

Research Article

Development of Pd Alloy Hydrogen Separation Membranes with Dense/Porous Hybrid Structure for High Hydrogen Perm-Selectivity

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For the commercial applications of hydrogen separation membranes, both high hydrogen selectivity and permeability (i.e., perm-selectivity) are required. However, it has been difficult to fabricate thin, dense Pd alloy composite membranes on porous metal support that have a pore-free surface and an open structure at the interface between the Pd alloy films and the metal support in order to obtain the required properties simultaneously. In this study, we fabricated Pd alloy hydrogen separation membranes with dense/porous hybrid structure for high hydrogen perm-selectivity. The hydrogen selectivity of this membrane increased owing to the dense and pore-free microstructure of the membrane surface. The hydrogen permeation flux also was remarkably improved by the formation of an open microstructure with numerous open voids at the interface and by an effective reduction in the membrane thickness as a result of the porous structure formed within the Pd alloy films.

1. Introduction

Pd-based membranes have attracted a great deal of attention for their use in hydrogen separation and purification owing to their high theoretical permeability, infinite selectivity, and chemical compatibility with hydrocarbon containing gas streams [1, 2]. Pd-based membranes are prepared in a composite form consisting of a dense Pd alloy film, which provides the high hydrogen perm-selectivity and a porous metal/ceramic support with appropriate mechanical strength to support the top layer [3–5]. Porous metal supports [4, 6–9] are promising candidates because of their better mechanical strength, resistance against cracking, ease of module fabrication and sealing, and thermal expansion coefficients similar to that of Pd and its alloys. However, typical metal supports like porous stainless steel support (PSS) and porous nickel support (PNS) have irregular, large surface pores, and very rough surfaces [7, 10–13]. These lead to the inhomogeneous sputter deposition of Pd on the porous metal support and

numerous pores at the surface of the membrane remain even after a heat treatment to achieve alloying and crystallization of Pd.

Many researchers have developed various surface pretreatments such as alumina sol-gel coating [7, 10, 13, 14] and micropolishing [4, 12, 13, 15] in order to remove the surface pores of porous metal supports. A sol-gel coated alumina layer is frequently introduced on PSS surface in order to moderate the average pore size, smoothen the surface, and prevent intermetallic diffusion of the metal support elements [7, 10, 14, 16]. The micropolishing pretreatment is very effective in leveling off the rough PNS surface and it almost completely plugs the surface pores.

Other researchers have focused on decreasing the thickness of the dense membrane in order to improve the hydrogen selectivity and permeability. In our previous studies [12, 13, 19], we reported on the fabrication of Pd alloy membranes with a dense and pore-free surface. These membranes

exhibited infinite hydrogen selectivity (H_2/N_2) at 723 K and a transmembrane pressure difference of 689 kPa. However, they did not have sufficient hydrogen permeability for various hydrogen separation applications because of the membrane with large thickness and closed structure at the interface between the Pd alloy films and the modified metal support. Therefore, it has been difficult to fabricate thin and dense Pd alloy films that are pore-free at the membrane surface and have an open structure near the interface in order to obtain high hydrogen perm-selectivity.

In this study, we developed Pd alloy membrane with dense/porous hybrid structure for obtaining both high hydrogen selectivity and permeability simultaneously. This membrane had high hydrogen selectivity owing to its dense and pore-free membrane surface, combined with improved hydrogen permeation flux not only because of its open microstructure with numerous voids near the interface but also because of the effectively reduced membrane thickness via the porous structure formed within the Pd alloy films. In this paper, we observed the morphology of the fabricated membranes and studied the formation mechanism of this hybrid structure. The effect of the dense/porous hybrid structure on the hydrogen perm-selectivity was also investigated.

2. Experimental

A PNS with good chemical affinity to Pd was prepared by compression of Ni powders and subsequent sintering. Ni powders were purchased from Sigma Aldrich Co. (with an average particle size of 5 μm) and from Nano Technology Co. (with an average particle size of 100 nm). In order to enhance the mechanical and thermal durability of the Ni support, the support surface was modified by mixing Ni powders with different average grain size of 5 μm and 100 nm in the ratio of 4 : 1 (wt%), respectively. Then, the mixture was milled for 24 h using a zirconia ball. The mixed-powders were compressed without binder in a cylindrical metal mold having a diameter of 1 inch. The compressed powders were heat treated at 973 K for 2 h under H_2 atmosphere. Additionally, a porous Al_2O_3 support was fabricated in a similar manner in order to identify the properties of the interface structures in dependence of the support material.

The sintered PNS was micropolished using an autopolisher (GLP S-20/25, purchased from GLP Korea) in order to fill the surface pores and, thereby, to smoothen the surface, which was carried out with #400 to #2000 grit SiC paper and then with a 3 $\mu\text{m}/1\mu\text{m}$ wet, fine diamond slurry. The support was then washed using isopropyl alcohol and acetone in an ultrasonic cleaner. Plasma surface modification of the Ni support was performed in a mixture of 10% H_2/Ar at a working pressure of 1.333×10^{-2} kPa and radio frequency (RF) power of 100 W for 5 min in order to remove surface impurities induced by air contamination and to activate the micropolished surface.

Using advanced continuous dc magnetron sputtering, Pd (99.95% target purity) and Cu (99.99% target purity) were in situ deposited on the modified Ni support to thicknesses in the range of 4~10 μm and 0.4~1 μm , respectively, under conditions of 298~673 K substrate temperature,

$1.333 \times 10^{-2} \sim 1.333 \times 10^{-4}$ kPa working pressure, 40~160 W dc power, and 20 sccm Ar flow. Furthermore, Cu metal was adopted for alloying and surface densification as well as for its low cost and high resistance against poisoning by hydrogen sulfide and sulfurous constituents [4, 12].

The Cu-reflow heat treatment was then applied to fill the voids at the surface of the membrane and to facilitate alloying and crystallization of the separate films. Alloying, crystallization, and densification of the Pd/Cu films were performed at 923 K for 2 h in a H_2/Ar mixture at a working pressure of 1.333×10^{-2} kPa. In our previous studies [4, 12, 13, 19], the obtained Pd-Cu alloy membranes had a dense, pore-free surface after the Cu-reflow process under the same conditions.

Two types of Pd alloy films with 4 μm and 10 μm thickness were prepared by sputter deposition and Cu-reflow processes. The Pd alloy films with a thickness of 4 μm were used to compare microstructures between closed interface, partially open interface, and open interface. We studied the heat treatment-induced interfacial reaction between Pd films and Ni particles. These samples were only applied for analyzing the cross-sectional structures. The Pd alloy films with a thickness of 10 μm were prepared for permeation test. After permeation test, the Pd alloy films with a thickness of 10 μm were used to identify the relation between the microstructure of films and their hydrogen perm-selectivity.

The hydrogen permeation flux and selectivity were measured using an apparatus that consisted of a membrane cell, furnace, temperature controller, pressure gauge/controller, and gas chromatograph, as described in the previous literature [12, 20]. The measuring temperatures were in the range of 623~723 K, and the transmembrane pressure difference was 50~200 kPa under the flow of mixed gas ($H_2 : N_2 = 1 : 1$ v/v). The morphology of the Pd alloy films was investigated by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The structures and compositions were determined by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), respectively.

3. Results and Discussion

For commercial applications of Pd alloy hydrogen separation membranes, both high hydrogen selectivity and permeability are required [3, 13, 21]. Therefore, much effort has been focused on achieving high hydrogen permeability while maintaining the high hydrogen selectivity. However, since these two properties are incompatible with each other, it has been difficult to enhance the two properties simultaneously. To further increase the hydrogen permeability, the dense Pd alloy layer must be thin, such that the hydrogen flux is linearly related to the reciprocal of the membrane thickness. In addition, it is necessary to form an open structure in the vicinity of the interface between the Pd alloy films and the modified metal support in order to reduce the hydrogen permeation resistance caused by the blocked interface.

Figure 1 shows FE-SEM cross-sectional photographs of the Pd alloy films formed on a porous nickel metal and alumina ceramic supports using the process described in

the previous section. As can be seen in Figure 1, the Pd-Cu alloy membranes had a dense, pore-free surface on top of the Al_2O_3 and modified Ni supports, essentially achieved by the Cu-reflow process that was applied to eliminate pores at the surface of the membrane and to facilitate alloying and crystallization of the separate Pd and Cu films [4, 12, 13, 19]. The interfaces between the Pd alloy films and the modified supports show entirely different microstructures depending on the support material. In case the Al_2O_3 ceramic was used as support, the Al_2O_3 ceramic did not satisfy the Hume-Rothery rules for a homogeneous solid solution with Pd metal because of the poor chemical affinity between Al_2O_3 and Pd. This poor affinity resulted in a separate and closed interface between Al_2O_3 and the Pd film deposited directly on it, which led to low hydrogen permeation caused by the interface resistance against hydrogen flow [13], as illustrated in Figure 1(a). On the other hand, the metals Pd and Ni, which have the same crystal structure, similar atomic radius, same valence, and similar electronegativity, completely satisfied the Hume-Rothery rules for a homogeneous solid-solution alloy [12, 22, 23]. This resulted in the observed open structure composed of a large number of open voids near the interface between the Pd film and the Ni support, as shown in Figure 1(b), which facilitated hydrogen gas flow via the open sites. Thus, it is expected that the hydrogen permeability can be significantly enhanced by the formation of this structure.

Figure 2 illustrates schematically the process and the mechanism for the formation of a three-dimensional (3D), widely open structure, which was fabricated via 3 steps including the micropolishing of PNS, continuous in situ Pd/Cu sputtering, and Cu-reflow heat treatment. Figure 2(a) shows the entire micropolishing process that was applied to obtain the pore-free and flat surface of the Ni support. Rough grinding was performed to remove larger pores at the surface using SiC paper and fine grinding to eliminate smaller pores and to maintain the smooth surface using a polishing cloth and wet diamond slurry. As shown in Figure 2(a), the sintered Ni support was composed of larger pores with a range of $0.1\sim 5\ \mu\text{m}$ and had a very rough surface. Such a surface state offers high hydrogen flux to the Pd alloy membranes, but it leads to inhomogeneous deposition of Pd on the Ni support during sputtering. Thus, the surface pores and scratches on the PNS were completely removed and the surface was leveled off by the micropolishing treatment, as can be seen from the surface morphology of the modified support in Figure 2(a). The modified Ni support with its pore-free and flat surface served as a high-quality substrate for the uniform, fine Pd nucleation by magnetron sputtering. Furthermore, most of the surface pores that had been filled by fine Ni debris during the micropolishing processes were regenerated after the Cu-reflow heat treatment. This may be attributed to the mutual diffusion of fine Pd deposits and small Ni particles near the interface and the resintering of the fine Ni particles in the modified Ni support by the thermal energy and activated reaction induced by the Cu-reflow heat treatment.

Continuous in situ Pd and Cu deposition using an advanced magnetron sputtering system was also newly introduced in order to enhance the properties of the Pd alloy hydrogen membranes. In case the sputtering was carried

out at a high substrate temperature of 673 K, a low working pressure of 1.333×10^{-4} kPa, and a high dc power of 160 W, we obtained uniform and dense Pd/Cu films, as shown in the FE-SEM and TEM images of Figure 2(b). The high mobilities and reactivities of Pd and Cu atoms activated by the high temperature, low working pressure, and high dc power facilitated the initial homogeneous nucleation of Pd nanoparticles, and eventually promoted the growth of uniformly fine-grained, dense films during successive sputtering depositions.

Finally, the sputtered Pd/Cu films were subjected to the Cu-reflow heat treatment at 923 K for 2 h in a mixture of 10% H_2/Ar in order to achieve complete alloying/crystallization and to ensure a dense/porous hybrid structure. Figure 2(c) shows the corresponding FE-SEM image, XRD pattern, and cross-sectional EDS composition depth profile of the membrane after the final heat treatment. Verified by FE-SEM and XRD, this membrane had a uniform, dense surface microstructure without micropores and formed a stable, single-phase Pd alloy. From the cross-sectional EDS composition depth profile, it was observed that Pd and Ni from the Pd alloy coating layer and the modified Ni support, respectively, mutually diffused at the interface during the Cu-reflow heat treatment process. These main components exactly satisfied the requirements to form a homogeneous solid solution, as suggested by the Hume-Rothery rules [12, 22, 23]; Pd and Ni metals with high chemical affinity are completely soluble in the solid state over the entire compositional range at 923 K, as illustrated by the Pd-Ni phase diagram given in Figure 2(d) [24]. The FE-SEM and TEM images shown in Figure 2 clearly exhibit 3D, widely open structure composed of a large number of voids near the interface between the Pd alloy films and the modified Ni support.

Considering the results of the FE-SEM, TEM, XRD, and EDS analyses, it should be concluded that uniform, fine Pd deposits and small Ni particles having good mutual chemical affinity are totally integrated at their interface by interdiffusion. Moreover, resintering of embedded Ni particles is generated in the modified Ni support by self-diffusion and the reaction of activated Ni particles during the Cu-reflow heat treatment. Thus, the results confirmed that the 3D, widely open structure of the Pd alloy membrane was formed by the combined effect of improved interfacial reaction (by using nanosized fine particles) and improved thermal/chemical reaction (resulting from activation by the Cu-reflow process). Furthermore, both material (Figure 2(d)) and process requirements (Figures 2(a), 2(b), and 2(c)) for the formation of the open structure within the Pd alloy films were satisfied simultaneously, schematically described in Figure 2. It is likely that very significant changes in the hydrogen perm-selectivity can be attributed to variations of the microstructures of the Pd alloy membranes.

Thin films prepared by sputtering show a wide range of microstructures and their relevant properties, both of which are highly dependent on the sputtering conditions. Figure 3 shows surface and cross-sectional FE-SEM images of as-deposited Pd/Cu and Pd-Cu alloy films after the Cu-reflow heat treatment in dependence of the sputter deposition

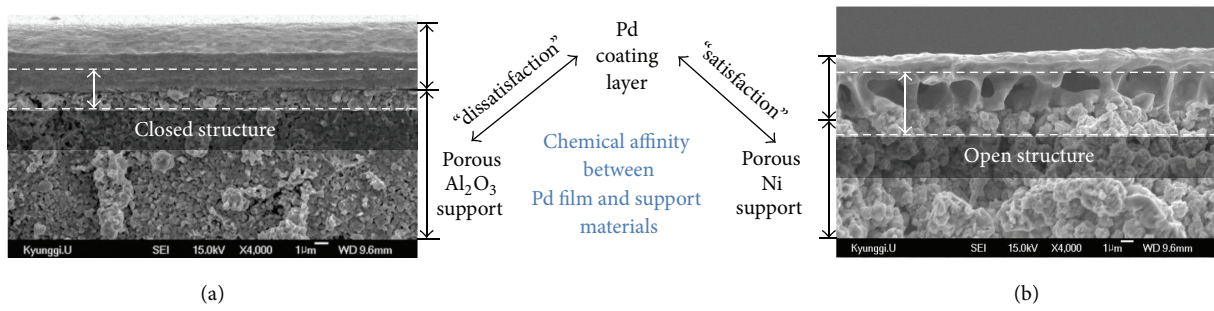


FIGURE 1: Chemical affinity between Pd film and support materials: (a) closed structure formed at interface between Pd film and porous Al₂O₃ support; (b) open structure formed at interface between Pd film and porous nickel support.

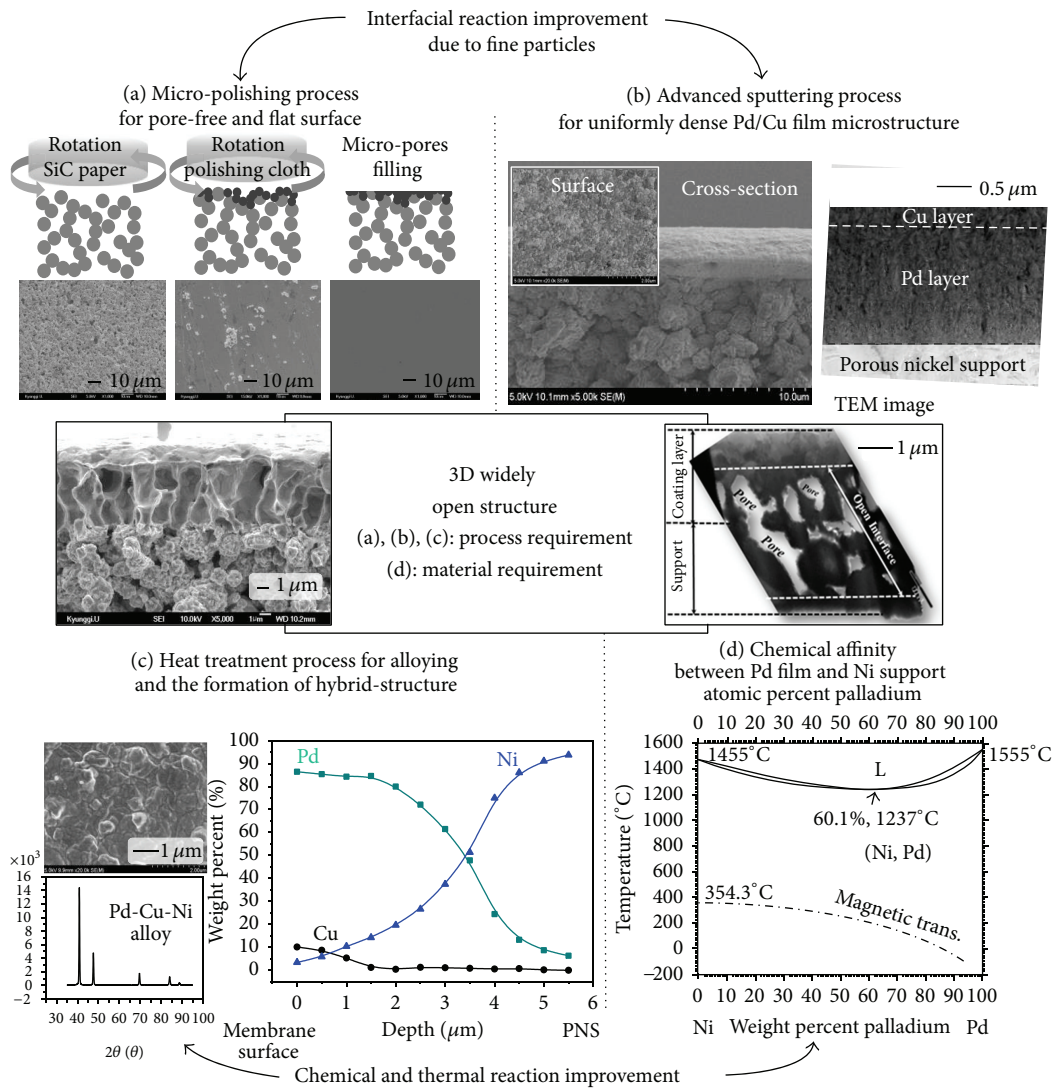


FIGURE 2: Process and mechanism for the formation of 3D widely open structure: (a) micropolishing process for pore-free and flat surface of the support (SEM images); (b) advanced sputtering process for uniformly fine films (SEM/TEM images); (c) heat treatment process for alloying, crystallization, and the formation of a dense/porous hybrid structure (SEM/XRD/EDS profile); (d) Pd-Ni alloy phase diagram.

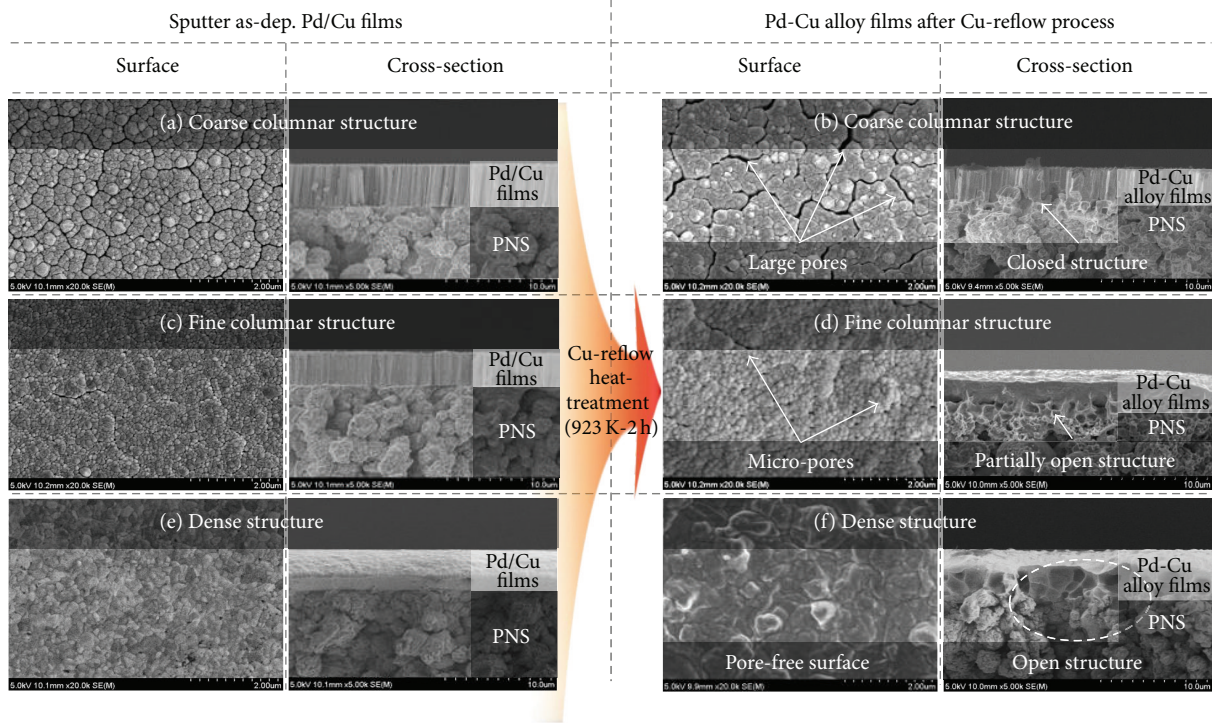


FIGURE 3: Surface and cross-sectional FE-SEM images of sputter as-deposited Pd/Cu and Pd-Cu alloy films after the Cu-reflow process for various sputtering variables: (a), (c), (e) sputter as-deposited films; (b), (d), (f) Pd-Cu alloy films after heat treatment.

conditions. As can be seen from the film microstructures shown in Figure 3, considerable structural differences in the as-deposited Pd/Cu and heat-treated Pd-Cu alloy films with a thickness of $4\ \mu\text{m}$ were observed, depending on the sputtering variables including the substrate temperature, working pressure, and dc power. As shown in Figure 3(a), when the sputtering was carried out at room temperature, a working pressure of 1.333×10^{-2} kPa, and dc power of 40 W, the resulting Pd/Cu coating layer had a coarse columnar structure and a very rough surface. Moreover, as evident from the morphology of the films shown in Figures 3(a) and 3(b), the inhomogeneous deposition of the films during the sputtering process resulted in abnormal grain growth, which led to large pores at the surface of the films and a closed structure near the interface after the Cu-reflow heat treatment at 923 K for 2 h in a H_2/Ar mixture. This ultimately caused the deterioration of the hydrogen perm-selectivity and long-term stability of the Pd alloy membranes. It can also be seen that the Pd/Cu films deposited by sputtering at the substrate temperature of 473 K, working pressure of 1.333×10^{-3} kPa, and DC power of 80 W had a fine columnar structure with smooth surface compared to the coarse columnar structure. After the Cu-reflow heat treatment, the Pd-Cu alloy films had a few micropores at the surface and a partially open structure near the interface, as illustrated in Figure 3(d). In contrast, as shown in Figure 3(e), the Pd/Cu films deposited by sputtering at a high substrate temperature of 673 K, an extremely low working pressure of 1.333×10^{-4} kPa, and high dc power of 160 W had a uniformly fine grained,

dense structure with pore-free surface. The reason for the formation of this desired film morphology is the same as that described above for Figure 2(b), namely, homogeneous nucleation of Pd nanoparticles. As shown in Figure 3(f), the Pd alloy hydrogen membranes having a dense, pore-free microstructure at the surface and a completely open structure near the interface between the Pd alloy films and the modified Ni support were obtained after the Cu-reflow heat treatment process, which is expected to increase the hydrogen permeability without reducing the ideal H_2/N_2 selectivity. Therefore, the microcrystalline morphology of the Pd/Cu film formed by the sputtering method plays an important role in improving the characteristics of the Pd alloy hydrogen separation membranes.

In order to further study the heat treatment-induced interfacial reaction between Pd films and Ni particles, we have investigated the change of the cross-sectional composition profile of the Pd alloy films and the Ni support for various interface structures that are shown in Figure 3. Figure 4 shows the cross-sectional composition depth profiles of the Pd-Cu alloy films with $4\ \mu\text{m}$ thickness after the Cu-reflow heat treatment at 923 K for 2 h for different interface structures between the Pd alloy film and the modified Ni support. The average compositions of the alloy films and the metal support including closed, partially open, and open interface structures were determined by EDS scan analyses. The scan path is marked by arrows in Figure 4. From the EDS results, it was observed that Pd, Cu, and Ni metals with high chemical affinity were mutually diffused during the

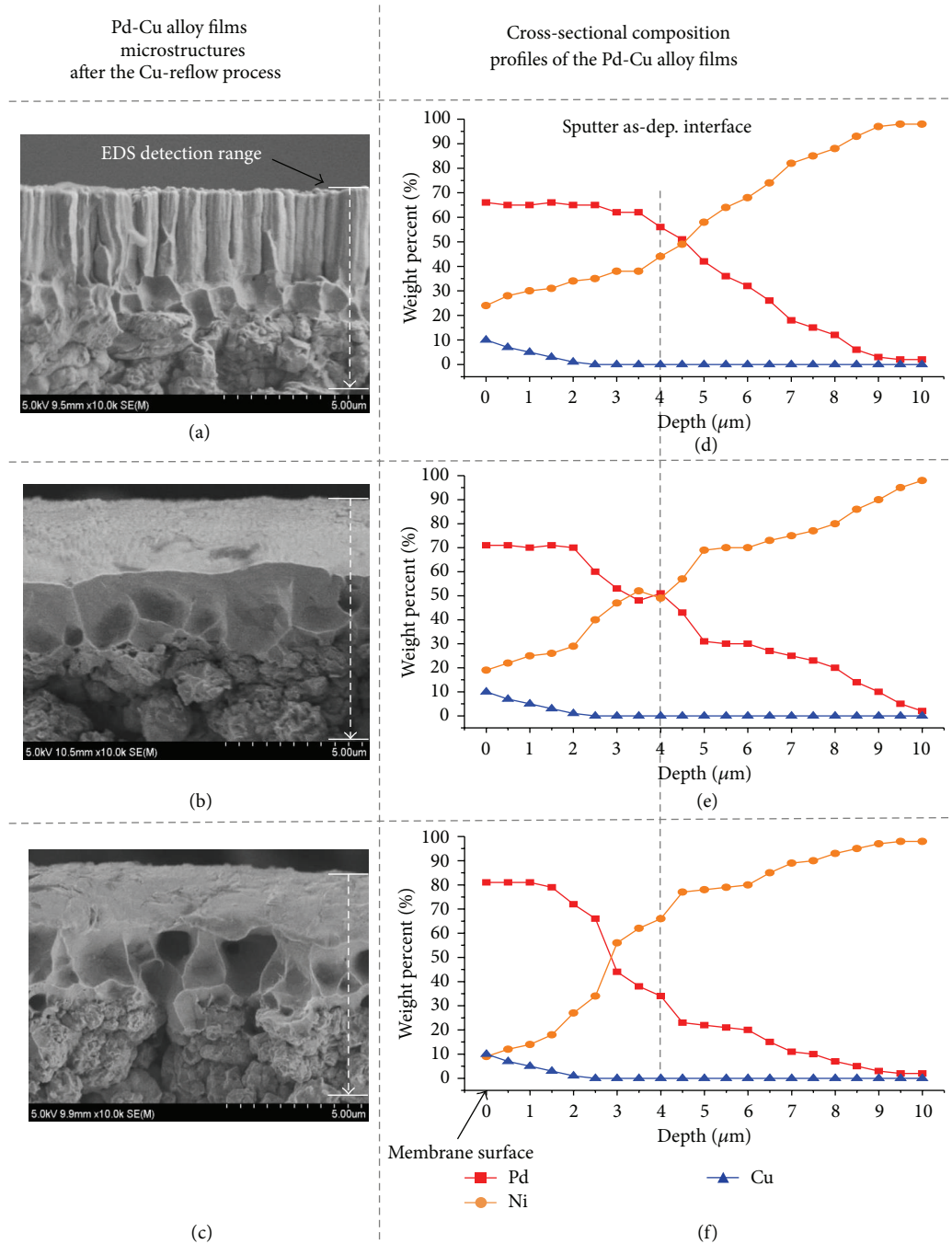


FIGURE 4: The cross-sectional FE-SEM images and composition profiles of the heat-treated Pd-Cu alloy films with $4\ \mu\text{m}$ thickness for various interface structures depending on the sputter as-deposited microstructures: (a), (d) closed interface; (b), (e) partially open interface; (c), (f) open interface; arrow lines in (a), (b), and (c) are EDS detection range.

Cu-reflow heat treatment. The largest amount of mutually diffused Pd and Ni atoms was found for Pd alloy films having a closed interface structure, as shown in Figures 4(a) and 4(d). That is, the composition of Ni at the membrane surface was estimated to be 23 wt% for the films with a closed interface structure (Figure 4(d)) and 8 wt% for an open interface structure (Figure 4(f)), indicating significant Ni interdiffusion into the Pd alloy films in the former case.

The reason for this experimental result can be attributed to the coarse columnar microstructures composed of large voids near columnar valleys, as mentioned above in case of Figure 3, which facilitated rapid mutual diffusion of Pd and Ni atoms during the Cu-reflow heat treatment. Furthermore, the interfacial reactivity of Pd deposits and Ni particles was rather high for the specimens with open interface structure (allowing rapid changes in the Pd and Ni composition at the

interface, as shown in Figure 4(f)) compared to the closed and partially open interface structures (corresponding to relatively gradual changes in the composition at the interface, as shown in Figures 4(d) and 4(e)). This could be explained by the significantly increased thermal reaction of uniformly distributed fine Pd and Ni particles (nanosize effect for the open interface specimen). This increased interfacial reactivity in case the open structure near the interface is in good agreement with the results discussed above for Figure 2. Therefore, the open structure composed of porous microstructures with numerous open voids near the interface was formed by the advanced sputtering method and subsequent Cu-reflow heat treatment process on modified Ni support.

The main focus of the present study is to assess the effect of the open structure near the interface on the hydrogen permeability. Therefore, hydrogen permeation tests were carried out and the hydrogen permeation flux of a fabricated membrane with dense/porous hybrid structure was compared to that of a conventional membrane having a closed interface structure. To identify the characteristics of the hydrogen membranes, the surface state and film thickness of the two membranes were kept the same (dense, pore-free morphology, and 10 μm in thickness, resp.). Thus, the influence of surface structure and membrane thickness on the hydrogen permeation flux for Pd alloy membranes was kept constant during the permeation tests. The membrane with large thickness of 10 μm was chosen to prevent degradation of the hydrogen permeability by intermetallic diffusion of Ni from the support into the membrane surface during the high-temperature of the Cu-reflow process. Consequently, the surface composition of the two membranes annealed at 923 K resulted in 90 wt% of Pd and 10 wt% of Cu. The Ni composition at the membrane surface was not detected by EDS analysis, and any variation of the hydrogen permeability as a function of the Ni content was ruled out given the constant surface composition.

Figure 5 represents the cross-sectional FE-SEM images of the developed and the conventional Pd alloy membranes manufactured under the above conditions. The pictures were obtained using these membranes after permeation test. The present membrane with dense/porous hybrid structure was obtained by the advanced process, as discussed in greater detail in Figure 2, whereas the conventional membrane having both purely dense structure and closed interface was fabricated by fine columnar Pd/Cu deposition and roughly polished surface treatment, as previously stated [4]. Such microstructural problem associated with the conventional method was the difficulty in forming open interface between the Pd alloy films and the metal support, which led to the adverse effect of the hydrogen permeability.

Figure 6 shows the hydrogen perm-selectivity of the present Pd-Cu alloy membranes having a dense/porous hybrid structure (open interface) as opposed to a purely dense structure (closed interface) formed by conventional membrane process. The hydrogen permeation flux and the ideal selectivity (H_2/N_2) were measured using our previously described measurement system [12, 20] at a transmembrane pressure difference of 50–200 kPa. The temperature was increased from room temperature to 723 K during the

measurements. Figure 6 represents the dependency of the hydrogen permeation flux and selectivity on the pressure difference at various temperatures. The hydrogen permeation flux depends on the pressure difference with the pressure exponent of 0.5 indicating Sievert's law flux dependence. The ideal H_2/N_2 selectivity of the two membranes was infinite within our measuring accuracy (the level of N_2 was below the detection limit of the measurement system during the permeation tests), regardless of the structure near the interface between the Pd alloy membranes and the modified Ni support. This is primarily because of the dense and pore-free surface morphology as a result of the Cu-reflow heat-treatment. The hydrogen permeation flux increased with increasing temperature and pressure difference and reached $2.4 \times 10^{-1} \text{ mol m}^{-2} \text{ s}^{-1}$ for the fabricated membrane with dense/porous hybrid structure (open interface) and $1.1 \times 10^{-1} \text{ mol m}^{-2} \text{ s}^{-1}$ for the conventional membrane with purely dense interface structure (closed interface) at 723 K and 200 kPa. Thus, the fabricated membrane with dense/porous hybrid structure had 2.2 times higher hydrogen permeation flux than the conventional one having a purely dense interface structure. This may be attributed to the open microstructure with numerous voids at the interface (the porous structure facilitates hydrogen flux without permeation resistance at the interface) and the effective thickness reduction of the dense structure from 10 μm to less than 5 μm as a result of the formation of the porous structure within the Pd alloy films (the hydrogen flux is inversely proportional to the thickness of the dense membrane) in comparison to the conventional membranes having a purely dense structure, as illustrated in Figure 5.

Ni content also has effect on hydrogen permeation. Our previous study shows that H_2 permeability increases with decrease of Ni content [13]. As shown in Figure 4, the dense/porous hybrid structure decreases Ni content as well as dense layer so that the hydrogen permeation flux increased.

Table 1 shows the comparison of hydrogen permeability between the present membrane and other literatures [17, 18]. We achieved 2.2 times higher hydrogen permeation flux by dense/porous hybrid structure. However, the present membrane has relatively low hydrogen permeability compared with Pd membranes deposited on porous ceramics and ceramic modified porous stainless steels because nickel decreased hydrogen solubility. Despite low hydrogen permeability, there are some advantages in Pd-Cu alloy membrane deposited on porous nickel support.

- (1) While Pd membranes easily suffer from hydrogen embrittlement due to the α - β phase transition at temperatures below the critical points of the Pd-H system [25], no α - β phase transition occurred in Pd-Cu alloy membrane [26]. Therefore, it was possible to design and build up a simple hydrogen purifier [27].
- (2) Very good adhesion between membrane layer and support provided very easy diverse modulation methods like knife-edge sealing [20] and diffusion bonding [28].

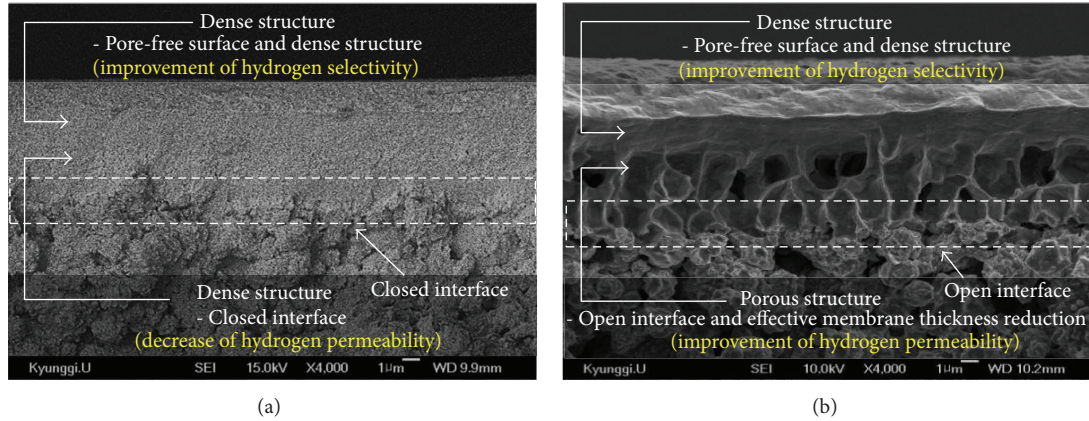


FIGURE 5: The cross-sectional FE-SEM images of (a) purely dense structured and (b) dense/porous hybrid structured Pd-Cu alloy films.

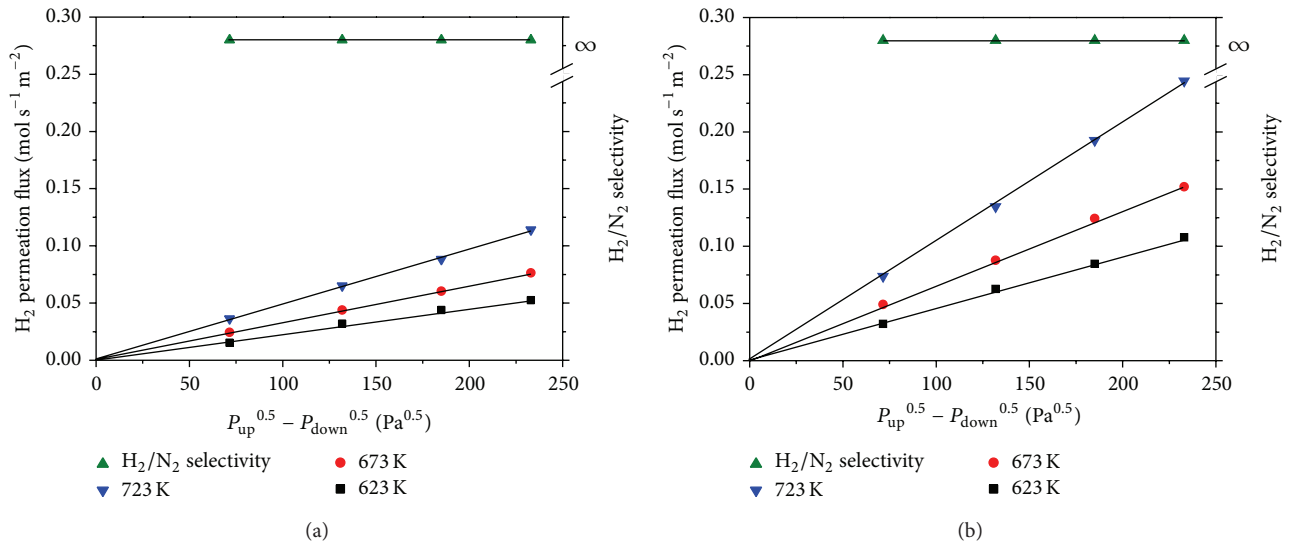


FIGURE 6: Hydrogen permeation flux and selectivity of membranes with (a) the purely dense structure and (b) dense/porous hybrid structure as a function of the pressure difference at various temperatures.

TABLE 1: Comparison of hydrogen permeability between the present membrane and other types of literature.

Support Material	Method	Membrane Material	Thick. (μm)	Temp. (K)	Permeability ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-0.5}$)	Selectivity (H_2/N_2)	Ref.
Al_2O_3	ELP*	Pd	3.5	773	$1.9\text{E} - 08$	4300	[17]
PSS	ELP	Pd	7.5	873	$1.9\text{E} - 08$	685	[18]
PNS	Sputtering	PdCu	12	773	$3.5\text{E} - 09$	Infinity	[13]
PNS	Sputtering	PdCu	10	723	$4.6\text{E} - 09$	Infinity	This work (purely dense structure)
PNS	Sputtering	PdCu	10	723	$9.9\text{E} - 09$	Infinity	This work (dense/porous hybrid structure)

*ELP: electroless plating.

In our previous study [4], a long-term annealing test was continued for 1500 h at a temperature of 823 K and the composition of elements in the membrane remained constant during the long-term annealing test.

It should be noted that the hydrogen permeation flux and the ideal H_2/N_2 selectivity of the Pd alloy membranes were simultaneously enhanced by introducing the unique dense/porous hybrid structure. In this study, we successfully fabricated Pd alloy hydrogen separation membranes with dense/porous hybrid structure on modified Ni support using advanced sputtering deposition and Cu-reflow heat treatment for high hydrogen perm-selectivity. Therefore, it is expected that this type of membrane will be applicable to industrial processes for hydrogen purification and a variety of further applications, including hydrogen separation.

4. Conclusions

We successfully developed Pd alloy hydrogen separation membrane with a dense/porous hybrid structure for high hydrogen perm-selectivity. The hydrogen selectivity of this membrane was increased by the dense and pore-free microstructure at the surface. The hydrogen permeation flux also was significantly improved not only because of the open microstructure with numerous open voids near the interface but also because of the effective thickness reduction of the dense membrane as a result of the formation of the porous structure within the Pd alloy films. This indicates that the requirements for simultaneous high hydrogen permeability and high hydrogen selectivity essential for commercial applications are satisfied by our modified fabrication process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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