Alloying effects on hydrogen permeability of V without catalytic Pd overlayer

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Abstract

Hydrogen permeability of air-treated V-based alloy membranes without Pd coating have been investigated.

The diffusion-limiting hydrogen permeation reaction takes place even without catalytic Pd overlayer on the surface. It is shown that pure V and its alloy membranes without Pd overlayer possess excellent hydrogen permeability and good durability at high temperature. The new description of hydrogen permeation based on hydrogen chemical potential has been applied and the hydrogen flux is analyzed in terms of the mobility of hydrogen atom and the PCT factor, f_{PCT} .

Keywords: Hydrogen permeable membrane, V-based alloy, Alloying effect, Hydrogen permeability, Air treatment, Hydrogen mobility

1. Introduction

Hydrogen permeable membranes are ones of the most important materials for hydrogen separation and purification technologies [1,2]. Group 5 metals, (vanadium (V), niobium (Nb) and tantalum (Ta)), are promising materials for hydrogen separation membranes, because of their lower cost and higher hydrogen permeability than currently used Pd-based alloys [3]. However, there is still a large barrier to the practical application due to their poor resistance to hydrogen embrittlement.

The hydrogen embrittlement of group 5 metals in hydrogen gas atmosphere at high temperature has been investigated by the *in-situ* small punch (SP) test method [4]. It is found that the ductile-to-brittle transition occurs drastically at the hydrogen concentration around 0.20 (H/M). Following these results, we have proposed a concept for alloy design and method to prevent the hydrogen embrittlement of group 5 metal-based hydrogen permeable membranes, while keeping high hydrogen flux through them [5-7].

On the other hand, it is well known that group 5 metals are oxidizable easily and its membrane surface is generally covered with their oxides, which is believed to have poor catalytic activity for hydrogen [8]. Therefore, for such non Pd-based alloy membranes, the catalytic Pd overlayers on the surface are considered to be essential to obtain practical hydrogen flux through them [9]. However, another problem arises when such Pd-coated composite membranes are used at high temperature, *i.e.*, a significant degradation of hydrogen permeability occurs within a short time due to the interdiffusion of base metal and palladium to form the intermetallic compound such as Pd₃Nb [10].

Recently, we have found a novel phenomenon that the surface-oxidized pure V membrane without Pd overlayer exhibits excellent hydrogen permeability at high temperature [11].

In this study, the hydrogen permeability of surface-oxidized pure V and V-based alloys are examined in order to investigate the alloying effects on the hydrogen permeability without Pd overlayer at high temperature.

2. Experimental

2.1 Sample preparation

A pure vanadium sheet with the thickness of about 96 and 203 μm (99.9 mass%, Taiyo Koko Co., Ltd.) is cut into disks with 12 mm in diameter. V-5mol%W, V-xmol%Cr ($x=4, 8$), V-y mol%Mo ($y=5, 10$) alloys are melted by using a tri-arc furnace in a purified argon gas atmosphere. The purity of the raw materials used in this study is 99.9 mass% for V (Taiyo Koko Co., Ltd.), 99.8 mass% for Cr (Tosoh Co., Ltd.) and 99.95 mass% for W and Mo (Rare Metallic Co., Ltd.). According to the V-W, V-Cr and V-Mo equilibrium binary phase diagrams, all these alloys are composed of a single bcc solid solution phase.

The as-cast ingots are cut into disks with about 12mm in diameter and 0.65mm in thickness by using a wire-cut electrical discharge machine. Both sides of the specimens are mechanically polished by alumina abrasive papers followed by the final polishing with 0.3 μm Al_2O_3 powders. The final thickness, L , of the specimens is approximately 0.4~0.5mm.

In addition, Pd-coated pure vanadium disk sample is prepared for comparison. Pure palladium of about

200 nm in thickness is deposited at 573 K under 1 Pa of pure argon gas atmosphere on both sides of the sample surfaces by using an RF magnetron sputtering apparatus.

2.2 Air treatment

Prior to the hydrogen permeation test, the oxidization and activation treatment are applied for each sample without Pd overlayer at high temperature. First, the disk sample is set into the hydrogen permeation apparatus. Subsequently, the sample cell is evacuated with turbo molecular pump (TMP). Then, it is heated up to 823 K under high vacuum condition. The oxidization treatment is performed by just breaking the vacuum to leak the ambient pressure of air into the system. The sample cell is evacuated again after about 2-minute interval. Subsequently, the sample cell is filled with about 0.4 MPa of G1-grade high purity (99.99999%) hydrogen gas for about one minute and evacuated. This activation process is repeated once again. The above oxidization and activation treatments are called “air treatment”.

2.3 Hydrogen permeation test

The hydrogen permeation tests are performed at 823 K. After the air treatment, G1-grade high purity hydrogen gas is introduced into both inlet (i.e., feed stream) and outlet (i.e., permeation) sides of the disk sample. The inlet and outlet hydrogen pressures applied in this study are listed in Table 1. Here, the inlet pressures are determined so that the hydrogen concentration at 823 K does not exceed the critical value of the ductile-to-brittle transition hydrogen concentration (DBTC, *i.e.*, 0.2(H/M)) [4]. For this purpose, the pressure–

composition-isotherms (PCT) are measured at 673~773 K by using a Sieverts-type apparatus. From the van't Hoff relation of the PCT curves of each alloy at 673~773 K, the PCT curve at 823 K is estimated and the results are shown in Fig. 1. The outlet pressure is fixed to be 0.2 MPa. The hydrogen fluxes, J , permeated through the disk samples with a unit area within a unit time are measured by the conventional gas permeation method using a mass flowmeter. It is noted that the atomic hydrogen flux, $\text{mol H m}^{-2} \text{s}^{-1}$, is evaluated in this paper, which is twice as large as the gaseous hydrogen flux, $\text{mol H}_2 \text{m}^{-2} \text{s}^{-1}$. A detailed explanation of the permeation test is given elsewhere [12].

2.4 XRD analysis of sample surface

In order to investigate the evolution of surface structure during the air-treatment, the X-ray diffraction experiments are performed for the samples after the oxidization and activation treatments using a Rigaku Ulutima IV diffractometer equipped with a Cu target.

Pure V membrane with about 200 μm in thickness is prepared. As an oxidization treatment, the sample is heat treated at 823K for 3.6 ks (1 hour) in an ambient pressure of air. On the other hand, as an activation treatment, the oxidized sample is heat treated at 823K for 3.6ks under 0.4MPa of G1-grade high purity hydrogen atmosphere.

The XRD analyses are also performed to investigate the structure of the inlet and outlet surfaces of the pure V membrane after the hydrogen permeation test.

3. Results and discussion

3.1 Hydrogen permeability of Pd-coated V membrane at high temperature

Generally, the hydrogen permeation coefficient, ϕ , is used to discuss the hydrogen permeation ability of metal membrane, which is the product of Fick's hydrogen diffusion coefficient, D , and the Sievelts' solubility constant, K . However, for group 5 metals and their alloys, the Sievelts' law is applicable only at very low hydrogen pressures and no longer valid at the ordinary condition of hydrogen permeation [13,14]. In such cases, hydrogen permeation coefficient, ϕ , should not be used as a measure of hydrogen permeability [13]. Therefore, in this study, the hydrogen flux itself is discussed because the amount of hydrogen permeated through the membrane with a unit area within a unit time is the most important factor for industrial application. The hydrogen flux, J , is divided by the inverse of the membrane thickness, $1/L$, in order to evaluate the normalized hydrogen flux, $J \cdot L$.

Figure 2 shows the time dependence of normalized hydrogen flux for Pd-coated pure V membrane with the thickness of 203 μm measured at 823 K under the pressure condition of inlet / outlet = 0.4 / 0.2 MPa. The initial flux is as high as about $50 \times 10^{-6} \text{ mol H m}^{-1} \text{ s}^{-1}$, but it decreases drastically within a short time. For example, the hydrogen flux becomes almost zero only after about half an hour. This degradation of hydrogen permeability is mainly due to the interdiffusion between base metal (*i.e.*, vanadium) and palladium to form intermetallic compound at the interface [10].

3.2 Hydrogen permeability of V-based alloys without Pd overlayer

The hydrogen permeation tests are performed for pure V and V-based alloy membranes without Pd overlayer. It is found that high hydrogen flux is detected immediately after starting the hydrogen permeation test by applying the pressure difference. Figure 3 shows the correlation between the hydrogen flux, J , and the inverse of the membrane thickness, $1/L$, for air-treated pure V without Pd overlayer. As shown in Fig. 3, there is a linear relationship between J and $1/L$. The line shown in Fig. 3 crosses at the origin indicating that the diffusion-limiting hydrogen permeation reaction takes place even without catalytic Pd overlayer on the surface.

Figure 4 shows the time dependences of the normalized hydrogen flux, $J \cdot L$, for pure V and V-based alloys. The hydrogen flux slightly increases during the first two hours especially for V-5mol%Mo and V-8mol%Cr alloys, although the reason remains unclear. As shown in Fig. 4, excellent hydrogen fluxes are observed for all the samples even without Pd overlayer. For example, the hydrogen flux for pure V membrane is about 70×10^{-6} mol H m⁻¹ s⁻¹, which is about 8 times higher hydrogen flux than practical Pd-25Ag alloy [15] with the same pressure condition. Also, V-based alloys exhibit about 1.5~1.7 times higher hydrogen flux than pure V. Thus, the alloying with Cr, Mo and W enhances the hydrogen flux obtained, although the pressure conditions for each alloy are different from that for pure V. For instance, the hydrogen flux for V-10Mo alloy with the pressure conditions of (inlet/outlet) = (0.95 MPa/0.2 MPa) is about 120×10^{-6} mol H m⁻¹ s⁻¹, which is about 5 times higher hydrogen permeability than Pd-25Ag alloy with the same pressure conditions.

Here, the relative magnitude of the hydrogen permeability compared with Pd-based alloy under the same pressure condition decreases by alloying. However, it is important to note that taking into account the

ductile-to-brittle transition of vanadium, the higher hydrogen pressure is applicable to the alloy membrane which leads to enhance the hydrogen flux.

The hydrogen flux changes depending on the alloy composition and they are classified roughly into three groups, *i.e.*, about $70 \times 10^{-6} \text{ mol H m}^{-1} \text{ s}^{-1}$ for pure V, about $100 \times 10^{-6} \text{ mol H m}^{-1} \text{ s}^{-1}$ for V-4Cr, V-5Mo, V-5W and about $120 \times 10^{-6} \text{ mol H m}^{-1} \text{ s}^{-1}$ for V-8Cr and V-10Mo.

In addition, the hydrogen flux is stable and nearly constant at least for more than 8 hours. Recalling that the Pd-coated V membrane degrades drastically within a short time, the air-treated pure V and its alloy membranes without Pd overlayer exhibit good durability at high temperature.

3.3 Evolution of surface structure during air treatment and hydrogen permeation

Figure 5 shows the XRD profiles for (a) as-received (b) oxidized at 823K for 3.6ks in air and (c) activated the oxidized sample at 823K for 3.6ks in 0.4MPa of high purity hydrogen atmosphere. For as received sample, only bcc V peaks are observed. After oxidization treatment, peaks mainly indexed as V_2O_5 appear. Some peaks for VO_2 are also observed.

After the activation treatment, the peaks for V_2O_5 and VO_2 disappear, and instead the peaks for V_2O_3 are observed. Thus, it is considered the surface of the sample is covered with V_2O_3 oxide after air treatment. The unknown peaks near the left side of bcc V may be V with hydrogen solid solution.

Figure 6 shows the XRD profiles of both inlet and outlet sides of the sample after hydrogen permeation test. As shown in Fig. 6(a), the peaks for V_2O_3 are almost dissipated at the outlet side, meaning that the V_2O_3 is

reduced into metallic V. Ultra-high purity hydrogen with active atomic form (hydrogen radical) is introduced through the membrane to the outlet side of the membrane surface during the hydrogen permeation, which may reduce the V_2O_3 oxide.

On the contrary, as shown in Fig. 6(b), the V_2O_3 oxide is still observed at the inlet side. According to the Ellingham diagram of vanadium oxide, the V_2O_3 is the stable phase at 823K even in the G1-grade high purity hydrogen atmosphere. The catalytic activity of vanadium oxides have been investigated extensively. The compounds with good catalytic properties are all found to have V in an oxidization state between 5^+ and 4^+ [16]. Therefore, it is understood that the crystalline V_2O_5 has the catalytic activity, but V_2O_3 does not have. The controlled oxidization and subsequent reduction process in hydrogen may create novel structure with catalytic properties. Further investigations on the surface oxide layer is now underway including cross section TEM observation, EELS spectrum analysis and XPS analysis.

3.4 Analysis of hydrogen permeability in view of hydrogen chemical potential

Recently, Suzuki *et al.* [13] have proposed a new description of the hydrogen permeation through metal membrane according to the diffusion equation based on the hydrogen chemical potential. The hydrogen flux, J , is described as a function of hydrogen concentration, c , and pressure, P , as follows,

$$J = \frac{RTB}{2L} \int_{c_2}^{c_1} c \frac{d \ln(P/P^0)}{dc} dc, \quad (1)$$

where L is the membrane thickness, R is gas constant, B is the mobility of hydrogen atom, T is absolute temperature and P^0 is standard hydrogen pressure (101325 Pa). c_1 and c_2 are hydrogen concentration at the

inlet and outlet sides of the membrane, respectively. Here, the term “ $d \ln(P/P^0)/dc$ ” reflects the shape of the pressure-composition-isotherm (PCT curve), meaning that the hydrogen flux, J , is linked with the shape of the PCT curve of the material. The integral term in Eq. (1) is defined as the PCT factor, f_{PCT} , because it is determined by the corresponding PCT curve. Then and Eq. (1) is simply expressed as follows.

$$J = \frac{RTB}{2L} f_{PCT} \quad (2)$$

The hydrogen fluxes shown in Fig. 4 are analyzed in view of the new description of hydrogen permeation based on hydrogen chemical potential. The PCT factor in Eq. (2) for each sample under each testing condition is estimated using the corresponding PCT curve at 823 K shown in Fig. 1 by applying the pressure condition shown in Table 1.

Then, the mobility of hydrogen atom, B , at 823 K is estimated from the relationship between the hydrogen flux, $J \cdot L$, and the PCT factor for each sample. Figure 7 shows the mobility of hydrogen atom for pure V and V-based alloys at 823 K. As shown in Fig. 7, the mobility of hydrogen atom for each sample is about 1.5×10^{-12} mol H m² s⁻¹ J⁻¹ and less changed by alloying, meaning that the diffusivity of hydrogen in vanadium is less sensitive with alloying elements at 823K studied in this paper.

Figure 8 shows the PCT factor for each sample estimated at 823 K under each testing condition. As shown in Fig. 8, the PCT factor increases by the addition of Cr, Mo and W. This is because the gradient of the PCT curve, *i.e.*, the term “ $d \ln(P/P^0)/dc$ ” in Eq. (1), increases by alloying Cr, Mo and W, as shown in Fig. 1. Similarly, as shown in Fig. 1, the PCT curve further shifts towards left and upper side with increasing the amount of alloying element, resulting in the further increment of the PCT factor. As shown in Fig. 8, the PCT

factor is roughly classified into three groups, the same trend of classification for the hydrogen flux is found as shown in Fig. 4.

As mentioned above, the mobility of hydrogen is nearly constant among the alloys at 823K tested in this study. Thus, following Eq. (2), the PCT factor is dominant to express the hydrogen flux, meaning that the alloying effects on the hydrogen solubility are important. In other words, the shape of the PCT curve is for high hydrogen permeability. The inlet and outlet pressure conditions applied to the membrane is also important to obtain high PCT factor, so high hydrogen flux. Further investigation about the temperature dependence on the mobility of hydrogen will be needed for the understanding of hydrogen permeability through V-based alloy membranes.

4. Summary

The hydrogen permeability of air-treated V-based alloy membrane without Pd overlayer have been investigated at high temperature. It is found that the diffusion-limiting hydrogen permeation reaction takes place through the air-treated pure V membranes even without catalytic Pd overlayer. It is shown that the pure V and its alloy membranes without Pd overlayer possess excellent hydrogen permeability. They also exhibit good durability at 823 K.

The mobility of hydrogen atom at 823 K is estimated according to the new description of hydrogen permeation based on hydrogen chemical potential. It is found that the mobility of hydrogen atom is nearly constant for all the alloys at 823K tested in this study, meaning that the diffusivity of hydrogen in vanadium is

less sensitive with alloying elements, Cr, W and Mo. On the other hand, the hydrogen flux correlates well with the PCT factor, f_{PCT} .

Taking into account the ductile-to-brittle transition of vanadium, the applicable limit of hydrogen pressure increases by alloying with Cr, Mo and W. As a result, the pressure condition with high PCT factor can be applied to the alloy membrane, which leads to enhance the hydrogen flux.

The analysis of hydrogen flux in view of the new description of hydrogen permeation based on hydrogen chemical potential is useful for understanding the hydrogen permeability of metal membrane.

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Fig. 1 PCT curves for pure V and V-based alloys at 823K estimated from those at 673~773 K.

Fig. 2 Time dependence of the normalized hydrogen flux, $J \cdot L$, for Pd-coated pure V membrane measured at 823K.

Fig. 3 Correlation between hydrogen flux, J , and the inverse of the membrane thickness, $1/L$.

Fig. 4 Time dependences of the hydrogen flux for pure V and V-based alloys measured at 823K. The hydrogen flux for Pd-25Ag alloy [15] at 823 K is also presented for comparison. The inlet and outlet hydrogen pressures are indicated in the parenthesis as (inlet/outlet (MPa)).

Fig. 5 XRD profiles for (a) as-received (b) oxidized at 823K for 3.6ks in air (c) activated the oxidized sample at 823K for 3.6ks in 0.4MPa of high purity hydrogen atmosphere.

Fig. 6 XRD profiles of (a) outlet and (b) inlet sides of the sample after hydrogen permeation test.

Fig. 7 The mobility of hydrogen atom for pure V and V-based alloys at 823 K.

Fig. 8 PCT factors for pure V and V-based alloys.

Table.1 Test conditions of the hydrogen permeation.

Sample	Temperature [K]	Inlet pressure [MPa]	Outlet pressure [MPa]
pure V	823	0.4	0.2
V-5W		0.6	
V-4Cr		0.6	
V-8Cr		0.9	
V-5Mo		0.6	
V-10Mo		0.95	