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Fabrication of palladium membrane with electroless deposition for hydrogen purification

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ABSTRACT

A palladium membrane has been prepared by electroless plating deposition method on the surface of a porous stainless steel disk as support. The disk surface was covered with an oxide barrier to prevent metal diffusion from the support to the palladium layer. The optimized thickness of the fabricated palladium layer to be dense enough was 46μm. The permeability of the membrane for hydrogen and nitrogen was investigated at 723, 773 and 823K and plotted vs. varying pressures. Additionally, the ratio of H_2/N_2 permeation selectivity of the membrane was around 3500.

KEYWORDS

Palladium membrane;
Porous stainless steel disk;
Oxide layer;
Electroless deposition;
Hydrogen separation.

INTRODUCTION

Palladium and palladium based alloy thin films have been considered abroad for their applications in the areas of gas sensors, electronic apparatures, hydrogen purifiers and magnetic storage devices[1]. Besides, in recent years, considering their unique properties as a feasible hydrogen permeance, thermal stability, sufficient mechanical strength and catalytic properties, palladium and pd-based alloys have been developed as a membrane.

Most of well-known palladium membranes is basically fabricated of two parts, support and palladium layer. Different techniques have been tried for fabrication of Pd and pd-based alloy composite membranes, such as physical vapor deposition (PVD)[2], chemical vapor deposition (CVD) and electroless plating[3]. Electroless plating is a popular technique for preparing thin Pd[4–6] and Pd-alloy[7,8] supported membranes with excellent hydrogen permeability.

Among all possible supports such as ceramics or vycor glasses[9,10], there are few which could match the beneficial aspects of porous sainless steel (PSS), regarding to its practical process, corrosion resistance, thermal stability, mechanical strength and thermal expansion coefficient which is the closest to that of palladium[11]. Metal diffusion through PSS into the palladium layer at high temperatures is considered as another PSS problem[12]. In this contribution, we made a oxide layer on the surface to prevent the described metal diffusion.

EXPERIMENTAL

Disk shape of 316L porous stainless steel grades

TABLE 1: Composition of the Pd plating bath

Subject	Amount
$Pd(NH_3)_4Cl_2 \cdot H_2O$ (g/l)	5
$Na_2EDTA\ 2H_2O$ (g/l)	42
NH_2OH (28%) (ml/l)	220
N_2H_4 (1 M) (ml/l)	4
pH	10-11

0.2m with 1mm thickness as a porous substrate was purchased from the Mott Metallurgical Corporation. A surface area of disk was 12.5cm^2. Cleaning process of the porous stainless steel support was performed in an ultrasonic bath with alkaline solution at 333K for 30min. This cleaning procedure was followed by immersing in water and isopropyl alcohol respectively then was dried at 373K for 3h. The porous stainless steel supports were oxidized in an air stream at 873K for about 6h. The rate of heating and cooling during the oxidation process was 5K/min. Prior to electroless plating step, the surface of disks was activated. The activation process involved, immersing the support in a dilute tin chloride solution for 5min, then by 5min rinsing in deionized water. It was followed with rinsing the disks in palladium salt solution for 5min, The above procedure was repeated 6 times. The chemicals used in the plating solutions were $PdCl_2$ (99.9%), Na_2EDTA, NH_4OH (35%), NH_4Cl, N_2H_4 (30%) purchased from Aldrich Chemicals. The deposition solution concentrations are represented in TABLE 1. The hydrazine was used as the reducing agent. The plating solution was renewed every 90 min, with rinsing with hot deionized water between each plating bath. The weight gains before and after the plating was used to determine the thickness of the membrane. Determining the hydrogen permeation flux through the membrane at 723-823K, we utilized a mass flow controller to feed a constant pressurized gas to one side of the disk while it was monitored with a pressure gauge and the other side, as the permeation side, was kept at atmospheric pressure.

RESULT AND DISCUSSION

Membrane preparation

According to the above mentioned method, palladium was precipitated on the support surface, followed by 14h of electroless plating, the fabricated membrane was completely dense in the pressure of 1 bar at room temperature. The gravimetery showed a thickness of 46μm. Then the membrane was treated at 673K under the nitrogen atmosphere for 6h. After that the nitrogen atmosphere was replaced with the hydrogen atmosphere for 4h.

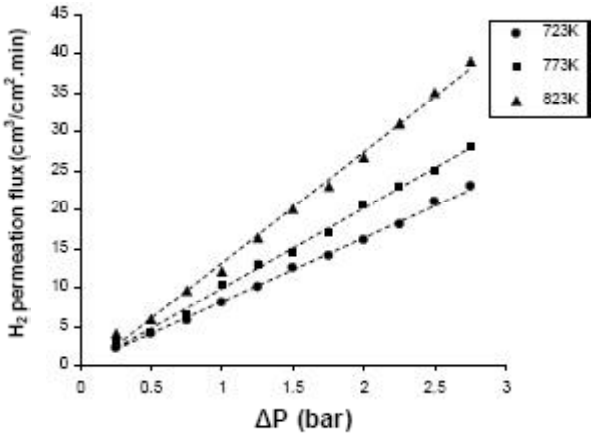

Figure 1: Results of hydrogen permeation tests at varying pressures

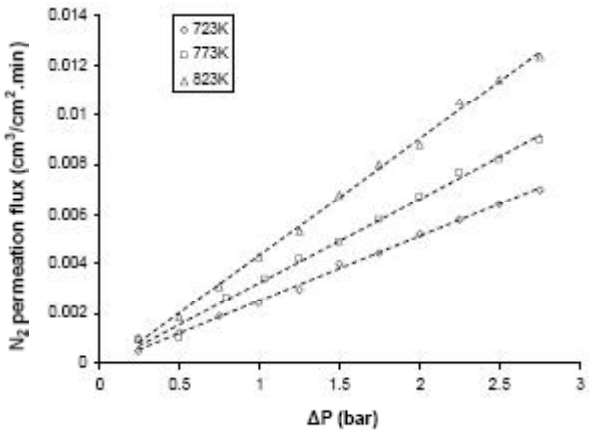

Figure 2: Results of nitrogen permeation tests at varying pressures

Membrane permeation properties

The characterized membrane was tested for H_2 and N_2 permeation at 773K. Activation process was done by exposing the membrane to N_2 atmosphere at 3 atm at 773K for 4 hours and then the whole process was repeated with H_2 atmosphere instead of N_2 for 5 hours.

Figures 1 and 2 represent the permeation fluxes of hydrogen and nitrogen through the membrane at the constant temperature of 723K. Pressure dependence of the hydrogen permeation flux through the palladium layer is indicated from positive slope of hydrogen per-

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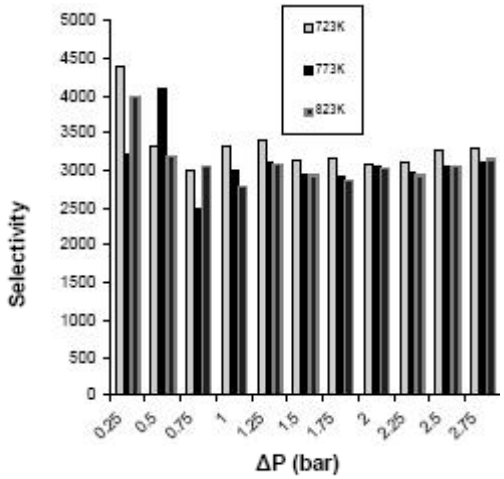

Figure 3: Selectivity of the membrane with respect to hydrogen

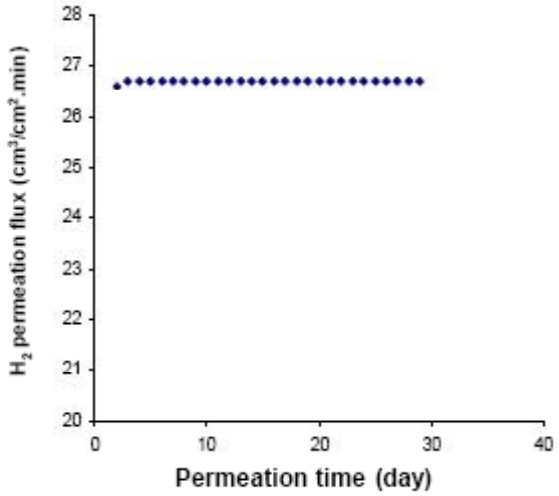

Figure 4 : Result of long duration hydrogen permeation test

meation vs. applied H_2 pressure. The H_2/N_2 selectivity of the membrane was computed by dividing the H_2 to N_2 permeation fluxes at a given pressure as shown in figure 3. According to the figure 3, temperature increase has not a regular and dramatic effect on the membrane selectivity. Figure 4 is showed the hydrogen permeation flux vs. time under ΔP of 2 bar at 823 K. As stated by this figure, hydrogen permeation is not affected by time passage. This could be explained by presence of oxide layer as a barrier to prevent metal diffusion from PSS through palladium layer.

CONCLUSION

A palladium membrane was fabricated by electroless deposition method on a modified PSS disk. The palladium layer was suitably dense with a thickness of about 46 μm. Permeability of the membrane for hydrogen and nitrogen was examined. The maximum permeation flux was 39 $cm^3/cm^2/min$. Additionally, the maximum permeation of nitrogen through the membrane was 0.01235 $cm^3/cm^2/min$. It confirms the proper denseness of the membrane.

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