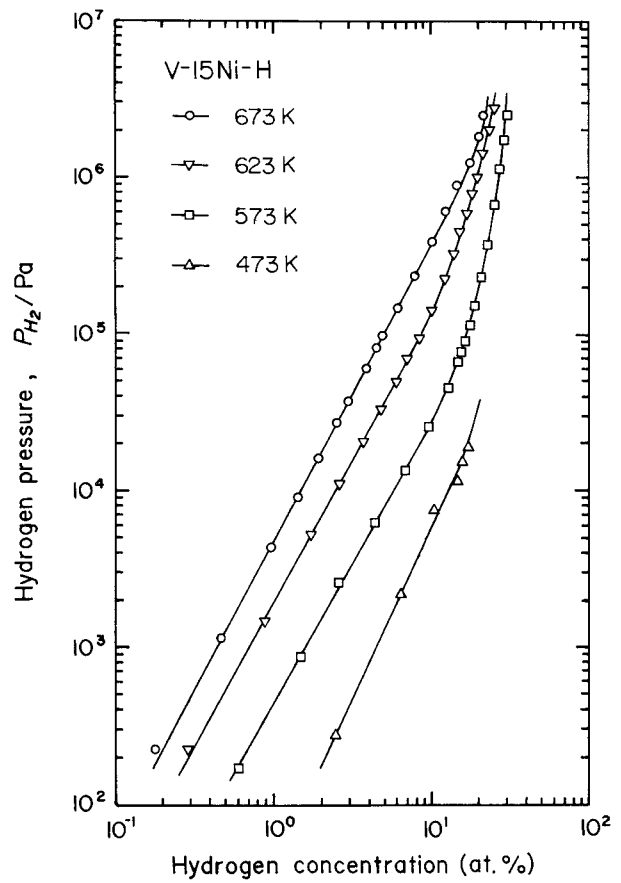


Fig. 7 Hydrogen pressure-composition isotherms for V-15 at% Ni alloy.

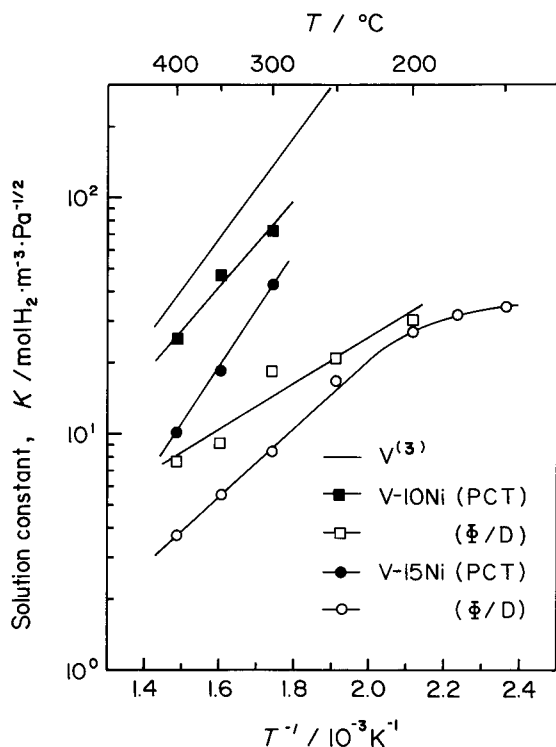


Fig. 8 Temperature dependence of hydrogen solution constants for vanadium-nickel alloys and vanadium⁽³⁾. Closed marks were obtained from P-C isotherms, and open marks were obtained dividing Φ by D .

permeation. Using the data of lattice expansion on hydrogen absorption⁽²⁷⁾, it is estimated that linear expansions on hydrogen absorption are 3.3 and 1.3% for vanadium and V-15 at% Ni alloy, respectively, at 573 K and under a hydrogen pressure of 1×10^5 Pa.

Some difference is observed between the K values determined by two kinds of methods: the K values determined by permeation measurements are in the range 1/10 to 4/10 of those determined by the gas-metal equilibration. The difference suggests that the true equilibrium of hydrogen solution was not established at the upstream interface even after the steady state permeation rate was reached. It will be discussed later.

IV. Discussion

1. Effect of nickel addition on hydrogen solubility and diffusivity

Interaction between substitutional solutes and hydrogen atoms have been investigated extensively in metal-hydrogen systems. In many investigations the interaction was discussed applying the localized trap model to the behavior of the terminal solubility for hydrogen (TSH)⁽²⁸⁾⁻⁽³³⁾. Recently, Shirley and Hall⁽³³⁾ proposed that elastic and electronic interactions both play important roles for hydrogen trapping.

On the other hand, Peterson *et al.*⁽²²⁾⁽³⁴⁾ reported that the evidence for hydrogen trapping could not be observed in studies on the isopiestic solubility of hydrogen

and the hydrogen diffusion in vanadium-based alloys (V-Nb, V-Cr and V-Ti). Their experiment suggests the inadequacy of applying a simple trap model to hydrogen diffusion and to hydrogen solution without formation of hydride. Tanaka and Kimura⁽⁶⁾ reported regarding the hydrogen diffusivity in vanadium-titanium alloys that the localized trap model becomes invalid for the alloys with more than 4 at% Ti. They also found no systematic relations between hydrogen diffusivity and the lattice parameter change on alloying to vanadium. The results of Peterson *et al.*⁽²²⁾⁽³⁴⁾ and Tanaka and Kimura⁽⁶⁾ suggest that the simple localized trap model is inadequate in vanadium-nickel alloys at high nickel concentrations such as 10 and 15 at%.

Table 2 lists the change in hydrogen solubility upon alloying various metals with vanadium. Comparing the hydrogen solubilities (H/M) of vanadium and V-10 at% Ni alloy, it is estimated that the number of the interstitial sites apparently blocked by one nickel atom is 1.8 at 673 K and under a hydrogen pressure of 1×10^5 Pa. As listed in the third column in Table 2, the blocking effect of nickel is smaller than those of cobalt, iron and chromium⁽³⁵⁾. The trend of blocking or trapping by the alloying elements appears in fairly good agreement with the trend of hydrogen solubility for these elements⁽³⁶⁾.

2. Interfacial equilibrium of hydrogen between palladium overlayer and bulk alloys

As shown in Fig. 8, the solubilities determined from Φ and D values were much smaller than those determined by the gas-alloy equilibration. It is in sharp contrast with the quite good agreement of K values for a single palladium membrane reported by Amano *et al.*⁽¹⁰⁾ Recently Tahara *et al.*⁽³⁷⁾ proposed a new boundary condition for the hydrogen permeation through the multi-layered membrane. Their boundary condition was introduced for a non-equilibrium condition, however, the detailed mechanism is not described in their paper.

In bulk alloys, a variety of trap sites such as interstitials⁽³⁸⁾ dislocations, voids and boundaries exist. Oriani⁽³⁹⁾ and Bucur⁽⁴⁰⁾ proposed that the diffusion flux which was measured at the exit side of the membrane had only the contribution from the hydrogen moving freely in normal sites. In that case, if the solubility determined by the gas-alloy equilibration includes a contribution from trap sites, there can be a difference between the two

Table 2 Change in hydrogen solubility (H/M) at 673 K and 10^5 Pa upon adding nickel, cobalt, iron, chromium or titanium to vanadium.

	H/M	$\left(\frac{\partial(H/M)}{\partial N_M}\right)_{T,P}$	Ref.
V	0.306	—	(2)
V-10Ni	0.126	-1.8	present work
V-10Co	0.020*	-2.9	(35)
V-10Fe	0.032*	-2.7	(35)
V-10Cr	0.069*	-2.4	(35)
V-10Ti	0.445*	+1.4	(35)

*: extrapolated from 1000 K.

kinds of solubilities. The solubility difference shown in Fig. 8, however, is too large to be ascribed only to the contribution from the trap sites, i.e., the difference in H/M ratio reaches about 0.2 at 573 K under a hydrogen pressure of 1×10^5 Pa.

Before the palladium overlayer is plated, oxide film formation is unavoidable. However since the rate determining step in the whole permeation process was found to be the diffusion in the bulk alloy, it is obvious that the oxide film has some defects which permit hydrogen atoms or molecules to reach the alloy rapidly. In such a condition, the effective area of the membrane and hence the steady state hydrogen permeation rate, which was determined by a mass flow meter, should be reduced. Therefore the Φ values calculated using the real membrane area should be reduced. The influence of the reduction in the effective area on D values is not clear. However, this influence on D values is considered to be included in the measured Φ values.

Thus, the difference between the K values determined by the two kinds of methods can be qualitatively explained well by reduction in the effective area of the membrane caused by the oxide film. It is, therefore, considered that the alloy membranes have a potential to exhibit still higher hydrogen permeability by improving the palladium coating technique.

V. Conclusion

Alloying a suitable amount of nickel with vanadium was found to suppress the hydrogen embrittlement without substantial decrease in the hydrogen permeability. The optimum nickel concentration was found to be about 15 at%. During a hydrogen permeation at 473 K, the palladium-plated V-15 at% Ni membrane showed five times as high hydrogen permeability as that of palladium, and did not show cracking even under a hydrogen pressure of 2×10^5 Pa. It has been suggested that still higher permeability may be obtained by improving the palladium coating technique. The palladium-plated V-15 at% Ni alloy membrane is one of the promising materials for hydrogen purification.

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