Oxide Glass/Amorphous Metal Alloy Laminated Membrane for Hydrogen Separation

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A five-layered membrane composed of an amorphous Ni–Nb–Zr alloy substrate (ca. 30 µm), thin proton–electron mixed conductive tungsten phosphate glass films (ca. 50 nm) and Ni coatings (ca. 20 nm) was fabricated by pulsed laser deposition and vacuum evaporation. A flux of hydrogen passed through the laminated membrane without Pd at 673 K at ca. 2×10^{-6} mol·cm^{-2}·s^{-1}, and no degradation was observed in the 10 h operation. The present results suggest that amorphous Ni–Nb–Zr alloy passivated with WO_3-based oxide glass is a promising material for H_2 filtering in a medium temperature range.

Hydrogen separation is a key technology for the realization of a hydrogen-based economy. Amorphous (a-) Ni–Nb–Zr alloys are expected to be alternative materials to replace expensive Pd-based membranes for hydrogen separation because of low cost, high hydrogen solubility and diffusivity, and high mechanical strength.[1–3] The hydrogen permeability at 573–673 K is in the order of 10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-1/2}$, which is comparable to that of Pd alloy. However, a-Ni–Nb–Zr alloys have fatal drawbacks for this application, i.e., they need thick Pd catalyst coating for promotion of H_2 dissociation and suppression of surface oxidation and react with the catalyst coating at the operation temperature.

Mixed proton and electron conducting materials are also candidates for hydrogen filter materials.[4–7] Tungsten phosphate glasses dissolve hydrogen at temperatures below the glass transition temperature (T_g) through reaction with W^{6+} ions to form redox pairs of W^{5+} and H^+, and electrons trapped on W^{5+} and charge compensating H^+ diffuse into the glass via hopping between W^{6+} and W^{5+}.[8–10] The hydrogen-reduced glasses show distinct protonic and electronic conductivity at 573–773 K.[11] Recently, we reported hydrogen permeation of thin tungsten phosphate glass films deposited by pulsed laser deposition (PLD).[12] The permeation rate of the oxide glass was found to be 2.0×10^{-6} mol·cm^{-2}·s^{-1} at 773 K when the difference of hydrogen partial pressures between the feed- and permeate-side (ΔP) and thickness of the glass layer were 0.2 MPa and ca. 100 nm, respectively.

Here we report fabrication of a five-layered membrane composed of a-Ni–Nb–Zr alloy substrate, thin tungsten phosphate glass films, and Ni coatings, and hydrogen permeation of the membrane without Pd in the temperature range 573–673 K. Ni coating works as a catalyst for dissociation of hydrogen although the thick plate is not applicable to a hydrogen separation membrane because of small permeability (ca. 3×10^{-11} mol·m^{-1}·s^{-1}·Pa$^{-1/2}$ at 673 K).[13] We propose that a-Ni–Nb–Zr alloy passivated with a thin tungsten phosphate glass layer to suppress surface oxidization and reaction with the Ni catalyst during operation at high temperatures is a good candidate for H_2 filtering.

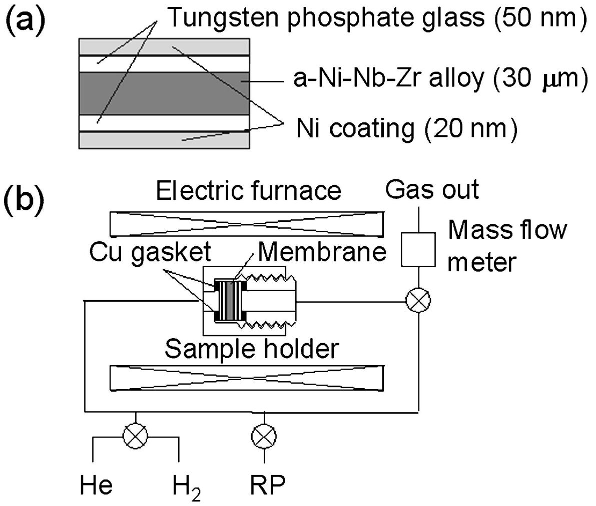

Figure 1. (a) Schematic cross-sectional view of the laminated membrane composed of a-Ni–Nb–Zr alloy substrate, thin tungsten phosphate glass films, and Ni coatings. Thin layers of the oxide glass and Ni coating were deposited by PLD and vacuum evaporation, respectively. (b) Experimental setup of the hydrogen permeation measurement. Sample membrane was fixed with Cu gaskets in the sample holder.

A five-layered membrane illustrated in Figure 1a was fabricated as follows: An a-$(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Co_5$ alloy ribbon with a crystallization temperature of ca. 730 K was prepared by single-roller melt-spinning technique in Ar atmosphere. The ribbon was cut into a circular shape and polished with lapping sheets and diamond pastes (12-mm diameter and 30-µm thick substrate). The substrate was etched with a dilute HF/HNO_3 solution and purified with ethanol and acetone. A thin film of tungsten phosphate glass (ca. 50 nm) was deposited on opposite surfaces of the substrate by PLD at room temperature. Bulk glass with chemical composition $37PO_{5/2}·6WO_3·18NbO_{5/2}·9BaO·30NaO_{1/2}$ was used as a target. An ArF excimer laser employed was operated at a 10 Hz repetition rate and a power density of ca. 4 J·cm^{-2} for ablation of the target. In order to prevent reduction of tungsten ion in the resulting oxide glass film during deposition, oxygen gas at 10 Pa was introduced into the PLD chamber. The molar ratio of cations in the film determined by the XPS measurement was ca. 28P:9W:23Nb:11Ba:29Na ($T_g > 773$ K). The glass film adhered strongly to the substrate and sustained no damage by the following handling. A thin Ni layer (ca. 20 nm) was then deposited on the surfaces of the oxide glass film by vacuum evaporation.

Hydrogen permeation rate of the laminated membrane was measured with a gas-permeation technique using a handmade apparatus shown in Figure 1b. Sample membrane was fixed with

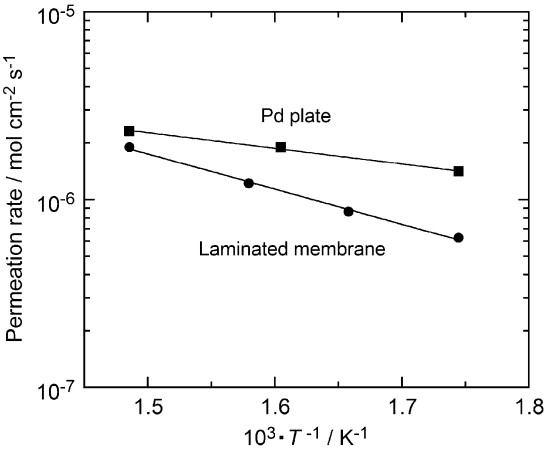

Figure 2. Temperature dependence of the hydrogen permeation rate of the five-layered membrane (●) and the Pd plate (■). $\Delta P = 0.3$ MPa was used.

Cu gaskets in the sample holder. The area for hydrogen permeation was approximately 0.25 cm^2. The membrane was heated up to 673 K in He atmosphere and then hydrogen was introduced in the permeation cell. The ΔP ranged up to 0.3 MPa. The flux of atmospheric hydrogen passed through the membrane at 673, 633, 603, and 573 K was measured using a mass flow meter. The permeation rate of a 250-μm Pd plate was also measured under the same condition for comparison (Pd-based alloy of a few hundred microns in thickness is generally utilized for hydrogen separation from a viewpoint of the mechanical strength).

Figure 2 shows the hydrogen permeation rate of the laminated membranes as a function of reciprocal absolute temperature T^{-1}. Thermally activated dependence was observed for both membranes and the permeation rate of the laminated membrane in the measured temperature range was comparable to that of the Pd plate. The permeation rate was constant 1.9×10^{-6} mol·cm^{-2}·s^{-1} at 673 K, which was stable not to change after 10 h. The activation energy of the laminated membrane for permeation was 36 kJ·mol^{-1}. In the membrane without Ni coating, hydrogen permeation was not detectable. Therefore, Ni coating worked as a catalyst for promotion of hydrogen dissociation.

The hydrogen flux passed through the laminated membrane can be estimated by considering an equivalent electrical circuit.[14] The total resistance for the hydrogen flux is given by $d/K = \Sigma(d_i/K_i)$, where d, K, and d_i, K_i are the thickness and the permeability of the laminated membrane or each layer i, respectively. From the equation, the flux though the laminated membrane was roughly determined by the oxide glass layer because the resistance of the a-Ni–Nb–Zr alloy substrate, and the Ni coating are smaller by more than one order of magnitude than that of the oxide glass layer. In fact, as shown in Figure 3, the permeation rate of the laminated membrane at 673 K was found to be proportional to $\Delta P^{0.73}$, indicating the hydrogen permeation was close to diffusion-limited ($\Delta P^{0.5}$).[15] However, the activation energy was twice the 18 kJ·mol^{-1} value reported in ref 12. The fact is due possibly to high resistance layers formed by reaction of the a-Ni–Nb–Zr alloy substrate with the oxide glass during the PLD. We are trying to detect the high-resistance layer by TEM observation and improve the hydrogen permeation rate by optimization of oxide glass composition and experimental condition.

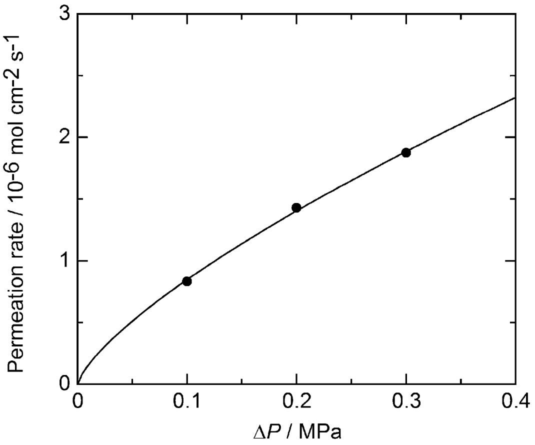

Figure 3. The hydrogen permeation rate of the five-rayered membrane at 673 K as a function of the ΔP. The hydrogen permeation rate was proportional to $\Delta P^{0.73}$.

In summary, it was found that a five-layered membrane composed of a-Ni–Nb–Zr alloy substrate, thin oxide glass films, and Ni coatings showed practical permeation rate in the temperature range 573–673 K and that the membrane was stable against heating at 673 K for 10 h.

References and Notes

1 S. Yamaura, Y. Shimpo, H. Okouchi, M. Nishida, O. Kajita, H. Kimura, A. Inoue, *Mater. Trans.* **2003**, *44*, 1885.
2 S. Yamaura, Y. Shimpo, H. Okouchi, M. Nishida, O. Kajita, A. Inoue, *Mater. Trans.* **2004**, *45*, 330.
3 S. Yamaura, M. Sakurai, M. Hasegawa, K. Wakoh, Y. Shimpo, M. Nishida, H. Kimura, E. Matsubara, A. Inoue, *Acta Mater.* **2005**, *53*, 3703.
4 J. Guan, S. E. Dorris, U. Balachandran, M. Liu, *Solid State Ionics* **1998**, *110*, 303.
5 X. Qi, Y. S. Lin, *Solid State Ionics* **2000**, *130*, 149.
6 H. Matsumoto, T. Shimura, T. Higuchi, H. Tanaka, K. Katahira, T. Otake, T. Kudo, K. Yashiro, A. Kaimai, T. Kawada, J. Mizusaki, *J. Electrochem. Soc.* **2005**, *152*, A488.
7 C. Zuo, T. H. Lee, S. E. Dorris, U. Balachandran, M. Liu, *J. Power Sources* **2006**, *159*, 1291.
8 H. Tawarayama, F. Utsuno, H. Inoue, H. Hosono, H. Kawazoe, *Chem. Mater.* **2006**, *18*, 2810.
9 H. Tawarayama, F. Utsuno, H. Inoue, S. Fujitsu, H. Kawazoe, *J. Power Sources* **2006**, *161*, 129.
10 H. Tawarayama, S. Sugata, H. Inoue, H. Hosono, H. Kawazoe, *Chem. Mater.* **2007**, *19*, 4385.
11 H. Tawarayama, H. Kawazoe, S. Sugata, H. Inoue, H. Hosono, *Ceram. Trans.* **2007**, *198*, 63.
12 H. Tawarayama, H. Kawazoe, H. Hosono, *Solid State Ionics*, in press.
13 Y. Yamanishi, T. Tanabe, S. Imoto, *Trans. Jpn. Inst. Met.* **1983**, *24*, 49.
14 K. Yamakawa, M. Ege, M. Hirscher, B. Ludescher, H. Kronmüller, *J. Alloys Compd.* **2005**, *393*, 5.
15 R. C. Hurlbert, J. O. Konecny, *J. Chem. Phys.* **1961**, *34*, 655.