Ta-W Alloy for Hydrogen Permeable Membranes

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The alloying effects of tungsten on the hydrogen solubility, the resistance to hydrogen embrittlement and the hydrogen permeability are investigated for Ta-based hydrogen permeable membranes. The hydrogen solubility is found to decrease by the addition of tungsten into tantalum or by increasing the temperature. It is also found that the mechanical properties (i.e., strength and ductility) for Ta-based alloy is better than that for Nb-based alloy in hydrogen atmosphere at high temperature. It is demonstrated that the Ta-5 mol%W alloy possesses excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions. For example, the hydrogen flux for Ta-5 mol%W alloy measured at 773 K under the pressure condition of inlet/outlet = 0.15/0.01 MPa is about 5 times higher than that for Pd-27 mol%Ag alloy measured at the same testing condition. [doi:10.2320/matertrans.MA201007]

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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 material cost as well as to improve the hydrogen permeability. Group 5 metals (i.e., Nb, V and Ta) 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 and vanadium in hydrogen gas atmosphere at high temperature have been investigated by the in-situ small punch (SP) test method.⁷,⁸ It was found that the ductile-to-brittle transition occurs drastically at the hydrogen concentration around \( H/M = 0.25 \) for pure niobium and \( H/M = 0.22 \) for pure vanadium at the temperature range between 573~773 K. This fact suggests that the resistance to hydrogen embrittlement of group 5 metals will be improved by keeping the hydrogen concentration below around \( H/M = 0.2 \) during the practical hydrogen permeation.

From these results, a concept for alloy design of Nb-based hydrogen permeable membranes has been proposed.⁹,¹⁰ Following this concept, Nb-based alloys that satisfy both high hydrogen permeability and strong resistance to hydrogen embrittlement have been designed and developed. For example, designed Nb-5 mol%W alloy possesses more than 4 times higher hydrogen permeability than Pd-26 mol%Ag alloy without showing any hydrogen embrittlement.¹¹ 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) around \( H/M = 0.2 \) 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, for example, by alloying.

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

2. Experimental Procedure

2.1 Sample preparation

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

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) of metals and alloys.¹²–¹⁴ Specimens of about 10 mm × 10 mm with the thickness of about 0.65 mm are prepared for Ta-5 mol%W alloy. Both sides of the specimen are mechanically polished by alumina abrasive papers followed by the final polishing.

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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 surface 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 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 (PCT) are measured by using a Sieverts-type apparatus in order to investigate the hydrogen solubility for Ta-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 at least 3 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 φ12 mm in diameter with a thickness of about 0.5 mm are prepared for Ta-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-Ag alloy is also prepared. Pd-27 mol% Ag alloy is arc-melted by using a tri-arc furnace in a purified argon gas atmosphere. The button ingot is cold-rolled and disk specimens of about φ12 mm in diameter with a thickness of about 0.05 mm are prepared. Then the disks are annealed at 1223 K for 3.6 ks in vacuum condition.

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 G1-grade hydrogen gas (99.99999% purity) 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 maximum hydrogen pressure is determined to be 0.15 MPa from the results of the PCT measurements shown in Fig. 1 in order to keep the hydrogen concentration below 0.2 (H/M) at 773 K. 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 system is evacuated and then cooled down to room temperature to take out the sample from the apparatus in order to check the sample damage due to hydrogen embrittlement.

### 3. Results and Discussion

#### 3.1 Alloying effects on the hydrogen solubility

The alloying effects of tungsten on the hydriding properties for tantalum are investigated by measuring the pressure-composition-isotherms (PCT) curves for Ta-based alloy. The PCT curves measured at 673 ~ 773 K for Ta-5 mol%W alloy are shown in Fig. 1. For comparison, the PCT curve for pure tantalum measured at 673 K reported by Veleckis and Edwards\(^16\) is also drawn in the figure for comparison.

#### 3.2 Mechanical properties of Ta-W alloy in hydrogen gas atmosphere

The in-situ SP tests are conducted for Ta-5 mol%W alloy in a constant hydrogen pressure of 0.01 MPa at 773 K. The load-deflection curves are shown in Fig. 2 together with the results for Nb-5 mol%W alloy measured at 773 K and for pure niobium measured at 773 K for comparison.
The load-deflection curve for pure niobium measured at 673 K shows very small ultimate 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 Ta-5 mol%W alloys measured at 773 K shows large ultimate load and deflection, meaning that ductile fracture takes place in these alloys. The dissolved hydrogen concentrations in these alloys at the testing conditions are about 0.07 \( H/M \) for Nb-5 mol%W and 0.04 \( H/M \) for Ta-5 mol%W alloys, respectively. These values are much lower than that for pure niobium at 673 K, i.e., \( H/M = 0.43 \). Thus, the resistance to hydrogen embrittlement improves by reducing the dissolved hydrogen concentration. In fact, no brittle cracking occurs for Ta-5 mol%W alloy membrane when hydrogen permeation tests is conducted under appropriate hydrogen permeation condition as explained later.

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

### 3.3 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, \( J \cdot d \). 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\(^{-1}\).

Figure 3 shows the normalized hydrogen flux, \( J \cdot d \), at 773 K for each testing condition. The pressure conditions are indicated in parentheses as (inlet/outlet (MPa)). The results of Pd-27 mol%Ag alloy measured at 773 K with the pressure condition of inlet/outlet = 0.15/0.01 MPa is about 5 times higher than that for Pd-27 mol%Ag alloy measured under the same pressure condition.

As shown in Fig. 3, the hydrogen flux changes depend on the applied hydrogen pressures. It is evident that the hydrogen flux is much higher for Ta-5 mol%W alloys than Pd-27 mol%Ag alloy. For example, the \( J \cdot d \) value for Ta-5 mol%W alloy measured under the pressure condition of inlet/outlet = 0.15/0.01 MPa is about 5 times higher than that for Pd-27 mol%Ag alloy measured under the same pressure condition.

Figure 4 shows a photo image of the sample of Ta-5 mol%W alloy after the hydrogen permeation test. There is no evidence of hydrogen embrittlement on the sample. Thus, the Ta-5 mol%W alloy possesses excellent hydrogen permeability together with strong resistance to hydrogen embrittlement and good mechanical properties in hydrogen atmosphere at high temperature.

### 4. Summary

The hydrogen solubility, the resistance to hydrogen embrittlement and the hydrogen permeability are investigated quantitatively for Ta-W system. The hydrogen solubility is found to decrease by the addition of tungsten into tantalum or by increasing the temperature. As a result, the Ta-5 mol%W alloy possesses strong resistance to hydrogen embrittlement.
Also, the mechanical properties (i.e., the strength and the ductility) for Ta-based alloy in 0.01 MPa of hydrogen pressure at 773 K is better than that for Nb-based alloy. It is demonstrated that the Ta-5 mol%W alloy exhibits excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions. For example, the $J \cdot d$ value for Ta-5 mol%W alloy measured at 773 K under the pressure condition of inlet/outlet = 0.15/0.01 MPa is about 5 times higher than that for Pd-27 mol%Ag alloy measured at the same condition.

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