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Influence of layer compositions and annealing conditions on complete formation of ternary PdAgCu alloys prepared by sequential electroless and electroplating methods

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HIGHLIGHTS

- Ternary PdAgCu alloy membranes were successfully prepared by the sequential electroless and electroplating methods.
- The average Pd composition required to form alloy was found to be approximately at least 60%wt.
- The alloy region was achieved for f Pd 60–73 wt%, Cu 18–30 wt% and Ag 2–13 wt%.
- Suitable annealing temperature in the range of 500–600 °C for an adequate period of treating time (20–60 h).

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ABSTRACT

PdAgCu ternary alloy membranes were synthesized by the sequential electroless plating of Pd following by electroplating of Ag and Cu onto stainless steel substrate. The composition of the composite was varied by changing the deposition times. The fabricated layers were annealed at the temperatures between 500 and 600 °C for 20–60 h. The Energy Dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) were employed to investigate the element distribution in the membrane which provided the insight on membrane alloying process. Complete formation of the alloy could be obtained when the Pd composition was greater than a critical value of 60 wt%, and Ag and Cu contents were in the range of 18–30 wt% and 2–13 wt%, respectively. Deposition times of Ag and Cu were found to affect the completion of alloy formation. Excess amount of the deposited Cu particularly tended to segregate on the surface of the membrane.

1. Introduction

Dense Pd and Pd-based alloy membranes supported on porous stainless steel (PSS) are well suited for hydrogen purification from various sources [1,2]. However, using pure Pd membranes could lead to undesired hydrogen embrittlement due to the $\alpha - \beta$ phase transition of palladium hydride under its critical temperature of 298 °C and pressure of 2 MPa [1,3]. This phase transition is accompanied by a considerable lattice expansion (c.3.5%), and the resulting internal stress generates defects such as pinholes and cracking of metal films [4]. In addition, pure palladium is easily subjected to surface poisoning by impurity gasses such as CO, CO_2, and H_2S. These severe problems, in conjunction with the high cost of Pd, have led to the exploration of a wide variety of Pd-alloy membranes. In general, the unique properties of Pd-based alloy membranes can be adjusted and customarily made by changing the substitute elements and their alloy compositions. With respect to pure Pd membranes, such the efforts would result in enhanced physical properties such as membrane strength, embrittlement resistance, sulfur tolerance); and improved separation performance such as increasing hydrogen permeability with exceptional selectivity; and cost reduction. The Pd–Ag–Cu system is one of the most promising candidates to possess improved performance mentioned above. Many studies have tried to incorporate Ag and Cu to develop binary Pd–Ag and Pd–Cu, and ternary Pd–Ag–Cu membranes. PdAg (20–30%) alloy membranes are very attractive for the

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practical use because of the low cost, higher hydrogen permeability and higher resistance to the damage due to the hydrogen embrittlement when compared to pure Pd membranes [5–7]. PdCu is a viable alternative since it shows high hydrogen permeability but with a better sulfur poisoning resistance [8–10]. The alloying of palladium with Cu gives a reduction of the cost of the membrane by reducing the amount of palladium needed [11]. Several deposition methods have been used to synthesize PdAgCu alloy membranes including sputtering [12,13], electroless plating [14–17] and electroplating [18]. The electroless and electrodeposition techniques were particularly uncomplicated and have economic advantages compared to the more sophisticated method [19]. However, the attempt to get membrane uniformity in forming the alloys under appropriate conditions is still very challenging. In heat treatment process, annealing temperatures that are not high enough and/or insufficient time for the diffusion can result in incomplete alloy formation [15,20]. But too high processing temperatures can cause or promote the diffusion of the substrate towards the top membrane layer, resulting in the formation of undesirable alloy phases. It has been reported by few studies [15–17] that forming homogeneous PdAgCu alloy by coating-diffusion process could be successfully achieved under suitable annealing temperatures in the range of 500–550 °C for different treating time depending on the details of the systems (for example, the deposition time for each layer). Additionally, the XRD and XPS results from a study by Tarditi et al. [16,17] confirmed that complete alloy formation of the PdAgCu membrane prepared by sequential electroless plating technique could be achieved under heat treatment at 500 °C for 162 h [17]. However, proper deposition times for each layer must be carefully controlled. Using density functional theory (DFT), a study by Ling et al. [21] suggested that fcc PdAgCu alloys with Pd greater than 66% atom could result in improved membrane performance. Yet, experimental confirmation of those findings has been rarely reported, especially on such membranes with mostly high Cu (20–30%) and moderate to low Ag contents (1–15%) [12,15,16,22]. Thus, it is interesting to investigate the effect of the layer deposition times of the membranes and their annealing conditions that affect the completion of alloy formation of Pd/Ag/Cu system prepared by sequential electroless plating and electroplating technique.

2. Materials and methods

2.1. Preparation of PdAgCu alloy membranes

Non-porous stainless steel disks (316L SS), cut into a 1 cm × 1 cm square shape with a thickness of 1 mm, were used as a substrate in studying of the effect of plating conditions to form palladium alloy, its morphology characteristics, and physical properties. Prior to the plating process, SS disks were ultrasonically cleaned in an alkaline solution consisting of 0.12 M $Na_3PO_4 \cdot 12H_2O$, 0.61 M Na_2CO_3, 1.13 M NaOH and 5 g/L detergent at 60 °C for one hour. Then the pre-washed disks were washed thoroughly three times with deionized water until the rinsing water had pH 7. Finally, the disks were immersed in isopropanol and dried at 120 °C for 3 h. The cleaned stainless steel was oxidized in a high temperature furnace at 600 °C for 6 h under ambient pressure. It was then activated to seed the surface layer with nuclei of palladium. The supports were sensitized by using 1 g/L $SnCl_2$ (pH 1) and activated by 0.1 g/L $PdCl_2$ (pH 1) repeatedly several times until their color changed into dark grey to ensure sufficient Pd coating on the surface [23,24].

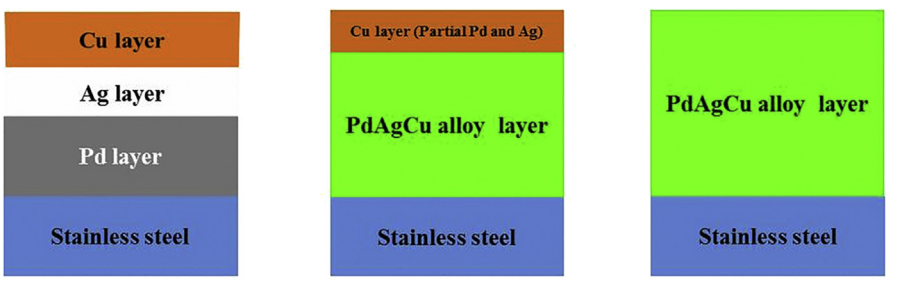
Pd was Firstly deposited onto the substrate by electroless plating method (ELP) using a solution consisting of 0.015 M $Pd(NH_3)_4Cl_2 \cdot H_2O$, 1.428 M NH_4OH, 0.108 M Na_2EDTA, and $N_2H_4 \cdot H_2O$. The clean and activated substrate was immersed in the solution at pH 11 and kept rotated at a constant temperature of 60 °C for 90 min. Sequentially, Ag was then deposited onto the Pd layer by electroplating (EP) technique. Silver anode and 10% $AgNO_3$ plating solution operated at 1.2 V were used to deposit Ag onto the substrates at room temperature for 3–15 s. Finally, a Cu layer was deposited on top of the PdAg layers using a copper bar as anode and 25% $CuSO_4$ plating solution, operated at 2.0 V for 30–180 s.

The Pd–Ag–Cu deposited layers were annealed at a suitable temperature (500–600 °C) [20,25] for a period of time (20–60 h) in argon atmosphere to promote intermetallic diffusion of the elements resulting in alloy formation of the membrane. The schematic of the alloy formation process of the fabricated layers under appropriate annealing conditions described above is illustrated in Fig. 1.

2.2. Membrane composition characterization

Composition analysis of the cross sectional area consisting of the deposited layers was examined by using Scanning Electron Microscope (SEM), JEOL model JSM-5800LV equipped with Energy Dispersive X-ray diffraction (EDX). The spatial resolution for the SEM–EDX lies between 0.8 and 1.2 μm with an accelerating voltage of 20 kV for the samples investigated. The distribution of element compositions was calculated from the line scan (EDX) results across the sample thickness.

Phase identification was also analyzed by X-ray diffractometer (XRD), Bruker AXS, Germany Model D8 Advance, equipped with a Cu Kα radiation (weighted average wavelength of 1.5406 ^{o}A) operating at 30 kV and 40 mA. The angular step size was 0.02°, the scan rate was 1-2° per min and 2θ was in the range of 15–90°. The XRD results were used to interpret the phase of alloy formation of the membranes.



(a) Non-annealed membrane (b) Annealed membrane with partial alloy formation (c) Annealed membrane with complete alloy formation

Fig. 1. Simplified illustration of the PdAgCu membrane structure before and after annealing.

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