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Measurement of hydrogen permeability of pure Nb and its alloys by electrochemical method

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Abstract

Niobium metal is one of the promising materials for hydrogen permeable membranes because of the highest hydrogen permeability among the 5A group metals including V and Ta. In the present study, using a limiting current method, the hydrogen permeability was measured precisely for the first time with pure Nb and Nb–5 mol%M binary alloys. Here, M were 4d transition metals, Zr, Mo, Ru and Pd. The measured hydrogen permeability of pure Nb agreed well with the value calculated from the diffusion coefficient and the hydrogen solubility. Also, it was found that the hydrogen permeability of niobium increased by the addition of Zr and Pd, but decreased by the addition of Mo and Ru.

Keywords: Hydrogen permeable membrane; Limiting current method; Niobium; Permeability

1. Introduction

Hydrogen is of wide interest as a clean energy carrier, for example, in power fuel-cells. A high purity hydrogen gas is requested for the operation of fuel-cells and the manufacture of semiconductors as well. Nowadays, Pd–Ag membranes are practically used for the hydrogen purification, but they are very expensive. So, there has been a great demand for new hydrogen permeable alloys to substitute for the currently used Pd–Ag alloys. Recently, special attention has been directed toward the 5A group metals in the periodic table such as vanadium, niobium and tantalum. Among these metals, niobium metal has the highest hydrogen permeability, but it possesses poor resisitance to hydrogen embrittlement. Because of this hydrogen embrittlement, it is rather difficult to measure accurately the hydrogen permeability of niobium using a conventional gas permeation method. As a result, accurate experimental data have never been reported for pure Nb and its alloys. However, such a measurement can be done using a limiting current method [1], which is one of the electrochemical methods.

The purpose of this study is to measure the hydrogen permeability for pure and alloyed Nb using a limiting current method. The alloying effects on the hydrogen permeability will provide us with a good clue to the design and development of Nb-based hydrogen permeable membranes.

2. Experimental procedure

2.1. Specimen preparation

The purity of raw materials used in this study are 99.9% for pure Nb and better than 99.9% for other alloying elements, Zr, Mo, Ru and Pd. About 30 g of button ingots were arc-melted and then homogenized at 1573 K for 86.4 ks under a high purity argon gas atmosphere, followed by quenching into cold water. The chemical compositions of the alloys were determined by the fluorescent X-ray analysis and the results are listed in Table 1. According to the X-ray diffraction experiment, any extra peaks other than the bcc reflections were

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Table 1
Chemical compositions of the alloys used in this study (mol%)

Alloy	Zr	Mo	Ru	Rh	Pd	Nb
Nb–5Zr	4.96	–	–	–	–	Bal.
Nb–5Mo	–	4.48	–	–	–	Bal.
Nb–5Ru	–	–	4.89	–	–	Bal.
Nb–5Pd	–	–	–	–	4.73	Bal.

not observed, so all the alloys were supposed to consist of a bcc single phase, in agreement with the binary phase diagram [2].

The button ingots were cut into the disks of about 20 mm in diameter and about 1 mm in thickness and polished mechanically to remove a surface oxide layer. To protect the disk surface against the corrosion in a molten salt as described later and also to activate the hydrogen dissolution reaction on the surface, a palladium layer with the thickness of about 10 μm was deposited by an electroless plating technique [3]. Prior to this Pd plating, pure Pd was deposited slightly on the disk surface using a conventional evaporation technique in order to make a number of Pd embryos on the surface which probably act as the nuclei for the crystal growth of Pd during the subsequent electroless plating. Furthermore, the surface treatment of the disk was done by scanning CO_2 laser beams on the surface to improve the adhesion of the Pd plate with the substrate.

2.2. Hydrogen permeability measurements

The hydrogen permeability was measured using a conventional two-electrode cell configuration. The electrochemical cell used is shown schematically in Fig. 1 and it is expressed as follows.

$$\mathrm{Ar{-}H_2} \left| \begin{matrix} \text{Sample} \\ (\underline{\mathrm{H}}) \end{matrix} \right\| \begin{matrix} \text{KOH}{-}\text{NaOH} \\ (\mathrm{H^+}) \end{matrix} \left\| \begin{matrix} \text{Pd} \\ (\underline{\mathrm{H}}) \end{matrix} \right| \mathrm{Ar} \qquad (1)$$

Here, the KOH–51.5% NaOH molten salt was used as an electrolyte. Its melting temperature is about 443 K. Using this electrochemical cell, a series of the polarization measurements was performed. For each applied potential, E, the equilibrium electric current, I, was measured and the value of the limiting current, I_L, was obtained from the I–E curve. The hydrogen permeability, Φ can be estimated by using the following relationship, if the hydrogen diffusion in metal is the rate limiting step in the hydrogen permeation process.

$$\Phi = I_L \frac{L}{zFA\sqrt{P_{H_2}}} \qquad (2)$$

Here, F is the Faraday constant and P_{H_2} is the applied hydrogen partial pressure at the upstream side of the metal sample. A and L are the effective area and the thickness of the specimen, respectively. Further detailed explanation of this method will be given in reference [1].

The P_{H_2} was set at 0.101 kPa in the present experiment and the polarization measurements were performed at 573 K under the potential range between 0 and 600 mV. No oxidation reaction of palladium occurred in this condition. The hydrogen permeability was measured for pure Nb and Nb–5 mol%M (M = Zr, Mo, Ru, Pd) alloys.

3. Results and discussion

3.1. Pure Nb

Fig. 2 shows the I–E curve for pure Nb obtained at 573 K. As shown in this figure, the electric current, I, increased with increasing applied potential, E, but it saturated to a certain value and the limiting current, I_L, was observed above 200 mV. Then, following Eq. (2), the hydrogen permeability was calculated to be 1.30×10^{-7} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$

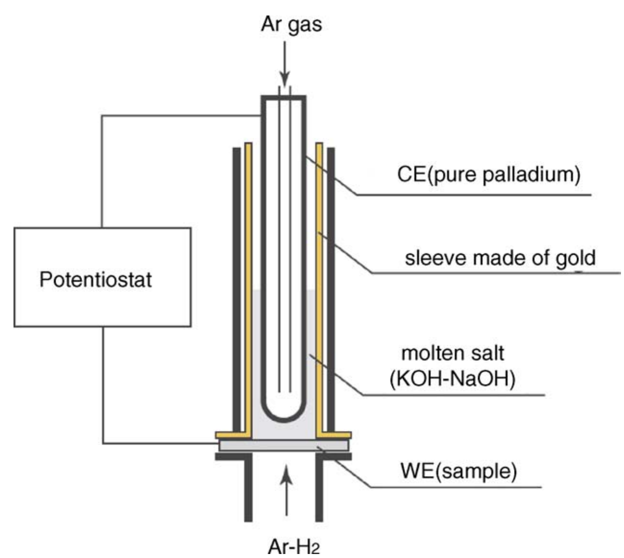

Fig. 1. Schematic illustration of the electrochemical cell using a limiting current method.

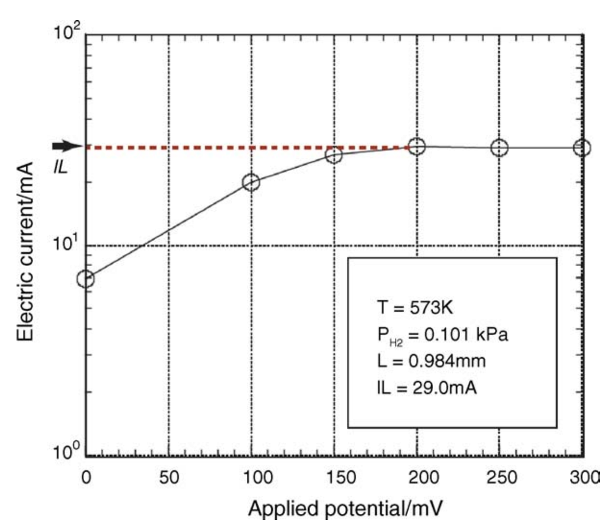

Fig. 2. Correlation between electric current and the applied potential measured at 573 K for pure Nb.

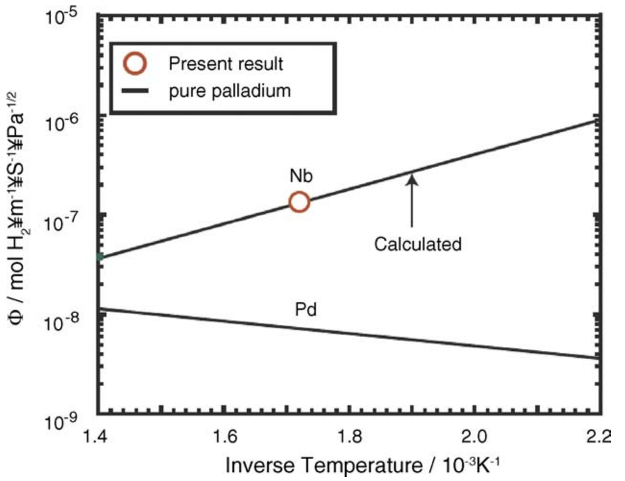

Fig. 3. Comparision of the experimental results of the hydrogen permeability of pure Nb with estimated result from the product of the hydrogen diffusivity and the hydrogen solubility.

for pure Nb. In Fig. 3, the present result was compared with the estimated result from the product of the hydrogen diffusivity [4] and the hydrogen solubility [5], each measured experimentally. There was good agreement between them. For comparision, the hydrogen permeability for pure Pd was also presented in Fig. 3. The permeability for pure Pd is about one order smaller than that of pure Nb at 573 K.

The hydrogen pressure used in the present limiting current method was as low as 0.101 kPa. This pressure was extremely small as compared to the pressure used in a conventional gas permeation method with a mass flow gauge. This is one of the great advantages, as the permeability can be measured accurately using this method even for materials showing poor resistance to hydrogen embrittlement.

3.2. *Nb–5 mol%M binary alloys*

The *I–E* curves measured at 573 K are shown in Fig. 4 for Nb–5 mol%M binary alloys (M = Zr, Mo, Ru and Pd).

As shown in this figure, the electric current saturated to a certain value and the limiting current, I_L, was observed clearly. The values of the I_L varied with M. The hydrogen permeability of these alloys were calculated following Eq. (2) and the results are summarized in Table 2 together with the result of pure Nb. The hydrogen permeability of niobium increased significantly by the Pd addition and slightly increased by the Zr addition. It was noted that the Pd addition into Nb could enhance the permeability despite that fcc Pd shows much lower permeability than bcc Nb.

On the other hand, the Mo addition lowered largely the hydrogen permeability of niobium. Also, the Ru addition slightly lowered the permeability.

Thus, the permeability of Nb–M alloys was obtained for the first time from the present experiment. To account for the measured alloying effect on the hydrogen permeability,

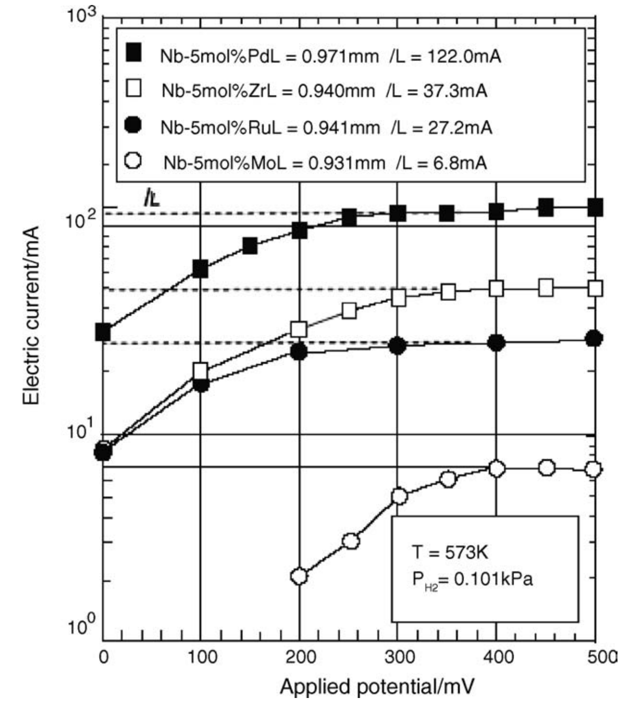

Fig. 4. Correlation between the electric current and the applied potential measured at 575 K for Nb mol% M (M = Zr, Mo, Ru and Pd).

Table 2
Hydrogen permeability measured at 573 K for Nb–5 mol%M (M = Zr, Mo, Ru and Pd)

Specimen	Φ (mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$)
pure-Nb	1.30×10^{-7}
Nb–5 mol%Zr	1.60×10^{-7}
Nb–5 mol%Mo	2.88×10^{-8}
Nb–5 mol%Ru	1.16×10^{-7}
Nb–5 mol%Pd	5.04×10^{-7}

the first principle calculations are now under way. Namely, the calculations are in progress to obtain both the hydrogen dissolution energy and the activation energy for the hydrogen diffusion in each alloy.

4. Summary

The hydrogen permeability of pure Nb and Nb–5 mol%M alloys (M = Zr, Mo, Ru, Pd) was measured at 573 K using a limiting current method. It was found experimentally that the hydrogen permeability changed largely with the addition of a small amount of alloying elements, M. The hydrogen permeability of Nb metal increased by the addition of Pd and Zr, but decreased by the addition of Mo and Ru.

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