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Ultra-thin Ni dense membrane prepared by polishing treatment of porous nickel support for high-temperature H_2 separation

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Abstract−Ultra-thin nickel dense membranes (~0.5 μm) were developed by polishing treatment of porous nickel supports. The polishing treatment involved the use of 400 grit sand paper, 1000 grit, and 1500 grit, which was able to remove the surface pores due to the ductility of the PNS. The hydrogen permeation test showed that 4.53×10^{-2} mol m^{-2} s^{-1} of hydrogen permeation flux through the membrane could be achieved at a temperature of 973 K and a pressure difference of 136 kPa. The nitrogen leakage tests confirmed that there were no pinholes on the surface of the ultra-thin nickel dense membrane.

Keywords: High-temperature, Hydrogen Separation, Ultra-thin Nickel Membrane, Polishing Treatment, Metal Membrane

INTRODUCTION

Hydrogen supply can be derived from fossil fuel sources, for example, by natural gas steam reforming and coal gasification. Hydrogen from fossil fuel sources contains other products such as CO, CO_2, N_2, H_2S, and H_2O, which should be separated from hydrogen before used in fuel cells, semiconductors, and oil refineries. H_2 selective membranes have been prepared and used for separation since they have been shown to be very efficient in the separation process. Ceramics, metals, polymers, and combination thereof have been used as materials in H_2 selective membranes [1,2]. Among the membranes, dense metal membranes, operating via a solution-diffusion mechanism, can produce pure H_2 because of its dense structure, which prevents the passage of other atoms and molecules, e.g., CO, CO_2, O_2, N_2, CH_4, H_2O. Thus, the advantage of metal membranes lies in their ability to separate H_2 to a high purity. Pd and its alloys are considered suitable material for the fabrication of hydrogen separation metal membranes because of their high hydrogen permeability and chemical stability in hydrocarbon-containing gas streams [3]. Pd-based membranes already form the basis of current bench-scale purifiers and methanol reforming units [4,5]. The main drawback of Pd-based membranes is their extremely high cost for large-scale applications [6]. For this reason, the search for durable and cost effective membranes is an active area of research. The potential of reducing the materials cost of H_2 separation membranes lies in replacing Pd as the main material of these membranes. Recent studies have suggested that metals other than Pd may be used in the fabrication of efficient metal membranes [7,8]. The metals with the highest permeability are early transition metals, such as Nb, Zr, V, and Ta. These metals form the body-centered-cubic (BCC) structure, except for Zr, which adopts a hexagonal close-packed (HCP) structure below 550 °C. The H_2 permeability of these metals and their amorphous alloy is significantly higher than that of Pd. However, they form a tightly-held oxide that inhibits surface reaction sites, and consequently these metals require a coating of catalyst such as Pd and its alloy [7]. The main limitation of such amorphous alloy membranes is the upper temperature limitation (~300 °C), which can result in crystallization and increase susceptibility to hydrogen embrittlement [9].

It is well known that nickel is far cheaper and enables selective hydrogen permeation. Despite this interesting possibility and the low price of nickel, very little has been published on the use of a nickel layer as an effective hydrogen separation membrane. Some studies have reported interesting results for microfiltration nickel membranes on ceramic supports [10,11]. The nickel membranes showed low H_2/N_2 selectivity (~28 at 600 °C) because the main diffusion mechanism of hydrogen was surface diffusion through the pores [10].

Thus, the objective of this study was the development of ultra-thin dense nickel membranes. An ultra-thin nickel layer was formed on porous nickel supports (PNS) using the polishing method with sand-paper. The membrane preparation method was very simple and cost effective. The high mechanical strength of the nickel dense membrane could allow for easy modulation with a metal O-ring and flange-type metal module. The gas permeation tests using H_2 and N_2 could be carried out at high temperature (~700 °C) because of its good thermal stability. The surface morphology and thickness of the membrane were characterized by SEM.

EXPERIMENTAL

1. Membrane Fabrication

The membrane preparation method is shown in Fig. 1. Ultra-thin nickel membranes were made by polishing treatment of PNS

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‡This article is dedicated to Prof. Sung Hyun Kim on the occasion of his retirement from Korea University.

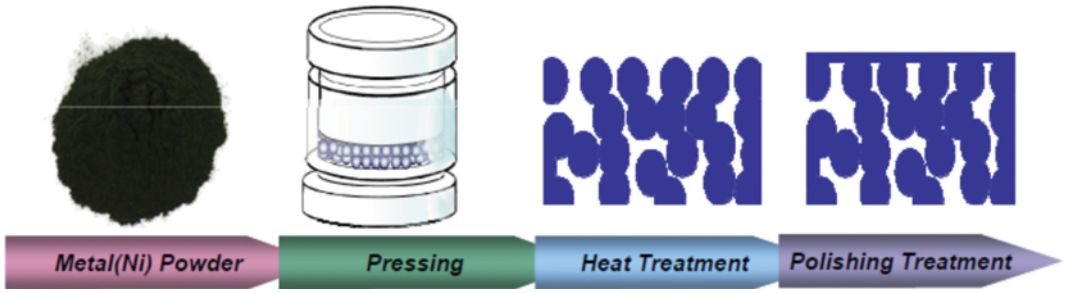

Fig. 1. Schematic showing procedure of Ni dense membrane preparation.

with three different types of sand-paper. The PNS was made by using an alumina modified nickel powder, which had an average size of 3.0 μm, adopted a spherical shape, and had a purity of 99.9%. To increase its thermal stability, the nickel powder was coated with an aluminum nitrate solution by using the incipient wetness impregnation method. An appropriate amount of aluminum nitrate ($Al(NO_3)_3 9H_2O$, Aldrich) was dissolved in deionized water, and the solution was added to the dried nickel powder to obtain 0.1 wt% Al. The nickel powder was then dried in a convection oven (120 °C) for 4 h and calcined at 400 °C for 4 h under 10%H_2+90%He mixture gas. 20 g of the alumina modified nickel powder was compressed without a binder in a cylindrical metal mold that had a diameter of 50 mm using a homemade press under high pressure (333 MPa). The compressed support was then treated at 1,173 K under H_2 for 2 h to improve its mechanical strength.

An ultra-thin nickel layer was formed by polishing method. The polishing process involved three steps and three different types of sandpaper. A grinder-polisher (Buehler) equipped with a sandpaper with a 400 grit was used in the first step. After the larger pores on the PNS were removed with the 400 grit sandpaper for 5 min, the scratches formed during the 400 grit sandpaper treatment and small pores remaining on the surface of the PNS were removed using 1000 grit sandpaper. The second polishing step was continued for ~10 min until the large scratches were removed. The last polishing step was conducted with 1500 grit sandpaper for ~10 min to remove the extra pores remaining on the surface of the PNS. The ultra-thin nickel membranes were then washed with deionized water and dried in a vacuum oven at 393 K for 2 h. The surfaces before and after polishing treatment were compared by SEM analysis.

2. Permeation Test

The prepared membranes were mounted in stainless steel permeation cells with metal O-rings. Permeation tests were conducted using hydrogen over a temperature range of 773 to 973 K, with a transmembrane pressure difference of 34-138 kPa. Nitrogen leak tests were conducted at the same conditions. The permeation rate of hydrogen was measured using a soap-bubble flow meter. Upon completion of the test, the membranes were slowly cooled under helium, broken and then the change in morphology and thickness was measured after the hydrogen permeation test using SEM.

RESULTS AND DISCUSSION

1. Membrane Characterization

Surface SEM images of PNS and polishing treated ultra-thin nickel dense membrane are compared in Fig. 2. The surface pore size of PNS made using the sintered metal method was ~5 μm. In a previous study, we tried to remove the surface pores to deposit a defect-free Pd and Pd alloy layer on the PNS [12]. Polishing treatment included three steps, 400 grit sandpaper, 1000 grit sandpaper, and alumina slurry, which effectively removed large pores and reduced the roughness. After polishing treatment, the PNS was almost impermeable. The last step of the polishing treatment included polishing using 1500 grit sandpaper. Due to the ductility of

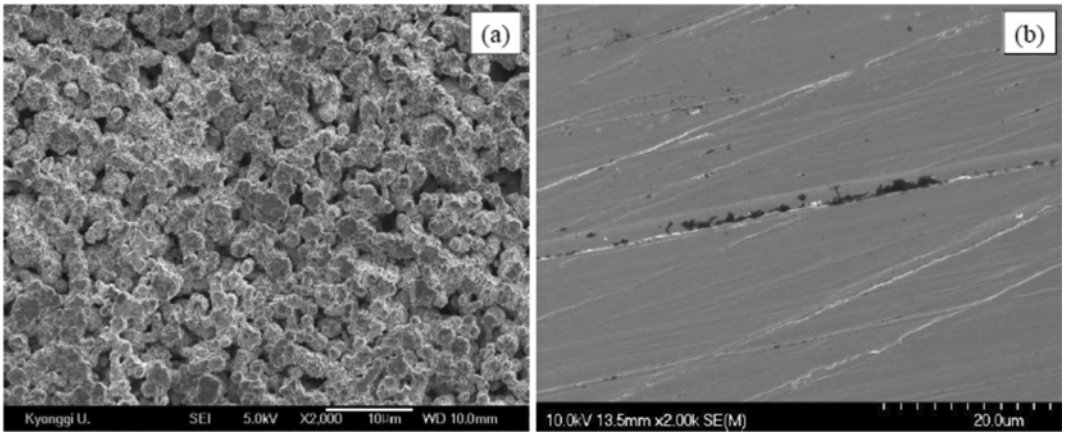

Fig. 2. Surface SEM images of fresh PNS (a) and polishing treated PNS (b).

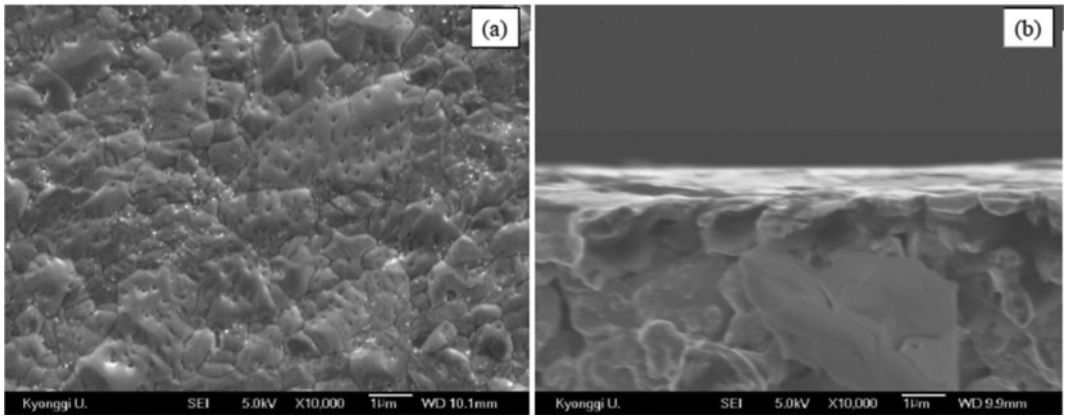

Fig. 3. Surface SEM images (a) and cross-sectional SEM image (b) of the ultra-thin nickel dense membrane.

the PNS, all the pores on the surface were blocked after the series of polishing treatments. The nitrogen leakage tests at room temperature confirmed that there were no pinholes on the surface of the polish treated PNS. As shown in Fig. 2(b), there were some scratches that were made by polishing with sand-paper. Even though there were some scratches, the membrane was lustrous enough to reflect light.

The ultra-thin nickel membrane was tested at 973 K using hydrogen and nitrogen. After the permeation tests were performed, the membrane was cooled, cut and the thickness of the dense nickel layer was analyzed. Fig. 3(a) shows the surface SEM images of the tested nickel dense membrane. After the permeation test at 973 K, the scratches disappeared and grains were observed on the surface of the nickel dense membrane. The average grain size was ~1 μm. Fig. 3(b) shows a cross-sectional SEM image of cut membrane. The thickness of the dense nickel layer was determined to be ~0.5 μm.

2. Permeation Tests

Gas permeation tests were conducted with pure hydrogen at temperatures ranging from 773 to 973 K and at pressure differences across the membrane ranging from 34 to 136 kPa. Fig. 4 shows the hydrogen permeation flux as functions of pressure and temperature. As expected, the hydrogen permeation flux increases with pressure difference and temperature and increased to 4.53×10^{-2} mol m^{-2} s^{-1} at a temperature of 973 K and a pressure difference of 0.136 MPa.

The hydrogen permeation flux (J, mol m^{-2} s^{-1}) is described by the following equation:

$$J=Q/l(P_{up}^{n}-P_{down}^{n}) \quad (1)$$

In which Q and l denote the hydrogen permeability (mol m m^{-2} s^{-1} Pa^{-n}) and the thickness (m) of the dense metal layer, respectively. P_{up} and P_{down} stand for the pressures on the feed and permeate sides. The dependency of the hydrogen flux on the pressure difference is shown in Fig. 5 and it shows that the pressure exponent of 0.5 gave good fits, meaning that the diffusion of hydrogen atoms through the dense nickel layer was rate-limiting from Sieverts' law. The nitrogen leakage tests, which were performed under the same conditions, confirmed that there were no pinholes on the surface of the ultra-thin nickel dense membrane.

Robertson [13] measured the permeability of hydrogen in pure nickel. He observed that there was no grain size effect on hydrogen permeability and the values he obtained were compared with

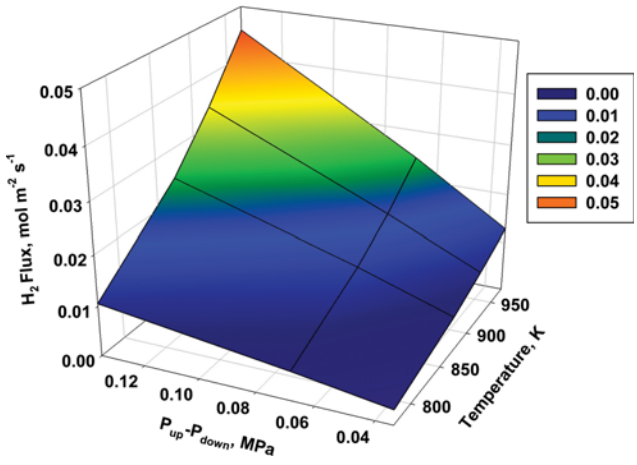

Fig. 4. Hydrogen permeation flux as functions of pressure and temperature.

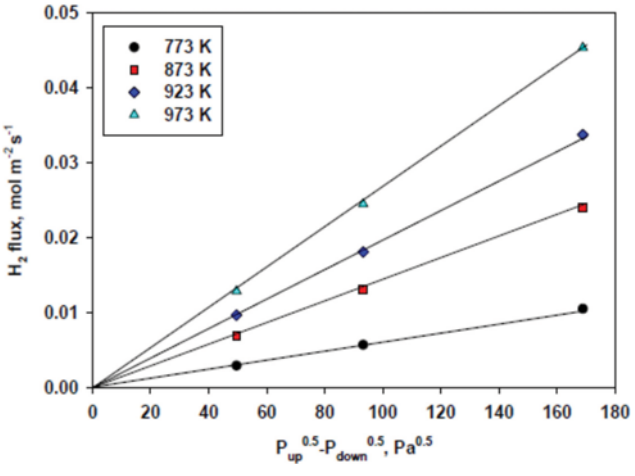

Fig. 5. Hydrogen permeation flux through the ultra-thin nickel dense membrane as a function of pressure difference with a pressure exponent of 0.5.

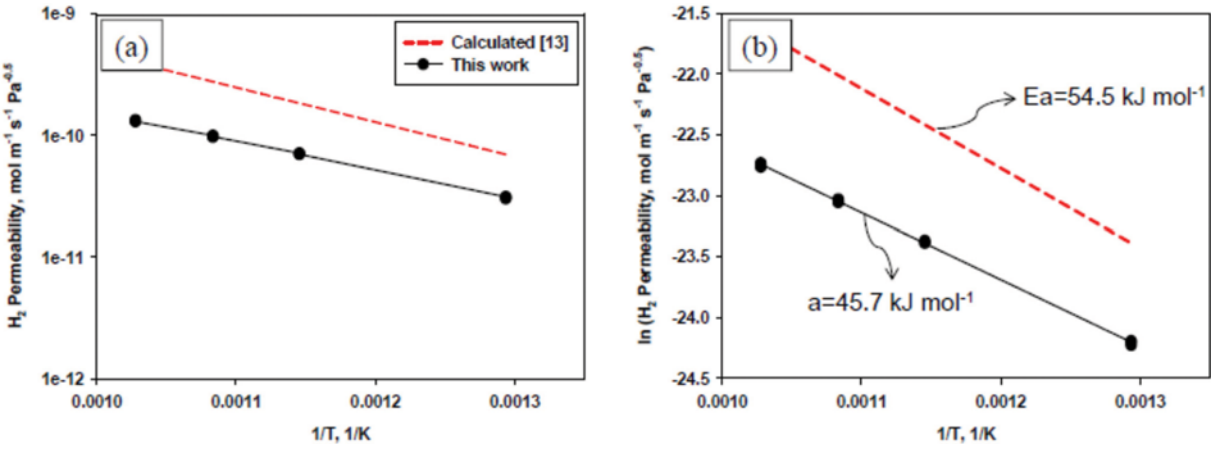

Fig. 6. Comparison of hydrogen permeability (a) and activation energy (b) between the values of this study and the value reported by Robertson [13].

our nickel membrane in Fig. 6(a). Hydrogen permeability of our ultra-thin membrane was ~1/3 of the value calculated by Robertson. The porosity of the PNS was calculated to be ~30%. The porosity could decrease the effective permeation area, leading to a decrease in hydrogen permeability.

Hydrogen transport through dense metal membranes is an activated process and can be described by the Arrhenius law:

$$\frac{Q}{l} = \frac{Q_0}{l}\exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where E_a is the activation energy (kJ mol^{-1}), R the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin units. As shown in Fig. 6(b), the activation energy of our ultra-thin nickel membrane, which was calculated based on the Arrhenius plot of overall hydrogen permeability, was 45.7 kJ mol^{-1}. This value is similar to the value (44.9-69.5 kJ mol^{-1}) summarized by Robertson [13].

CONCLUSIONS

Morphological analysis, hydrogen permeation tests and nitrogen leakage tests for the ultra-thin nickel dense membrane prepared by polishing treatment of PNS revealed that:

- It is possible to create a defect-free ultra-thin (~0.5 μm) nickel dense membrane by polishing treatment of PNS.
- The pressure exponent was 0.5, meaning that diffusion of hydrogen atoms through the dense nickel layer was rate-limiting and the hydrogen flux increased to 4.53×10^{-2} mol m^{-2} s^{-1} at a temperature of 973 K and a pressure difference of 136 kPa.
- The membrane was stable enough to be operated at a high temperature of 973 K.

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