

Hydrogen permeable Pd/Cu alloy composite membrane prepared by vacuum electrodeposition

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1. INTRODUCTION

The palladium-based membranes have been the focus of many studies because of their potential in hydrogen purification or membrane reactors including catalytic dehydrogenation reactions[1]. However, due to hydrogen embrittlement, the use of pure palladium membrane for the hydrogen separation is restricted. Alloying of palladium with other metals such as silver, copper, or nickel has been used to reduce the well known hydrogen embrittlement. The commercially available palladium-based membranes are of self-supported type (200 μm at least), made by conventional metallurgical process[2]. Although these membranes had high selectivities, the process proved uneconomical because the membranes material cost is high and the hydrogen flux was too low. Thus, current researchers are trying to prepare a composite-type membrane composed of a thin selective layer (thickness 5~20 μm) deposited on a porous support. Palladium-based membranes prepared by the most common techniques, sputter deposition, chemical vapor deposition, electrodeposition, and electroless deposition, were reviewed by Shu et al.[1].

In a previous study, we have demonstrated that a new technique, a so-called vacuum electrodeposition technique could serve as a simple way for coating the thin Pd alloy films on a mesoporous SUS support[3]. The present work focuses on the fabrication of Pd-Cu alloy composite membranes that can maintain low inert gas flux while high permselectivity towards hydrogen.

2. EXPERIMENTAL

Disk shape of 316L stainless steel (SUS) used as porous substrate was purchased from the Mott Metallurgical Corporation. To make the surface more smooth and prevent intermetallic diffusion, one of the substrate sides was pretreated before deposition: dispersing submicron nickel powder (Aldrich Co.) on the surface under low vacuum, sintering for 5 hr at 1073 K under high vacuum, coating of monodisperse silica layer by sol-gel process, cleaning in distilled water for 10 min, and activating in 5 wt% H_2SO_4 solution subsequently. The opposite side of the deposition surface was evacuated to 600 Torr by the aspirator and a thin film consisting of multilayer of palladium and copper was formed on the mesoporous substrate alternately. Heat treatment of the coating layer was carried out at 1073 K for 5 hr under high vacuum. The morphologies of the deposited films and substrates were observed by scanning electron microscope (SEM,

JEOL JSM-840A). The composition and phase structures of the deposited films were determined by the energy dispersive spectroscopic analysis(EDS) and X-Ray diffraction(Diano XRD 8200), respectively. Distribution of palladium alloy was measured by means of electron probe microanalyzer (EPMA). The permeations of individual gases, hydrogen and nitrogen, were carried out at 623, 723, and 823K, respectively. Permeate pressure in all runs was kept constant at 1 atm. The selectivities are defined as the ratio of the hydrogen permeance to the nitrogen permeance under the same transmembrane pressure difference.

3. RESULTS & DISCUSSION

With commercially available SUS substrates, pinhole-free deposition of palladium alloy membranes could not be achieved even after a long tedious deposition because of the large defects present initially. Thus, a nickel powder dispersing method was employed in order to mitigate the surface roughness. This technique appeared to be very effective in decreasing the surface roughness and controlling the average pore size of the substrate surface. In addition, using a vacuum condition during electrodeposition of alloy metals on a treated mesoporous support allowed the solution to approach inside the pores, thereby preparing a well adhered Pd alloy composite membrane[3].

We showed that a miscible palladium-copper alloy film formed by the coating and diffusion treatment was produced at 1073K. Also, electron probe microanalyzer (EPMA) experiments shows that palladium alloy layer maintains thermal stability for a long time owing to coating of intermediate SiO₂ layer. The supported palladium-copper alloy membrane obtained in this study yielded excellent separation performance for hydrogen : hydrogen permeance of $2.6 \times 10^{-2} \text{ cm}^3/\text{cm}^2 \cdot \text{cmHg} \cdot \text{s}$ and hydrogen/nitrogen(H₂/N₂) selectivity was above 70000 at 723 K.

4. REFERENCE

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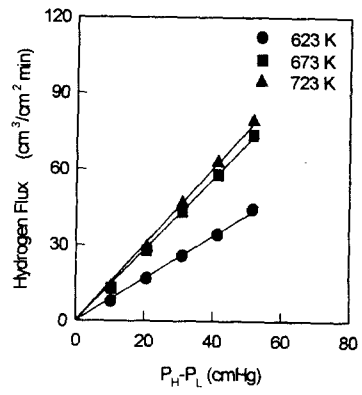


Fig. 1. Hydrogen flux for a Pd/Cu alloy composite membrane prepared on the treated substrate by vacuum electrodeposition.

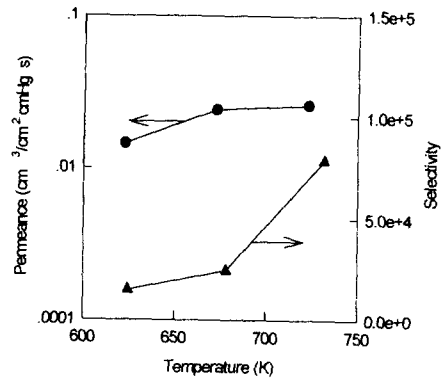


Fig. 2. Performance for a Pd/Cu alloy composite membrane prepared on the treated substrate by vacuum electrodeposition.