특별강연 2

Multiple Layer Caoting and Diffusion Treatment Technique for Fabrication of Pd-Ag Alloy Membranes

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INTRODUCTION

In practice, the wide use of pure Pd membranes for H_2 separation is limited by H_2 embrittlement. For this reason, the commercially used Pd based membranes are made from Pd-Ag alloys in which the silver content is about 23 wt.%. Additions of silver also have advantage of significant increasing the H_2 permeability. Therefore, a new generation of highly permselective Pd-Ag alloy membranes with large H_2 permeation flux may emerge if the dense Pd-Ag alloy composite membranes are developed.

Several research groups reported the preparations of Pd-Ag alloy membranes by various fabrication techniques [1, 2]. The most commonly employed method for the preparation of Pd-Ag alloy membranes is so called two layer coating and diffusion treatment technique. In this method, Pd and Ag are coated on a substrate using various thin film fabrication technique and then the prepared membrane is sintered at high temperature (> 800 °C) to form Pd-Ag alloy. Most of these Pd-Ag alloy membranes used ceramic supports because of high temperature sintering process. However, in the case of ceramic supports, a remaining problem is the structural instability during thermal cycling due to the mismatch of thermal expansion coefficients between the metallic film and the nonmetallic support. On the other hand, the thermal expansion coefficient of stainless steel is very close to that of Pd, insuring good mechanical properties of the composite membrane during temperature cycling. In addition to the structural stability, PSS supports have the simplicity of module construction. Thus, porous stainless steel (PSS) supports appear to be one of the most promising supports for palladium based membranes. However, atomic interdiffusions of metals between the Pd based film and the stainless steel components occurring at high temperature (> 500 °C) can deteriorate the Pd-Ag alloy membrane in their hydrogen permeability [3]. Therefore, the application of Pd-Ag alloy membranes in hydrogen

separations and catalytic reactions depends largely on the successful development of a low temperature fabrication method for Pd-Ag membranes on PSS supports. The objectives of the present work are: (1) to develop a low temperature fabrication method for dense Pd-Ag alloy composite membranes on PSS supports; (2) to develop Pd-Ag alloy membranes with improved hydrogen permeation properties and thermal stability; and (3) to study the characteristics of the prepared membranes for hydrogen separation and purification.

EXPERIMENTAL

Support

The porous 316L stainless steel cups (O.D. - 15.9, wall thickness - 1.6 mm and length - 19), purchased from Mott Metallurgical Corporation, were used as supports. The grade of these porous stainless steel (PSS) was 0.5 μm (95% rejection) with the biggest pore diameter of 5 μm and an average pore diameter of 3 μm. The porosity of the PSS was 17%. The PSS cups were electrically welded to non-porous stainless steel tubes.

Plating

The membrane prepared here consists of multiple layers of Pd and Ag, as shown in Fig. 1. This unique mutiple layer configuration makes it possible for Pd-Ag layers to transform into alloy phase by the low temperature sintering process due to the small diffusion distance of two different metals. In order to have the multiple layer structure, the membrane went through successive activation, plating and drying cycles. The schematic diagram of the activation, plating and drying cycle is presented in Fig. 2. The purpose of the surface activation was to seed the PSS surface with palladium nuclei, which during the electroless plating initiated an autocatalytic process of the reduction of a metastable metal salt complex on the target surface. Because electroless plated Pd layer acts as nuclei for Ag growing, activation process was performed only before Pd plating. The activation procedure consisted of successive immersions in an acidic $SnCl_2$ bath (sensitizing) followed by an acidic $PdCl_2$ bath. The typical composition of the activation bath is presented in Table 1.
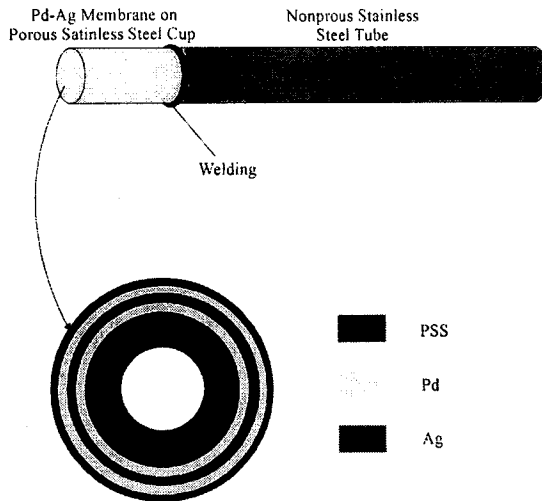
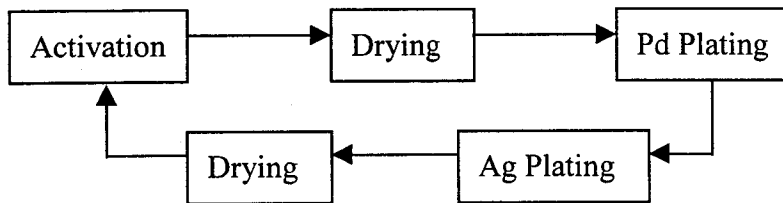Fig. 1 Structure of a multiple layer Pd-Ag membrane

Fig. 2 Schematic diagram of activation, plating and drying cycle

Table 1.　Composition of the activation solutions

	Sn - solution	Pd - solution
$SnCl_2 \cdot 2H_2O$, g/l	1.0	-
PdCl2, g/l	-	0.1
HCl (~37%), ml	1	1
Temperature, °C	20	20
Duration, min.	5	3-5

Table 2.　Compositions of the palladium plating bath

$(Pd(NH_3)_4Cl_2\,H_2O$	4.0　g/l
Na_2 EDTA	40.1　g/l
NH_4 OH (28%)	198　ml/l
H_2NNH_2 (1M)	5.6　ml/l
pH	~10.4
Temperature	60°C

Table 3.　Compositions of the silver plating bath

$AgNO_3$	0.519　g/l
Na_2 EDTA	40.1　g/l
NH_4 OH (28%)	198　ml/l
H_2NNH_2 (1M)	5.6　ml/l
Temperature	60°C

After activation and drying, Pd was plated with the Pd plating solution for 1 and half hours. Table 2 shows a typical Pd plating bath composition. The deposition of Pd on the activated PSS supports was done by placing the PSS supports in an electroless plating bath surrounded by a water jacket for temperature control. After 1 and half hours Pd plating, Ag was plated on the membrane for 3 hours. Table 3 shows typical compositions of the Ag plating bath used here. After the plating, the membrane was rinsed with DI water, dried at 120°C for two hours, and weighed. Compared to Pd, Ag has a relatively low activity in the catalytic reaction and thus, the electroless plating of Ag need to be initiated by foreign nuclei such as Pd. For this reason, the Pd is always deposited prior to the Ag plating. Since the concentration of Ag salt in the plating solution was low, longer plating time (3 hours)

was applied in order to obtain the desired Ag concentration (about 20 wt.%).

In order to transform the deposited Pd-Ag into an alloy, the membrane was sintered at 550 °C for 5 hours under H_2 atmosphere. The presence of H_2 can prevent the silver films from oxidizing. Moreover, the interaction between H_2 and Pd favors the segregation of palladium toward the membrane surface and thus, it makes it easier to form Pd-Ag alloy. During the sintering process, the variation of H_2 permeation flux was monitored.

Gas permeation experiment

The H_2 and He permeation fluxes were measure at different temperatures and pressures. Figure 3 shows the schematic diagram of the gas permeation setup. The feed gas flowed upward through the outside of the membrane (shell side), and the permeate gas was collected on the tube side. The upstream pressure was monitored by a capacitance pressure transducer and the permeate side pressure was kept atmospheric. The gas permeation rate (the volumetric flow rate) was measured in the permeate side at atmospheric pressure and room temperature.
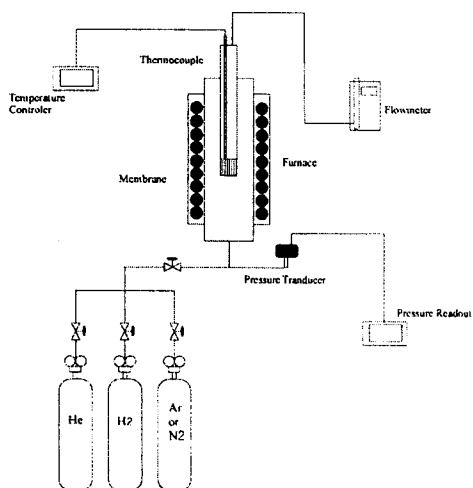

Fig. 3 Schematic diagram of gas permeation cell

RESULTS AND DISCUSSION

A multiple layer Pd-Ag membrane was prepared by a separate electroless plating. In order to obtain gas-tight membrane, 8 times of the activation, plating and drying cycles were performed and the total membrane thickness was about 25 μm. The average thickness of a single Pd-Ag layer was about 3.5 μm after a single activation, plating and drying cycle. After low temperature (550°C)sintering process, XRD characterization was performed and it confirms that the prepared membrane has Pd-Ag alloy phase.

The prepared membrane was loaded into the permeation cell and He and H_2 permeation fluxes were measured at various temperatures from 200 to 350 °C. Fig. 4 shows the variation of H_2 and He permeation flux during the gas permeation experiment, respectively. The H_2 permeation flux was stable at each temperature for more than 100 hours. Even though the membrane was gas-tight at room temperature, small He permeation was detected after heating to 350°C. The He flow might be contributed by the permeation through the open pores created during the heating process [4]. The He permeation flux increased at the first stage of the permeation experiment at 350 °C, but it became stable over the rest of experiment at the temperature from 200 to 350 °C.
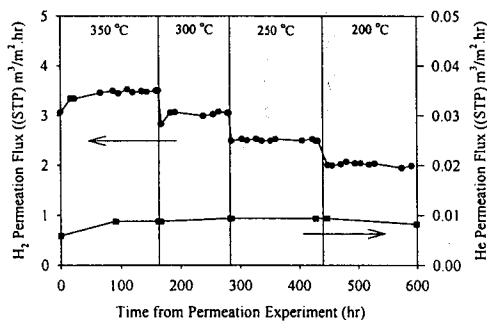

Fig.4 He and H_2 permeation flux through the Pd-Ag alloy membrane

The H_2 permeation flux through the Pd-Ag membrane was measured at different temperatures and pressure. The pressure dependency of H_2 flux is shown in Fig. 5. The H_2 flux through the Pd-Ag membrane showed linear relationship to $(P_h^{1/2} - P_l^{1/2})$. It means that the membrane follows Sievert's law.

CONCLUSION

A multiple layer Pd-Ag membrane was prepared by the successive activation, plating and drying cycle. The membrane was about 25 μm thick and consists of 8 thin Pd layers and 8 thin Ag layer in alternative order. The membrane was sintered at relatively low temperature, 550 °C for about 5 hours under H_2 atmosphere and then the membrane showed Pd-Ag alloy phase. Thus, it is clear that the multiple layer coating and diffusion treatment techniqe can prepared Pd-Ag membrane with relatively low temperature sintering process. The membrane showed higher H_2 permeation flux than that of Pd membrane and the H_2 permeation follows Sievert's law.
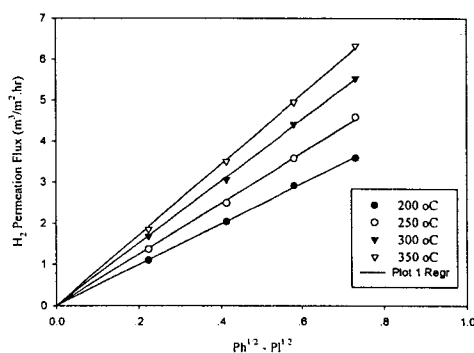
Fig. 5 Pressure dependency of H_2 permeation flux

REFERENCES

1. Shu, J., B.P.A.Grandjean, E. Ghali, and S. Kaliaguine, "Simultaneous deposition of Pd and Ag on porous stainless steel by electroless plating", *J. Memb. Sci.*, **77**, 181 (1993).
2. Uemiya, S., T. Matsuda, and E. Kikuchi, "Hydrogen permeable palladium-silver alloy membrane supported on porous ceramics", *J. Memb. Sci.*, **56**, 315 (1991b).
3. Shu, J., A. Adnot, B.P.A.Grandjean and S. Kaliaguine, "Structurally stable composite Pd-Ag alloy membranes: Introduction of a diffusion barrier", *Thin Solid Films*, **286**, 72 (1996).
4. Mardilovich P.P., Y. She, M.-H. Rei and Y.H. Ma, "Defect Free Palladium Membranes on Porous Stainless Steel Support", *AIChE Journal,* **44**, 2, 310 (1998).