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Hydrogen permeation characteristics of V-15Ni membrane with Pd/Ag overlayer by sputtering

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Abstract

Pd–Ag alloy coated V-15Ni composite membranes were prepared by co-sputtering of separate pure Pd and Ag targets using a DC multi-target sputtering system where voltage for each target can be controlled independently. The film composition was controlled by changing the target voltage. Hydrogen permeation characteristics of as-prepared composite membranes were investigated using the gas permeation technique in the temperature range of 423–673 K. The hydrogen permeation of the composite membranes was mainly bulk-diffusion limited at a temperature higher than 473 K. At 473 K or lower, the hydrogen permeability of the composite membranes increased with the Ag content until 30 at%.

Keywords: Hydrogen permeation; Composite membrane; Vanadium; Palladium

1. Introduction

Most scientists and researchers agree that the future energy economy is mainly based on hydrogen [1]. Pure hydrogen is the ideal fuel in terms of fuel-cell performance [2]. In addition, the demands for high purity hydrogen are increasing rapidly in a variety of technologies such as semiconductor manufacture, and petrochemical processing. At present, the most effective method to produce high purity hydrogen uses hydrogen separation membranes [3]. Palladium and its alloys are the most commonly used materials for hydrogen separation membranes but they are too expensive for large-scale use [4]. Therefore, many efforts are focused on the development of low cost and high performance hydrogen separation membranes [5]. This is creating a continued interest in composite membranes for hydrogen separation. The composite membrane usually consists of porous or non-porous substrates and palladium or its alloy overlayer as catalytic and protection overlayer. Although the porous or high hydrogen permeable material, such as porous ceramic [6–8] and vanadium group metals [4,9–12], are selected as substrates, the performance of the overlayer is important in determining the hydrogen permeability of the composite membranes since the hydrogen-separation membrane for practical application is thin and the surface effects are significant [9]. It is well known that the addition of Ag to palladium can improve its hydrogen permeability. Pd–Ag alloy also has a higher resistance to embrittlement than pure palladium so that Pd–Ag alloy-coated composite membrane has attracted much attention. Up to date, almost all the film deposition techniques have been used in the fabrication of Pd–Ag alloy film, including chemical vapor deposition [13,14], electroless plating [15], and sputtering [8,14,16–18]. Among these methods, sputtering is attractive since it is less laborious, has higher speed and lower cost. However, previous research has utilized a single Pd–Ag alloy target and it is difficult to control the composition of the Pd–Ag film. Nevertheless, the composition of the Pd–Ag film should be controlled to optimize the hydrogen permeability since there is an optimum Ag concentration [15,19].

In this work, we prepared Pd–Ag films with different Ag ratio on the V-15Ni membrane by co-sputtering of separate Pd and Ag targets. The voltage applied to each target can be controlled independently, which makes it flexible for control of the composition of the Pd–Ag film.

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2. Experimental

Pure vanadium and nickel were used as raw materials and ingots of V-15Ni alloy were prepared by arc melting in an argon atmosphere. The ingots were cold rolled into strips with the thickness of about 40 μm. The strips were annealed at 1573 K for 15 min under a vacuum of 4×10^{-4} Pa and rapidly cooled by argon flow. The strips were then cut into 12-mm diameter circular substrates and chemically cleaned. Pd–Ag films were prepared in a DC sputtering system with two separate Pd and Ag targets (purity of both, 99.99%) in argon atmosphere. Voltage for each target can be controlled in the range of 0–600 V. At first, the Pd–Ag films were deposited on stainless steel substrates in order to optimize the sputtering conditions. The compositions of Pd–Ag films were analyzed using EDX. The thickness of as-sputtered films was measured using AFM. Then, the Pd–Ag films with the thickness of about 100 nm were deposited on each side of as-prepared V-15Ni substrates under the optimized sputtering conditions. The target–substrate distance and work pressure were set at 60 mm and 1.6 Pa, respectively. The voltage of Pd target was fixed at 400 V while the voltage of Ag target varied between 0 and 400 V. To avoid the surface oxidation of the V-15Ni substrate, the Pd–Ag alloy film was prepared as follows. One side of the V-15Ni substrate was cleaned using fast atom bombardment (FAB) for 25 min and transferred directly into sputtering chamber in vacuum without exposing to air. After sputtering, the sample was transferred back into the FAB chamber and the same procedure repeated for the other side. As-sputtered films were checked by XRD.

Hydrogen permeation tests were carried out using high purity hydrogen within the temperature range of 423–673 K, using a conventional gas-permeation apparatus described in our previous report [12]. The steady-state hydrogen permeability was determined by a mass flow transducer (Kofloc 3920E, Kojima Instrum.).

3. Results and discussion

Fig. 1 shows the dependence of the film composition on the voltage of Ag target while the voltage of Pd target was kept at 400 V. The Ag ratio of as-sputtered films was proportional to the voltage of Ag target. Thus, the voltage applied to Ag target can be determined for the required composition of Pd–Ag film. XRD analysis indicated that all the sputtered films were fcc single phase with the (1 1 1) orientation, i.e. a solid solution of palladium (Fig. 2). The measurements of relative density showed that the relative densities of the Pd–Ag films were higher than 92%. Therefore, a dense Pd–Ag alloy film was prepared using the multi-target sputtering system in this work. Such a dense film is important for the protection of vanadium-based membrane since vanadium is subject to oxidation.

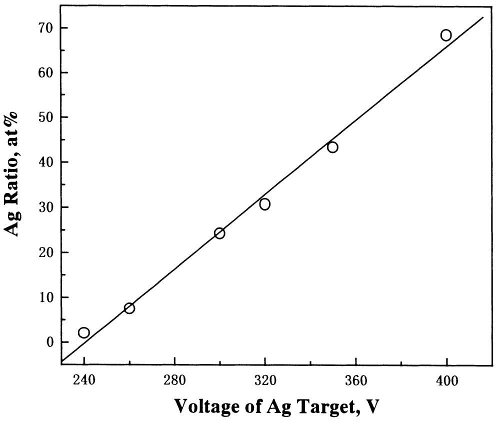

Fig. 1. Dependence of film composition on the voltage of Ag target. The voltage of Pd target was fixed at 400 V.

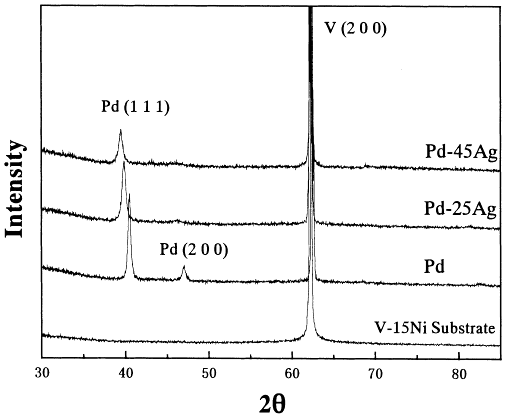

Fig. 2. XRD patterns of as-prepared composite membranes.

Fig. 3 shows the hydrogen permeability of as-prepared composite membranes under the upstream pressure of 4×10^4 Pa. At a higher temperature than 473 K, the hydrogen permeability of the composite membranes had no obvious dependence on the Ag content. At 473 K or lower,

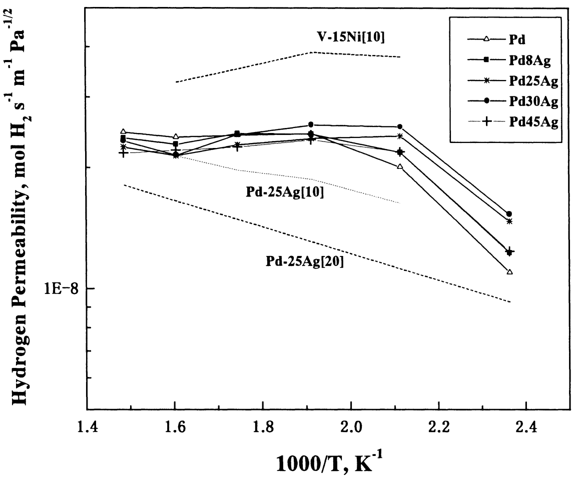

Fig. 3. Hydrogen permeability of as-prepared composite membranes.

the hydrogen permeability of the composite membrane increased as the Ag content increased until 30 at%. At 423 K, the Pd–30Ag alloy-coated composite membrane had the highest hydrogen permeability or 1.53×10^{-8} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$, which was about higher by 43% than that of the Pd-coated composite membrane or 1.07×10^{-8} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$. It revealed that the addition of Ag to palladium improved the hydrogen permeability of the composite membrane at low temperatures. The optimal Ag content was in the range of 25–30 at%, which is slightly higher than the case of bulk Pd–Ag alloy [15,19]. The composite membranes prepared in this work had higher hydrogen permeability than the Pd–25Ag alloy sheet [10,20] but lower than a V-15Ni sheet [10]. Considering the inevitable surface-related effects in this work, the Pd–Ag alloy-coated composite membranes showed great potential as a replacement of the Pd-based hydrogen separation membranes.

The upstream pressure dependence of hydrogen permeation flux through the composite membranes was examined. Similar relationships between the upstream pressure and the hydrogen permeation flux were found for all the composite membranes so that only the Pd–25Ag alloy-coated composite membrane was presented in Fig. 4 for discussion. Fig. 4 shows that the slope of relationship between the hydrogen flux and the upstream pressure in the logarithmic scale was about 0.52 at 573 K. It is known that the slope is 0.5 if the hydrogen permeation is bulk-diffusion limited. Therefore, the hydrogen permeation of the Pd–25Ag alloy-coated composite membrane was mainly bulk-diffusion limited at high temperature. The upstream pressure dependence of hydrogen flux at 423 K can be divided into two sections: linear and saturated. The slope of the linear section was about 0.62, which was higher than that at 573 K. It indicated that the surface-related reaction became significant in the hydrogen permeation with decreasing temperature. Hence, the composition control of Pd–Ag films was necessary in order to improve the hydrogen permeability of the composite membrane. As the upstream pressure exceeded 4×10^4 Pa, the value of flux at 423 K became saturated gradually in Fig. 4. Three mechanisms may be responsible for the saturation of hydrogen permeation flux: rate-limiting absorption upstream, rate-limiting desorption downstream, and bulk saturation [21]. It was found that all the hydrogen flux through the composite membranes became saturated as the upstream pressure was about 4×10^4 Pa, so that the flux saturation here may be due to the bulk saturation. A more detailed investigation is underway.

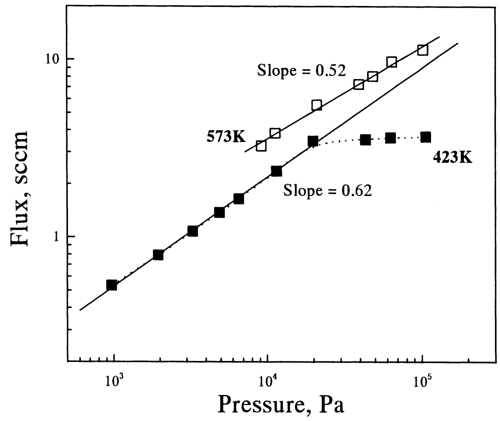

Fig. 4. Upstream pressure dependence of hydrogen flux through the Pd–25Ag alloy-coated composite membrane at 423 and 573 K, respectively.

4. Conclusion

In this work, a novel technique for the preparation of Pd–Ag film was proposed and carried out. The composition of a Pd–Ag film can be controlled by varying the voltages of each target. At low temperatures, the hydrogen permeability of the composite membranes was improved by the addition of Ag. The Pd–30Ag-coated composite membrane had the highest hydrogen permeability among as-prepared composite membranes at 423 K.

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