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ARTICLE

Synthesis of Pd-Ag Membranes by Electroless Plating for H_2 Separation

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Abstract: Both sequential-deposition and co-deposition based on electroless plating method for the preparation of Pd-Ag composite membranes were investigated. The morphology, phase structure, compositional homogeneity and compactness of the prepared membranes were compared. The results show that Pd-Ag membranes prepared by co-deposition are dendritic, inhomogeneous, and poorly compact, while those by multilayer sequential deposition are more homogeneous and compact. The multi-layer sequential deposition requires higher temperature and longer time for annealing to form Pd-Ag alloy. The Pd particles size is decreased by separate Ag layer and the surface of Pd-Ag membrane is smoother.

Key words: Pd-Ag composite membrane; electroless plating method; codeposition; sequential deposition

The composite membrane configuration with a thin Pd or Pd alloy membrane supported on a porous substrate has attracted much attention due to its infinite theoretical hydrogen selectivity, higher hydrogen permeability, and higher resistivity[1-10]. Defects-free ultrathin Pd-Ag membrane is the key point to Pd composite membrane reactor for H_2 separation. In pursuit of defect free, thin and stable membranes, various techniques have been investigated over the past decades by numerous research groups. Of all the methods, electroless plating (EP) for thin film deposition appears to be quite attractive due to the possibility of the uniform deposition on complex shapes, very simple equipment and ease to scale up on large size substrate and therefore is more suitable for the industrial applications[11-16].

The electroless deposition procedures for Pd-Ag alloy membranes consist of depositing the two elements simultaneously (codeposition) or sequentially (layer by layer). In the sequential deposition, alternate layers of Pd and Ag are deposited from their individual plating baths. The Pd and Ag layers are then annealed to obtain a uniform alloy film. However, most efforts have been focused on the Pd-Ag codeposition because the codeposits require more mild annealing conditions than those required for the sequential deposition[17,18]. Thus the overall membrane synthesis procedure becomes significantly simple[14,19,20]. But the deposition of alloys at exact composition is the main challenge through electroless plating because controlling codeposition of two metals is difficult.

In the present study, for palladium-silver composites, both the deposition of palladium and silver at the same time and separate deposition of two metals were investigated. The deposition properties of the two methods, which are very important for the synthesis of homogeneous Pd-Ag alloys, such as uniformity, compactness, phase structure, compositional homogeneity and particle sizes of individual metals, were examined.

1 Experiment

Palladium and silver were deposited on the outside surface of the porous stainless steel (PSS) tube provided by powder metallurgy, through the electroless plating method. The PSS tube was 60 mm in length with an outside diameter of 5.6 mm and a wall thickness of 1 mm. The average pore size was 0.5 μm and the porosity of the support was 25% (as shown in Fig.1).

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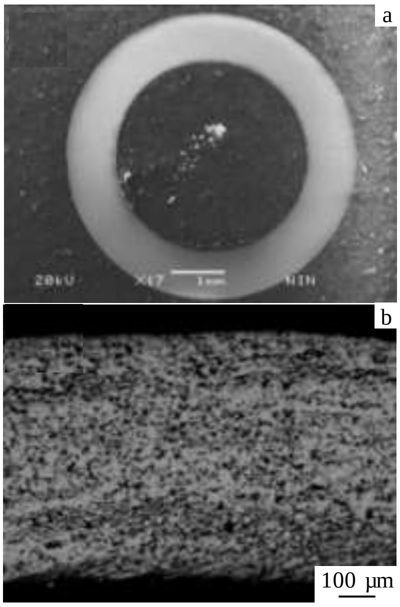

Fig.1 SEM image (a) and optical morphology(b) of the PSS

Prior to deposition, the PSS tubes were cleaned in ultrasonic bath at 60 °C for 120 min in alkaline solution to remove any unwanted contaminants. After cleaning, the PSS tubes were deposited with a TiO_2 layer by a sol-gel process to introduce the intermetallic diffusion barrier between the PSS and Pd-Ag layer. Then, the modified substrates were activated with $PdCl_2$ and $SnCl_2$ solutions. The activation solution consisted of 1 mL/L HCl (~37%). The activation process was performed for 4 times. The composition of the electroless plating solution for Pd and Ag deposition is shown in Table 1.

The composite Pd-Ag membranes were plated using a sequential deposition and a codeposition of Pd and Ag by electroless plating. The plating step was repeated until the desired thickness of the membrane was reached. After each deposition, the samples were rinsed with deionized water, and then dried in an oven at 120 °C for 3 h. Finally, the membrane was annealed in an argon flows.

The phase structure of the membranes plating by the two methods were identified using X-ray diffraction (XRD, D/MAX-2500pc, Japan) with Cu Kα radiation. The morphology and composition of the deposits were examined using JSM-6700 field emission scanning electron microscope and the attached energy-dispersive X-ray spectroscope (EDS).

2 Results and Discussion

2.1 Pd-Ag codeposition

Fig.2 shows the top and cross-section views of the Pd-Ag composite membrane prepared by the codeposition method. As can be seen from this figure, the Pd-Ag codeposits show much highly nonuniform growth in the perpendicular direction, but little in the lateral direction to the substrate surface. Therefore, little substrate pore coverage is expected. The addition of silver results in a dendritic structure of the PdAg layer. According to the mixed potential theory, the plating rate of Ag is higher than that of Pd. So, the growth of Pd and Ag grains cannot keep the same rates for all directions. The deposits by codeposition show preferential deposition on the top of the substrate pores compared with the inside of the pore, which lack uniform deposition over the entire surface of the substrate.

Fig.3 shows the typical distribution of Pd and Ag in the deposits obtained by the EDS spot scan analysis. Points (1, 2, and 3) show relatively higher Ag concentration in comparison to the bottom points (4 and 5) and the results are listed in Table 2. The inhomogeneous distribution of Ag is due to its deposition occurring at the severe mass transfer controlled condition from the coplating bath.

The XRD patterns of the deposition are shown in Fig.4. It

Table 1 Bath composition for Pd electroless, Ag electroless and Pd-Ag codeposition

Chemical	Pd bath	Ag bath	Pd-Ag bath
$PdCl_2$/g·L^{-1}	2	-	1.37
$AgNO_3$/g·L^{-1}	-	0.75	0.43
$Na_2EDTA_2H_2O$/g·L^{-1}	40	40	40
$NH_3\cdot H_2O$ (28%)/mL·L^{-1}	200	200	300
H_2NNH_2(1 mol/L)/mL·L^{-1}	5	5	6
pH	10~11	10~11	10~11
Temperature/°C	60	60	60

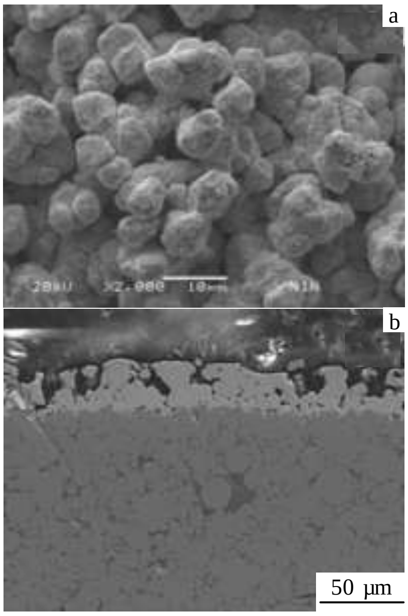

Fig.2 SEM images of Pd-Ag composite membranes by electroless codeposition (Pd/Ag=77/23): (a) top view and (b) cross-section view

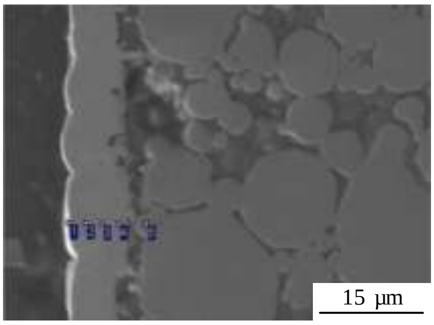

Fig.3 Typical Pd and Ag distribution obtained in the deposits by codeposition

Table 2 Membrane composition in the deposits by codeposition in Fig.3 (wt%)

Points	Ag	Pd
1	42	58
2	20	80
3	37	63
4	5	95
5	10	90

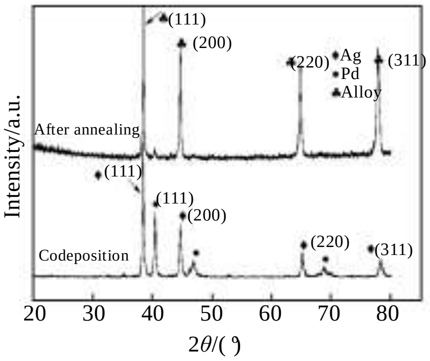

Fig.4 XRD patterns of the samples prepared by co-deposition and after annealing at 600 °C for 10 h in Ar gas

can be seen that for the as-deposited sample, all of these peaks are located between the peaks of Pd (111) and Ag (111), Pd (200) and Ag (200), Pd (220) and Ag (220), Pd (311) and Ag (311), indicating that the Pd-Ag deposits obtained are bimetallic, not alloy. However, the diffraction peaks of the obtained Pd-Ag membrane after annealing appear at 2θ=40.05°, 46.52°, 67.96°, 81.89°, 86.36°, which reveals that after annealing the obtained Pd-Ag deposits form a homogeneous alloy.

2.2 Pd-Ag sequential deposition

2.2.1 Two-layer sequential deposition

The Pd-Ag composite membranes were prepared by separate deposition of the two metals on the support. Pd was deposited first followed by Ag deposition (two-layer sequential deposition) as shown in Fig.5. The Pd-Ag deposition consists of one layer of Pd (5~6 μm) and one layer of Ag (2~3 μm). The deposits are homogeneous, smooth, and dense over the entire substrate surface.

The XRD patterns of the two-layer sequential deposits are illustrated in Fig.6. The Pd and Ag deposits are crystalline and do not show any preferred crystal orientation. The presence of Pd and Ag phase means that as obtained deposits are not entirely of alloy phase after annealing at 700 °C for 24 h in Ar gas. After annealing at 900 °C for 48 h in Ar gas, the deposits entirely form alloy phase. The codeposition of Pd and Ag as membrane preparation method offers advantages such as fast synthesis procedure and easy annealing of the deposits in comparison to the two-layer sequential plating method.

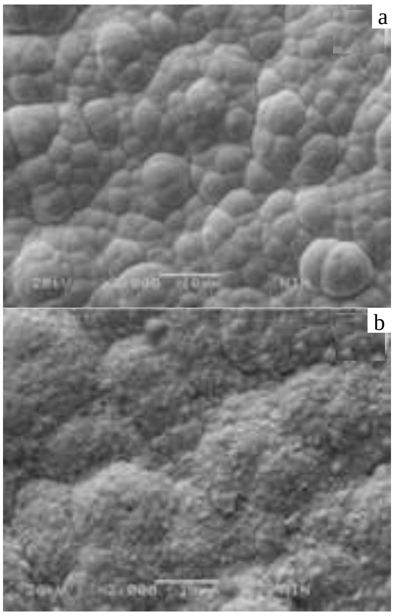

Fig.5 Deposition characteristics of Pd electroless deposits (a) and Ag electroless deposits by two-layer sequential deposits (b)

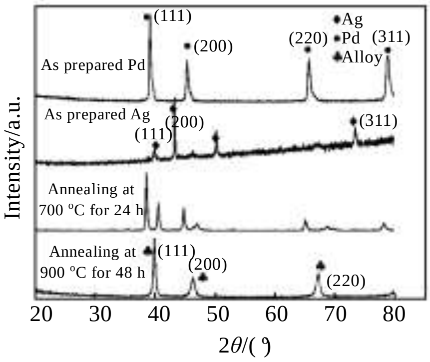

Fig.6 XRD patterns of the samples prepared with two-layer sequential deposition

2.2.2 Multi-layer sequential deposition

The Ag electroless deposits show very similar growth characteristics to that of electroless plated Pd as observed from Fig.7a, 7b, 7d, 7e. They show very uniform growth over the substrate surface and the deposits show the equal growth on the top and inside the pore of the substrate. The good lateral growth of the deposits is a desired characteristic for the synthesis of thin and hydrogen selective membrane. The Pd and Ag sequential deposits show very uniform morphology as is evident from Fig.7c and 7f. The deposition consists of four alternate layers of Pd (2.2 μm) and Ag (1 μm) each (total 8 layers). The Pd particles size is decreased by the alternate Ag layer and the surface of Pd-Ag membrane is smoother.

Fig.8 shows the typical distribution of Pd and Ag in the deposits obtained by the EDS spot scan analysis. Points (1, 2, 3 and 4) show homogeneous distribution of Pd and Ag in Table 3. Point 5 shows that Pd and Ag atomics deposit into the pore of the support. The deposits obtained by sequential deposition are more homogeneous in Pd and Ag composition than the deposits obtained by codeposition.

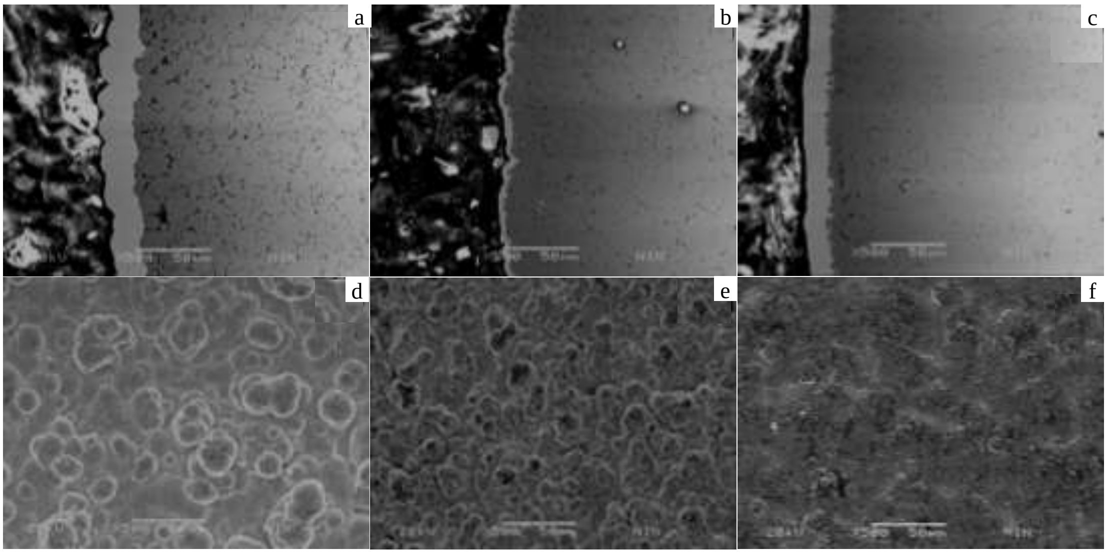

Fig.7 Deposition characteristics of Pd electroless deposits (a, d) Ag electroless deposits (b, e), and sequential deposits (c, f)

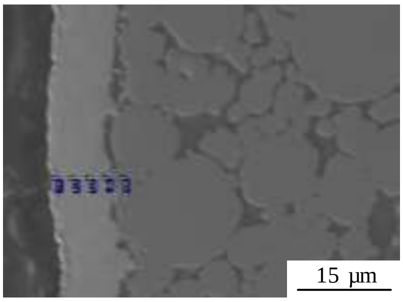

Fig.8 Typical Pd and Ag distribution obtained in the deposits prepared by sequential deposition

Table 3 Membrane composition in the deposits by multi-layer sequential deposition in Fig.8 (wt%)

Points	Ag	Pd
1	26.5	73.5
2	26.6	73.4
3	26.9	73.1
4	26.8	73.2
5	10	90

3 Conclusions

1) Codeposition is not a suitable method for preparing Pd-Ag composite membranes. The main reasons are as follows: (i) The Pd conversion in this reaction is low. Obtaining a specific Pd-Ag ratio on the membrane is very difficult; (ii) The Pd and Ag concentrations in the initial solution are low and as a result the amount of Pd-Ag deposited is also low; (iii) The deposited film is non-homogeneous and irregular. Dense, even thick (>25 μm) film could not be successfully prepared even after 8 consecutive one hour plating sessions; (iv) The morphology of the codeposits obtained by conventional bath is nonuniform with the deposits showing dendritic structure and poor substrate pore coverage.

2) The composite membranes prepared by separate deposition of metals (sequential deposition) are very uniform including composition and morphology and good lateral growth of the deposits on the substrate surface, which is suitable for preparing the Pd-Ag membrane. However, PdAg layers prepared by sequential method require longer alloying time and higher temperature than

that of codeposition to form alloy. The Pd particles size is decreased by the alternate Ag layer and the surface of Pd-Ag membrane is smoother.

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多层分步镀方法制备用于氢气分离的 Pd-Ag 膜

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摘 要：用基于化学镀方法的钯银共沉积和分步沉积 2 种方法制备了 PdAg 膜。对比研究了 2 种方法制备的钯银膜的形貌、相结构、成分均匀性和致密性。实验结果表明共沉积法获得的钯银膜是树枝状的，成分不均匀，且致密性很差。分步沉积获得的钯银膜成分均匀、沿侧面生长趋势好，更适合制备超薄致密的用于氢气分离的钯银合金膜。多层分步镀形成 Pd-Ag 合金需要更高的温度和更长时间的热处理。Ag 层的交替使得 Pd 的晶粒减小，并且最终沉积的膜表面更光滑。

关键词：PdAg 膜；化学镀；共沉积；分步沉积

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