

Hydrogen Permeation of Pd₆₀Cu₄₀/V-15Ni Composite Membrane under Mixing Gases of H₂+H₂S

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ABSTRACT Pd-Cu alloy covered V-15Ni composite membranes have been prepared in this work. XRD, SEM and AES analysis were performed to characterize the composite membranes. Hydrogen permeation of the composite membrane under pure hydrogen and mixing gas with H₂S impurity were studied, and the composition and thickness of Pd-Cu overlayers were optimized. It shows that the Pd₆₀Cu₄₀/V-15Ni composite membrane has higher permeability than other overlayer compositions. In the temperature range of 573~673K, the Pd₆₀Cu₄₀/V-15Ni composite membrane shows a good resistance to H₂S impurity; when the temperature is lower than 573K, the effect of H₂S impurity becomes more serious and the hydrogen permeability of Pd₆₀Cu₄₀/V-15Ni composite membrane decreases rapidly with increasing of H₂S concentration.

Key words: Hydrogen permeation; Pd-Cu alloy; V-15Ni alloy; Composite membrane; H₂S

1. INTRODUCTION

As a clean and recoverable energy carrier, hydrogen is becoming more and more important and attractive due to the worldwide energy crisis and environment problem [1]. Pure hydrogen is not only the fuel for fuel cell but also very important feedstock for many industrial and high-tech applications [2,3]. Currently there are several methods for preparing pure hydrogen, among them; metallic membrane separation is one of the most cost-effective and promising methods for high purity hydrogen. Pd and its alloys are most extensively used for hydrogen separation, however it is too expensive to use in a large scale [4, 5]. To develop new membrane materials with low cost and high performance for hydrogen separation, many efforts have been made in recent years [6]. Several kinds of high permeable materials [7-11] are under development at present. Among them, the V-15Ni alloy, which was developed by Nishimura et al [8], shows good workability and resistance to hydrogen embrittlement and higher permeability than Pd and Pd alloys. However, V-15Ni membrane is easy to oxidize and not active to hydrogen molecule dissociation; depositing a thin overlayer of Pd or Pd alloys on the V-15Ni membrane to form a composite membrane is proved to be a good solution, and the cost of such composite membranes will be far

lower than those of pure Pd or Pd alloys membranes. A lot of research had been done on Pd/V-15Ni and Pd-Ag/V-15Ni composite membranes [12-16] and higher hydrogen permeability than pure Pd and Pd-Ag alloy membranes was obtained. In comparison with Pd and Pd-Ag alloys, Pd-Cu alloys (wt.% Pd > 60) membranes have similar hydrogen permeability [17] with them, and it is cheaper than Pd and Pd-Ag alloys, furthermore, they shows better resistance to poisoning and deactivation by H₂S, the most frequent impurity in hydrogen mixed gas [18,19]. Recently we did a preliminary work on a Pd-Cu/V-15Ni composite membrane for hydrogen permeation [20-21], as a successive work on hydrogen permeation of Pd-Cu/V-15Ni composite membranes, effect of H₂S on hydrogen permeation properties of the composite membrane will be reported in this paper.

2. EXPERIMENTS

Circular V-15Ni membrane samples with a diameter of 12mm, which were processed with the same procedures as in previous work [8,9], were used as the substrates for deposition of Pd-Cu overlayer. They were firstly mechanically polished and then chemically polished using a solution with a composition of hydrofluoric acid solution (48 wt.%): nitric acid solution (70 wt.%): lactic acid solution (90 wt.%) = 1:1:1 in

volume. After chemical polishing, the substrates are 300 μ m in thickness. To minimize oxide and other surface impurity, the chemically polished membrane was further cleaned by fast ion bombardment (FAB) in the FAB chamber for 30 minutes, and then directly sent into the sputtering chamber for film deposition. Pd-Cu films were prepared in a DC sputtering system with separate Pd and Cu targets (purity of both, 99.99 at.%) in argon atmosphere. To ensure composition homogeneity of the film, the substrate holder could rotate at different speed and the distance between target and substrate is adjustable. Voltage for each target can be varied in the range of 0–600 V. The Pd–Cu films were deposited on each side of the as-prepared V-15Ni substrates under the following sputtering conditions: the base pressure for sputtering was 6.0×10^{-6} Pa, the target–substrate distance and work pressure were set at 60 mm and 1.6 Pa respectively, and films are deposited at room temperature. The voltage of Pd target was fixed at 340 V while the voltage of Cu target varied between 0 and 600 V to control the overlayer composition. The composition of Pd-Cu films was analyzed using EDX and AES, the thickness of as-sputtered films was measured using FE-SEM.

Hydrogen permeation measurements for the composite membrane were carried out from 423 to 673K under pure H₂ and a mixing gas of H₂+H₂S respectively, with an upstream pressure about 40kPa, using a permeation apparatus described in the previous work [9]. By measuring the hydrogen permeation flux (J), upstream pressure (P_1) and downstream pressure (P_2) at steady state, the hydrogen permeability (Φ) could be determined by the equation: $\Phi = JL(P_1^{1/2} - P_2^{1/2})^{-1}$, where L is the thickness of sample. Usually P_2 is very small and could be neglected.

3. RESULTS AND DISCUSSION

As reported in our previous work [21], keeping the voltage of Pd target constant at 340V, Cu concentration of the overlayer could be expressed as a function of Cu target voltage: x_{Cu} (wt%) = $0.45V_{Cu} - 138$ ($V_{Pd} = 340V$, $V_{Cu} > 300V$), where V_{Pd} and V_{Cu} are the voltage of Pd and Cu target respectively, so the composition of Pd-Cu overlayer could be controlled easily by adjusting the voltage of Cu target, hereinafter the overlayer composition is expressed as Pd_{100-x}Cu_x, where x refers to weight percent.

Fig. 1 shows the surface morphology of the as-deposited Pd₆₀Cu₄₀ film. It can be seen that the film has a very fine microstructure, and it looks very dense and there is no evident pinhole in the film.

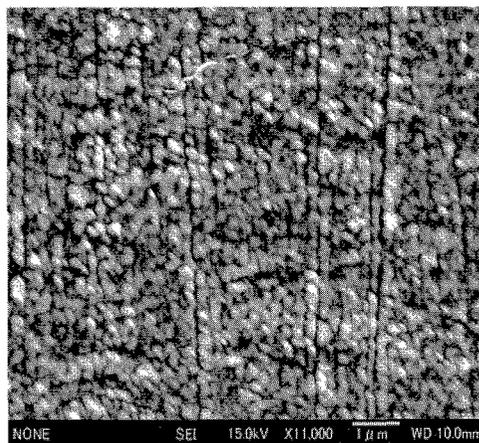


Fig.1 SEM morphology of the Pd₆₀Cu₄₀/V-15Ni composite membrane deposited for 60s.

Fig.2 shows a back scattering electron image of the cross-section of the Pd₆₀Cu₄₀/V-15Ni composite membrane, the overlayer deposition time is 60s. Where the white strip corresponds to the Pd₆₀Cu₄₀ overlayer, the gray area is the V-15Ni membrane, while the dark zone is the epoxy resin used for embedding the membrane sample. It can be seen that the overlayer is very dense and the thickness is about 200nm. The inset in bottom left corner is an AES depth profile of the Pd₆₀Cu₄₀/V-15Ni composite membrane, the AES sputtering rate is 20 nm/min. It can be seen that both Pd and Cu show very homogeneous distribution along the thickness direction.

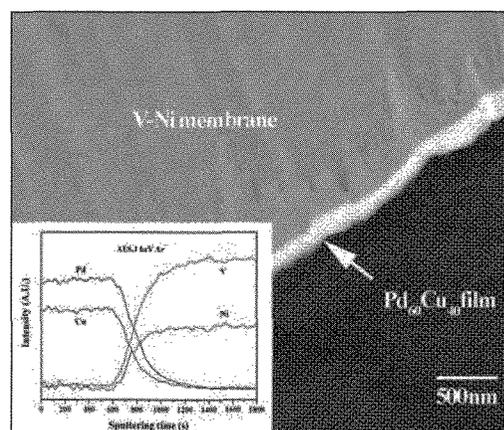


Fig. 2 The cross-sectional BSE image and AES depth profile of the Pd₆₀Cu₄₀/V-15Ni membrane deposited for 60s (AES sputtering rate: 20nm/min.)

For hydrogen permeable composite membrane, thinner and dense overlayer is more preferable because it means less Pd metal. Therefore thickness control is very important to the Pd-Cu alloy overlayer. To study the relationship between the overlayer thickness and depositing time, we deposited the Pd₆₀Cu₄₀ films for

different times and measured their thickness with the back scattering electron images of their cross-section and showed the results in Fig.3. It can be seen that the overlayer thickness shows a linear dependence on depositing time. For $V_{Pd} = 340V$ and $V_{Cu} = 395V$, the depositing rate is about 3.5nm/s.

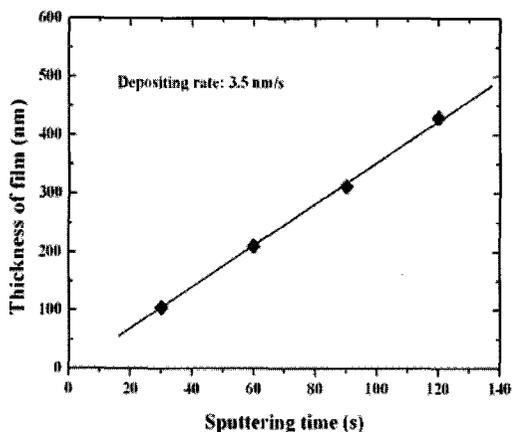


Fig. 3. Variation of the Pd₆₀Cu₄₀ overlayer thickness with depositing time ($V_{Pd}=340V$, $V_{Cu}=395V$)

Fig. 4 shows the relationship between the hydrogen permeability of the composite membranes and their overlayer composition. It can be seen that the hydrogen permeability increases with Cu content until 40 wt.% Cu, and then it decreases rapidly with Cu content increasing. The Pd₆₀Cu₄₀/V-15Ni composite membrane presents the highest hydrogen permeability. The overlayer with Cu content higher than 40 wt.% is not suitable for hydrogen permeation.

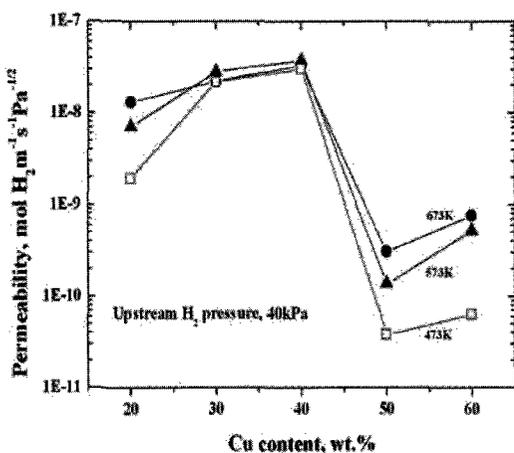


Fig. 4 Variation of the hydrogen permeability with the Cu content of the overlayer

Hydrogen permeability of the Pd₆₀Cu₄₀/V-15Ni composite membrane with different overlayer thickness that corresponds to deposition time as 30s, 60s, 90s and 120s respectively was shown in Fig.5. The hydrogen

permeability of the composite membrane first increases when the deposition time increases from 30s to 60s, and the 60s sample which corresponds to an overlayer thickness about 200nm has the highest hydrogen permeability among all the samples, and the maximum permeability was obtained at 573K as $3.72 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$. As for the composite membrane deposited for 30s, the overlayer was very thin (about 100nm) and its coverage to the V-15Ni substrate was also not so complete, SEM observation shows there are some sparse sites in the overlayer, so it is understandable that it has lower permeability than that of the composite membrane deposited for 60s. Further increasing the overlayer thickness, the hydrogen permeability decreases. Ignoring the interface or surface effect, according to the Barrie's model [22], the hydrogen permeability for dense composite membrane could be expressed as:

$$\frac{L_1 + L_2 + L_3}{\Phi} = \frac{L_1}{\Phi_1} + \frac{L_2}{\Phi_2} + \frac{L_3}{\Phi_3}$$

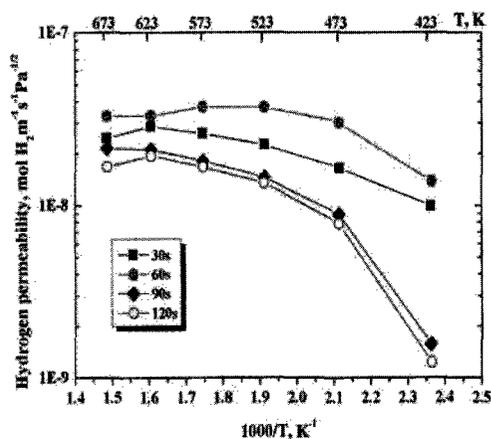


Fig.5 Variation of the hydrogen permeability of composite membrane with the deposition time of the Pd₆₀Cu₄₀ overlayer

Where L_i denotes the thickness of the i^{th} layer, and Φ_i and Φ mean the hydrogen permeability of the i^{th} layer and the composite membrane respectively. Considering that the hydrogen permeability of the Pd₆₀Cu₄₀/V-15Ni composite membrane is quite larger than that of single Pd₆₀Cu₄₀ membrane [20], it is reasonable to deduce that the hydrogen permeability of V-15Ni membrane (Φ_2) is larger than that of Pd₆₀Cu₄₀ membrane (Φ_1). Therefore hydrogen permeability of the Pd₆₀Cu₄₀/V-15Ni composite membrane (Φ) decreases with increasing the thickness of the Pd₆₀Cu₄₀ overlayer (L_1) could be qualitatively explained by Barrie model. Further research is under way.

To study the effect of H₂S impurity on hydrogen permeability of Pd₆₀Cu₄₀/V-15Ni composite membrane, the Pd₆₀Cu₄₀/V-15Ni composite membrane with Pd₆₀Cu₄₀ overlayer thickness of 200nm was measured in a mixing gases of H₂+H₂S with different H₂S concentration, and the results were shown in Fig.6. It can be seen that Pd₆₀Cu₄₀/V-15Ni composite membrane shows a good resistance to H₂S impurity in the temperature range of 573~673K; when the temperature is lower than 573K, the effect of H₂S impurity becomes more serious and the hydrogen permeability of Pd₆₀Cu₄₀/V-15Ni composite membrane decreases rapidly with the increasing of H₂S concentration. What should be pointed out is, all data in Fig.6 were obtained with the same sample measured sequentially in different mixing gases. That is to say, the composite membrane could recover its hydrogen permeability in high temperature (573-673K), even if it was degraded by H₂S at low temperature (473-573) in the previous measurement. Therefore the permeability degradation by H₂S in low temperature should not be attributed to physical destruction to the composite membrane, and the increasing surface adsorption of H₂S to the membrane in low temperature, which lowers the hydrogen solubility of the membrane should be the main reason.

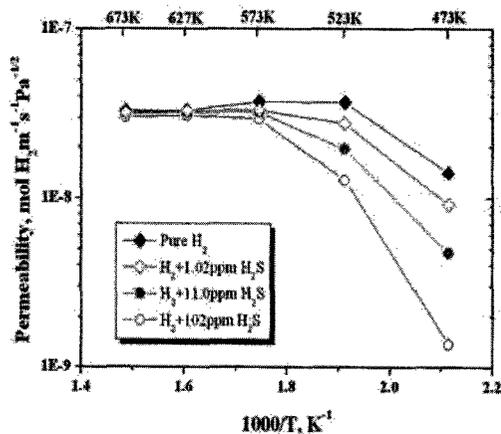


Fig. 6. Variation of the hydrogen permeability with the H₂S content (the overlayer thickness: 200nm)

4. CONCLUSION

Pd-Cu alloy covered V-15Ni composite membranes have been prepared in this work. XRD, SEM and AES analysis were performed to characterize the composite membranes. Hydrogen permeation of the composite membrane under pure hydrogen and mixing gas with H₂S impurity were studied, and the composition and thickness of Pd-Cu overlayers were optimized. It shows that the Pd₆₀Cu₄₀/V-15Ni composite membrane has

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