Alloy Design of Nb-Based Hydrogen Permeable Membrane with Strong Resistance to Hydrogen Embrittlement

Hiroshi Yukawa1,*1, Tomonori Nambu2, Yoshihisa Matsumoto3, Naoshi Watanabe1,*2, Guoxing Zhang1 and Masahiko Morinaga1

1Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
2Department of Materials Science and Engineering, Suzuka National College of Technology, Suzuka 510-0294, Japan
3Department of Mechanical Engineering, Oita National College of Technology, Oita 870-0152, Japan

The alloying effects of Ru and W on the hydrogen solubility, the resistance to hydrogen embrittlement and hydrogen permeability are investigated quantitatively for Nb-based hydrogen permeable alloys. It is found that the hydrogen solubility decreases by the addition of alloying element into niobium or by increasing the temperature. As a result, the resistance to hydrogen embrittlement is improved by reducing the hydrogen concentration. On the other hand, the hydrogen flux, \( J \), through the alloy membrane increases linearly with increasing difference of hydrogen concentration, \( \Delta C \), between both sides of the membrane. It is shown that the Nb-5 mol%X (X = Ru and W) alloys possess excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions, i.e. temperature and hydrogen pressures. Also, the hydrogen diffusion coefficients during the practical hydrogen permeation at high temperature are evaluated from the linear relationship between the hydrogen flux and the hydrogen concentration difference. It is found that the hydrogen diffusion coefficient of pure Nb is much lower than the reported values measured for dilute hydrogen solid solutions. Surprisingly, the hydrogen diffusion is found to be faster in Pd-26 mol%Ag alloy with fcc crystal structure than in pure niobium with bcc structure at 773 K during the hydrogen permeation. It is also interesting that the addition of Ru or W into niobium enhances the hydrogen diffusion of the practical hydrogen permeation at high temperature. [doi:10.2320/matertrans.MA200805]

(Received April 2, 2008; Accepted May 9, 2008; Published June 25, 2008)

Keywords: hydrogen permeable membrane, niobium based alloy, hydrogen embrittlement, hydrogen solubility, hydrogen diffusion coefficient

1. Introduction

Hydrogen permeable alloys are one of the most important materials for the hydrogen purification technologies.1,2 For example, Pd-Ag alloys are widely used practically for the separation and purification of hydrogen gas. Recently, special attention has been directed towards V- and Nb-based alloys,3–6 because they possess higher hydrogen permeability than currently used Pd-Ag alloys.7,8 However, there is still a large barrier to the practical use due to their poor resistance to hydrogen embrittlement.

The mechanical properties of Nb in a hydrogen gas atmosphere at high temperature have been studied by Gahr and Birnbaum.9 They proposed the ductile-to-cleavage transition boundary in the Nb-H system for Pd-uncoated specimens. However, the hydrogen concentration in their specimens are questionable because the Pd coating on the Nb surface is essential for the hydrogen dissociation reaction from molecular \( H_2 \) into atomic H and subsequent absorption reaction into bulk to take place smoothly even in a hydrogen gas atmosphere at high temperature.3,10

Recently, Nambu et al. investigated the hydrogen embrittlement of Pd-coated Nb by the in-situ small punch (SP) test method.6 It was found that the ductile-to-brittle transition occurs drastically at the hydrogen concentration around \( H/M = 0.25 \) at the temperature 573–773 K. This critical hydrogen concentration is much low as compared to the ductile-to-cleavage boundary proposed by Gahr and Birnbaum.9 The alloying effects on the hydrogen solubility and hydrogen embrittlement have also been studied.11

From these results, a concept has been proposed for alloy design of Nb-based hydrogen permeable membrane with high hydrogen permeability and strong resistance to hydrogen embrittlement.

Fig. 1 A schematic illustration showing the concept for alloy design of Nb-based hydrogen permeable membrane with high hydrogen permeability and strong resistance to hydrogen embrittlement.

---

*Corresponding author, E-mail: hiroshi@numse.nagoya-u.ac.jp
**Graduate Student, Nagoya University
critical value during the practical hydrogen permeation. Therefore, it is necessary to reduce the heat of hydrogen dissolution into Nb. In other words, the pressure-composition-isotherms (PCT) curve of Nb should be controlled and shifted toward left and upper side as shown in Fig. 1 in some ways, for example, by alloying.

On the other hand, according to the Fick’s law, the hydrogen flux, J, increases proportionally with increasing the hydrogen concentration gradient, \( \Delta C / d \), between the inlet and outlet sides of the membrane with the thickness of d. Therefore, high hydrogen permeability will be expected when large hydrogen concentration difference, \( \Delta C \), is obtained for the designed alloy at a given hydrogen permeation condition as shown in Fig. 1. The hydrogen diffusion coefficient, \( D \), during the hydrogen permeation is also an important factor controlling the hydrogen permeability of the alloy.

In this study, following this concept, the alloying effects of Ru and W on the hydrogen solubility and the resistance to hydrogen embrittlement of Nb are investigated. Also, the hydrogen permeability of the alloys is measured and analyzed in view of the difference of hydrogen concentration, \( \Delta C \), between both sides of the membrane.

### 2. Experimental Procedure

#### 2.1 Sample preparation

The purities of the raw materials used in this study are 99.96 mass% for Nb and 99.95 mass% for Ru and W. Nb-X mol%Ru (X = 5, 10, 15) and Nb-5 mol%W alloys are arc-melted by using a tri-arc furnace in a purified argon gas atmosphere. According to the Nb-Ru and Nb-W phase diagrams, all these alloys are solid solution single phase.

#### 2.2 Hydrogen pressure-composition-isotherm (PCT) measurement

The pressure-composition-isotherms (PCT) are measured at 673–773 K in order to investigate the hydrogen solubility. A small piece of the sample is set into the PCT apparatus and then evacuated. Subsequently, it is heated up to the measuring temperature. 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 the hydrogen absorption and desorption reactions to be take place smoothly without Pd coating.

#### 2.3 In-situ SP test

The hydrogen embrittlement is investigated by the in-situ small punch (SP) test method. The plate-shaped specimens of about 10 mm × 10 mm with the thickness of 0.5 mm are prepared for pure Nb, Nb-5 mol%Ru and Nb-5 mol%W alloys. Both sides of the specimens are mechanically polished by emery papers followed by the final polishing with 0.3 μm Al₂O₃ 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.

The load-deflection curves are measured by the in-situ SP tests conducted under a constant hydrogen pressure of 0.01 MPa at 673–773 K 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.⁶

#### 2.4 Hydrogen permeation test

The hydrogen permeation tests are performed at 773 K by the differential pressure method in order to evaluate the hydrogen permeability.¹² The hydrogen flux is estimated by monitoring the pressure change of the reserve tank with known volume. The disk specimens of about φ12 mm in diameter with the thickness of 0.5 mm are prepared for pure Nb, Nb-5 mol%Ru and Nb-5 mol%W alloys. They are polished mechanically and coated with pure Pd 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 hydrogen fluxes, \( J \), permeated through the disk samples are measured. After the hydrogen permeation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrogen pressure, ( P ), MPa</th>
<th>( \Delta P / ), MPa</th>
<th>( \Delta C / ), H/M</th>
<th>Hydrogen flux, ( J \cdot ), mol H ( \cdot ) m ( -1 ) ( \cdot ) s ( -1 )</th>
<th>Hydrogen diffusion coefficient, ( D ), m²s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-5 mol%Ru</td>
<td>0.10 0.01</td>
<td>0.09 0.14</td>
<td>53.8 × 10⁻⁶</td>
<td>4.40 × 10⁻⁹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05 0.04</td>
<td>0.04 0.07</td>
<td>30.1 × 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-5 mol%W</td>
<td>0.05 0.01</td>
<td>0.04 0.12</td>
<td>40.7 × 10⁻⁶</td>
<td>4.05 × 10⁻⁹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03 0.02</td>
<td>0.02 0.07</td>
<td>23.1 × 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Nb</td>
<td>0.02 0.01</td>
<td>0.02 0.10</td>
<td>26.6 × 10⁻⁶</td>
<td>3.07 × 10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>Pd-26 mol%Ag</td>
<td>0.26 0.06</td>
<td>0.20 0.02</td>
<td>11.6 × 10⁻⁶</td>
<td>5.98 × 10⁻⁹</td>
<td></td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Alloying effects on the hydrogen solubility

The results of the PCT curves measured at 673 K for Nb-X mol%Ru (X = 5, 10, 15) alloys are shown in Fig. 2. For comparison, the PCT curve for pure Nb reported by Lässer et al.\textsuperscript{13} is also drawn in the figure. As shown in this figure, the PCT curve shifts toward left and upper side with increasing Ru content in the alloy, resulting the decrement of the dissolved hydrogen content in it. The hydrogen solubility further decreases with increasing the temperature as shown in Fig. 3. Similar results are also obtained for Nb-5 mol%W alloy as shown in Fig. 4. Comparing Fig. 3 with Fig. 4, it is found that the alloying effects are larger for Ru than W on the hydrogen solubility of Nb.

3.2 Alloying effects on the hydrogen embrittlement

The in-situ SP tests are conducted under 0.01 MPa of hydrogen at 673–773 K. The results of the load-deflection curves are shown in Fig. 5 for Nb-5 mol%Ru and Nb-5 mol%W alloys together with the results for pure Nb. Comparing the curves for pure Nb and Nb-5 mol%Ru measured at 673 K, it is found that the load-deflection curve changes by the addition of 5 mol%Ru. For example, the test, the sample is evacuated and then cooled down to room temperature in order to check the damage of the sample due to hydrogen embrittlement.
maximum load and the deflection are increased by alloying 5 mol% of Ru into Nb. Similarly, as shown in Fig. 5, the curve for Nb-5 mol%W measured at 773 K shows very large maximum load and deflection. These results indicate that the addition of Ru or W improves the mechanical properties (i.e., the strength and the ductility) of Nb in 0.01 MPa of hydrogen gas atmosphere at high temperature.

The SP absorption energy, $E_{SP}$, is estimated from each load-deflection curve shown in Fig. 5 and the results are summarized in Fig. 6. The equilibrium hydrogen concentration for each sample is estimated from the results of the PCT measurements shown in Figs. 3 and 4, and they are indicated in the figure. As shown in Fig. 6, the SP absorption energy for pure Nb is very small indicating a severe hydrogen embrittlement occurs under 0.01 MPa of hydrogen atmosphere where a large amount of hydrogen dissolves in it.

On the other hand, the $E_{SP}$ values for Nb-5 mol%Ru and Nb-5 mol%W alloys are very large. They are about 4 times and 10 times higher than that for pure Nb, respectively. The hydrogen concentrations in these Nb-5 mol%Ru and Nb-5 mol%W alloys at the testing condition are approximately $H/M = 0.045$–0.11, significantly lower than that in pure Nb, $H/M = 0.42$. Thus, the addition of Ru or W into Nb improves the resistance to hydrogen embrittlement by reducing hydrogen concentration.

In fact, both Nb-5 mol%Ru and Nb-5 mol%W alloys possess strong resistance to hydrogen embrittlement when tested under appropriate hydrogen permeation condition. For example, a photo image of the sample of Nb-5 mol%Ru alloy after the permeation test described later is shown in Fig. 7. There is no evidence of hydrogen embrittlement during the hydrogen permeation. Similar results are obtained for all the samples examined in this study except for Nb-5 mol%W alloy tested under the pressure condition of inlet/outlet = 0.10/0.01 MPa. In this pressure condition, the hydrogen content in Nb-5 mol%W alloy exceeds the critical value, $H/M = 0.25$, for the ductile-to-brittle transition as mentioned before, so that a cracking occurs due to hydrogen embrittlement when evacuated after the permeation test.

### 3.3 Hydrogen permeability

The steady-state hydrogen fluxes, $J$, are measured by the hydrogen permeation tests. They are normalized by the inverse of the sample thickness, $1/d$. The values of normalized hydrogen flux, $J \cdot d$, are summarized in Table 1. It is noted here that the atomic hydrogen flux, mol H m$^{-1}$s$^{-1}$, is evaluated in this paper, which is twice of the gaseous hydrogen flux, mol H$_2$ m$^{-1}$s$^{-1}$.

Figure 8 shows the change in the normalized hydrogen flux, $J \cdot d$, 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)).
hydrogen flux is much higher for Nb-5 mol%Ru and Nb-5 mol%W alloys than Pd-26 mol%Ag alloy, despite that the applied hydrogen pressure, $P$, as well as the pressure difference, $\Delta P$, is lower for Nb alloys than Pd-Ag alloy. For example, the $J \cdot d$ value for Nb-5 mol%Ru alloy measured under the pressure condition of inlet/outlet $= 0.10/0.01$ MPa is about 4.5 times higher than that for Pd-26 mol%Ag alloy measured under the pressure condition of inlet/outlet $= 0.26/0.06$ MPa. Similar results are also obtained for Nb-5 mol%W alloy.

Such high hydrogen fluxes for Nb-Ru and Nb-W alloys will be attributable to the high hydrogen concentration difference, $\Delta C$, between the inlet and outlet sides of the membrane. In fact, as shown in Table 1, the $J \cdot d$ value is high when the hydrogen concentration difference, $\Delta C$, is large. However, the hydrogen diffusion coefficient, $D$, will also affect on the hydrogen flux, as expressed by the Fick’s law, $J = D \times \Delta C / d$.

### 3.4 Hydrogen diffusion coefficient during hydrogen permeation

In order to investigate the alloying effects on the hydrogen diffusion coefficient, $D$, during the hydrogen permeation, the hydrogen flux is analyzed in view of the difference of hydrogen concentration. Figure 9 shows the correlation between the normalized hydrogen flux, $J \cdot d$, and the difference of hydrogen concentration, $\Delta C$. As shown in Fig. 9, there is a linear relationship between them. Each straight line shown in Fig. 9 crosses at the origin, indicating that the diffusion limiting hydrogen permeation reactions take place through the membrane following the Fick’s first law.

Then, the hydrogen diffusion coefficient during the hydrogen permeation can be evaluated from the linear relationship shown in Fig. 9. The results of the hydrogen diffusion coefficients are summarized in Table 1. Here a linear relationship is assumed for Pd-26 mol%Ag alloy at 773 K by a straight line, although there is only one data point as shown in Fig. 9. For comparison, the reported hydrogen diffusion coefficients at 773 K for pure niobium14–16) and Pd-25 mass%Ag alloy7) are presented in Table 2. It is found that the hydrogen diffusion coefficient during the hydrogen permeation in Pd-26 mol%Ag alloy measured at 773 K are in good agreement with the values estimated from the expression, $D = 3.07 \times 10^{-7} \exp[-25902/RT]$ (m$^2$/s), reported by Serra et al. for Pd-25 mass%Ag alloy.7)

On the other hand, the hydrogen diffusion coefficient for pure niobium obtained in this study is quite different from the reported values for dilute hydrogen solid solutions. For example, the hydrogen diffusion coefficient for pure niobium during the hydrogen permeation at 773 K is $3.07 \times 10^{-10}$ m$^2$/s, which is significantly lower than the previous works measured by the relaxation method.14–16) These results are in consistent with the past findings that the hydrogen diffusion coefficient for pure niobium decreases with increasing the hydrogen concentration.17) Surprisingly, the hydrogen diffusion during the hydrogen permeation is found to be faster in Pd-26 mol%Ag alloy with fcc crystal structure than that in bcc niobium at 773 K. It is also interesting that the addition of Ru or W into niobium increases the hydrogen diffusion coefficient during the hydrogen permeation. From the results of PCT measurements shown in Figs. 3 and 4, the addition of Ru or W reduces the stability of hydrogen in niobium. In other words, the hydrogen potential at the interstitial site of bcc niobium will become shallow by the addition of these alloying elements, which will lead to decrease the activation energy for the hydrogen diffusion. Further experiments will be needed and are now in progress in order to examine the alloying effects on the pre-exponential factor and the activation energy of the hydrogen diffusion coefficients during the hydrogen permeation.

### 4. Conclusion

The alloying effects on the hydrogen solubility and the resistance to hydrogen embrittlement are investigated quantitatively for Nb-based hydrogen permeable alloys. It is found that the hydrogen solubility decreases by the addition of alloying element into niobium or by increasing the temperature. As a result, the resistance to hydrogen embrittlement is improved by reducing the hydrogen concentration. On the other hand, the hydrogen flux, $J$, through the alloy membrane increases linearly with increasing difference of hydrogen concentration, $\Delta C$, between both sides of the sample surface.

On the basis of the concept of alloy design for Nb-based hydrogen permeable membrane, Nb-based alloys with high hydrogen permeability and strong resistance to hydrogen embrittlement can be designed and developed. For example, the designed Nb-5 mol%Ru and Nb-5 mol%W alloys possess excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate hydro-
gen permeation conditions, i.e. temperature and hydrogen pressures.

In addition, the hydrogen diffusion coefficients during the hydrogen permeation through pure Nb and its alloys at high temperature are evaluated from the linear relationship between the normalized hydrogen flux, $J \cdot d$, and the hydrogen concentration difference, $\Delta C$.

Acknowledgement

This research was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, by the Japan Society for the Promotion of Science (JSPS) and by Industrial Technology Research Grant Program from New Energy and Industrial Technology Department Organization (NEDO) of Japan.

REFERENCES