Alloying effects of Ru and W on hydrogen diffusivity during hydrogen permeation through Nb-based hydrogen permeable membranes

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ABSTRACT

The hydrogen permeability have been measured for pure niobium and Nb-5 mol%X ($X =$ Ru and W) alloys in order to investigate the alloying effects of ruthenium and tungsten on the hydrogen diffusivity during hydrogen permeation. The hydrogen diffusion coefficient during hydrogen permeation is estimated from a linear relationship between the normalized hydrogen flux, $J \cdot d$, and the difference of hydrogen concentration, ΔC, between the inlet and the outlet sides of the membrane. It is found that the addition of ruthenium or tungsten into niobium increases the hydrogen diffusion coefficient during the hydrogen permeation. On the other hand, the activation energy for hydrogen diffusion in pure niobium under the practical permeation condition is much higher than the reported values measured for dilute hydrogen solid solutions. It is interesting that the activation energy for hydrogen diffusion is decreased by alloying of ruthenium or tungsten into niobium.

1. Introduction

The palladium and its alloys are well known as the hydrogen permeable metal membrane for the separation and purification of hydrogen gas [1–4]. Recently, there has been a great demand for the development of new hydrogen permeable alloys to be substituted for currently used palladium-based alloys, in order to reduce the materials cost as well as to improve the performance of the hydrogen permeability [5]. Niobium metal exhibits the higher hydrogen permeability than palladium-based alloys, so niobium and its alloys are ones of the most promising materials for hydrogen permeable membranes [6–10].

Recently, Zhang et al. [11] have investigated the hydrogen diffusion coefficients for pure niobium under the practical condition of hydrogen permeation at 773 K. The hydrogen diffusion coefficient in pure niobium during the hydrogen permeation was found to be much lower than that reported values measured for dilute hydrogen solid solution [12–14]. It was also found that the hydrogen diffusion coefficient for pure niobium with body-centered-cubic (bcc) crystal structure is smaller than that in pure palladium or Pd–Ag alloy with face-centered-cubic (fcc) crystal structure under the practical condition of hydrogen permeation [11].

In this study, the hydrogen permeability have been measured for pure niobium and Nb-5 mol%X ($X =$ Ru and W)

Table 1 – Hydrogen permeation conditions and hydrogen diffusion coefficients for pure Nb, Nb-5 mol%Ru and Nb-5 mol%W alloys.

Sample	Temperature, T (K)	Hydrogen pressure, P (MPa)		ΔP (MPa)	ΔC (H/M)	Hydrogen diffusion coefficient, D ($m^2\,s^{-1}$)
		Inlet	Outlet			
Pure Nb	773	0.030	0.010	0.020	0.10	2.97×10^{-9}
		0.020		0.010	0.05	
	753	0.022	0.005	0.017	0.12	1.87×10^{-9}
		0.015		0.010	0.07	
	733	0.015	0.005	0.010	0.10	1.24×10^{-9}
		0.009		0.004	0.04	
	713	0.010	0.003	0.007	0.10	0.81×10^{-9}
		0.005		0.002	0.03	
	693	0.007	0.003	0.004	0.09	0.49×10^{-9}
		0.005		0.002	0.04	
Nb-5 mol%Ru	773	0.100	0.010	0.090	0.14	4.13×10^{-9}
		0.075		0.065	0.11	
		0.050		0.040	0.08	
	723	0.050	0.010	0.040	0.12	2.34×10^{-9}
		0.030		0.020	0.07	
	673	0.020	0.005	0.015	0.10	1.09×10^{-9}
		0.010		0.005	0.04	
Nb-5 mol%W	773	0.050	0.010	0.040	0.11	4.06×10^{-9}
		0.030		0.020	0.06	
	723	0.020	0.005	0.015	0.10	1.89×10^{-9}
		0.012		0.007	0.05	
	673	0.008	0.003	0.005	0.08	0.67×10^{-9}
		0.006		0.003	0.05	

alloys in order to investigate the alloying effects of ruthenium and tungsten on the hydrogen diffusivity during hydrogen permeation. The temperature dependence of hydrogen diffusion coefficient is also analyzed to estimate the activation energy for hydrogen diffusion under the practical conditions.

2.   Experimental procedure

2.1.   Sample preparation

Both Nb-5 mol%Ru and Nb-5 mol%W alloys are melted by using a tri-arc furnace under a purified argon gas atmosphere. The purities of the raw materials used in this study are 99.96 mass% for niobium and 99.95 mass% for ruthenium and tungsten. According to the Nb–Ru and Nb–W binary phase diagrams, all these alloys are solid solution single phase.

2.2.   Hydrogen permeation test

For hydrogen permeation tests, the as-cast ingots are cut into disks with about φ12 mm in diameter and about 0.65 mm in thickness by using a wire-cut electrical discharge machine. For comparison, disks of pure niobium are prepared. A rod of φ12 mm in diameter with the purity of 99.96 mass% is cut into disks with the thickness of about 0.65 mm and they are annealed in a high purity argon gas atmosphere at 1473 K for 259.2 Ks.

Both sides of the disks are mechanically polished by emery papers followed by the final polishing with 0.3 μm Al₂O₃ powders. The final thickness, d, of the samples are approximately 0.48–0.50 mm. Then, a protective layer of pure palladium of about 200 nm in thickness is deposited on both sides

of the sample surfaces by using an RF magnetron sputtering apparatus at 573 K.

The hydrogen permeation tests are performed at 673–773 K by the differential pressure method. First, the disk sample is set in the hydrogen permeation apparatus and then evacuated. Subsequently, it is heated up to the measuring temperature and then high purity (99.99999%) hydrogen gas is introduced to both sides of the disk sample. The testing conditions of the temperature and hydrogen pressures are listed in Table 1. The inlet and outlet hydrogen pressures are determined from the PCT curves reported by Veleckis and Edwards [15] for pure niobium and Yukawa et al. [10] for Nb–Ru and Nb–W alloys so that the hydrogen concentration do not exceed the value H/M < 0.25 to avoid sample cracking due to hydrogen embrittlement [10]. The hydrogen fluxes permeated through the disk samples are measured by monitoring the pressure of the reserve tank with known volume. A detailed explanation of the permeation test is given elsewhere [6].

3.   Results and discussion

3.1.   Hydrogen diffusion coefficient during the hydrogen permeation

In this study, the hydrogen diffusion coefficients during the hydrogen permeation are evaluated following the Fick's law for membrane with the thickness of d.

$$J = D \frac{C_{in} - C_{out}}{d} = D \frac{\Delta C}{d},$$

where C_{in} and C_{out} are the hydrogen concentration at the inlet and outlet sides of the membrane. Here C_{in} and C_{out} are