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Preparation of palladium–silver alloy membranes for hydrogen separation by the spray pyrolysis method

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Abstract

A Pd–Ag alloy membrane is formed on the outer surface of a porous alumina hollow-fiber support by spray pyrolysis of a $Pd(NO_3)_2$ and $AgNO_3$ solution in a H_2–O_2 flame. The mass fraction of silver in the membrane obtained at a support-surface temperature of 1240–1340 K is as low as 0.04, while its fraction in the total metal mass dissolved in the spray solution is 0.1–0.4. This is explained by the higher partial pressure of silver compared to that of palladium. An additional spray pyrolysis with a silver nitrate solution provides a proper silver content in the alloy membrane. The thickness of the alloy membrane is 1.5–2 μm, and the separation factor of hydrogen to nitrogen is about 24 at 773 K. The membrane surface is observed by high-resolution SEM, and the evolution of the morphology is discussed from the view of the deposition mechanism.

Keywords: spray pyrolysis; palladium–silver alloy membranes; gas permeation; separation of hydrogen/nitrogen

1. Introduction

It is well known that hydrogen permeates a palladium film by the solution–diffusion mechanism [1], and palladium films have been employed to separate hydrogen from other gases [2,3]. Hydrogen embrittlement, a defect of palladium, is reduced by alloying with group Ib metals such as silver [4]. The permeation rate of hydrogen through the Pd alloy membrane is increased by decreasing film thickness. This need for a thinner, stronger film can be met by forming a Pd alloy film on the surface of an inorganic porous support [5].

Recently, several works have been performed on the preparation of composite membranes and their application to membrane reactor systems [6–8]. Uemiya et al. [9,10] formed a Pd–Ag alloy membrane on a porous alumina tube by the chemical plating method. The film was 4.5–6.4 μm thick, more than one order of magnitude thinner than Pd films reported in the literature [11]. Their membrane exhibited a high selectivity for hydrogen, but was obtained by repeating the activation pro-

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cess many times, which is not a simple procedure.

Meanwhile, the spray pyrolysis technique has been established to produce fine particles of metal oxides [12,13] or noble metals [13–16]. A solution of metal salts is sprayed into a heated gas stream and is pyrolyzed. High-temperature superconducting powder of Y–Ba–Cu–O systems is formed by this method in an electric furnace [17,18]. The hydrogen–oxygen flame is particularly clean and is commercially applied for the production of optical fiber. Ultrafine titanium oxide particles are produced in the flame of hydrocarbons [19]. Fine metal particles of Pd, Ag and Pd–Ag alloy are also prepared by the pyrolysis of metal nitrate solutions sprayed ultrasonically [15]. A thin conductive film of Pd–Ag alloy is formed on a substrate by firing a layer of Pd and Ag particles mixed in an organic vehicle [20]. However, the spray pyrolysis method has never been applied to the formation of Pd membranes with the aim of hydrogen separation.

In the present study, a thin Pd–Ag alloy membrane is prepared by spray pyrolysis of a Pd and Ag nitrate solution on a porous alumina hollow-fiber support. The effects of the metal salts concentration in the solution and the flame temperature on the surface morphology of the membrane are investigated, and the mechanism of membrane formation is discussed. A gas permeation test of the membrane is also carried out.

2. Experimental

2.1. Support

The porous α-alumina hollow fiber used was supplied by NOK Corporation. To make the fiber surface uniform, a γ-alumina thin layer was coated on the outer surface by the following method [21]: First, a boemite (γ-AlOOH) sol was prepared by the procedure reported by Yoldas [22]. The concentration of the sol was 1.0 mol-L^{-1}. The hollow fiber, whose lower end was closed, was dipped in the sol for 5 sec. The fiber was dried overnight in air, and was then heated to 1023 K at a rate of 80 K-hr^{-1} in an air stream. The properties of the support fiber are summarized in Table 1. The surface and fractured section of the support fiber were observed with a field emission scanning electron microscope (FESEM, Hitachi S-900). As shown in Fig. 1(a), the surface of the γ-alumina film is quite smooth, and the pores are smaller than 5–10 nm. Figure 1(b) shows the contact between the fine γ-alumina and coarse α-alumina layers.

TABLE 1

Properties of support fiber and γ-alumina membrane

Support fiber	
	outer diameter = 2.5 mm
	inner diameter = 1.6 mm
	porosity = 0.4
	average pore diameter = 120 nm
Sol-gel derived membrane	
	average thickness = 5 μm
	average pore diameter = 5 nm

2.2. Spray solution

An aqueous solution of palladium nitrate was prepared by dissolving palladium black in nitric acid. Palladium black was obtained by dissolving a palladium powder (99.9% pure; Rare Metallic Co., Ltd., Japan) in aqua regia and precipitating with sodium formate (98% pure; WAKO Pure Chemical Industries Ltd., Japan). Silver nitrate (99.8% pure; WAKO Pure Chemical Industries Ltd., Japan), without further purification, was added to the palladium nitrate solution.

2.3. Spray pyrolysis and characterization of membrane

The spray pyrolysis technique was used for preparing the Pd–Ag alloy membrane. A sche-

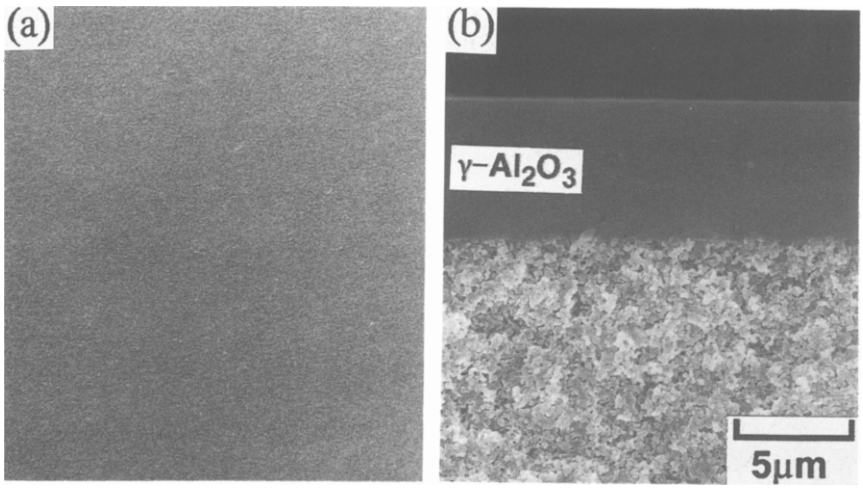

Fig. 1. Scanning electron micrographs of (a) top surface, and (b) fractured section of γ-alumina film.

matic diagram of the experimental apparatus is shown in Fig. 2. The aqueous solution of palladium nitrate and silver nitrate was atomized by the ultrasonic vibrator. The aerosol evolved was carried to the burner nozzle by an oxygen stream. Large liquid drops were trapped by the collision plates installed in the tube below the nozzle. Hydrogen gas was fed through the outer tube, and oxygen gas containing the aerosol through the inner tube. Then a H_2–O_2 flame was formed with a cylindrical coaxial burner. To keep the flame stable, it was covered with an open glass tube (6.5 cm I.D. and 38 cm long) having two holes on opposite sides of the wall. The position of the support fiber in the flame was changeable axially. The support fiber was rotated at a rate of 200 rpm and was moved to and fro horizontally during the deposition. Thus the alloy membrane was formed at the central part of the support fiber. The experimental conditions are listed in Table 2.

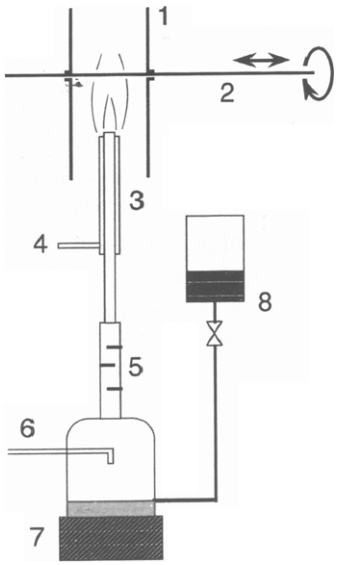

Fig. 2. Experimental apparatus of spray pyrolysis. (1) Glass column; (2) hollow support fiber; (3) cylindrical coaxial burner; (4) hydrogen gas; (5) baffle plates; (6) oxygen gas; (7) ultrasonic vibrator; (8) aqueous solution of metal nitrates.

The temperature of the support hollow fiber in the flame was measured with a Pt–Rh thermocouple (wire diameter = 0.1 mm), which was slid inside the hollow fiber. The temperature of the inner wall of the fiber was considered as that of its outer surface because the wall thickness was as thin as 0.45 mm. The emissivity of the alumina surface is close to unity but that of the alloy membrane is small. So the surface temperature of the support in the flame was de-

TABLE 2

Experimental conditions

	Spray pyrolysis of $Pd(NO_3)_2$ and $AgNO_3$	Spray pyrolysis of $AgNO_3$
Spray solution		
conc. of $Pd(NO_3)_2$ (mol-L^{-1})	0.021	-
conc. of $AgNO_3$ (mol-L^{-1})	0.014	0.1
mass fraction of Ag	0.4	1
feed rate (m^3-sec^{-1})	4×10^{-9}	4×10^{-9}
Flow rate		
hydrogen (m^3-sec^{-1})	4.17×10^{-5}	4.17×10^{-5}
oxygen (m^3-sec^{-1})	2.5×10^{-5}	2.5×10^{-5}
Reaction time (min)	100	45

termined after complete formation of the metal membrane.

The composition of alloy membrane was determined by ICP-AES (Seiko I., SPS 1200) after dissolving in aqua regia. The crystalline structure of membrane was analyzed by X-ray diffraction with CuKα radiation (XRD, Shimadzu XD-D1).

2.4. Permeation

Gas permeation tests were carried out with hydrogen and nitrogen by using the apparatus shown in Fig. 3. The whole surface of the support fiber except for the test part bearing the alloy membrane was coated with a Na_2O–B_2O_3–SiO_2 glass sealant, and the membrane exposed was about 10 mm long. The feed gas permeating from the outside to the inside of the membrane was carried by a stream of argon. The flow rate was measured with a soap-film flow meter, and the gas composition was analyzed by gas chromatography. The pressure outside the membrane was varied while that inside it was kept at atmospheric pressure. The gas permeation coefficient for a thin film was calculated from the fiber dimensions, permeate flow rate, and feed pressure.

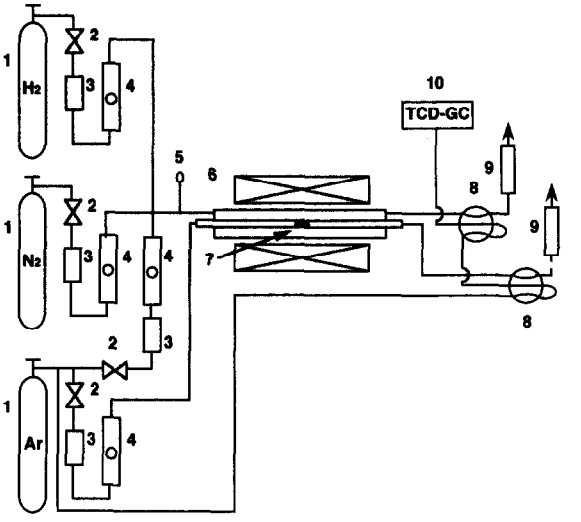

Fig. 3. Equipment for gas permeation. (1) Cylinder; (2) stop valve; (3) mass flow controller; (4) flow meter; (5) pressure gauge; (6) furnace; (7) Pd–Ag membrane; (8) six-way sample valve; (9) soap film meter; (10) gas chromatograph.

$$Q_i = \frac{q_i(\mathrm{STP})}{2\pi r L \Delta p_i} \quad (1)$$

where q_i is the volumetric flow rate of species i at STP, Q_i is the permeation coefficient of species i, L is the membrane length, Δp_i is the difference in partial pressure of species i, and r is the membrane radius. The separation factor between H_2 and N_2 was calculated from Q_{H_2}/Q_{N_2}.

3. Results and discussion

3.1. Formation of Pd alloy membrane

Figure 4 shows the changes in morphology of the alloy membrane during its formation. The support was positioned 5 cm above the nozzle mouth of the burner. As shown in Fig. 4(a), metal particles smaller than 1 μm in diameter

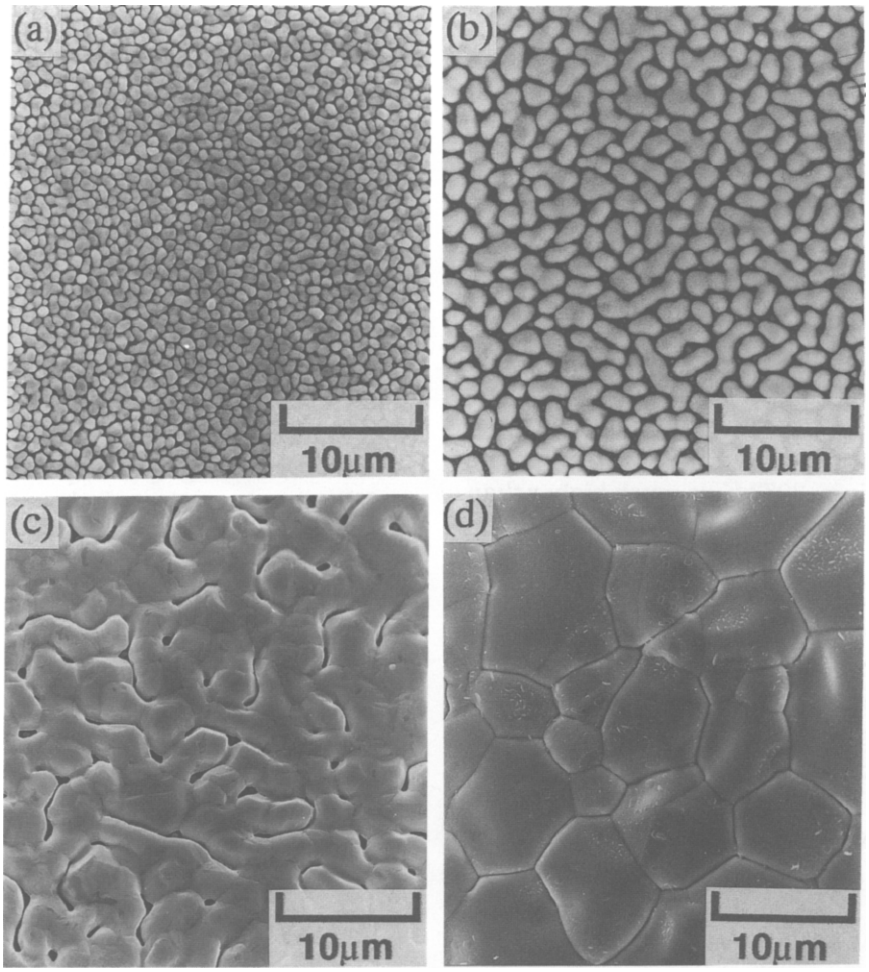

Fig. 4. Changes in surface morphology of palladium–silver alloy membrane during its formation. Deposition period: (a) 3 min, (b) 10 min, (c) 30 min, (d) 100 min.

were observed in the early stage of deposition (3 min). After 10 min deposition, as Fig. 4(b) reveals, these particles sintered with one other to connect several particles. These islands continued to grow and formed a film, as shown in Fig. 4(c). At this stage, however, boundaries surrounding the islands remained. A continuous palladium–silver alloy membrane was obtained at 100 min as shown in Fig. 4(d). The thickness of the alloy membrane, determined from SEM observation of the fractured surface, was 1.5–2 μm. The silver content in the alloy membrane was only 4 wt.% although the silver concentration in the spray solution was 10–40 wt.% of the total metal.

3.2. *Temperature of fiber in flame*

The adiabatic flame temperature is estimated to be higher than 2000 K from thermodynamic calculation, but the surface temperature of the support in the flame is much lower because it is affected by thermal radiation. The temperature of the support fiber placed on the

central axis of the burner nozzle was 1320 K. At horizontal distances of 3 mm and 6 mm from the central axis the temperature became 1340 K and 1240 K respectively.

3.3. Mechanism of membrane formation

The mechanism of membrane formation is shown schematically in Fig. 5. Droplets of the solution are formed by ultrasonic vibration and introduced into the flame. Palladium nitrate is first decomposed to PdO and then reduced to palladium metal at 973 K. Since the boiling point of palladium, 3273 K, is much higher than the adiabatic flame temperature, palladium and palladium alloy containing silver are entrained by the gas stream in the form of metal droplets which then collide with the support hollow fiber as shown in Fig. 4(a). Nagashima et al. [20] found that the alloying between palladium and silver particles formed by spray pyrolysis proceeded even at 873 K. Actually, the XRD analysis of the membrane prepared in the present study gave only Pd–Ag alloy peaks, showing that a support temperature of 1240–1340 K was high enough for the formation of Pd–Ag alloy.

The decomposition temperature of silver nitrate is 717 K, and the boiling point of silver is 2483 K, which is close to the adiabatic flame temperature. Nagashima et al. [15] produced fine particles of silver in a H_2–O_2 flame by the spray pyrolysis method, finding that homogeneous nucleation from silver vapor was important. In the present experiment, a part of the silver deposited was continuously revaporized to the gas phase, and therefore the silver content in the membrane was lower than that in the solution. The composition of the membrane was not largely changed during pyrolysis.

We also investigated the effects of flame temperature and solution concentration on the morphology of the Pd–Ag alloy membrane. Expecting to prevent the vaporization of silver from the membrane, a H_2–air flame was used instead of the H_2–O_2 flame, and the hydrogen flow rate was reduced to 2.9×10^{-5} m^3-sec^{-1}. The temperature of the membrane in the flame was 1073–1223 K. After a 100-min deposition period, small particles were built up on the surface as shown in Fig. 6. The temperature in the H_2–air flame was too low for the formation of a flat membrane, and the growth of particles pro-

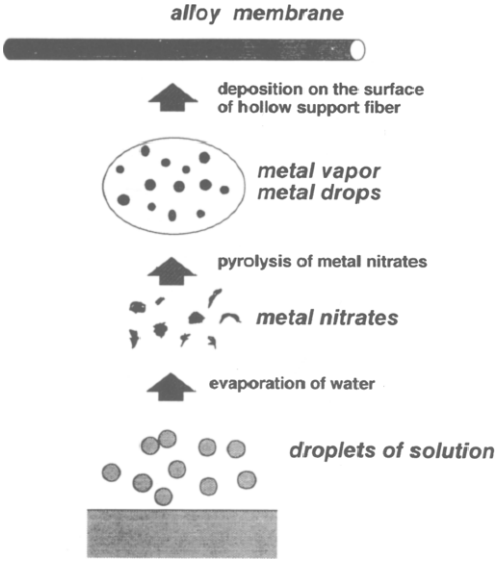

Fig. 5. Mechanism of Pd–Ag alloy membrane formation.

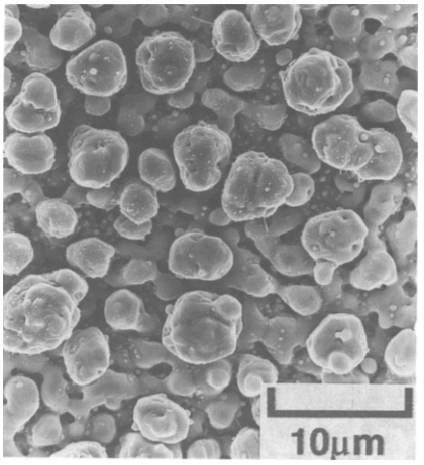

Fig. 6. Surface morphology of Pd–Ag alloy membrane formed in H_2-air flame.

ceeds. When the nitrate concentration in the solution was doubled, the other conditions being kept unchanged from those in Table 2, the morphology of the alloy membrane did not change.

3.4. Hydrogen selectivity

To increase the silver content in the membrane, spray pyrolysis was repeated with a concentrated silver nitrate solution of 0.1 mol-L^{-1}. Then a Pd–Ag alloy membrane containing 24 wt.% silver was obtained. This composition is equivalent to that of the membrane used for hydrogen separation reported by Uemiya et al. [10]. The membrane obtained had the same structure as shown in Fig. 4(c).

Figure 7 shows the permeation coefficients of hydrogen and nitrogen through the Pd–Ag alloy membrane on the γ-alumina support surface. The permeation coefficients through the support fiber itself are much larger than overall values and are in agreement with the previous work [21]. The separation factor of hydrogen to nitrogen through the γ-alumina support alone is in the range of 3 to 4. This implies that diffusion there is controlled by the Knudsen mechanism. In the alloy membrane, on the other hand, the permeation coefficient of hydrogen increases with increasing temperature according to the solution–diffusion mechanism. The separation factor was 24 at 773 K.

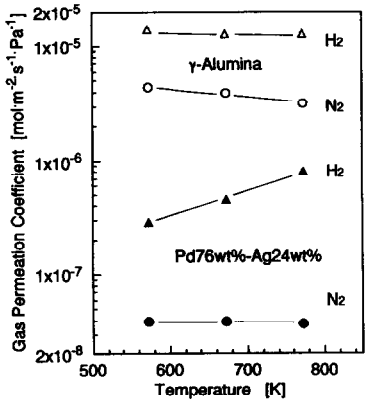

Fig. 7. Gas permeation through Pd–Ag alloy membrane and γ-alumina support fiber.

Theoretically, the separation factor of hydrogen to nitrogen through a palladium membrane is infinite. This means that the low values obtained in this study are due to pinholes and impurities. Since we could not find pinholes larger than 5 nm with the FESEM, leaks seem to occur through pores smaller than 5 nm in the present case. The separation factor will be increased by increasing membrane thickness, but this inherently decreases the flux. An optimum thickness should be determined by balancing selectivity and flux.

4. Conclusion

By applying spray pyrolysis for the first time, a Pd–Ag alloy membrane was formed on a thin α-alumina hollow fiber tailored with γ-alumina film. The silver content in the membrane was lower than that in the solution. This was explained by the evaporation of silver from the membrane. An alloy membrane containing 24 wt.% silver was obtained by modifying the palladium membrane by an additional spray pyrolysis with a silver nitrate solution. The thickness of the alloy membrane was 1.5–2 μm. The separation factor of hydrogen to nitrogen of the resulting membrane was about 24 at 773 K. This implies that there is a slight leakage of nitrogen, but the spray pyrolysis method is much simpler than the chemical plating method. The present membrane can be used when a very high purity of hydrogen is not required.

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