Hydrogen Permeation of Eutectic Nb-Zr-Ni Alloy Membranes Containing Primary Phases

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Hydrogen permeability (Φ) of eutectic Nb-Zr-Ni alloy membranes containing the primary phases ZrNi or bcc-(Nb, Zr) was measured using a gas flow meter. Φ of the Nb₁₀Zr₄₅Ni₄₅ alloy containing the primary ZrNi phase (16 vol%) was 2.35×10^{-8} [mol H₂ m⁻¹ s⁻¹ Pa^{-0.5}] at 673 K, while Φ of the Nb₂₀Zr₄₀Ni₄₀ alloy containing the primary bcc-(Nb, Zr) phase (18 vol%) was 2.73×10^{-8} [mol H₂ m⁻¹ s⁻¹ Pa^{-0.5}] at 673 K. These values were higher than that of pure Pd and of the Nb₃₉Ti₃₁Ni₃₀ alloy that shows the highest Φ value in the Nb-Ti-Ni system. The present work strongly supported our previous proposal that multiphase alloys containing eutectic structures, which suppress a hydrogen embrittlement, are promising as novel hydrogen permeation membranes.

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1. Introduction

In recent years, many attempts to develop palladium free permeation membranes for separation and purification of hydrogen gas have been made. Nishimura *et al.* have systematically investigated hydrogen permeability (Φ) of vanadium-based alloys and reported that they show higher Φ than that of pure palladium.¹⁻⁵ Nevertheless, these alloys suffer from a severe hydrogen embrittlement, so that they are not practically used as a hydrogen membrane. Hydrogen permeability (Φ) is expressed as the product of hydrogen diffusivity (D) and hydrogen solubility (K). Consequently, we must raise D , K or both in order to raise Φ . Metals having large hydrogen solubility are susceptible to the hydrogen embrittlement, which results in that high Φ and resistance to the hydrogen embrittlement are incompatible in the single-phase alloys. The present authors have proposed new concept for alloy designing of hydrogen permeation membranes on the basis of the idea for sharing the functions. That is, they have designed new multiphase alloy membranes consisting of the primary bcc-(Nb, Ti) phase that contributes to hydrogen permeation and the eutectic B2-TiNi and bcc-(Nb, Ti) phases that suppress the hydrogen embrittlement.⁶ However, Φ of these Nb-Ti-Ni alloys are only comparable to that of pure Pd, so that a further improvement of Φ is strongly desired. It is expected that Φ of Nb-Zr-Ni system is at least comparable with that of Nb-Ti-Ni one.

The main purpose of the present work is to search for the eutectic structure in the Nb-Zr-Ni system and to demonstrate that the eutectic alloys are effective in suppression of the hydrogen embrittlement.

2. Experimental

The Nb-Zr-Ni alloy ingots (mol%) were prepared by arc melting using Nb (99.9 mass%), Zr (99.7 mass%) and Ni (99.9 mass%) in a purified argon atmosphere. Disks of 12 mm

in diameter and 0.5–0.7 mm in thickness were cut from these ingots using a spark erosion machine. Microstructural and structural examinations of these disks were carried out using a scanning electron microscope (SEM) and an X-ray diffractometer (XRD), respectively. Both sides of these disks were polished using buff with 0.5 μ m Al₂O₃ particle, and then coated by Pd with 190 nm thickness using a RF sputtering machine to prevent oxidation during permeation experiments. After these disks were sealed by copper gaskets, both sides of the disk were evacuated using a diffusion pump to below 3×10^{-3} Pa, then heated to 673 K and kept for 20 minutes. Hydrogen gas (99.99999%) of 0.2–0.55 MPa and 0.1 MPa was introduced in the upstream side and in the downstream side, respectively. Hydrogen flux passing through the disks was measured by a hydrogen flow meter (KOFLOC Model-3300). If the hydrogen content in these alloys is proportional to the square root of the hydrogen pressure, *i.e.* obeys the Sieverts' law, the relation between the hydrogen flux J passing through the disks and Φ is expressed by the following equation;

$$J \times L = \Phi(P_u^{0.5} - P_d^{0.5}) \quad (1)$$

where L is a thickness of the disk, and P_u and P_d are the hydrogen pressure in the upstream and the downstream sides, respectively.

3. Result and Discussion

Figures 1(a) and (b) show XRD patterns of Nb₁₀Zr₄₅Ni₄₅ and Nb₂₀Zr₄₀Ni₄₀ alloys in the as-cast state, respectively. The Bragg peaks of both alloys are indexed on the basis of the B_f-type ZrNi (*Cmcm*) intermetallic compound and the bcc-(Nb, Zr) solid solution.

The SEM photographs of Nb₁₀Zr₄₅Ni₄₅ and Nb₂₀Zr₄₀Ni₄₀ alloys are shown in Figs. 2(a) and (b), respectively. The Nb₁₀Zr₄₅Ni₄₅ alloy consists of thin rod-type primary ZrNi phase and very fine eutectic structure of ZrNi and (Nb, Zr) phases. The volume fraction of the primary phase is about 16%. It is worth noticing that permeation experiments are possible in this alloy in spite of containing much ZrNi phase

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Fig. 1 XRD patterns of the as-cast (a) Nb₁₀Zr₄₅Ni₄₅ alloy and (b) Nb₂₀Zr₄₀Ni₄₀ alloy, respectively. The Bragg peaks of these alloys are indexed on the basis of ZrNi and (Nb, Zr) phases.

Fig. 2 SEM photographs of the as-cast (a) Nb₁₀Zr₄₅Ni₄₅ alloy and (b) Nb₂₀Zr₄₀Ni₄₀ alloy, respectively. The primary phase is ZrNi for (a) the Nb₁₀Zr₄₅Ni₄₅ alloy, while (Zr, Nb) for (b) the Nb₂₀Zr₄₀Ni₄₀ alloy.

that fails usually by the hydrogen embrittlement. On the other hand, we observe a small (Nb, Zr) primary phase and very fine eutectic structures of ZrNi and (Nb, Zr) phases in the Nb₂₀Zr₄₀Ni₄₀ alloy. The volume fraction of the primary (Nb, Zr) phase is about 18%. These facts suggest that the eutectic

Fig. 3 Plots of $(J \times L)$ vs $(P_u^{0.5} - P_d^{0.5})$ for Nb₁₀Zr₄₅Ni₄₅ and Nb₂₀Zr₄₀Ni₄₀ alloys at 673 K.

point should exist in the composition between these two alloys, where the crystal structure of the primary phases changes according to the alloy composition.

Figure 3 shows the plots of $(J \times L)$ versus $(P_u^{0.5} - P_d^{0.5})$ for these alloys at 673 K. The permeation rate $(J \times L)$ is proportional to $\Delta P^{0.5}$. The linear relation coefficients R^2 are obtained by a linear regression analysis. The R^2 values are over 0.96, which implies that the hydrogen flux passing through this alloy obeys eq. (1) at the temperature range of 573–673 K. That is, hydrogen permeation of this alloy is controlled by hydrogen diffusion. Φ of this alloy, *i.e.* the slope of $(J \times L)$ vs $(P_u^{0.5} - P_d^{0.5})$ line, is 2.35×10^{-8} [mol H₂ m⁻¹ s⁻¹ Pa^{-0.5}] for the Nb₁₀Zr₄₅Ni₄₅ alloy and 2.73×10^{-8} [mol H₂ m⁻¹ s⁻¹ Pa^{-0.5}] for the Nb₂₀Zr₄₀Ni₄₀ alloy at 673 K, respectively. Unfortunately, the Nb₁₀Zr₄₅Ni₄₅ alloy was broken by the hydrogen embrittlement at 573 K and lower temperature. The Arrhenius plots of Φ for these two alloys are shown in Fig. 4. Plots of Pd and the Nb₃₉Ti₃₁Ni₃₀ alloy⁶⁾ are included in this figure, which have been measured using a same experimental apparatus. Φ of these alloys increases

Fig. 4 Arrhenius plots of hydrogen permeability (Φ) for Nb₁₀Zr₄₅Ni₄₅ and Nb₂₀Zr₄₀Ni₄₀ alloys together with that of pure Pd and the Nb₃₉Ti₃₁Ni₃₀ alloy.

with increasing temperature as the same manner to that of the $\text{Nb}_{39}\text{Ti}_{31}\text{Ni}_{30}$ alloy. Φ of these alloys is higher than that of pure Pd above 573 K. Furthermore, it should be noted that Φ of these alloys is higher than that of the $\text{Nb}_{39}\text{Ti}_{31}\text{Ni}_{30}$ alloy, although the Nb content of the former alloy (13.4 mass%) is about quarter lower than that of later one (52.8 mass%). These alloys show high hydrogen permeability in spite of low Nb content in comparison with the $\text{Nb}_{39}\text{Ti}_{31}\text{Ni}_{40}$ alloy, which implies the possibility of low cost hydrogen permeation alloys in this system. The present work strongly supported our previous proposal that multiphase alloys containing eutectic structures, which suppress the hydrogen embrittlement, are promising as novel hydrogen permeation membranes.

4. Summary

We have examined the hydrogen permeation characteristics of multi-phase Nb-Zr-Ni alloys. The $\text{Nb}_{10}\text{Zr}_{45}\text{Ni}_{45}$ alloy constitutes of the ZrNi primary phase and the eutectic structure of ZrNi and bcc-(Nb, Zr) phases. On the other hand, the $\text{Nb}_{20}\text{Zr}_{40}\text{Ni}_{40}$ alloy constitutes of the (Nb, Zr) primary phase and the eutectic structure of ZrNi and bcc-(Nb, Zr) phases. Hydrogen embrittlement does not occur in both alloys during permeation measurements above 623 K. The hydrogen permeability (Φ) of these alloys is higher than that

of pure Pd above 573 K. Furthermore, these alloys show high Φ in spite of the low Nb content in comparison with that of the $\text{Nb}_{39}\text{Ti}_{31}\text{Ni}_{40}$ alloy, which implies the possibility of low cost hydrogen permeation alloys in this system.

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