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Hydrogen permeation and diffusion of metallic composite membranes

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Abstract

We have investigated hydrogen permeation of Pd/V–15Ni/Pd and Pd–25Ag/V–15Ni/Pd–25Ag alloy composite membranes with about 40-μm and 1-mm thickness in the temperature range of 423–673 K. Hydrogen permeation of Pd–25Ag/V–15Ni/Pd composite membranes with about 40-μm thickness was also examined. There were two directions for the hydrogen permeation of Pd–25Ag/V–15Ni/Pd composite membranes. Higher permeation flux was obtained in the Pd–25Ag/V–15Ni/Pd composite membrane when the Pd–25Ag overlayer was at the upstream side and the Pd overlayer was at the downstream side. Overall hydrogen diffusion coefficients of the composite membranes were independent of the permeation pressure and overlayer, while hydrogen permeation flux had strong dependence on the overlayer composition and sequence. Membrane thickness and overlayer had profound effects on hydrogen permeation of composite membranes. The overlayer effects were discussed.

Keywords: Palladium; Composite membrane; Hydrogen permeation

1. Introduction

The latest decade has witnessed increasing interest in dense composite membranes for hydrogen separation and purification because of rapid development of membrane reactors and fuel cells. These dense composite membranes comprise thin palladium overlayer and highly hydrogen-permeable substrates, e.g., vanadium group metals [1–9], amorphous metals [10], and proton-conductive ceramics [11]. The dense composite membranes, particularly, metallic composite membranes are preferable for use at low temperature for reasons of metallic interdiffusion; they are preferred in the ultra-thin form for high permeation flux. Hydrogen permeation of the dense metallic composite membrane, in fact, is not well understood. Negative effects of the overlayer are usually ignored. Only pure palladium is used as the overlayer material. Our previous work showed that overlayer improvement could enhance hydrogen permeation even when the composite membrane was saturated with hydrogen at low temperature [12]. It is necessary to further scrutinize the effects of overlayer.

This study used 40-μm (thin) and 1-mm thick (thick) V–15Ni substrates to show overlayer effects directly. Hydrogen permeation of Pd/V–15Ni/Pd and Pd–25Ag/V–15Ni/Pd–25Ag composite membranes was studied. We also prepared Pd–25Ag/V–15Ni/Pd composite membranes with 40-μm thickness. There were two directions for hydrogen permeation of the thin Pd–25Ag/V–15Ni/Pd composite membranes. The first permeation direction was that Pd–25Ag overlayer was at the upstream side and Pd overlayer was at the downstream side. The second direction was the opposite direction.

2. Experimental

Pure vanadium (99.9%) and nickel (99.9%) were used as raw materials. Ingots of V–15Ni alloy were prepared by arc melting in an argon atmosphere. V–15Ni alloy substrates

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Table 1
Types of as-prepared composite membranes

	Thickness of V–15Ni substrate	Overlayer	
		Inlet side	Outlet side
Sample 1	1 mm	Pd	Pd
Sample 2	1 mm	Pd–25Ag	Pd–25Ag
Sample 3	40 μm	Pd	Pd
Sample 4	40 μm	Pd–25Ag	Pd–25Ag
Sample 5	40 μm	Pd	Pd–5Ag
Sample 6	40 μm	Pd–25Ag	Pd

with about 40-μm thickness and 1-mm thickness were prepared as described, respectively, in previous studies [2,12]. All substrates were annealed at 1573 K under a vacuum of 4×10^{-4} Pa and rapidly cooled by argon flow in order to obtain bcc single phase. The V–15Ni substrates were cleaned using a chemical solution and fast atom bombardment (FAB) in sequence before sputtering [12]. Special attention was paid during the cleaning procedure in order to obtain the same surface conditions for all the substrates. A Pd–Ag film of about 100 nm in thickness was prepared using a DC multi-target sputtering system with two separate Pd and Ag targets. Six kinds of composite membranes were prepared (see Table 1).

Hydrogen permeation and diffusion tests were carried out using high pure hydrogen within the temperature range of 423–673 K, using a conventional gas-permeation apparatus described in our previous report [13]. The duration of permeation at each temperature was about 1 h. Hydrogen permeance (Φ) of the composite membrane could be determined via measurement of hydrogen permeation flux (J), upstream pressure (P_u) and downstream pressure (P_d) at steady state [14],

$$J = \Phi(\sqrt{P_u} - \sqrt{P_d}) = \Phi\sqrt{P_u} \quad (1)$$

The downstream pressure was neglected since the downstream side was kept in vacuum during hydrogen permeation. The hydrogen permeance (Φ, mol H_2 s^{-1} m^{-2} $Pa^{-0.5}$) of the laminated membranes is related to the thickness and to the permeability of individual laminas of materials under the hypotheses of perfect gas behavior and validity of Sievert's law [14,15]:

$$\Phi = \frac{1}{\sum_{i=1}^{n}(d_i/P_i)} \quad (2)$$

where d_i and P_i are the thickness and permeability of the ith layer, respectively. In this work, overall hydrogen permeability (P_e) of the composite membrane was used instead of permeance,

$$P_e = \Phi L = \frac{L}{\sum_{i=1}^{n}(d_i/P_i)} = \frac{1}{\sum_{i=1}^{n}(d_i/L)(1/P_i)} \quad (3)$$

where L denotes the total thickness of composite membrane. The overall hydrogen permeability is then related to the permeability and to the thickness ratio of individual laminas of materials that constitute the composite membrane. Once the thickness ratios of individual laminas of materials are decided, the value of P_e is only related to the permeability of individual laminas of materials and has no dependence on the total thickness of composite membrane.

The overall hydrogen diffusion coefficients of the composite membranes were measured by a time-lag method. All the samples were examined using FE-SEM.

In addition, the hydrogen permeability of 48-μm and 0.5-mm-thick Pd–25Ag alloy samples (VACOM GmbH, Germany) was measured for comparison. The 48-μm-thick Pd–25Ag alloy membrane was cold-rolled using the 0.5-mm-thick Pd–25Ag alloy. All Pd–25Ag alloy membranes were annealed at 973 K in vacuum before hydrogen permeation.

3. Results and discussion

Fig. 1 shows temperature dependence of overall hydrogen permeability of as-prepared composite membranes. Hydrogen permeability of Pd–25Ag alloy membranes prepared in this work and from related literature [16,17] was also plotted for comparison. The V–15Ni alloy composite membranes had higher hydrogen permeability than the Pd–25Ag alloy membranes in the temperature range of 423–673 K. The thin V–15Ni alloy composite membranes had overall hydrogen permeability about two to three times higher than the 48-μm-thick Pd–25Ag alloy membrane. The V–15Ni alloy composite membranes also had higher mechanical strength than the Pd–25Ag alloy membrane. The V–15Ni/Pd–Ag composite membranes were excellent candidates to replace expensive Pd-based alloy membranes in applications below 673 K.

At temperatures higher than 473 K, overall hydrogen permeability of the thick composite membranes increased with the decrease of temperature, whereas that of the thin composite membranes varied slightly. There was no apparent difference between overall hydrogen permeability of the Pd– and Pd–25Ag-coated membranes when the substrate thickness

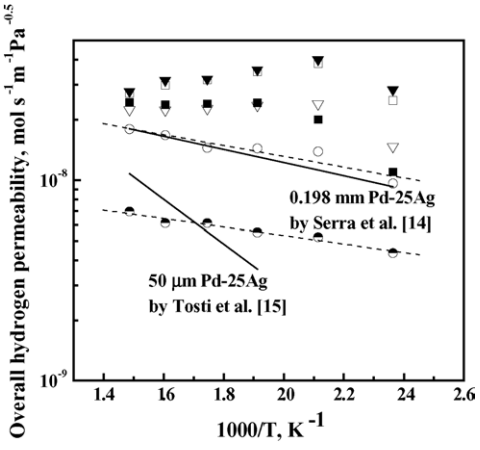

Fig. 1. Overall hydrogen permeability of as-prepared composite membranes: Sample 1 (□); Sample 2 (▼); Sample 3 (■); Sample 4 (▽); as-prepared Pd–25Ag alloy membranes in 0.5-mm (◯) and 48-μm (◓) thickness, respectively.