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Novel preparation of Pd/Vycor composite membranes

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Abstract

Pd/Vycor® composite membranes were prepared using electroless plating from both typical hydrazine-based and formaldehyde modified baths. The electroless palladium film obtained from the modified bath has a higher luster, smaller grain size, and is denser than the typical bath. Using a new preparation technique which combines electroless plating and osmosis, the microstructure of the palladium film can be manipulated to yield both porous and dense films without altering the chemistry of the plating bath.

1. Introduction

Recently, we have reported a novel preparation technique for metal–ceramic composite membranes [1,2] based on electroless plating and osmosis. The technique allows the direct manipulation of film structure (porosity and thickness) without affecting the chemistry of the plating bath. Using this technique, composite membranes with thin and dense Pd, Ag and Pd/Ag films were plated on microporous ceramic, glass and stainless steel supports [1–3].

In this paper, we present two methods of improving the quality of the Pd film plated on porous Vycor glass. The first is by modifying the plating solution, while the second is by the use of osmosis.

2. Experimental

Porous Vycor glass tube (Corning Inc.) with an average pore size of 50 Å was used as support for the Pd composite membranes. Although the pore size is reported to be between 10 Å to 150 Å, the scanning electron micrograph shown in Fig. 1a indicates that micron size grooves run parallel to the tube axis. Thus, commercial porous glass has two different pore structures as shown in the schematic diagram (Fig. 1b). The tube was 10 mm in diameter with a wall thickness of 1.5 mm.

The porous Vycor tubes as received from the supplier were cut to desired length and cleaned in a 30% hydrogen peroxide solution at 80°C for 1 h to remove hydrocarbons adsorbed in the pores. After rinsing in deionized water, the tubes were cleaned ultrasonically in trichloroethylene followed by rinsing in ethanol and deionized water. The cleaned tubes were then stored in deionized water.

Prior to electroless plating, the Vycor tube surface was activated using Sn(II) and Pd(II) solutions (see Table 1). The tubes were first immersed for 5 min in Sn(II) solution followed by 5 min in distilled water. The sensitized tubes were then immersed for 5 min in Pd(II) solution

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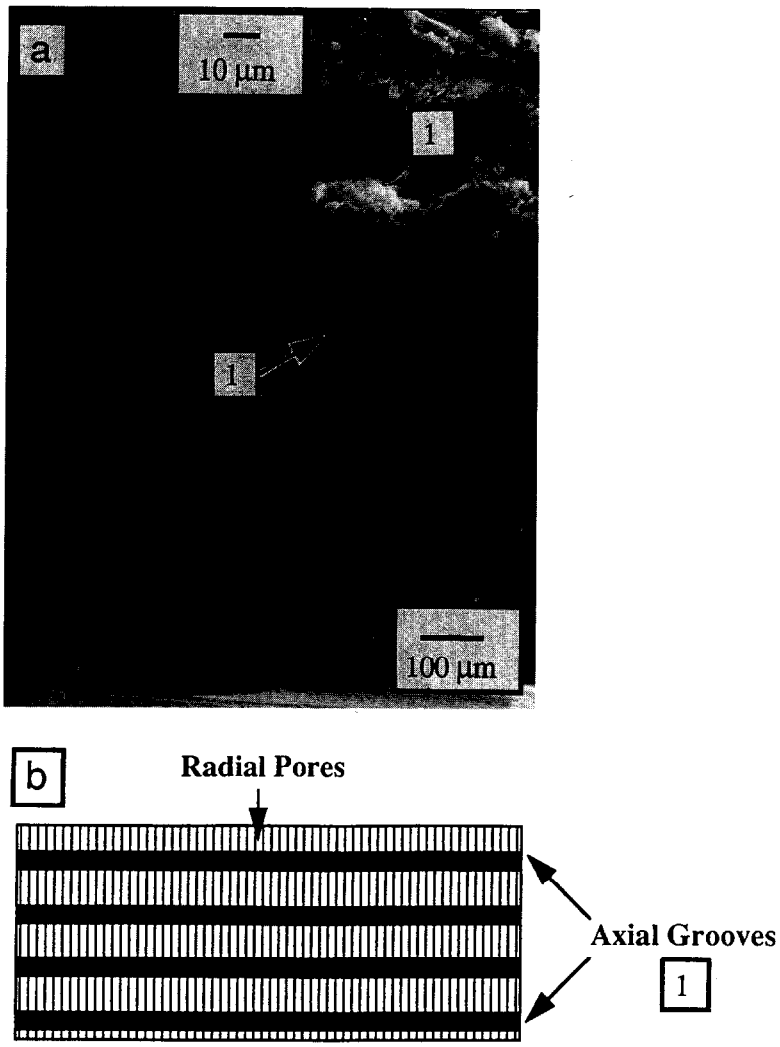

Fig. 1. (a) Scanning electron micrograph and (b) schematic diagram of the porous Vycor glass tube. (1) Axial grooves.

Table 1
Composition of the sensitizing and activating solutions

Sn(II) sensitizing solution		Pd(II) activating solution	
$SnCl_2$	1 g/l	10% $(NH_3)_4Pd(NO_3)_2$	2 ml/l
HCl (28–30%)	1 ml/l	HCl (28–30%)	1 ml/l

followed by 5 min in distilled water. The latter step forms the Pd seeds needed to activate the glass surface. This procedure is repeated 10 times to insure uniform activation of the tubes. The activated tubes (yellow-brown color) were then dried at 60°C for 24 h and stored in a dessicator.

The Pd electroless plating bath was based on a formulation developed by Rhoda [4] which has been used widely in preparing Pd composite membranes on both ceramic [5], porous glass [6] and porous stainless steel supports [7]. It consists of a Pd-ammine complex stabilized with ethylenediamine tetraacetate (EDTA) and uses hydrazine

Table 2
Composition of the Pd electroless plating baths

Bath composition	Bath 1	Bath 2
$(NH_3)_4Pd(NO_3)_2$ (10 wt.-%)	50 ml/l	50 ml/l
Na_2EDTA	40 g/l	40 g/l
NH_4OH (30 wt.-%)	200 ml/l	200 ml/l
N_2H_4 (1 M)	6 ml/l	6 ml/l
Formaldehyde (37 wt.-%)	0	1 ml/l
Buffer (pH 10)	100 ml/l	100 ml/l

as a reducing agent (Table 2, Bath 1). Our modification involves addition of 1–2 ml/l formaldehyde and a typical bath composition used in this study is shown in Table 2, Bath 2. The tubes to be plated were immersed in the plating bath at 65°C and allowed to plate for 90 minutes with occasional stirring. After plating, the tubes were rinsed with deionized water and sectioned into smaller pieces using a diamond saw for scanning electron microscopy (SEM) of film structure and thickness.

3. Results and discussion

3.1. A new modified plating bath composition

Using electroless plating, one way of improving the quality of the deposited film is to develop a better plating solution. The Pd/Vycor composite membrane shown in Fig. 2a was prepared using the Bath 1 composition. The deposited film is dull grey and can be scratched easily. The accompanying SEM micrographs (Fig. 2b and Fig. 2c) show that the film is made up of irregular faceted grains of nonuniform size. From the cross-section micrograph (Fig. 2c), it appears that the film has a rough surface with three-dimensional conical growths, and a measured thickness of 3.5 μm.

Fig. 2d shows a Pd/Vycor membrane prepared using the modified Bath 2 composition. The deposited film has a high surface luster and is relatively scratch-proof. The film microstructure in Fig. 2e has smaller grain size as compared to the Bath 1 formulation (Fig. 2b) used typically in prior studies [4–7]. In addition, the grains do not exhibit any facets and are also more uniform in size. Fig. 2f shows that the film is smoother, and for the same plating duration a thinner (0.8 μm) but denser film is obtained.

Formaldehyde is a well known reducing agent and the work of Bindra et al. [8] describes in detail the role of formaldehyde as an electron donor in metal plating via electrocatalytic oxidation and decomposition. We have found that the addition of formaldehyde to a hydrazine based bath results in a longer induction period but yields a more uniform plating. Our study has shown that there is an optimum amount of formaldehyde that can be added to the plating bath. There is no discernible film improvement with less than 1 ml/l of formaldehyde, while with more than 2 ml/l, total inhibition of plating was observed. It appears that formaldehyde acts as a moderating agent during the plating process. A further study of this phenomenon is currently in progress.

3.2. A novel preparation technique involving electroless plating and osmosis

A way of improving the film quality without resorting to changing the plating bath composition is to carry out electroless plating under osmotic pressure [1–3]. This was achieved by immersing the porous Vycor glass in Bath 1, while an *inert* solution was pumped through the tube. The concentration difference of solutes across the membrane gives rise to osmotic pressure and results in a net flux of water across the membrane from the dilute to the concentrated solution. Two inert solutions, a 3 M $CaCl_2$ solution and distilled water, were utilized.

Fig. 3a and Fig. 3b show SEM micrographs of a palladium composite membrane prepared by conventional electroless plating from Bath 1 composition, with the exception that only half the amount of palladium was used. As compared to Fig. 2b and Fig. 2c, the film has a more uniform grain size and is thinner (1.2 μm versus 3.5 μm). Two other palladium membranes were also prepared simultaneously, from the *same* plating solution and conditions. In the first case (Fig. 3c and Fig. 3d), a 3 M $CaCl_2$ solution was pumped through the tube while it was immersed in the plating solution. Fig. 3c shows that the resulting palladium film is denser with smaller grains as compared to conventional electroless plating (Fig. 3a and 3b), and also the film is thinner, 0.9 μm (Fig. 3d). In the second case (Fig. 3e and Fig. 3f), distilled water was pumped through the tube and the film structure is different. Unlike the previous cases, although the grains are small

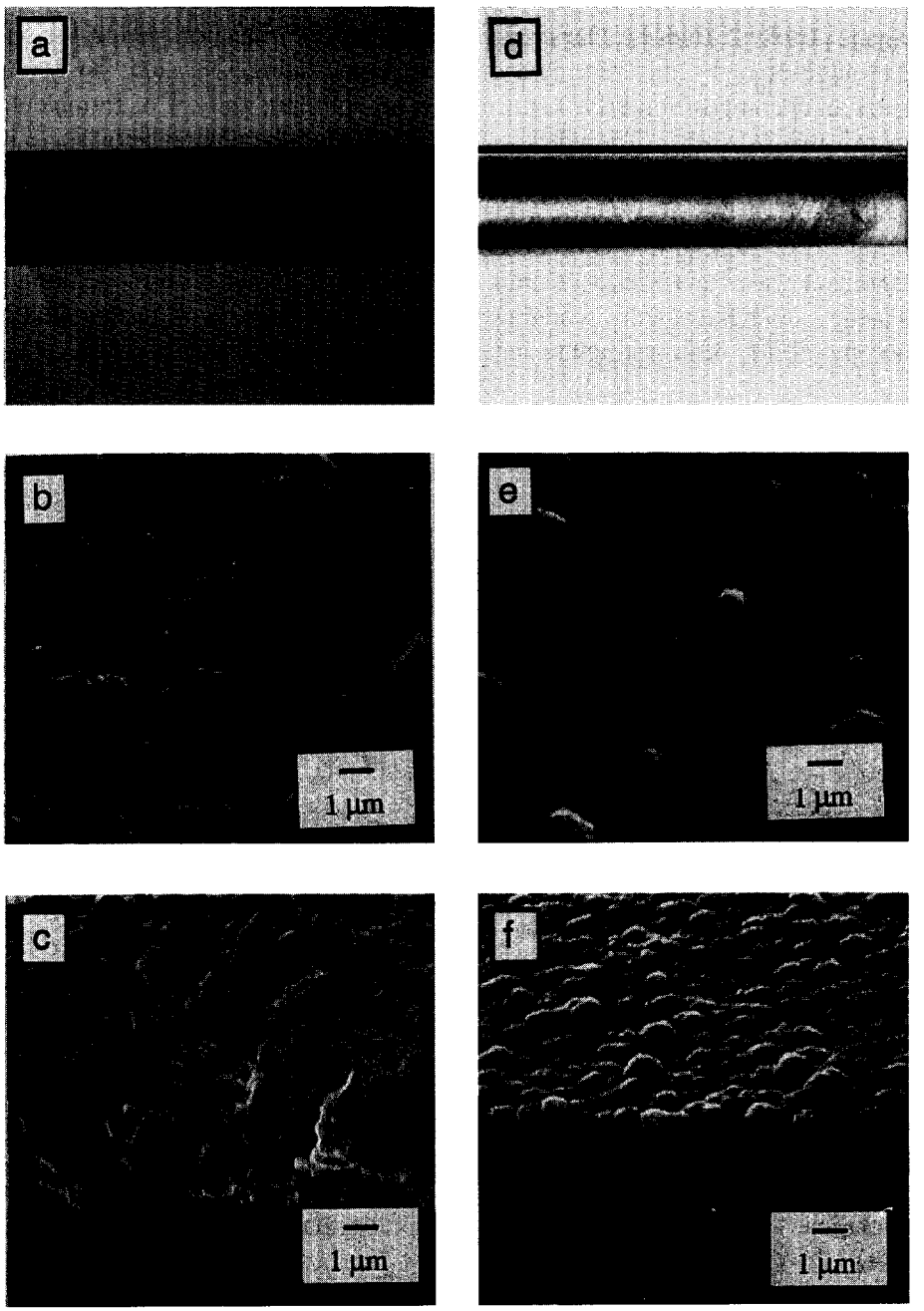

Fig. 2. Photograph and SEM micrographs of Pd/Vycor composite membrane prepared by Bath 1 (a)–(c), and Bath 2 (d)–(f).

(Fig. 3e), there is evidence of porous structure (Fig. 3f). In addition, the film is thicker (1.6 μm) and rougher due to formation of conical growths.

It can be seen from Fig. 3 that the electroless palladium deposited under osmosis has a different film structure as compared to conventional electroless plating. In Fig. 3c and Fig. 3d, where the tube-side solution (3 M $CaCl_2$) is more concentrated than the plating bath, the osmotic pressure is directed normal to the film and the resulting flux is from the plating bath to the tube-side. The effect is two-fold; first, the palladium deposit is densified against the support surface, and second, mass transfer of reactant to the plating

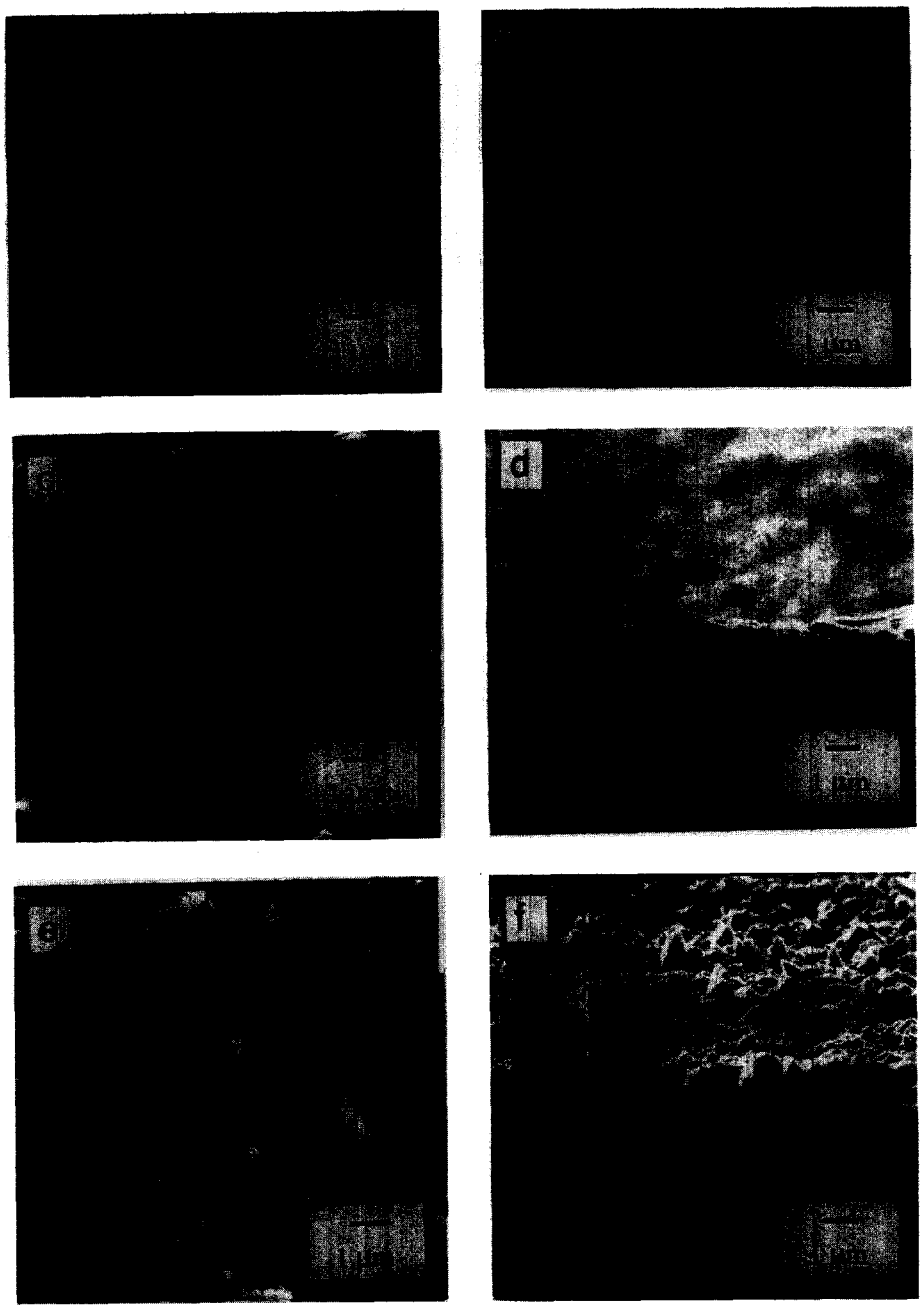

Fig. 3. SEM micrographs of the surface and cross-section of Pd/Vycor composite membranes prepared by (a) and (b) typical electroless plating, and by the new preparation technique under (c) and (d) 3.0 M $CaCl_2$ solution and (e) and (f) distilled water.

surface is enhanced. In the case of Fig. 3e and Fig. 3f, the direction of osmotic pressure and flux is reversed. This hinders mass transfer of reactants to the surface and may account for the rougher, conical growths observed.

4. Concluding remarks

In this work, we have discussed two methods for improving the quality of electroless Pd film deposited on porous Vycor glass. These methods

involve modifying the plating bath composition and the use of osmosis. In forthcoming publications, we shall examine in greater detail the effects of various plating parameters, including the addition of formaldehyde, amount of palladium precursor and osmotic pressure. The thermal stability of both Pd and Pd–Ag alloy films will also be analyzed.

Acknowledgements

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