FULL PAPER

Preparation and hydrogen permeation properties of Pd–Al₂O₃ matrix composites

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We propose Pd–Al₂O₃ matrix composites as hydrogen separators instead of pure Pd films. The Pd–Al₂O₃ is lower cost, more stable at higher temperatures as well as higher mechanical strength. The plasma electronic sintering method was effective for preparing 25(30) vol % Pd–Al₂O₃. The hydrogen permeation flux (J_{H_2}) or total electrical conductivity (σ_t) of the 30 vol % Pd[with polyvinylpyrrolidinone (PVP)]–Al₂O₃ was one order of magnitude higher than that of the 25 vol % Pd(with PVP)–Al₂O₃, suggesting percolation conduction of 30 vol % Pd. The 30 vol % Pd(with no PVP)–Al₂O₃ was further higher than that of the 30 vol % Pd(with PVP)–Al₂O₃, because of connections among larger Pd grains for the sample with no PVP. The σ_t or J_{H_2} of the 30 vol % Pd(with no PVP)–Al₂O₃ was one magnitude lower than that of Pd films.

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1. Introduction

Pd films are applicable to hydrogen separators to purify hydrogen gas from syngas.^{1)–4)} The hydrogen permeation depends on temperatures as well as thicknesses of Pd films.^{4),5)} The higher temperatures or thinner films show higher hydrogen permeability. Thus the hydrogen separators based on Pd films need better durability at elevated temperatures than 500°C. In addition, Pd is a precious metal. That's why the industries need reasonable hydrogen separators with a few amount of Pd. With the point of view, many studies propose developing composites of Pd films on porous alumina substrates, instead of pure Pd. The Al₂O₃ possesses more stable at higher temperatures as well as higher mechanical strength, compared to the Pd. The former studies have tried to prepare thinner Pd films on the porous alumina substrates and then investigated hydrogen permeation properties. This approach is advantageous to reduce the required Pd amount as well as improve H₂ permeability.^{6)–12)} However, the preparation processes are complicated compared to that of the simple Pd film. They need to precisely tune many preparation conditions for the films and the substrate conditions such as porosities. The gas leakage throughout thinner Pd films is a subsequent problem. Instead of the Pd films on the porous Al₂O₃, we propose another possibility that Pd–Al₂O₃ matrix composites show hydrogen permeability as well

as electrical conductivity, coming from percolation phenomena. We suppose more simple preparation process as well as higher mechanical strength, compared to the Pd films on ceramic porous substrates. The interconnected network of the Pd phase in the composite contributes to hydrogen migration as well as electrical conduction, resulting in the H₂ permeation. This study tries to develop a Pd–Al₂O₃ matrix composite membrane to permeate only hydrogen gas. The first purpose of this study is to prepare dense Pd–Al₂O₃ matrix composites. This study focused on two strategies for preparing the Pd–Al₂O₃ matrix composites. The first one is concerning about Pd particles used for the composite preparation. The normal commercial Pd powder is not useful for the composite preparation because larger Pd particles create a lot of pores during sintering. It leads to a porous composite sample. This study prepared smaller Pd particles by using a reflux method as described in the Sect. 2. Second one is a sintering method. We try a plasma electronic sintering (PECS) method for the sintering. This is because Pd is easily oxidized at elevated temperatures up to ~800°C under ambient air, although the Pd metal is stable at higher temperatures than 850°C.^{13),14)} The ordinary solid state reaction (SSR) method is not suitable because it needs elevated sintering temperatures under ambient air. As a result, the Pd is easily oxidized during heating or cooling. The PECS method is possible to sinter under vacuum at elevated temperatures for shorter time (= about 10 min.), compared to the SSR method. Based on the PECS method, this study investigated a good condition to prepare dense Pd–Al₂O₃ matrix composites.

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Then this study investigated the electrical conductivity as well as the hydrogen permeation properties of the prepared Pd–Al₂O₃ matrix composite. In particular, we focus on the composition of the 25 vol % Pd–75 vol % Al₂O₃ as well as the 30 vol % Pd–70 vol % Al₂O₃. This is based on the former study concerning about the Ni–alumina composites. Aldrich et al. reported that approximately 25 vol % of Ni formed the interconnected network of the Ni phase for the conduction in the composites.^{15),16)} The fact suggests that ~25 vol % of Pd is enough for the interconnected network of Pd phase. We discuss the influence of difference in the Pd volume fraction between 25 and 30 vol % on the Pd dispersion on the microstructure, the electrical conductivities and the hydrogen permeation fluxes.

2. Experimental procedures

Figure 1 shows the scheme of procedure to prepare the Pd particles. Pd particles were prepared by using a heating reflux method.^{17),18)} Pd(NO₃)₂ solution (Pd concentration: 50 g/l) and a protective agent: polyvinylpyrrolidinone (PVP; Mw = 40000) were mixed with a deionized water for 20 min, where the weight ratio of the PVP to the Pd was approximately 10 wt.%. After then, ethanol was added as a reducing agent and mixed for 20 min. The volume ratio between the ethanol and the deionized was 1:1. The mixed solution was heating-refluxed at 90°C for 3.5 h. The obtained Pd particles were separated from the solvent by using a centrifuge with 6500 rpm. Subsequently, the deionized water was added with the Pd particles and centrifuged again. Finally, the Pd particles were dried. For the some Pd particles, no PVP was added for the preparation procedures.

The α -Al₂O₃ (99.99%) with the prepared Pd particles was molded into pellets and then sintered by using a PECS method. The volume fractions of the prepared composite were 25 vol % Pd–75 vol % Al₂O₃ and 30 vol % Pd–70 vol % Al₂O₃. For the 25 vol % Pd–75 vol % Al₂O₃, the Pd particles protected by the PVP were used. For the 30

vol % Pd–70 vol % Al₂O₃, the Pd particles protected by the PVP and no PVP were used. We denote the three prepared composite samples as 25Pd(PVP), 30Pd(PVP) and 30Pd(no PVP), respectively. A mold with diameter of 15.6 mm ϕ and the carbon sheet with the thickness of 0.2 mm were used for the molding. The molded pellets were sintered at 1200°C for 5 min. under the 80 MPa by using the PECS. The programming rate for the heating/cooling was 50 °C/min.

The relative density of the sintered samples were investigated by the Archimedes' method. To investigate the microstructure of the prepared samples using a scanning electronic microscope (SEM; JSM-6360LV; Jeol Co. Ltd.). Therein the backscattered electron (BAE) images were observed to distinguish the containing elements clearly. Before the observation, gold was coated on the samples by a sputtering equipment to avoid the charge build-up.

The crystalline phase of the prepared sample was characterized at room temperature using X-ray powder diffraction (XRPD; RAD-C; Rigaku Co. Ltd.) with Cu K α radiation, where the conditions of XRPD voltage and current were respectively, 45 kV and 40 mA.

The electrical conductivities were measured using a DC four-point method at room temperature under the ambient air, by using a resistance meter (MCP-T610; Mitsubishi Chem. Co. Ltd.).

The H₂ permeation fluxes of the prepared samples were investigated under H₂ partial pressure gradients in the temperature range of 450–600°C. A pellet sample with thickness of 0.8 mm was set between two quartz tubes, where a glass ring was used for gas sealing. Before running the H₂ permeation measurement, the sample was heated up to 640°C. At this temperature, gas sealing was made during melting the glass ring. Then Ar gas was flowed on the P_{low} side with a flow rate of 20 sccm; 8%H₂–N₂ mixed gas on the P_{high} side with a flow rate of 30 sccm. The H₂ gas permeating from the P_{high} side to the P_{low} side was detected by using a gas chromatograph (CP-4900 Micro GC; Varian Inc.). To estimate the intrinsic hydrogen permeation flux, a little amount of leakage hydrogen gas was deducted. The leakage gas was estimated from the nitrogen gas detected on the P_{low} side.

The electrical conductivities as well as the H₂ permeation fluxes of the Pd–Al₂O₃ composites were compared to those of the Pd film with thickness of 0.8 mm. For this, a commercial Pd film (99.9%; Tanaka Kikinokogyo Co. Ltd.) was used.

3. Results and discussion

Figure 2 portrays XRPD patterns of the prepared Pd particles with PVP and no PVP. Each observed XRPD pattern corresponds to the reported Pd phase.¹⁹⁾ No secondary phase appeared in the XRPD pattern. The XRPD pattern of the Pd particles with PVP was broader than that of the Pd particles with no PVP, indicating that the particle size of Pd protected with PVP was smaller compared to the Pd particles with no PVP.

Fig. 1. The scheme of procedure to prepare the Pd particles.

Fig. 2. XRPD patterns of the Pd particles protected with PVP and no PVP. For the reference, the ICDD (No. 46-1043) of Pd¹⁹⁾ is also illustrated.

Figure 3 presents XRPD patterns of the Pd–Al₂O₃ composites prepared by the PECS method. The observed reflections corresponding to the Al₂O₃ phase²⁰⁾ as well as the Pd phase¹⁹⁾ appeared in each prepared sample. No secondary phases appeared. The results mean that no reaction between Pd and Al₂O₃ appears. Also, no Pd oxidation appeared during sintering. Thus the sample prepared by the PECS method was completely Pd–Al₂O₃ composite.

Table 1 tabulates relative densities of the prepared samples. The 25Pd(PVP) sample showed higher density, compared to the 30Pd(PVP). It suggests that the higher amount of Pd makes the sintering difficult. There was no remarkable difference between the 30Pd(PVP) and the 30Pd(no PVP). Figure 4 displays BAE images of the prepared composite samples. The white- and black-parts in the images correspond to Pd and Al₂O₃, respectively. For the 30Pd(PVP), the smaller Pd grains well dispersed in the Al₂O₃ matrix. On the other hand, the Pd grains aggregated in the 30Pd(no PVP). For both of the 30Pd(no PVP) and the 30Pd(PVP), surface microstructures showed higher dispersion of smaller Pd grains, compared to microstructures of the cross-sections. The 25 Pd(PVP) showed no remarkable difference in microstructures between the surface and the cross-section.

Figure 5(a) presents the investigated hydrogen permeation flux J_{H_2} for the prepared Pd–Al₂O₃ composite. In addition, Fig. 5(b) shows the J_{H_2} of the Pd film (thickness: 0.8 mm) for the comparison. The J_{H_2} of the 30Pd(PVP) was higher than that of the 25Pd(PVP), meaning that the greater amount of Pd contributed to higher permeability. The 30Pd(no PVP) showed higher permeability than that

Fig. 3. XRPD patterns of the prepared Pd–Al₂O₃ matrix composites. For the reference, the ICDD of Pd (No. 46-1043)¹⁹⁾ as well as Al₂O₃ (No. 71-1123)²⁰⁾ is also presented.

Table 1. The relative densities, activation energies E_H of the J_{H_2} and total electrical conductivities σ_t for the prepared Pd–Al₂O₃ composite and Pd film

Sample	Density [%]	E_H (kJ/mol)	σ_t [S cm ⁻¹]
25Pd(PVP)	93.6	16.6	1.98×10^2
30Pd(PVP)	88.7	12.9	1.84×10^3
30Pd(no PVP)	87.7	12.5	5.21×10^3
Pd film	—	12.4	9.50×10^4

of the 30 Pd(PVP). Although the Pd grains were larger in the 30Pd(no PVP) as depicted in Fig. 4, the Pd grains interconnected each other. The connection results in the enough conduction and forms hydrogen migration pathways. Smaller Pd grains in the 30Pd(PVP) well dispersed as shown in Figs. 4(c) and 4(d). However, the interconnection between Pd grains was not enough. The insufficient connection is a possible reason for the lower permeability. The J_{H_2} of the Pd film was one magnitude higher than those of the Pd–Al₂O₃ composites. Each Pd–Al₂O₃ composite showed no deterioration during keeping at elevated temperatures of 450 to 600°C, suggesting a good stability. The Pd film showed slight deterioration at temperatures of 600, 575 and 550°C.

Figure 6 presents Arrhenius plots of Pd–Al₂O₃ matrix composites as well as Pd film obtained from Fig. 5. Each sample showed a simple Arrhenius relation. Table 1 tabulates activation energies E_H evaluated from the Arrhenius plots. The E_H of the 25Pd(PVP) was larger than those of the other samples, suggesting that the connection among Pd grains was not enough for the hydrogen migration. The

Fig. 4. SEM images of (a) surface and (b) cross-section of 25Pd(PVP), (c) surface and (d) cross-section of 30Pd(PVP) and (e) surface and (f) cross-section of 30Pd(no PVP).

E_H of the other samples showed similar values to that of the Pd film investigated in this study. The activation energy of the H₂ permeation reported in the Pd films on the ceramic porous substrates is in the range of 8 to 16 kJ/mol.^{6–12)} The results mean that the H₂ permeation mechanism for the composites in this study is the same as those of the Pd films.

Figure 7 portrays the σ_t at room temperature and the J_{H_2} at 600°C as function of Pd volume fraction. Table 1 also lists the σ_t value of each sample. With increases of Pd volume fraction from 25 to 30 vol %, the σ_t abruptly improved, suggesting that the 30 vol % Pd formed interconnected network of the Pd phase in the matrix composite. The J_{H_2} was similar behavior to that of the σ_t . The both of J_{H_2} and σ_t for the 30Pd(no PVP) was one magnitude smaller than those of the Pd film. The facts mean that the electrical conductivity is closely related to the H₂ permeability. To improve the H₂ permeability, we need to increase the conduction pathways in the composite.

4. Conclusions

This study investigated a good condition to prepare the dense Pd–Al₂O₃ matrix composites using the PECS method, where Pd particles protected with PVP or no PVP were used. Then this study investigated influence of the difference in Pd volume fractions between 25 and 30 vol % as well as microstructures of the composites on hydrogen permeation properties or electrical conductivities. The J_{H_2} or σ_t of the 30 Pd(PVP) was one order of magnitude higher than that of the 25Pd(PVP), suggesting the percolation conduction of the 30Pd(PVP) sample. The J_{H_2} or σ_t of the 30Pd(no PVP) was higher than that of the 30Pd(PVP), because the interconnections among Pd grains were better for the conduction in the 30 volPd(no PVP). The Pd grains in the 30Pd(PVP) well dispersed, but the connection was poor, resulting in the lower conduction. The σ_t or J_{H_2} of the 30Pd(no PVP) was one order of

Fig. 5. H₂ permeation flux and the measuring duration time for (a) the prepared Pd-Al₂O₃ matrix composites and (b) Pd film at each temperature.

Fig. 6. Arrhenius plot of H₂ permeation flux for the prepared Pd-Al₂O₃ matrix composites as well as Pd film.

Fig. 7. Relation among Pd volume fraction, (a) total electrical conductivity σ_t at room temperature and (b) H₂ permeation flux at 600°C.

magnitude lower than that of the Pd film. Increasing conduction pathways is a strategy to improve the H₂ permeability in the composite.

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