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Characteristics of dense palladium alloy membranes formed by nano-scale nucleation and lateral growth



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ABSTRACT

In this study, fine, uniform nano-scale layers of Pd were deposited by an advanced sputtering system with high vacuum, high temperature, and high power to overcome the limitations of existing sputtering systems. Thin Pd films formed by continuous sputtering exhibited vertical growth, combined with the lateral growth of Pd clusters due to the improved reactivity of Pd nano-particles, the diffusion of activated Pd atoms at high temperature, and the self-catalyst effect of the porous nickel support (PNS). Additionally, uniformly dense Pd structures were formed by the successive deposition of Pd particles, and Pd clusters formed with a uniform density. A fine Pd–Au alloy membrane manufactured by this advanced sputtering system not only improved hydrogen selectivity due to the pinhole-free membrane surface but also increased hydrogen permeability because the thin film had a thickness less than 6 μm and a uniformly fine grained structure. Additionally, the Pd alloy membrane exhibited enhanced durability because the inter-diffusion of the support component to the membrane surface was prevented by the low temperature of the heat treatment for crystallization and the low alloying temperature.

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1. Introduction

The demand for high purity hydrogen has increased rapidly for several industrial processes such as chemical synthesis, chemical hydrogenation, and the manufacturing of semiconductors, liquid crystal displays (LCDs), light emitting diodes (LEDs), and fuel cells. Membrane-related processes are promising technologies for the production of high purity hydrogen. They offer a number of potential advantages with regards to energy and cost-effectiveness [1–5]. In particular, Pd-based alloy hydrogen separation membranes have attracted a great deal of attention for their use in hydrogen purification and separation due to their infinite hydrogen selectivity, high hydrogen permeability, and chemical compatibility with hydrocarbon containing gas streams [6–8]. Pd and Pd-based alloy hydrogen separation membranes are fabricated as composites consisting of a thin Pd-based layer and a porous metal support with the appropriate mechanical strength. In addition, Pd-based alloy films are mainly prepared on porous stainless steel supports (PSS), porous nickel supports (PNS), and porous ceramic

supports by electroless plating, CVD, electro-plating or sputtering [9–12]. Among these methods, sputtering provides excellent control of the composition, film thickness, and microstructure of the coated film. Additionally, multi-functional films can be obtained by the precise adjustment of sputtering process variables including substrate temperature, pressure, power, and substrate bias. However, sputter-deposited Pd or Pd-based alloy films exhibit a large columnar microstructure when the conventional sputtering is performed at a low substrate temperature, high pressure, and low power. Therefore, the micro-pores are formed near the larger columnar grained-structure on the surface of the membrane after heat treatment for stable Pd alloying and crystallization, resulting in Pd alloy membranes with low hydrogen selectivity [13]. To overcome this problem, we introduced Cu-reflow technology after Pd–Cu sputtering [14–16]. However, our previous membranes did not have a high enough hydrogen permeability for the various hydrogen separation applications because of the increased thickness of the Pd alloy films required to produce micro-pore free surfaces, and because of the intermetallic diffusion from the metal support to the membrane surface caused by the high temperature required for stable Pd alloying and crystallization. To attain both high hydrogen selectivity and permeability, Pd-based alloy membranes need to be thin, dense films with no intermetallic diffusion from the porous metal support.

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This study reports the development of a Pd–Au alloy membrane by advanced DC magnetron sputtering consisting of a uniformly fine and dense microstructure. The advanced DC magnetron sputtering consisted of in-situ, successive deposition systems, facilitating fine, uniform initial nucleation. In this way, the lateral growth combined with the vertical growth to form a pinhole-free surface. Consequently, in this paper, we investigated the mechanism by which this dense structure was formed, and observed the morphology of the fabricated membranes. Furthermore, the hydrogen perm-selectivity of this membrane was also investigated.

2. Experimental

2.1. Preparation of support

A PNS with good chemical affinity to Pd was prepared by the compression of Ni powder and subsequent sintering. Ni powder was purchased from Sigma Aldrich Co. (with an average particle size of 5 μm) and from Nano Technology Co. (with an average particle size of 100 nm). To enhance the mechanical and thermal durability of the PNS, the support surface was modified by mixing Ni powders with different average grain sizes of 5 μm and 100 nm at a ratio of 4:1 (wt%), respectively. Then, the mixture was milled for 24 h using a zirconia ball. The mixed powders were compressed without binder in a cylindrical metal mold with a 2 in. diameter. The compressed powders were heat treated at 1173 K for 2 h under H_2 atmosphere. The sintered PNS was micro-polished using an auto-polisher (GLP S-20/25, purchased from GLP Korea) to fill the surface pores and thus smoothen the surface. This was carried out with #400 to #2000 grit SiC paper followed by a 3 $\mu\text{m}/1 \mu\text{m}$ wet, fine diamond slurry. The modified PNS was then washed using isopropyl alcohol and acetone in an ultrasonic cleaner. The micro-polishing was implemented to improve the hydrogen perm-selectivity of Pd–Au alloy membranes. Plasma surface modification of the Ni support was then performed in a mixture of 10% H_2/Ar at a working pressure of 1.333×10^{-2} kPa and a radio frequency (RF) power of 100 W for 5 min to remove surface impurities induced by air contamination and to activate the micro-polished surface.

2.2. Fabrication of dense Pd–Au alloy films

Using advanced continuous DC magnetron sputtering, Pd (99.95% target purity) and Au (99.99% target purity) were deposited in-situ on the modified PNS with thicknesses in the range of 5 to 5.5 μm and 0.5–1 μm , respectively, at a substrate temperature of 283–673 K, a process pressure of 1.333×10^{-1} – 1.333×10^{-3} kPa, a DC power of 40–160 W, and an Ar flow of 20 sccm. Especially, Au metal was used for alloying and surface densification as well as to increase the resistance against poisoning by hydrogen sulfide and sulfurous constituents [17–19]. Thus, the Pd/Au films on the modified PNS samples could be obtained by successive in-situ DC magnetron sputtering. Additionally, three types of Pd films were prepared by sputter deposition as a function of sputtering times of 60 s, 100 s, and 300 s. These Pd films were only used to compare the nucleation and growth of Pd films by analyzing coarse columnar structure, fine columnar structure, and density. Furthermore, three types of the Pd–Au membranes with a thickness of 6 μm were then prepared for heat treatment and permeation testing.

2.3. Heat treatment and hydrogen permeation testing of dense Pd–Au alloy membrane

Heat treatment was used to fill the voids at the surface of the membrane, to increase the density of the microstructure, and to

facilitate the alloying and crystallization of the separate films. Alloying, crystallization, and densification of the Pd–Au membranes were performed at 673–923 K for 2 h in a H_2/Ar mixture at a working pressure of 1.333×10^{-2} kPa. The heat treatment temperature was varied to determine the optimal temperature. Next, the hydrogen permeation flux and selectivity were measured using an apparatus consisting of a membrane cell, furnace, temperature controller, pressure gauge/controller, and gas chromatograph, as previously described in the literature [15,20]. The measurement temperatures were in the range of 723 K, and the transmembrane pressure difference was 100–750 kPa under a mixed gas flow (H_2 : N_2 =1: 1 v/v). The separation area was 16.6 cm^2 . Furthermore, the morphology of the Pd films was investigated by atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The structures and compositions were determined by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), respectively.

3. Results and discussion

3.1. Properties of dense Pd films

To observe the microstructural properties of the Pd films, the films were deposited on the modified PNS depending on the sputtering conditions, as shown in Fig. 1. The Pd film was fabricated at room temperature, a process pressure of 1.333×10^{-1} kPa, and a DC power of 40 W, with a surface roughness of 114 nm, as shown in the AFM image presented in Fig. 1(a). This film exhibited a coarse columnar structure, heterogeneous deposition, and many voids throughout the entire coating thickness as illustrated by FE-SEM and TEM images of Fig. 1(e) and (i). As a result of this structure, higher points on the growth surface received more sputtered atoms than the valleys due to the shadowing effect. In addition, the adatom surface mobility was low, and the non-uniform initial nucleation tended to grow in the direction of the available coating flux. As a result, the sputtered atoms and adatom had insufficient energy, with the result that the Pd clusters growing on the deposited film could not become dense. Therefore, to increase the density of the microstructure of the Pd film, the sputtering variables affecting the deposited films should be properly controlled.

As shown in Fig. 1(b) and (c), when the sputtering was performed at substrate temperatures of 423 K and 673 K under a process pressure of 1.333×10^{-1} kPa and DC power of 40 W, the columnar structure of the Pd films was gradually modified and then disappeared. The Pd films deposited at a higher substrate temperature exhibited a fine columnar structure and a smooth surface. Moreover, the grain boundaries in the deposited Pd film at a higher substrate temperature appeared to be very dense, and the deposited Pd particles and adatom became significantly fine. These considerable structural differences resulted from increased nanoparticle reactivity, adatom surface mobility, and surface self-diffusion which had effects on lateral growth, densification, and the restraint of columnar structure formation at elevated substrate temperature. Furthermore, grain boundary migration and recrystallization occurred during film growth. Thus, the increase in the substrate temperature increased bulk self-diffusion, grain boundary migration, and thermo-induction for metal atom diffusion [21].

Next, when the process pressure was decreased from 1.333×10^{-1} to 1.333×10^{-3} kPa at room temperature and a DC power of 40 W, the deposited Pd films exhibited a fine columnar structure with a smoother surface than the coarse columnar structure, as shown in Figs. 3(f) and (g). Moreover, this fine

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