

Characterization of Thin Palladium-based Membranes for the Application of On-site Hydrogen Production

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Metallic membranes play important roles in membrane reactor technology for on-site hydrogen production application. Pd and Pd-25Ag alloy membranes with the thickness of 2.5 μm were successfully prepared on silicon support using microfabrication technology in this work. Silicon-supported Pd alloy membranes were characterized by in-situ hydrogen microscope within the temperature range of 423 ~ 673 K. The Si-supported Pd-25Ag alloy membrane showed excellent resistance to hydrogen-induced brittleness whereas the Si-supported Pd membrane had fractured upon hydrogenation-dehydrogenation cycle. Ni-supported Pd membrane in 2.5 μm thick was also successfully prepared for permeation characterization. Hydrogen permeation of the Ni-support Pd membrane was carried out in a conventional gas permeation apparatus using pure hydrogen and gas mixture of hydrogen and 28.3 Vol.% CO_2 , respectively. Grain growth had occurred in the Ni-supported thin Pd membrane during hydrogen permeation. Surface resistance was significant and increased with the addition of CO_2 .

Keywords: Palladium, Membrane, Hydrogen separation

1. INTRODUCTION

Commercial application of polymer electrolyte fuel cell (PEFC) on portable power source technology is halted because effective methods are not available yet for on-board storage of hydrogen. Therefore, it is interesting to develop membrane reactor technology as an alternative method for the on-board storage of hydrogen [1-5]. High purity hydrogen could be directly produced using methanol and other liquid hydrocarbon fuels by membrane reactor. Hydrogen separation membranes are important to performance of membrane reactor because they determine hydrogen purity and productivity. The most commonly used materials for hydrogen separation membranes are palladium-based. There are numerous publications on preparation and characterization of thin Pd alloy membranes for hydrogen separation application. However, much of recent effort has been devoted to the preparation of thin Pd alloy membranes supported by porous ceramic and metals. It is difficult to obtain thin Pd alloy membrane without pinhole on the porous support because of rough surface [6]. The porous supports also have significant resistance to mass transfer. As a result, it is difficult for us to know intrinsic permeation behavior of thin Pd alloy membranes [7]. The knowledge is necessary for us to design and optimize membrane reactor for practical application.

Recently, microfabrication method has been successfully employed for preparing pinhole-free Pd alloy membranes on silicon with channel and microsieve structure [1, 2, 4, and 8]. Owing to brittleness of silicon, it is difficult to characterize hydrogen permeation of thin Pd based alloy membranes using conventional gas permeation apparatus in which gas-tightness relies on metallic gasket. It is therefore difficult for us to directly compare literature results with each other.

In this work, we would utilize Ni metal instead of Si as support for hydrogen permeation of thin Pd alloy membrane. As a result, it is possible to carry hydrogen permeation experiment in conventional gas permeation apparatus. In addition, we are interested in clarifying whether silicon-supported Pd alloy membranes would fracture or not upon

hydrogenation-dehydrogenation cycle because our previous work showed that thin Pd alloy membranes supported by materials with low hydrogen solubility would fracture owing to hydrogen-induced stress [9]. Pd and Pd-25Ag alloy membrane would be prepared on Si and characterized.

2. EXPERIMENTAL

Fig. 1 shows schematic structure of thin Pd alloy membranes prepared in this work. Silicon support was used for the hydrogenation-dehydrogenation observation. Ni support was used for hydrogen permeation characterization because of excellent mechanical properties and low hydrogen permeability.

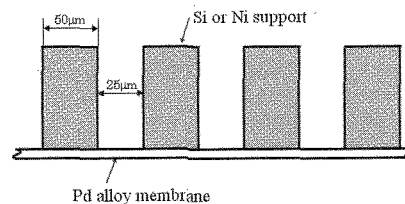


Fig.1 Schematic structure of thin Pd alloy membranes supported by Ni and Si. Ni and Si support was 50 and 400 μm thick, respectively.

Thin Pd and Pd-25Ag alloy membranes were prepared using a multi-target sputtering system. A dc power source was used for Pd (99.99% purity) target. An RF power source was used for Ag (99.99% purity) target. Pinhole-free Pd and Pd-25Ag alloy membranes were successfully prepared in argon atmosphere using the optimized parameters as follows. The base and work pressure was 2.6×10^{-5} Pa and 0.2 Pa, respectively. The dc power was 200 W for the Pd target. The RF power was 100 W for the Ag target. The target/substrate distance was 150 mm.

Fig. 2 shows fabrication procedure of thin Pd-based membrane supported by silicon. 2 μm -thick SiO_2 layer was formed on silicon wafer by thermal oxidation (Fig. 2 (1)). Then window

was opened in BHF solution (Fig. 2 (2 and 3)). After resist was removed, Si wafer was etched by dry etching until there was a Si layer with thickness of about 20 μm left (Fig. 2 (4)). Then Pd and Pd-25Ag layer with the thickness of about 2.5 μm were prepared by the aforementioned multi-target sputtering method (Fig. 2 (5)). The Pd-based layer was finally released by dry etching (Fig. 2 (6)).

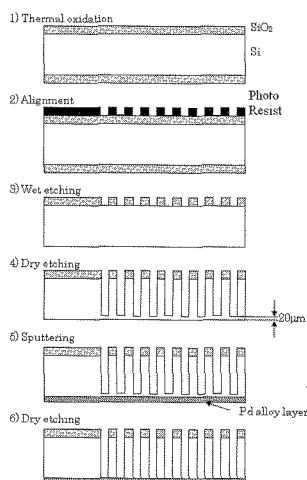


Fig. 2 Fabrication procedure of thin Pd-based membrane supported by Ni layer.

Fig. 3 shows fabrication procedure of thin Pd-based membrane supported by Ni layer. Thin Pd-based layer was deposited on silicon wafer by the multi-target sputtering (Fig. 3 (a)). 65 μm -thick negative resist (XP-KMPR 1050, KAYAKU MICROCHEM) was spin-coated and patterned (Fig. 3 (b)). Then 50 μm -thick Ni layer was prepared by electroplating (Fig. 3 (c)). After the negative resist was removed, Si wafer was etched away in KOH solution (Fig. 3 (d and e)). As-prepared membranes were then cleaned by electron cyclotron resonance (ECR) method before permeation experiment in order to remove contaminations formed during the fabrication procedure. The preparation of Ni-supported Pd-25Ag alloy membrane, however, was failed in this work due to internal stress. Only Ni-supported Pd membrane was successfully prepared.

In-situ hydrogenation-dehydrogenation of Si-supported Pd-based membranes was carried out in a high temperature hydrogen microscope within the temperature range of 423 ~ 673 K. The instrumental details had been described in our previous work [9]. The experimental details in the microscope were as follows.

- (1) The chamber was evacuated to 5×10^{-4} Pa after the loading of sample;
- (2) Sample was heated to 673K by 10 K/minute.
- (3) Pure hydrogen was introduced to 8.0×10^4 Pa and kept for 10 minutes; then evacuated;
- (4) Sample was cooled to 573K, 473K and 423K by 10 K/minute, respectively, and Step (3) was repeated.

Hydrogen permeation of the Ni-supported Pd membrane was carried out in a conventional gas permeation apparatus within the temperature range of 473 ~ 673 K and the hydrogen pressure of ~ 40 KPa. High purity hydrogen (99.9999%) and gas mixture of hydrogen and 28.3 Vol.% CO_2 was used, respectively. Aluminum gaskets were used for necessary gas-tightness. The Ni-supported Pd membrane was loaded into the permeation apparatus and annealed at 673 K in vacuum for 30 minutes before permeation. 20 kPa air was introduced into the upstream side while the downstream side was still kept in evacuation. The upstream pressure was recorded in order to examine whether

membrane sample was leakage-free or not. If there were pinholes or other defects in membrane sample, the upstream pressure would decrease gradually or the Ni-supported Pd membrane would fracture soon under the high upstream pressure. After the gas-tightness examination, both the upstream and downstream side were opened to air and kept for 5 minutes for baking treatment. It is thought such a procedure is necessary to remove contaminations on the surface of Pd membranes. Air was evacuated and pure hydrogen or the gas mixture was then introduced into the upstream side. The downstream side was kept in vacuum by continuous pumping during hydrogen permeation. All samples were examined in SEM before and after permeation experiments.

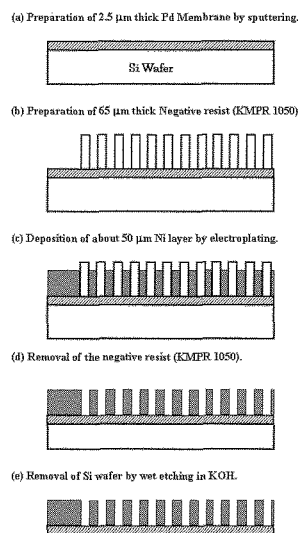


Fig. 3 Fabrication procedure of thin Pd-based alloy membrane supported by Si layer.

3. RESULTS AND DISCUSSION

Fig. 4 shows representative cross-sectional SEM image of Si-supported Pd alloy membranes. The thin Pd alloy membranes were dense and crack-free. Thin Pd alloy membranes showed good process compatibility with silicon-based microfabrication technology.

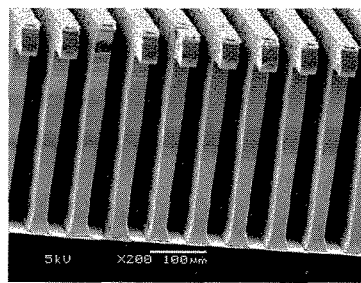


Fig. 4 SEM image of the as-prepared micro Pd-25Ag membrane.

The Si-supported Pd membrane was fractured during the hydrogenation-dehydrogenation cycle. This is keeping with our prior observations [9]. On the contrary, there was no peel-off, pinhole or any other visible failure in the Si-supported Pd-25Ag membrane after the same hydrogenation-dehydrogenation cycle. The Si-supported Pd-25Ag membrane had excellent resistance to hydrogen-induced brittleness. Fig. 5 is SEM image of the Si-supported Pd-25Ag membrane after the

hydrogenation-dehydrogenation cycle. This was different from our previous results [9]. We thought that it might result from that the channel structure had positive effects. Hydrogen-induced stress might be released by the channel structure. This was important for practical applications of Pd alloy membrane on membrane reactor technology.

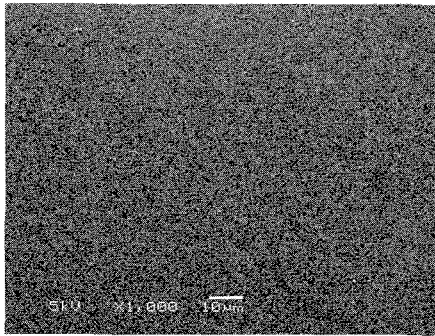


Fig. 5 SEM image of the Si-supported Pd-25Ag alloy membrane after the hydrogenation-dehydrogenation cycle.

Fig. 6 (a) shows cross-sectional SEM images of the Ni-supported Pd membrane. The Pd membrane was about 2.5 μm thick. There were some deflections in the Ni-supported Pd membrane because of internal stress. It was also partly owing to that the sample was directly prepared by the scissor. Fig. 6 (b) is top view of the Ni-supported Pd membrane. The channel width was about 28 μm , which was slightly deviated from the designed value.

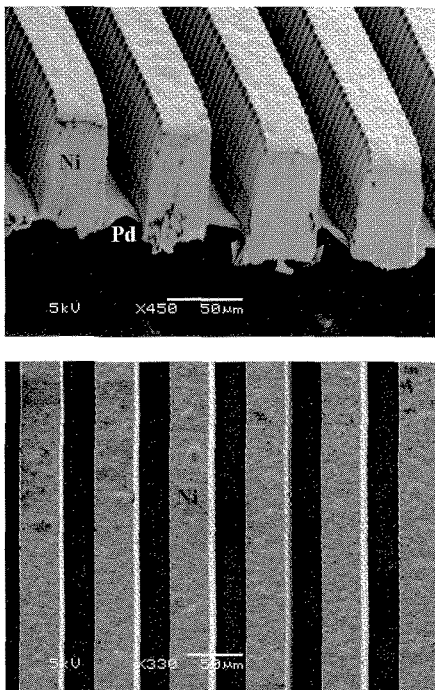


Fig. 6 SEM images of the Ni-supported Pd membrane.

Figs. 7 show SEM images of the Ni-supported Pd membrane after hydrogen permeation within the temperature range of 473 ~ 673 K. There were grains with different sizes between the upstream and downstream side of the Ni-supported Pd membrane. Grain sizes ranged from several tens nanometers to several microns on the downstream surface. The average size of grains at the upstream side was smaller than that of grains at the

downstream side. The largest grains at the upstream side had the diameter of about 1 μm , while those at the down stream side had the diameter of 4 or 5 μm . The grain growth of Pd and Pd-Ag alloy membranes had been observed [8-9, 11, and 12]. Our previous study showed that the grain growth at the downstream side of palladium membrane was larger than that at the upstream side. This was consistent with the observations in this work. It indicated that grain growth had occurred during hydrogen permeation of the Ni-supported Pd membrane. It was unclear about the specific mechanism of the grain growth. It might result from annealing effect of permeation process and hydrogen-induced stress. The thin palladium membrane was only about 2.5 μm thick, which was smaller than some big grains at the downstream side. It could be inferred that some grains were transmembrane. It was unknown whether the grain growth had negative effects or not on hydrogen permeation of Pd membrane [13, 14]. The presence of high volume of grain boundary is benefit for hydrogen diffusion in solid whereas grain growth was unwanted in the views of thermal stability. It was possible to suppress the grain growth of the Pd membrane with addition of Ag element into Pd metal [9].

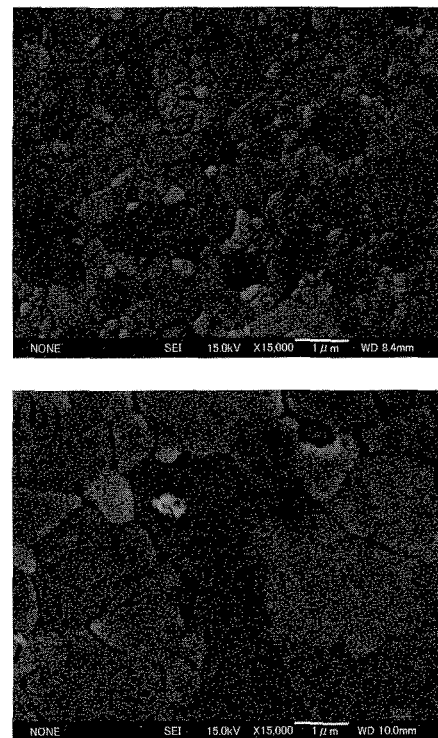


Fig. 7 SEM images of the Ni-supported Pd membrane after permeation. a) Upstream side; b) Downstream side.

Fig. 8 is Arrhenius plots of hydrogen permeability of the Ni-supported Pd membrane using pure hydrogen and gas mixture of hydrogen and 28.3 Vol.% CO_2 . Hydrogen permeability of the Ni-supported Pd membrane apparently decreased with the presence of 28.3 vol.% CO_2 . For example, hydrogen permeability was about $5.19 \times 10^{-9} \text{ mol H}_2 \text{ s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$ but decreased to $2.89 \times 10^{-9} \text{ mol H}_2 \text{ s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$ with the addition of CO_2 at 573K. Better linear relationship could be observed for pure hydrogen permeation. It seemed that CO_2 gas had significantly negative effect on hydrogen permeation of thin Pd membrane.

Hydrogen permeation through dense metal membrane could be described using the following equation:

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

where J , Φ , P_U , P_D and L denote permeation flux, permeability, upstream pressure, downstream pressure and membrane thickness, respectively. n is pressure exponent. In this work, the downstream side was kept in vacuum by continuous pumping so that the equation could be written as follows:

$$J = \frac{\Phi P_U^n}{L} \quad (2).$$

The pressure exponent would be 0.5 if the permeation is diffusion-limited; it would be 1 if the permeation is surface reaction-limited [14].

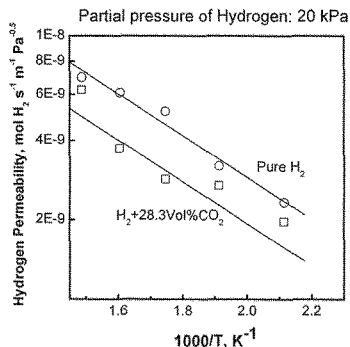


Fig. 8 Arrhenius plot of temperature dependency of hydrogen permeability of the Ni-supported Pd membrane.

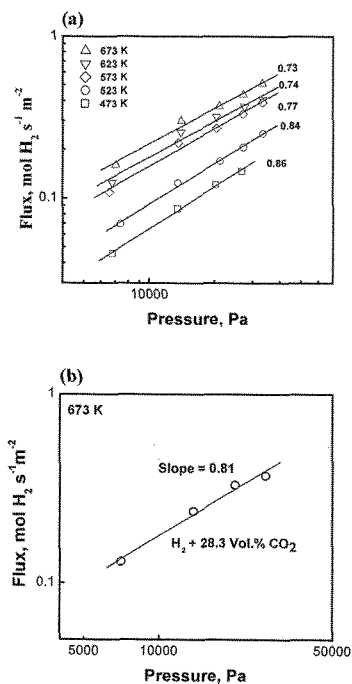


Fig. 9 Pressure dependency of permeation flux through the Ni-supported Pd membrane under different conditions.

Fig. 9 (a) shows pressure dependence of hydrogen permeation flux through the Ni-supported Pd membrane using pure hydrogen. There were good linear relationships. Pressure exponent could be calculated from the slope of linear curves, which was also denoted as number in Fig. 9 (a). The pressure exponents had apparent dependency on temperature. The pressure exponent increased from 0.73 to 0.86 when temperature decreased from 673 K to 473 K. The hydrogen permeation was limited by both surface resistance and bulk diffusion. The fraction of surface

resistance increased with the decreasing temperature. Figure 9 (b) shows that the pressure exponent was about 0.81 for hydrogen permeation at 673 K with the addition of CO₂ gas. It was higher than 0.73 in Fig. 9 (a). There was higher surface resistance with presence of CO₂ gas in high concentration. Further work is necessary to clarify the phenomenon.

4. CONCLUSION

In this work, dense thin Pd and Pd-25Ag membrane were successfully prepared on Si and Ni supports using the microfabrication method. Tin Pd alloy membranes showed excellent process compatibility with microfabrication technology. The Si-supported Pd-25Ag alloy membrane had high resistance to hydrogen-induced brittleness whereas the Si-supported Pd membrane did not. It was observed that CO₂ gas had apparent negative effects on hydrogen permeation of the Ni-supported Pd membrane. Surface resistance increased with decreasing permeation temperature, suggesting that more effort has to be devoted to the surface status of Pd alloy membrane for practical applications.

5. REFERENCES

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