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V–W alloy membranes for hydrogen purification

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ABSTRACT

The alloying effects of tungsten on the hydrogen solubility and the hydrogen permeability are investigated for V-based hydrogen permeable membranes. The hydrogen solubility is found to decrease by the addition of tungsten into vanadium or by increasing the temperature. It is shown that the ductile fracture occurs for V–5 mol%W alloy even in the hydrogen pressures of 0.3 MPa at 773 K. It is also found that the mechanical properties (i.e., strength and ductility) of V-based alloy are better than that of Nb-based alloy in hydrogen atmosphere at high temperature. It is demonstrated that the V–5 mol%W alloy possess excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions, i.e., temperature and hydrogen pressures.

1. Introduction

Mass production of high purity hydrogen gas is necessary for the future clean energy systems. Hydrogen permeable membranes are important materials for hydrogen separation and purification technologies [1,2]. For example, Pd-based alloys (e.g., Pd–Ag alloy) are widely used practically for these purposes. Recently, there has been a great demand for the development of new hydrogen permeable alloys in order to reduce the material cost as well as to improve the hydrogen permeability. Nb-based and V-based alloys are ones of the most promising materials for hydrogen permeable membranes because of their lower cost and higher hydrogen permeability than currently used Pd-based alloys [3–6]. However, there is still a large barrier to the practical application due to their poor resistance to hydrogen embrittlement.

Recently, the mechanical properties of niobium in hydrogen gas atmosphere at high temperature have been investigated by the *in situ* small punch (SP) test method [7]. It was found that the ductile-to-brittle transition occurs drastically at the hydrogen concentration around H/M = 0.25 at the temperature range between 573 and 773 K. This fact suggests that the resistance to hydrogen embrittlement of niobium will be improved by keeping the hydrogen concentration below this critical value during the practical hydrogen permeation.

On the other hand, in view of the hydrogen chemical potential in metals, the hydrogen flux, J, through the membrane with a thickness of d can be expressed as,

$$J = -cB\frac{\Delta\mu}{d}, \tag{1}$$

where c is the hydrogen concentration, B is the mobility and $\Delta\mu$ is the difference of hydrogen chemical potential between the inlet and outlet sides of the membrane. Assuming that the equilibrium conditions are achieved at both inlet and outlet sides of the membrane with the hydrogen pressures of P_{inlet} and P_{outlet}, the difference of hydrogen chemical potential, $\Delta\mu$, can be expressed as follows [8].

$$\Delta\mu = \frac{1}{2}RT\,\ln\left(\frac{P_{\text{inlet}}}{P_{\text{outlet}}}\right) \tag{2}$$

High hydrogen permeability will be expected when the parameter $c \times \Delta\mu$ is large for the designed alloy membrane at a given hydrogen permeation conditions, i.e., hydrogen pressures [8].

From these results, we have proposed a concept for alloy design of Nb-based hydrogen permeable membranes [8,9]. Following this concept, Nb-based alloys with high hydrogen permeability and strong resistance to hydrogen embrittlement have been designed and developed. For example, designed Nb–5 mol%W alloy tested at 773 K under the pressures condition of inlet/outlet = 0.05/0.01 MPa possesses more than 4 times higher hydrogen permeability than Pd-26mol%Ag alloy tested at the same temperature under the pres-

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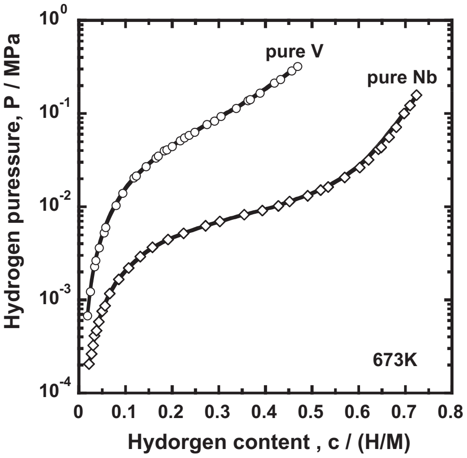

Fig. 1. PCT curves for pure Nb and pure V at 673 K [11].

sure condition of inlet/outlet = 0.26/0.06 MPa, without showing any hydrogen embrittlement [10].

According to the concept for alloy design, it is necessary to reduce the dissolved hydrogen concentration below the DBTC (Ductile-to-Brittle Transition hydrogen Concentration) in order to improve the resistance to hydrogen embrittlement. For this purpose, the heat of hydrogen dissolution into metals should be reduced. In other words, the pressure–composition–isotherms (PCT) curve should be controlled and shifted toward left and upper side in some ways.

Fig. 1 shows the PCT curves for pure niobium and pure vanadium at 673 K reported by Veleckis and Edwards [11]. As shown in this figure, the PCT curve for pure vanadium is located at left and upper side of that for pure niobium. Thus, following to the concept for alloy design, it is expected that V-based alloys possess stronger resistance to hydrogen embrittlement than Nb-based alloys.

In this study, the concept for alloy design is further applied to V-based alloys. The alloying effects of tungsten on the hydrogen solubility, the resistance to hydrogen embrittlement and the hydrogen permeability are investigated for V-based alloy in a fundamental manner.

2. Experimental procedure

2.1. Sample preparation

V–5 mol%W alloy is prepared by using a tri-arc furnace in a purified argon gas atmosphere. Here, tungsten (W) is selected as an alloying element in this study because tungsten has less affinity for hydrogen than vanadium. Therefore, the hydrogen concentration is expected to be reduced by the addition of tungsten into vanadium. In addition, V–W is the continuous solid solution system so that the alloy is composed of single solid solution phase with simple bcc crystal structure. The purity of the raw materials used in this study is 99.95 mass% for both vanadium and tungsten.

2.2. *In situ* small punch (SP) test

The mechanical properties of the plate-shaped specimens are evaluated by the *in situ* small punch (SP) test method using a special setup of the SP apparatus equipped with a gas flow system. Here, the SP testing technique is well known as an effective evaluation method to estimate the DBTT (Ductile-to-Brittle Transition Temperature) [12–14]. Specimens of about 10 mm × 10 mm with the thickness of about 0.65 mm are prepared for pure vanadium and V–5 mol%W alloy. Both sides of the specimens are mechanically polished by alumina abrasive papers followed by the final polishing. The thickness of the specimen is reduced to 0.50 ± 0.01 mm by the final polishing with 0.3 μm alumina powders. 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 apparatus. This palladium layer on the surfaces protects the sample from the oxidation. It also acts as catalyst for hydrogen dissociation reaction and subsequent dissolution into metal to take place smoothly.

The load–deflection curves are measured by the *in situ* SP tests conducted with the loading rate of $v = 8.3 \times 10^{-3}$ mm/s. The SP absorption energy is estimated by taking the area under each load–deflection curve until the specimen fails. The detailed explanation of the *in situ* SP test is found in elsewhere [7].

2.3. Hydrogen pressure–composition–isotherm (PCT) measurement

The pressure–composition–isotherms are measured by using a Sieverts-type apparatus in order to investigate the hydrogen solubility for V–5 mol%W alloy. A small piece of the sample is set into the PCT apparatus and then evacuated. Subsequently, it is heated up to 773 K. Then, about 5 MPa of hydrogen is introduced and cooled down to room temperature. This process is repeated several times prior to the measurement in order to activate the sample surface for hydrogen absorption and desorption reactions to take place smoothly without palladium coating. The PCT curves are measured at 673–773 K up to about 5 MPa.

2.4. Hydrogen permeation test

The hydrogen permeation tests are performed at 773 K by the conventional differential gas pressure method in order to evaluate the hydrogen permeability. Disk specimens of about Ø 12 mm in diameter with a thickness of 0.5 mm are prepared for V–5 mol%W alloy. They are polished mechanically and coated with pure palladium by the same procedure mentioned above. For comparison, a sample of Pd–26 mol%Ag alloy is also prepared.

The disk sample is set to the hydrogen permeation apparatus and then evacuated. Subsequently, it is heated up to 773 K, and then a high purity hydrogen gas is introduced to both sides of the specimen. The testing conditions of the inlet and outlet hydrogen pressures applied in this study are listed in Table 1. The inlet and outlet hydrogen pressures are controlled within the accuracy of ±0.1 kPa. The hydrogen fluxes, *J*, permeated through the disk samples are measured by using mass flow meter or by monitoring the pressure change of the reserve tank with known volume. A detailed explanation of the permeation test is given elsewhere [15].

After the hydrogen permeation test, the sample condition (i.e., gas leak due to cracking) is checked by applying helium gas pressure. Finally, the sample is evacuated and then cooled down to room temperature to take out the sample from the apparatus in order to check the damage of the sample due to hydrogen embrittlement.

3. Results and discussion

3.1. Ductile-to-brittle transition hydrogen concentration for pure vanadium

The *in situ* SP tests are conducted for pure vanadium at 623 or 673 K under several hydrogen pressure conditions. The SP absorption energy, E_{SP}, is estimated from each load–deflection curve, and the results are summarized in Fig. 2 as a function of dissolved hydrogen concentration, *C* (H/M). Here, the hydrogen concentration for each testing condition is estimated from the PCT curves for pure vanadium at 623 or 673 K reported by Veleckis and Edwards [11]. As shown in Fig. 2, the SP absorption energy for pure vanadium is very large when a small amount of hydrogen dissolves in it, indicating that a ductile fracture takes place in this condition. The value of E_{SP} decreases drastically with increasing dissolved hydrogen concentration. From these results, it is found that the DBTC for pure vanadium exists at around H/M = 0.22.

This fact suggests that the resistance to hydrogen embrittlement of vanadium will be improved by keeping the hydrogen concentration below the DBTC, i.e., H/M = 0.22, during the practical hydrogen permeation.

Table 1
Pressure conditions of the hydrogen permeation tests.

Sample	Hydrogen pressure, *P* (MPa)	
	Inlet	Outlet
V–5 mol%W	0.30 0.20 0.15	0.01
Pd–26 mol%Ag	0.26	0.06

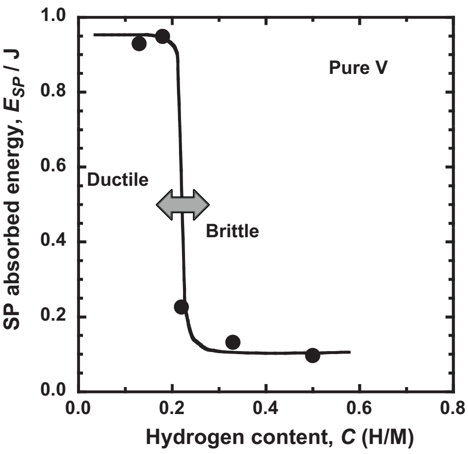

Fig. 2. Correlation between SP absorption energy and dissolved hydrogen concentration in pure vanadium.

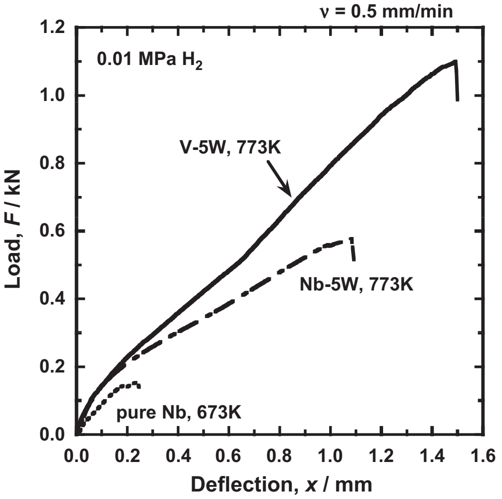

Fig. 4. Load–deflection curves for V–5 mol%W and Nb-5 mol%W alloys measured at 773 K in hydrogen atmosphere. The curve for pure Nb measured at 673 K is also drawn in the figure for comparison.

3.2. Alloying effects on the hydrogen solubility

The alloying effects on the hydriding properties for vanadium are investigated by measuring the pressure–composition–isotherms curves for V-based alloy. The PCT curves measured at 673–773 K for V–5 mol%W alloy are shown in Fig. 3. For comparison, the PCT curve for pure vanadium at 673 K reported by Veleckis and Edwards [11] is also drawn in the figure. As shown in Fig. 3, the PCT curve shifts by the addition of 5 mol%W into vanadium. As a result, the dissolved hydrogen concentration decreases at a same hydrogen pressure. The hydrogen solubility further decreases with increasing the temperature as shown in Fig. 3.

3.3. Mechanical properties of V–W alloy in hydrogen atmosphere

The *in situ* SP test is conducted for V–5 mol%W alloy in a constant hydrogen pressure of 0.01 MPa at 773 K. The results of the load–deflection curve are shown in Fig. 4 together with the results for Nb–5 mol%W alloy measured at 773 K and for pure niobium measured at 673 K for comparison.

The load–deflection curve for pure niobium measured at 673 K shows very small maximum load and deflection, indicating that brittle fracture due to severe hydrogen embrittlement occurs for pure niobium under this testing condition. On the other hand, the load–deflection curves for both Nb–5 mol%W and V–5 mol%W alloys measured at 773 K shows large maximum load and deflection, meaning that ductile fracture takes place for these alloys. The dissolved hydrogen concentration in these alloys at the testing condition is about H/M = 0.07 and 0.03 for Nb–5 mol%W and V–5 mol%W alloys, respectively. These values are much lower than that for pure niobium at 673 K, i.e., H/M = 0.43.

Here, it is noted that the maximum load and the deflection for V-based alloy are larger than that for Nb-based alloy, indicating that the mechanical properties (i.e., the strength and the ductility) for V–W alloy is better than that for Nb–W alloy in hydrogen gas atmosphere at high temperature.

The *in situ* SP tests are also conducted for V–5 mol%W alloy in 0.01, 0.1, 0.2 and 0.3 MPa of hydrogen atmosphere at 773 K. The dissolved hydrogen concentrations are estimated from the PCT curve for 773 K shown in Fig. 3. The results of the load–deflection curves are shown in Fig. 5. As shown in the figure, the load–deflection curve changes when the hydrogen pressure increases. However, each sample still shows high ductility even for the sample tested in 0.3 MPa of hydrogen atmosphere. In this pressure condition the dissolved hydrogen concentration is about H/M = 0.2, near DBTC of vanadium. Thus, the resistance to hydrogen embrittlement improves by reducing the dissolved hydrogen concentration below the DBTC. In fact, no brittle cracking occurs for V–5 mol%W alloy

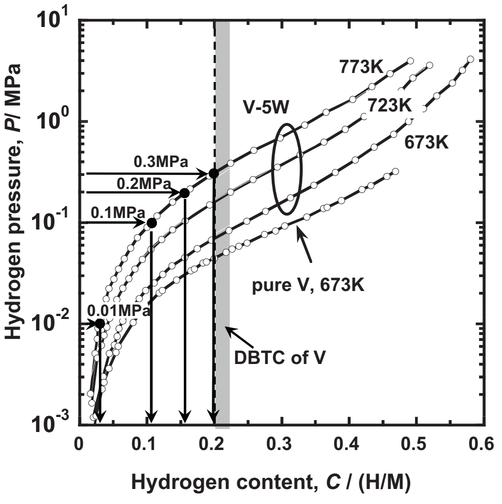

Fig. 3. PCT curves for V–5 mol%W alloy measured at 673–773 K. PCT curve for pure V measured at 673 K [11] is also drawn in the figure for comparison.

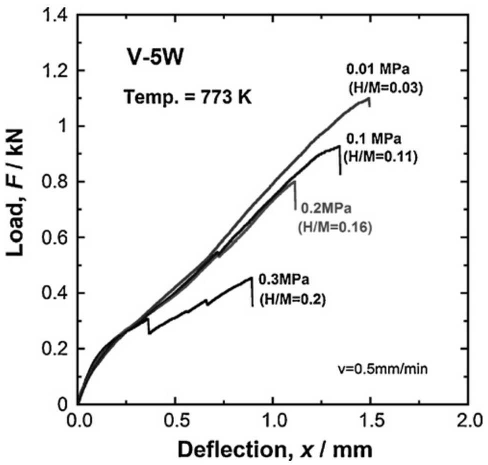

Fig. 5. Load–deflection curves for V–5 mol%W alloys measured at 773K.

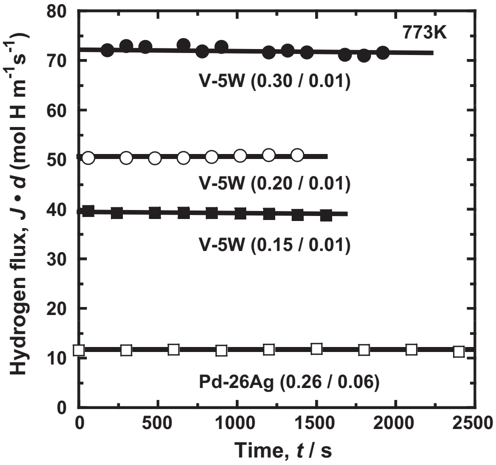

Fig. 6. Changes in the normalized hydrogen flux, *J*·*d*, during the measurements at 773 K. The inlet and outlet hydrogen pressures for each measurement are indicated in parentheses in the figure as (inlet/outlet (MPa)).

membrane when hydrogen permeation tests are conducted under appropriate hydrogen permeation condition as explained later.

3.4. Hydrogen permeability

The steady-state hydrogen fluxes, *J*, are measured by the hydrogen permeation tests. They are divided by the inverse of the sample thickness, 1/*d*, in order to estimate the normalized hydrogen flux, *J*·*d*. It is noted here that the atomic hydrogen flux, mol H m^{-1} s^{-1}, is evaluated in this paper, which is twice as large as the gaseous hydrogen flux, mol H_2 m^{-1} s^{-1}.

Fig. 6 shows the change in the normalized hydrogen flux, *J*·*d*, during the measurement at 773 K for each testing condition. The pressure conditions are indicated in parentheses in the figure as (inlet/outlet (MPa)). The results of Pd–26 mol%Ag alloy measured at 773 K with the pressure condition of inlet/outlet = 0.26/0.06 MPa are also presented in the figure for comparison. As shown in Fig. 6, the hydrogen flux is stable and nearly constant during each measurement.

As shown in Fig. 6, the hydrogen flux changes depend on the applied hydrogen pressures. It is evident that the hydrogen flux is much higher for V–5 mol%W alloys than Pd–26 mol%Ag alloy. For example, the *J*·*d* value for V–5 mol%W alloy measured under the pressure condition of inlet/outlet = 0.30/0.01 MPa is more than 7 times higher than that for Pd–26 mol%Ag alloy measured under the pressure condition of inlet/outlet = 0.26/0.06 MPa. As mentioned before, the hydrogen permeability of Nb–5 mol%W alloy is about 4 times higher than Pd–26 mol%Ag alloy. Thus, the amount of hydrogen flux increases about 1.75 times for V–5 mol%W than Nb–5 mol%W, although the pressure conditions are different each other because higher hydrogen pressures can be applied to V-based alloy than Nb-based alloy.

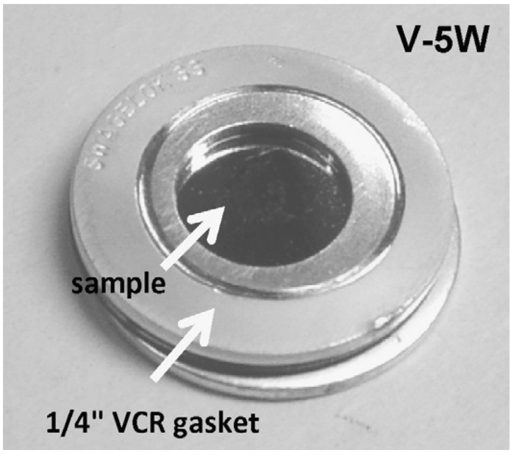

Fig. 7. Photo image of a disk sample of V–5 mol%W alloy evaluated and cooled down to room temperature after the hydrogen permeation test.

Fig. 7 shows a photo image of the sample of V–5 mol%W alloy after the hydrogen permeation test. There is no evidence of hydrogen embrittlement on the sample. Thus, V–5 mol%W alloy possess excellent hydrogen permeability together with strong resistance to hydrogen embrittlement and good mechanical properties in hydrogen atmosphere at high temperature.

4. Summary

The mechanical properties of pure vanadium in hydrogen atmosphere are investigated by the *in situ* SP test method. It is found that the SP absorption energy decreases drastically with increasing dissolved hydrogen concentration at the hydrogen concentration around H/M = 0.22. Thus, the DBTC (Ductile-to-Brittle Transition hydrogen Concentration) for pure vanadium is determined to be about H/M = 0.22.

The hydrogen solubility is found to decrease by the addition of tungsten into vanadium or by increasing the temperature. As a result, the V–5 mol%W alloy possesses strong resistance to hydrogen embrittlement. Also, the mechanical properties (i.e., the strength and the ductility) for V-based alloy in 0.01 MPa of hydrogen pressure at 773 K are better than that for Nb-based alloy. It is demonstrated that the V–5 mol%W alloy exhibits excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions, i.e., hydrogen pressures and temperature.

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