

Development of a new porous metal support of metallic dense membrane for hydrogen separation

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Abstract

Porous nickel support was successfully made by uniaxial pressing of nickel powder for gases separation or metal support of Pd and/or Pd-alloy dense membrane. Since the used nickel powder was prepared by pulsed wire evaporation (PWE) method, it has a good thermal stability. Furthermore, a broad particle size distribution from 20 to 5000 nm cleared out the powder mixing step in the procedures of fabrication of porous nickel support. From the pore characterization and SEM analysis, it was clarified that the fabricated porous nickel support had so small uniform pore size of 33 nm and very smooth surface so that it can be offered as new material for the substrate of palladium and/or palladium-based alloy membrane. As a result of single gas permeation test using H₂ and N₂, permeance was constant with increasing transmembrane pressure difference and the selectivity was around 3.7, which indicated that the gas permeation was contributed by Knudsen diffusion. Since it has thermal resistance up to 650 °C, sputtering followed by copper reflow could be applied to the formation of Pd–Cu–Ni ternary film on it. Furthermore, it showed the defect-free dense membrane characteristic.

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1. Introduction

Variety of porous supports has been used for dense palladium-based alloy dense membranes recently. A lot of studies describe different methods to fabricate such composite membranes. The commonly used methods are sputtering [1–4,9], electroless plating [1,4–6], CVD [7–9] and electroplating [5,11]. The thin palladium or palladium-based alloy layer is prepared on the surface or inside the pores of porous supports by those methods. Many researchers have developed the support for palladium or palladium-based alloyed membrane. The materials having been commercially used for porous supports are ceramics [1,3,4,7–9,11], glass [2] and stainless steel [5,6,10]. Recently, silicon wafer covered with SiO₂ and TiO₂ have been reported [12].

For high quality of metallic composite membrane support should be porous, smooth facial, highly permeable, thermally stable and metallic adhesive. Furthermore, it has to have defect-free surface. Moreover, in order to produce in large quantity of membrane the method of fabrication should be as simple as possible. On the other hand, the thickness of palladium or palladium-based alloy film depends on the deposition method and the pore size of the support. Uemiya [13] reported that the thickness of palladium layer strongly depended on the supports quality, such as narrow pore size distribution and the amount of defects on the surface. The suggested relations between the thickness of Pd layer and pore size were 13 μm in thickness versus 0.3 μm in pore size, 4.5 μm versus 0.2 μm, 2.2 μm versus 0.1 μm and 0.8 μm versus 5 nm. Mardilovich et al. [5] showed that the minimum thickness of palladium required to achieve a dense layer by electroless plating was approximately three times the diameter of the largest pores in the support.

Among the supports, non-metal, such as ceramic and glass has weak adhesion to metallic thin film and difficulty to seal into

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commercial component. The weak adhesion, different thermal expansion coefficients and the volume change of the membrane in contact with hydrogen may cause stability problems [3,14,15]. Tosti et al. [4] demonstrated that the Pd and Pd alloy thickness was very important for the membrane stability against the stress generated in the membrane-support interface. In additions, they found that shear stress at interface metal-ceramic decreased with a decrease in a palladium membrane thickness. They also found that the adhesion value (about 10 MPa) of Pd-ceramic for electroless and sputtered membranes were less than the shear stress at >500 K.

On the other hand, porous stainless steel support has been used to improve mechanical strength of the support. From the viewpoint of a practical application, porous stainless steel has the merit of getting more readily sealed into a commercial unit. However, atomic interdiffusion of metals between the thin Pd/Pd alloy layer and the stainless steel components occur during high temperature processing. To inhibit the atomic interdiffusion, Shu et al. [16] introduced titanium nitride as a diffusion barrier. However, Pd-Fe interdiffusion occurred at high temperature and the permeation flux was reduced. Furthermore, the diffusion barrier effectively separated the palladium-based alloyed film and the support.

There are some applications of other metal support. Zhang et al. [17] obtained Pd-Ag alloyed film on V-15Ni alloy. However, metallic interdiffusion and selective oxidation of vanadium were deteriorated Pd-Ag membrane. Furthermore, they insisted that the stainless steel with low hydrogen affinity cracks the palladium-based alloy film or become porous during hydrogenation/dehydrogenation. And they suggested that the higher hydrogen affinity support has the higher resistance to hydrogen-induced failure it is. However, Tosti [18] found that metal, such as Nb with hydrogen permeability higher than palladium crack the palladium-based alloy during hydrogen permeation. In addition, he suggested that nickel with permeability lower than palladium is a good metal for an ideal permeation behavior. However, since they used dense nickel for support of palladium film, hydrogen permeability was too low.

This paper focuses on a possibility of porous nickel membrane as support of metallic composite membrane and a scaling up of porous nickel support for membrane modulation. In order to fabricate and scaling up a porous substrate, nickel powder was pressed by uniaxial pressing in the metal cylindrical mold having diameter of 50 mm. Furthermore, defects free Pd alloy layer was successfully deposited on the porous nickel support by sputtering followed by Cu-reflow technique. The permeation test was carried out at temperatures in the range of 25–500 °C. The membranes were characterized by scanning electron microscopy (SEM) and mercury porosimeter.

2. Experimental

2.1. Fabrication of porous support

Sub-micron nickel powder, purchased from Nano Technology Co., was used as a raw material for porous nickel support. As shown in Fig. 1, the particle size of nickel powder is from

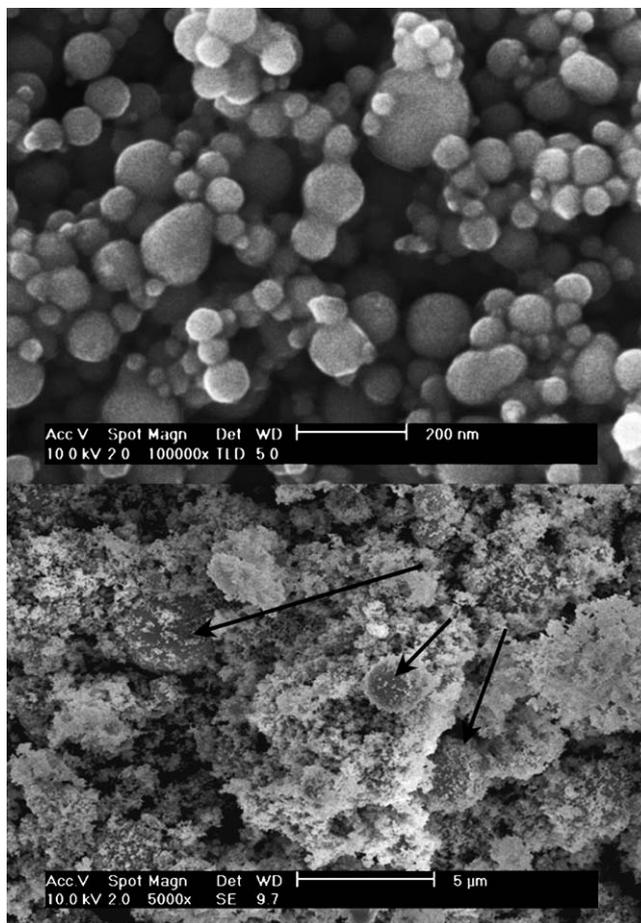


Fig. 1. SEM image of the used nickel powder: The arrows points are micron-particles.

20 to 5000 nm and the powder has smooth spherical shape with purity of 99.9% of nickel. Nickel powder was compressed without binder in metal cylindrical mold having diameter of 50 mm using a home made press under high pressure (333 MPa) and then the compressed support was treated at 650 °C under H_2 condition for 1 h for mechanical strength.

2.2. Fabrication of Pd-Cu-Ni ternary alloy membrane

Pd and Cu were deposited on porous nickel supports (PNS) by magnetron sputtering method. To increase the adhesion and activation of the support, the surface was treated by H_2/Ar plasma surface modification. This surface modification was carried out in a 10% H_2/Ar mixture at 66.6612×10^2 mPa (50 mTorr) working pressure with radio frequency 100 W for 5 min. A pure palladium (99.9%) and copper (99.9%) targets of 0.3175 cm (1/8 in.) in thickness and 5.08 cm (2 in.) in diameter, purchased from Kurt J. Lesker Co., were used as the sputtering source. The supports were approximately kept 70 mm from sputtering gun during deposition. Before deposition, the sputtering chamber was evacuated to 1.333224×10^{-5} Pa (1.0×10^{-7} Torr) and then filled with ultra high purity argon. All membranes were deposited at 1.333224×10^2 mPa (1 mTorr) in ultra high purity argon. Prior to Cu-sputtering at 18 W (600 V, 30 mA) for 10 min

Pd was sputtered at 42 W (350 V, 120 mA) for 40 min. The membrane thickness could be controlled by sputtering time with deposition rates of palladium and copper at 958 and 233 Å/min, respectively.

The temperature of substrate was controlled at 400 °C. After Pd–Cu deposition, the sputtering chamber was gradually cooled at room temperature. Subsequently, Cu-reflow and Pd–Cu–Ni alloy formation was performed at 650 °C for 2 h. Prior to copper reflow the muffle furnace was evacuated to 1.333224×10^{-5} Pa (1.0×10^{-7} Torr) and then filled with 10% H₂/Ar mixture gas. The temperature was increase to the 650 at the rate of 7 °C/min and the mixture gas was continuously introduced during the Cu-reflow.

2.3. Permeation measurements

Permeation test was conducted with single gases of hydrogen and nitrogen at temperatures in the range of 25–500 °C and at transmembrane pressure differences of 0.034–0.152 MPa for the porous nickel support (PNS). For the Pd alloy/PNS dense membrane, the test carried out with single gases of hydrogen and nitrogen at temperatures in the range of 350–500 °C and at transmembrane pressure differences of 0.083–0.358 MPa. The permeation apparatus consists of a membrane cell, furnace, temperature controller, pressure gauge/controller and mass flow controller as shown in Fig. 2. Gases were introduced by mass flow controller (MCF, Brooks 5850 E series) and transmembrane pressure difference was regulated by pressure controller (Alicat PC-30PSIG-D). The permeation rate of individual gases was measured by a soap-bubble flow meter. The prepared support and Pd alloy/PNS were inserted in the membrane cell as shown

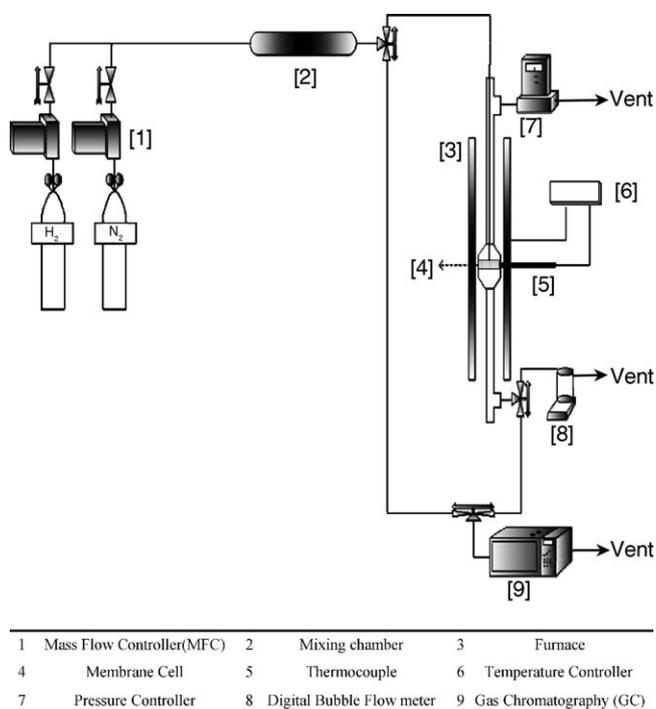


Fig. 2. The schematic diagram of a permeation test apparatus.



Fig. 3. The photograph of a single membrane unit.

in Fig. 3 and tightened to the cell by graphite seal. Selectivity was defined as the ratio of the permeance of hydrogen to that of nitrogen at the same transmembrane pressure difference and operating temperature.

2.4. Characterization of porous nickel support and Pd alloy membrane

The scanning electron microscopy (SEM) was used to characterize the surface and cross-section of the prepared support and Pd alloy membrane. Pore size distribution, average pore size, total pore volume and porosity of the prepared support were measured by mercury porosimeter. The composition of the metal elements was detected by EDS. To determine the extent of intermetallic diffusion at the Pd alloy layer/porous nickel support after long term test, EDS line scanning was used.

3. Results and discussion

3.1. Porous nickel support made by uniaxial pressing process

In previous paper, the porous nickel membrane with diameter of 2.54 cm (1 in.) was successfully fabricated [19]. However, to be designed into module, membranes need to be large enough. For this reasons, the porous nickel membrane had been scaled up to 50 mm in diameter as shown in Fig. 4. In previous study, mixture powder of 0.15 and 5 μm in average particle diameter made membrane higher packing degree than single size. The powder used in this study, supplied from Nano Technology Co., had broad particle size from 20 to 5000 nm. It means that the pre-mixing step could be eliminated. Furthermore, the selectivity and permeance were depended on press pressure while those were constant at below 680 MPa. Even though, in this study, the pressure was 333 MPa because of press capacity, the membrane was successfully fabricated with mechanical strength to be sealed into commercial unit and showed similar permeation results. Furthermore, as shown in Fig. 5, the membrane made

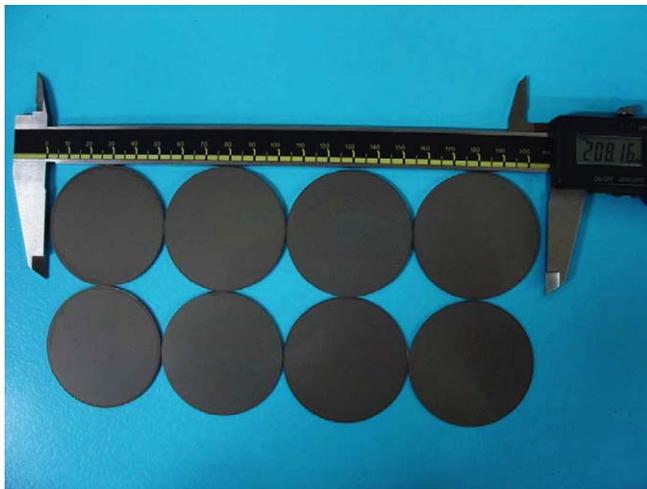


Fig. 4. The photograph of the developed porous nickel support: diameter is 50 mm; thickness is 1.2 mm.

with Chang-Sung Co.'s powder, which was made by precipitation method was too much sintered at 650 °C in hydrogen condition. The metal sintering made large and few amount of pores. In another study [20], we introduced the copper reflow method to make defect free Pd–Cu–Ni ternary alloyed mem-

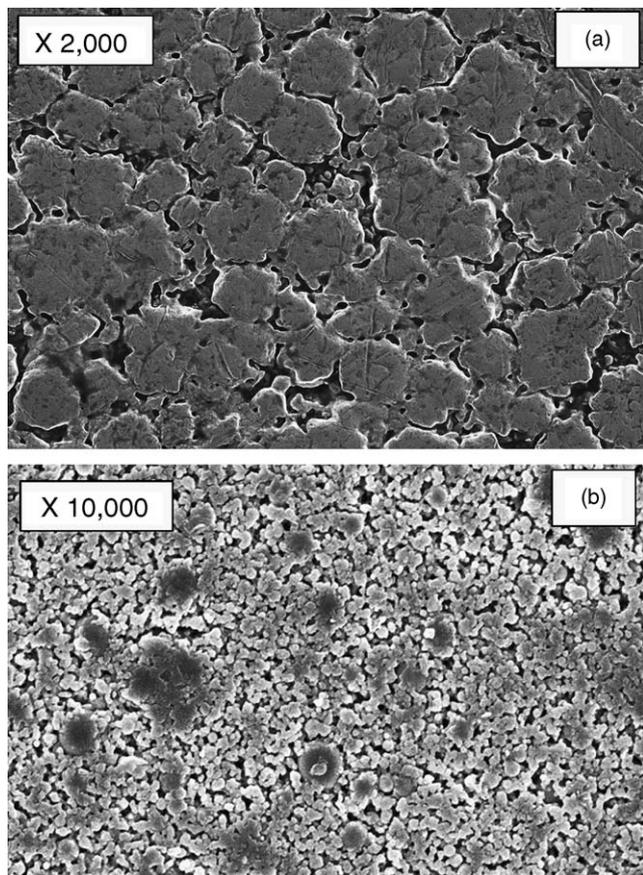


Fig. 5. The SEM images of porous nickel support after heat treatment: treatment condition is at 650 °C in H₂ for 1 h; (a) is the PNS fabricated of Ni powder made by precipitation method and (b) is the PNS fabricated of Ni powder made by pulsed wire evaporation method.

Table 1

The pore properties of the developed porous nickel support measured by mercury porosimeter

Average pore diameter (nm)	33
Total pore area (m ² g ⁻¹)	6.4
Total pore volume (cm ³ g ⁻¹)	0.05
Porosity (%)	30

brane deposited on those nickel porous membrane. However, since the Cu-reflow and alloy formation take place over 650 °C in hydrogen condition, sub-nickel layer was electroplated to reduce the pore size. To eliminate the nickel electroplating procedure, we had to change the raw material and found other nickel powder, which has thermal resistance in hydrogen condition at this temperature.

Fig. 6 is comparison between developed porous nickel support and commercial ones. SEM images in Fig. 6 shows that porous nickel support has very small pores with uniformity and smooth enough surface to be applied to the support without surface modification. Commercial porous supports had relatively large pore size of 0.5 μm so that it is modified by γ-Al₂O₃, sub-micron nickel powder and/or SiO₂ (500 nm) to obtain smoother surface and reduce the average pore size [1,3,6–9]. However, comparing to commercial α-alumina and porous stainless steel, the surface of porous nickel support is smooth enough and the pore diameter is so small as to apply to the support for metallic dense membrane. Table 1 and Fig. 7 are the results of mercury porosimeter of the porous nickel support. As shown in Table 1, the porous nickel support has total pore area of 6.4 m² g⁻¹, total pore volume of 0.053 cm³ g⁻¹ and porosity of 30%. Fig. 7 gives the pore size distribution of the porous nickel support. As shown in Fig. 7, it has average pore size around 33 nm with uniformity, which is very small comparing to α-alumina and porous stainless steel of 0.2 and/or 0.5 μm. From the results of pore properties and surface analysis, it is clarified that this kind of porous nickel support is good enough to be support of metallic dense membrane comparing to commercial porous supports because the surface of commercial porous materials needs to be modified by several step to be used for the support of the Pd dense membrane for large pore size of 0.2 or 0.5 μm.

3.2. Pd alloy dense metallic membrane deposition on the porous nickel support

We introduced the sputtering and copper reflow method on the porous nickel support to make defect free Pd alloy dense membrane. Since the copper reflow took place over 650 °C in hydrogen condition, the nickel porous support should be resistant at this temperature. As shown in Fig. 8, the Pd alloy defect-free film with 4 μm of thickness was formed at 650 °C. The weight composition of Pd:Cu:Ni was 89:4.5:6.5 from EDS analysis. It means that the nickel diffused through the Pd–Cu layer at 650 °C. However, after permeation test for 10 days at 500 °C, there were any indications of nickel diffusion from the EDS line scanning.

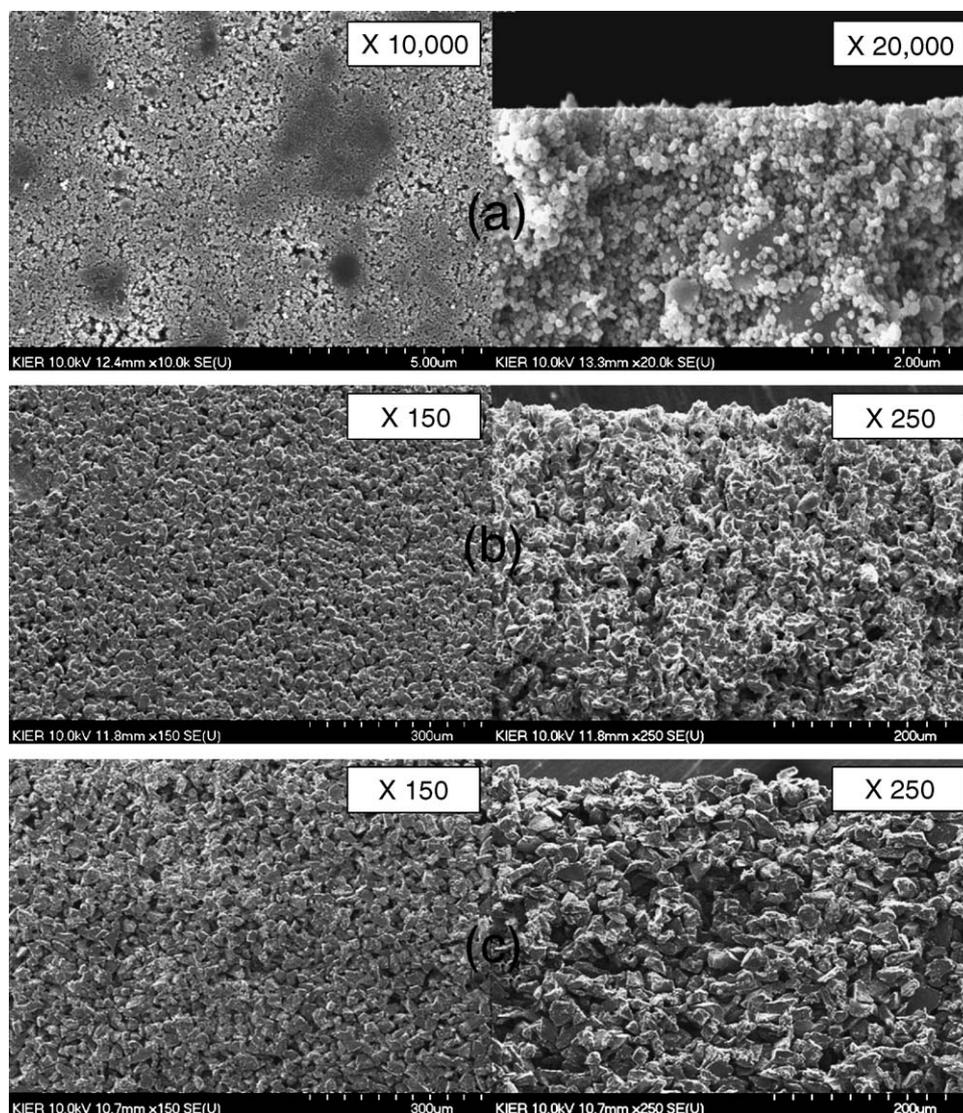


Fig. 6. The SEM images of the porous supports for metallic dense membrane: (a) is the invented porous nickel support, (b) is commercial porous stainless steel and (c) is commercial porous α - Al_2O_3 ; left is surface and right is cross-section images.

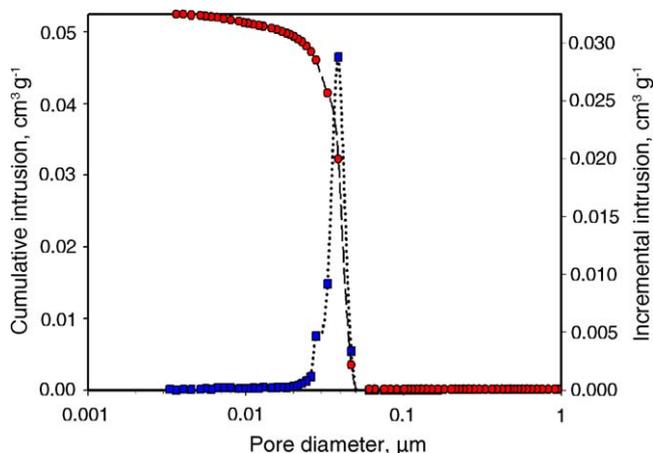


Fig. 7. The pore distribution of porous nickel support measured by mercury porosimeter: circle is cumulative intrusion; rectangular is incremental intrusion.

3.3. Gas permeation

The permeation test was carried out with single gases of H_2 and N_2 . The test temperature was from 25 to 500 °C and the transmembrane pressure difference from 0.034 to 0.152 MPa. Fig. 9 shows single gases of hydrogen and nitrogen permeance and the selectivity of H_2/N_2 of porous nickel support. As shown in Fig. 9, there is a decrease of gases permeances with increasing permeation temperature which is differ from earlier result while the selectivity of H_2/N_2 was constant as 3.7 which is similar to the earlier result [19]. And as shown in Fig. 9, H_2 and N_2 permeance were nearly constant with transmembrane pressure difference. It indicates that the gas permeation is contributed by Knudsen diffusion. The reason of permeance decrease with increase in temperature is that the characters of the used two kinds of nickel powders are different from each other.

Fig. 10 shows pure hydrogen flux of Pd alloy/PNS. Permeation test was conducted with single gases at temperatures in the

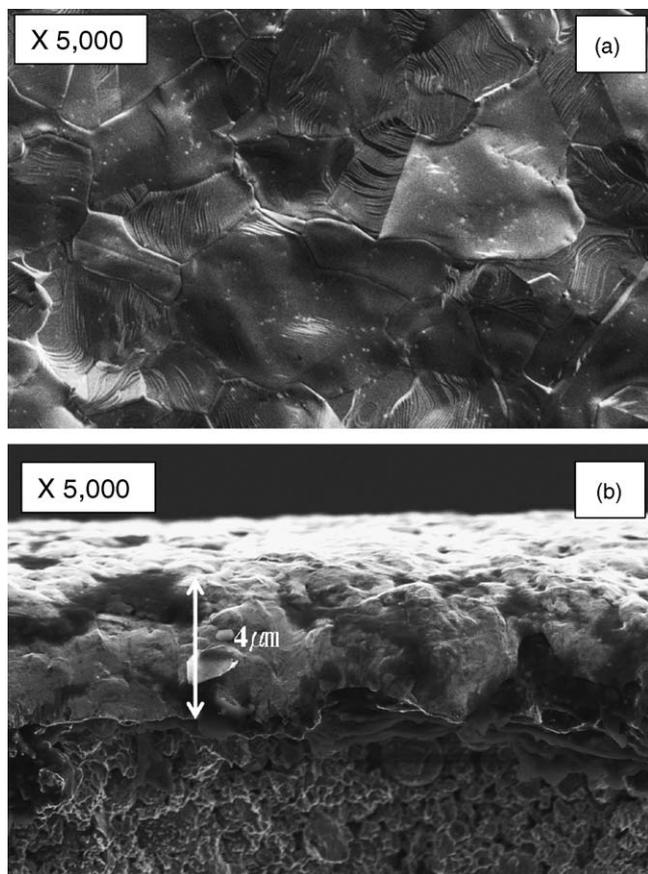


Fig. 8. The surface SEM images of Pd alloy/PNS after copper reflow: (a) is the surface image and (b) is the cross-section image.

range of 350–500 °C and at the transmembrane pressure differences of 0.083–0.358 MPa. The nitrogen was not detected during the test period. The hydrogen flux increased with increasing temperature and transmembrane pressure difference. It indicated that the Pd alloy deposited on porous nickel support showed

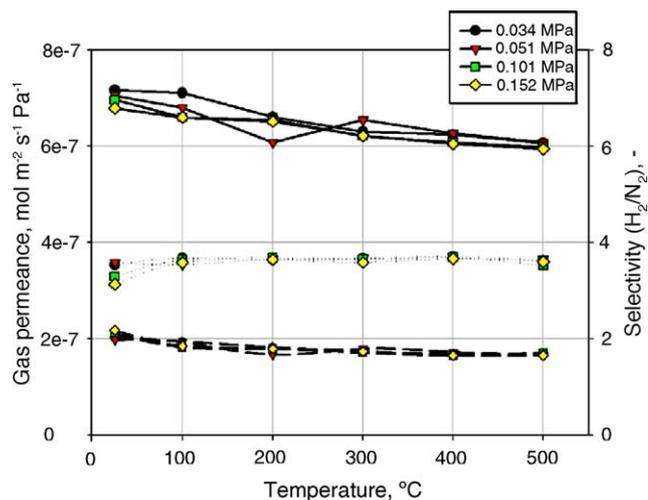


Fig. 9. The effect of temperature on the gas permeance and H_2/N_2 selectivity of PNS: circle is at 0.034 MPa; triangle is at 0.051 MPa; rectangular is at 0.101 MPa; diamond is at 0.151 MPa; solid line is H_2 permeance; dotted line is selectivity; dashed line is N_2 permeance.

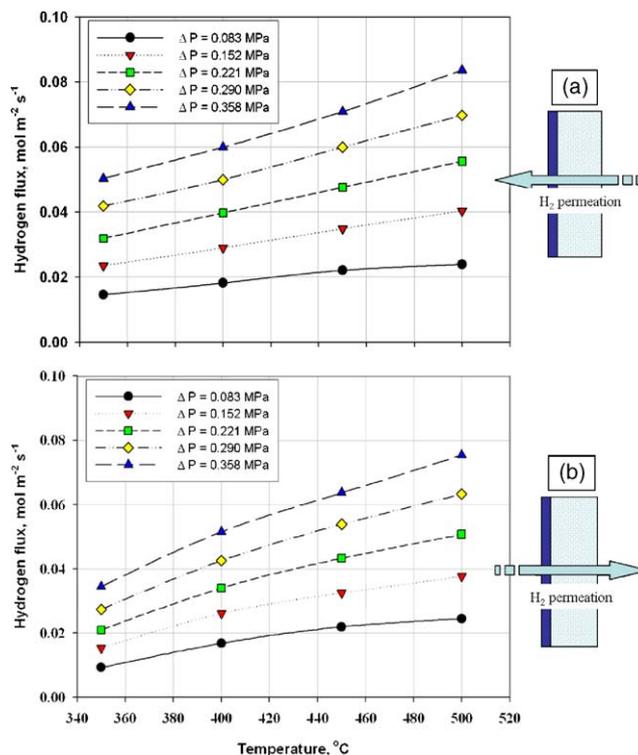


Fig. 10. The effect of temperature and operation mode on hydrogen permeation flux of Pd alloy/PNS: (a) is the operation mode of support to film (SF) and (b) is the operation mode of film to support (FS); nitrogen was not detected at any temperature and transmembrane pressure difference.

defect-free dense membrane. After permeation test carried out in operation SF (Support to Film) mode, we changed the permeation mode to FS (Film to Support). From the result shown in Fig. 10, the hydrogen flux was somewhat decreased with mode change from SF to FS. From the permeation test of porous nickel support, the ideal permselectivity of H_2/N_2 was around 3.7. It indicates that the porous nickel support has Knudsen diffusion which causes the decrease of permeation flux with mode change from SF to FS.

4. Conclusions

The porous nickel support was successfully scaled up by diameter of 50 mm. To improve the thermal stability, we changed the raw material, which was prepared by physical method, pulsed wire evaporation method, rather than chemical method, precipitation method. From single gas permeation test, the permeation was contributed by Knudsen diffusion. As metal substance, porous nickel support could provide several advantages, such as the mechanical strength, thermal stability and sealing to the commercial unit. Furthermore, this kind of porous nickel support has very small uniform pore size of 33 nm comparing to commercial porous ceramic and stainless steel substrate. Therefore, porous nickel support can be offered as new support material for palladium and palladium-base alloyed composite membrane. Moreover, it had so high mechanical strength that it could resist at 0.358 MPa. For this reason, it is anticipated that the developed porous nickel support can be applied to industrial process, such

as washable porous metal HEPA filter, hot gas filter, sparger, etc.

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