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Analysis of pressure–composition–isotherms for design of non-Pd-based alloy membranes with high hydrogen permeability and strong resistance to hydrogen embrittlement

A. Suzuki [a,1], H. Yukawa [a,*], T. Nambu [b], Y. Matsumoto [c], Y. Murata [a]

[a] Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-Cho, Chikusa-ku, Nagoya 464-8603, Japan
[b] National Institute of Technology, Suzuka College, Shiroko-Cho, Mie 510-0294, Japan
[c] National Institute of Technology, Oita College, Maki, Oita 870-0152, Japan

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ABSTRACT

The hydrogen permeability of Pd–27 mol%Ag alloy membrane has been analyzed in view of the new description of hydrogen permeation based on hydrogen chemical potential. The hydrogen flux is consistently proportional to the PCT factor, f_{PCT}, which reflects the shape of the corresponding pressure–composition–isotherm (PCT curve), regardless of whether hydrogen solubility is expressed in a format of the Sievert's law or not. From the two points of the PCT factor, f_{PCT}, and DBTC (the ductile-to-brittle transition hydrogen concentration), the concept for alloy design of non-Pd-based alloy membranes is obtained. As an example, V–9 mol%Al alloy is designed for applied temperature and pressure condition. For this condition, this alloy membrane possesses excellent hydrogen permeability with strong resistance to hydrogen embrittlement.

1. Introduction

Hydrogen permeable alloy membranes are important key materials for hydrogen separation and purification [1–5]. For example, Pd–Ag or Pd–Cu alloy membrane is widely used practically for these purposes [5]. Recently, there has been a great demand for the development of new hydrogen permeable alloys instead of Pd-based alloys in order to reduce the material cost as well as to improve the hydrogen permeability [6–11]. Nb-based and V-based alloys are promising materials for hydrogen permeable membranes to be substituted for currently used Pd-based alloys. This is because they are less expensive and possess higher hydrogen permeability than currently used Pd-based alloys. However, for such non-Pd-based alloys, a brittle fracture sometimes occurs during the operation at high H_2 pressure gas atmosphere, which impedes the practical use of these alloy membranes [6,12].

Recently, the mechanical properties of niobium (Nb) and vanadium (V) membrane in hydrogen gas atmosphere at high temperature have been investigated by the *in–situ* small punch (SP) test method [13,14]. It is found that a ductile-to-brittle transition occurs drastically at the hydrogen concentration around 0.2–0.25 (H/M) for both Nb and V membranes [13,14]. This critical hydrogen concentration is reffered to as the DBTC (the Ductile-to-Brittle Transition hydrogen Concentration). In order to prevent a brittle fracture of the membrane with group 5 metals such as Nb and V, the hydrogen concentration in the membrane must be controlled and kept below the DBTC, i.e., 0.2 (H/M), during the operation of hydrogen permeation.

On the other hand, the hydrogen diffusion in metal membranes is generally the rate-limiting process of the total reaction of hydrogen permeation through them. Therefore, the following Fick's first law is commonly applied to metal membranes to discuss the property of them.

$$J = -D\frac{dc}{dx}, \tag{1}$$

where J is the hydrogen flux of hydrogen atom, D is the hydrogen diffusion coefficient, and dc/dx is the gradient of the hydrogen concentration across the membrane. In the Fick's law, dc/dx is the driving force for hydrogen diffusion. Eq. (1) is modified as follows and applied to metal membrane with thickness of L.

$$J = D\frac{\Delta c}{L}, \tag{2}$$

where Δc is the difference of hydrogen concentration at feed and permeation sides of the membrane. Combined Eq. (2) with the

* Corresponding author.
E-mail address: hiroshi@nagoya-u.jp (H. Yukawa).
[1] Research Fellow of Japan Society for the Promotion of Science.

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Sieverts' law, $c = K\sqrt{P}$, the hydrogen permeation coefficient, $\phi = D \times K$, is derived and used as a measure to show the hydrogen permeability of metals and alloys, where K is the Sieverts' solubility constant [11]. However, there are many exceptional cases that the experimental results of hydrogen flux through membrane cannot be explained consistently by using the parameter, ϕ. Therefore, it is important to derive a consistent description of hydrogen permeation through metal membrane.

It is known that the hydrogen diffusion is not always driven by the hydrogen concentration gradient, dc/dx. Strictly speaking, the driving force for hydrogen diffusion is the gradient of the hydrogen chemical potential, $d\mu/dx$. Recently, Suzuki et al. have proposed a new description of hydrogen permeation through metal membrane based on hydrogen chemical potential [15]. The diffusion equation based on the chemical potential is expressed as follows [16]:

$$J = -cB\frac{d\mu}{dx}, \tag{3}$$

where B is the mobility of hydrogen atom. Assuming the following three conditions, Eq. (3) can be modified into Eq (4). (i) The hydrogen permeation reaction reaches to the steady state condition, (ii) the equilibrium condition is established between gaseous hydrogen and dissolved hydrogen atom on the top surface of the metal membrane (iii) the mobility, B, is independent of the hydrogen concentration.

$$J = \frac{RTB}{2L}\int_{c_2}^{c_1} c\frac{d\ln(P/P^0)}{dc}dc = \frac{RTB}{2L}f_{\mathbf{PCT}}, \tag{4}$$

where R is the gas constant, T is absolute temperature, L is the membrane thickness, c_1 and c_2 are the hydrogen concentrations at the feed and permeation sides of the membrane, respectively. P is applied hydrogen pressure and P^0 is the standard hydrogen pressure (i.e., 101,325 Pa). The integral term in Eq. (4) is redefined as the PCT factor, f_{PCT}, because it can be determined by analyzing the corresponding pressure–composition–isotherm (PCT curve) of the alloy. The validity of Eq. (4) has been confirmed by various hydrogen permeation tests with pure niobium and Nb-based alloy membranes [15,17]. It is noted that the hydrogen flux, J, is proportional to $1/L$ when the diffusion of hydrogen atom is the rate-limiting process of the total reaction of hydrogen permeation through metal membrane.

In this study, the hydrogen permeability of Pd-based alloys have been analyzed in view of Eq. (4) in order to confirm that the property of hydrogen permeable metal membrane can be understood consistently by Eq. (4). In addition, the concept for the alloy design of non-Pd-based alloy membranes is discussed in view of the PCT curves based on Eq. (4) and it is applied to the design of V–Al alloy as an example.

2. Experimental procedure

2.1. Sample preparation

A plate of Pd–27 mol%Ag alloy with thickness of 49 μm is prepared, and cut into disk with a diameter of about 12 mm. They are annealed in a high purity argon gas atmosphere at 1273 K for 10.8 ks.

On the other hand, V–5 mol%Al, V–9 mol%Al, V–16 mol%Al and V–20 mol%Al alloys are melted by using a tri-arc furnace in a purified argon gas atmosphere. The raw materials used in this study are 99.9 mass% for vanadium and 99.999 mass% for aluminum. According to V–Al equilibrium phase diagram, all these alloys are composed of a single solid solution phase with simple bcc crystal structure.

For hydrogen permeation test, the as-cast ingot of V–9 mol%Al is cut into disk with about 12 mm in diameter and 0.65 mm in thickness by using a wire-cut electrical discharge machine. Both sides of the specimen are mechanically polished by emery papers followed by the polishing with 9 μm and 1 μm diamond slurry. The final thickness, L, of the specimen is 0.541 mm. Subsequently, pure palladium of about 200 nm in thickness is deposited at 573 K on both sides of the sample surfaces by using an RF magnetron sputtering aparatus.

2.2. Pressure–composition–isotherms

The pressure–composition–isotherms (PCT curves) are measured for Pd–27 mol%Ag, V–5 mol%Al, V–9 mol%Al, V–16 mol%Al and V–20 mol%Al alloys by using a Sieverts-type apparatus in order to investigate the hydrogen solubility. A small piece of each sample is set into a cell and activated several times prior to the measurements. The PCT curves are measured at 473 K and 773 K for Pd–27 mol%Ag, and at 773 K for V–5 mol%Al, V–9 mol%Al, V–16 mol%Al and V–20 mol%Al alloys.

2.3. Hydrogen permeation test

The hydrogen permeation tests are performed at 473 K and 773 K by the conventional gas permeation method. The testing conditions of the temperature as well as the feed and permeation hydrogen pressures applied in this study are listed in Table 1. The hydrogen fluxes, J, permeated through the disk samples are measured by monitoring the pressure change of a reserve tank with known volume for Pd–27 mol%Ag alloy membrane, and by using a mass flowmeter for V–9 mol%Al membrane. It is divided by the inverse of the membrane thickness, $1/L$, in order to estimate the normalized hydrogen flux, $J \cdot L$. Under the steady-state diffusion-limiting condition, J is proportional to $1/L$ for each metal or alloy membrane at the same temperature and pressure condition as expressed in Eq. (2) or Eq. (4). Therefore, $J \cdot L$ is independent of the membrane thickness, L, and the hydrogen permeation property of the samples with different thickness can be compared. It is noted here that the atomic hydrogen flux, mol H m^{-1} s^{-1} is evaluated in this study, which is twice as large as the gaseous hydrogen flux, mol H_2 m^{-1} s^{-1}. A detailed explanation of the permeation test is given elsewhere [8].

Table 1
Temperature and pressure conditions of hydrogen permeation tests.

Test no.	Sample	Temperature, T (K)	Hydrogen pressure, P (MPa)	
			Feed	Permeation
1	Pd–27 mol%Ag	773	0.050	0.005
2			0.100	0.010
3			0.260	0.060
4			1.000	0.100
5			1.000	0.010
6		473	0.050	0.005
7			0.100	0.010
8			0.260	0.060
9			1.000	0.100
10			1.000	0.010
11	V–9 mol%Al	773	0.550	0.100