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Hydrogen solubility and permeability of Nb–W–Mo alloy membrane

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ABSTRACT

The alloying effects of molybdenum on the hydrogen solubility, the resistance to hydrogen embrittlement and the hydrogen permeability are investigated for Nb–W–Mo system. It is found that the hydrogen solubility decreases by the addition of molybdenum into Nb–W alloy. As a result, the resistance to hydrogen embrittlement improves by reducing the hydrogen concentration in the alloy. It is demonstrated that Nb–5 mol%W–5 mol%Mo alloy possesses excellent hydrogen permeability without showing any hydrogen embrittlement when used under appropriate hydrogen permeation conditions, i.e., temperature and hydrogen pressures.

1. Introduction

Palladium (Pd) and its alloys are well-known as hydrogen permeable materials to be used for the separation and purification of high purity hydrogen gas [1]. Recently, there has been a great demand for the development of new hydrogen permeable alloys to be substituted for currently used Pd-based alloys, in order to reduce material cost as well as to improve the hydrogen permeability [2–5]. Niobium (Nb) is less expensive than palladium and exhibits the highest hydrogen permeability among metals [6], so it is one of the most promising materials for hydrogen permeable membranes. However, there is still a large barrier to the practical use due to its 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 [7,8]. It was found that the ductile-to-brittle transition occurs at the hydrogen concentration around H/M = 0.25 at the temperature range between 573 and 773 K without showing any micro-structural changes (i.e., phase transition or precipitation of secondary phase) [9]. 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, the hydrogen diffusion in metal membrane is generally the rate-limiting process of the total reaction of the hydrogen permeation through it. Therefore, the hydrogen flux, J, through the membrane with a thickness of d can be expressed by the following diffusion equation,

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

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 can be expressed as follows [10].

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

where R is gas constant and T is absolute temperature. As expressed in Eq. (1), high hydrogen flux, J, 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., inlet and outlet hydrogen pressures [10].

From these results, a concept for alloy design of Nb-based hydrogen permeable membrane has been proposed [10,11]. Following this concept, Nb–5 mol%W alloy with a single solid solution phase have been designed and developed which possesses high hydrogen permeability without showing any hydrogen embrittlement when used under appropriate permeation conditions [10].

In this study, the concept has been applied to Nb–W–Mo ternary system in order to improve further the resistance to hydrogen

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Table 1
Nominal compositions of the samples.

Sample	Concentration, c/(mol%)		
	W	Mo	Nb
Nb–5W	5	–	bal.
Nb–5W–5Mo	5	5	bal.
Nb–5W–10Mo	5	10	bal.
Nb–5W–15Mo	5	15	bal.

embrittlement at high hydrogen pressures as well as the hydrogen permeability of Nb–W alloy. The alloying effects of molybdenum into Nb–W alloy on the hydrogen solubility, the resistance to hydrogen embrittlement and the hydrogen permeability are investigated in a fundamental manner.

2. Experimental procedure

2.1. Sample preparation

The purities of the raw materials used in this study are 99.96 mass% for niobium and 99.95 mass% for tungsten and molybdenum. Nb–W–Mo alloys are prepared by using tri-arc furnace in a purified argon gas atmosphere. The nominal compositions of the alloys prepared in this study are listed in Table 1. According to the Nb–W, Nb–Mo and Mo-W equilibrium phase diagrams, all the alloys are composed of a single solid solution phase with simple bcc crystal structure [12].

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

In order to examine the hydrogen solubility for Nb–5 mol%W–x mol%Mo (x = 5, 10, 15) alloys, the pressure-composition-isotherms (PCT) are measured by using a Sieverts-type apparatus. A small piece of the sample is placed in a cell and then the cell is evacuated by using TMP pump. Subsequently, it is heated up to 773 K, and then high purity hydrogen (99.99999% purity) of about 5 MPa is introduced and cooled down to room temperature. This process is repeated at least three times prior to the PCT measurement in order to activate the sample surface for the hydrogen absorption and desorption reactions to take place smoothly. The PCT curves are measured at 673–773 K and up to about 5 MPa of hydrogen pressure.

2.3. In situ small punch (SP) test

The mechanical properties of Nb–5 mol%W–5 mol%Mo alloys in hydrogen gas atmosphere are investigated quantitatively by the *in situ* small punch (SP) test method. Plate-shaped specimens of about 10 mm × 10 mm with a thickness of about 0.6 mm are prepared by using a wire-electric discharge machine. Both sides of the specimens are mechanically polished by using alumina abrasive paper followed by the final polishing. The thickness of the specimen is reduced to 0.5 ± 0.01 mm by the final polishing with 0.3 μm Al_2O_3 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 in order to protect the sample surface from oxidation. The Pd-coating on the surface also acts as a catalyst to eliminate the hindrance to the hydrogen dissociation and dissolution reactions on the surfaces of the membrane.

The load–deflection curves are obtained by the *in situ* SP tests conducted under a constant hydrogen pressure of 0.01 MPa at 673 K or 773 K. The plate-shaped specimen is placed in the apparatus and, then punched by a Si_3N_4 ball (ϕ 2.4 mm in diameter) with a constant loading rate (i.e., the cross-head speed), $v = 8.3 \times 10^{-3}$ mm/s. The SP absorption energy, E_{SP}, 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 given elsewhere [7].

2.4. Hydrogen permeation test

The hydrogen permeation tests are performed for Nb–5 mol%W–5 mol%Mo alloy at 773 K. Disk specimens of about ϕ 12 mm in diameter with a thickness of about 0.5 mm are prepared. They are polished mechanically and coated with pure palladium by the same procedure as mentioned above. For comparison, samples of Nb–5 mol%W and Pd–26 mol%Ag alloys are also prepared.

The disk sample is set into the hydrogen permeation apparatus and then evacuated. Subsequently, it is heated up to 773 K, and then a high purity hydrogen gas (99.99999% purity) is introduced into both sides of the specimen. The inlet and outlet hydrogen pressures applied in this study are listed in Table 2. These hydrogen pressures are determined from the PCT curves so that the hydrogen concentration does not exceed the critical value H/M < 0.25 [7] to avoid the brittle cracking due to hydrogen embrittlement. The hydrogen fluxes, J, permeated through the disk samples are measured by a conventional gas permeation method. A detailed explanation of the hydrogen permeation test is given elsewhere [13].

Table 2
Pressure conditions of the hydrogen permeation test.

Sample	Hydrogen pressure, P/MPa	
	Inlet	Outlet
Nb–5W–5Mo	0.10	0.01
	0.07	
	0.05	
Nb–5W	0.05	0.01
Pd–26Ag	0.26	0.06

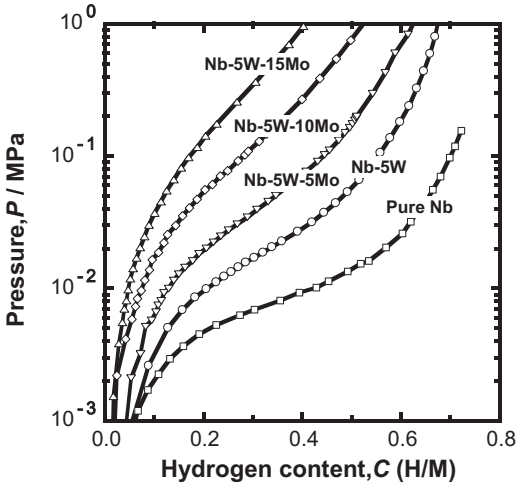

Fig. 1. PCT curves for Nb–5 mol%W–x mol%Mo (x = 5, 10 and 15) alloys measured at 673 K. The PCT curves for pure niobium measured at 673 K [14] and Nb–5 mol%W alloy measured at 673 K [11] are also drawn in the figure.

3. Results and discussion

3.1. Alloying effects of Mo on the hydrogen solubility of Nb–W alloy

The PCT curves for Nb–5 mol%W–x mol%Mo (x = 5, 10, 15) measured at 673 K and 773 K are shown in Figs. 1 and 2, respectively. For comparison, the results for pure niobium reported by Veleckis and Edwards [14] and Nb–5 mol%W reported by Yukawa et al. [11] are also drawn in the figures. As is evident from these figures, the PCT

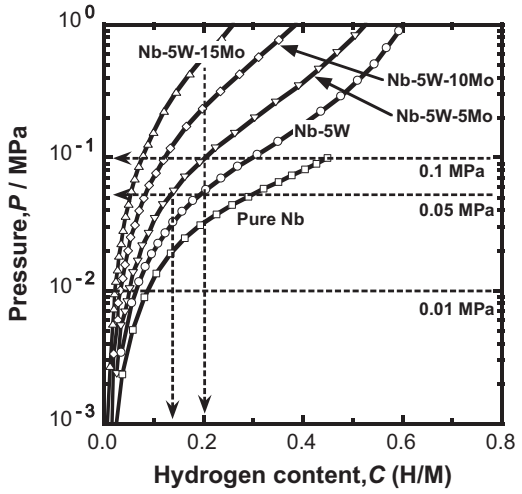

Fig. 2. PCT curves for Nb–5 mol%W– x mol%Mo (x = 5, 10, and 15) alloys measured at 773 K. The PCT curves for pure niobium measured at 773 K [14] and Nb–5 mol%W alloy measured at 773 K [11] are also drawn in the figure.