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Deposition of Pd-Cu Thin films on V-15Ni Membrane and Their Hydrogen Permeation

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ABSTRACT Pd-Cu/V-15Ni composite membranes were deposited for the first time by co-sputtering in this paper. XRD, SEM and AES were performed to characterize the composite membrane. Cu concentration of the Pd-Cu overlayer shows a linear dependence on the Cu target sputtering voltage (V_{Cu}) when Pd target voltage is constant and $V_{Cu} > 300V$. SEM observation shows that the overlayer films have very dense and fine microstructure; XRD and AES analysis reveal that the films are well alloyed and have homogeneous composition distribution. The depositing rate is about 3.4nm/s when the Pd and Cu target voltages are set as 340V and 395V respectively. The obtained $Pd_{60}Cu_{40}$/V-15Ni composite membrane shows higher hydrogen permeability than that of $Pd_{60}Cu_{40}$ alloy membrane and presents good feasibility to replace the $Pd_{60}Cu_{40}$ alloy membrane for hydrogen purification in the temperature range of 423-673K.

Key words: Hydrogen permeation; Pd-Cu films; Vanadium nickel alloy; Composite membrane

1. INTRODUCTION

Hydrogen energy is becoming more and more important and attractive to us due to the worldwide energy crisis and environment pollution [1]. Pure hydrogen is not only the fuel for fuel cell but also very important for many industrial and high-tech applications [2,3]. Currently the most cost-effective method for high purity hydrogen production is membrane separation. Pd and its alloys are most extensively used for hydrogen separation, however it is too expensive to use in a large scale [4, 5]. Many efforts have been made to develop new membrane materials with low cost and high performance for hydrogen permeability [6]. Several kinds of high permeable materials (e.g. V, Ta and their alloys [7-10], amorphous alloy [6] and ceramics [11]) are under development at present. Among them, V-15Ni alloy, which was developed by Nishimura et al [8], are very competitive for its higher permeability than Pd and Pd-Ag alloys, good workability and resistance to hydrogen embrittlement. However, V-15Ni membrane is easy to oxidize and not active to hydrogen molecule dissociation, deposition a thin overlayer of Pd or Pd-Ag alloys on V-15Ni to form a composite membrane is proved to be a good solution, and the cost of these composite membranes is greatly reduced than that of pure Pd or Pd-Ag alloys. Zhang [12-14] and Ozaki [15,16] et al. did a lot of works on Pd/V-15Ni and Pd-Ag/V-15Ni composite membranes 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], it is cheaper that Pd and Pd-Ag alloys, furthermore, they shows better resistance to poisoning and deactivation by H_2S, the most common impurity in hydrogen mixed gas [18,19]. So it will be very meaningful to develop a Pd-Cu/V-15Ni composite membrane for hydrogen permeation. To our knowledge, there is no related work reported on this topic yet. As a part of our research work on hydrogen permeation of Pd-Cu/V-15Ni composite membranes, firstly Pd-Cu/V-15Ni composite membrane were prepared by DC co-sputtering method, and their hydrogen permeation properties were reported in this paper.

2. EXPERIMENTS

Ingots of V-15Ni alloy were prepared by arc melting using vanadium (99.9 at.%) and nickel (99.95 at.%) in an argon atmosphere. The ingots were cold rolled into strips with the thickness of about 300μm. 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, the substrates were firstly mechanically polished and then chemically polished using a solution with a composition of hydrofluoric acid: nitric acid: lactic acid = 1:1:1 in volume. 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 two 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 with 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 with different compositions and thickness 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 study the relationship between thin film composition and Cu target voltage. The composition of Pd-Cu films was analyzed using EDX and AES, the thickness of as-sputtered films was measured using FE-SEM, and the structure of the as-sputtered films was analyzed with a JDX-3500 X-ray diffractometer.

Hydrogen permeation measurements for the composite membrane were carried out from 423 to 673K under pure H_2 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

Fig.1 shows the variation of Cu concentration in the as-sputtered Pd-Cu films with the sputtering voltage of Cu target, where Pd target is constant at 340V. It can be seen that there are two parts in figure 1. At I segment, Cu concentration is close to zero when Cu target voltage is lower than 300V, indicating that there is very less Cu sputtering under this condition. On the other hand, Cu concentration increases rapidly and linearly with the target voltage at II part, so the composition of Pd-Cu overlayer could be controlled easily by adjusting the voltage of Cu target.

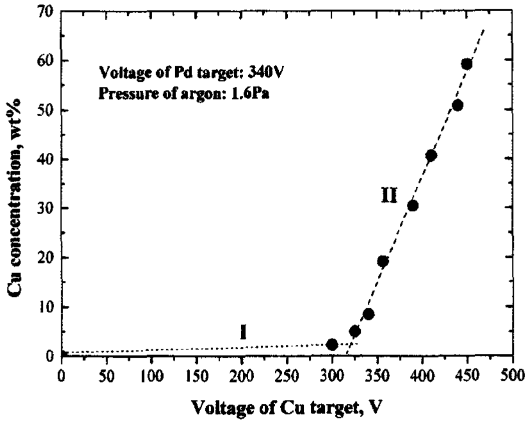

Fig.1 Variation of Cu concentration of the as-sputtered films with the voltage of Cu target

Overlayer films with different Cu contents as 0, 40, 50wt.% were deposited on V-15Ni substrates, and their structure were checked by XRD and shown in Fig.2. It can be seen that there is no new peak but Pd (111) and (200) peaks move to high degree position with Cu content increasing, indicating that the as-sputtered $Pd_{60}Cu_{40}$ and $Pd_{50}Cu_{50}$ overlayers have the same structure as that of pure Pd films, that is to say, the as-sputtered Pd-Cu films have a fcc Pd(Cu) solid solution structure, which is quite different the bulky Pd-Cu binary phase diagram [20].

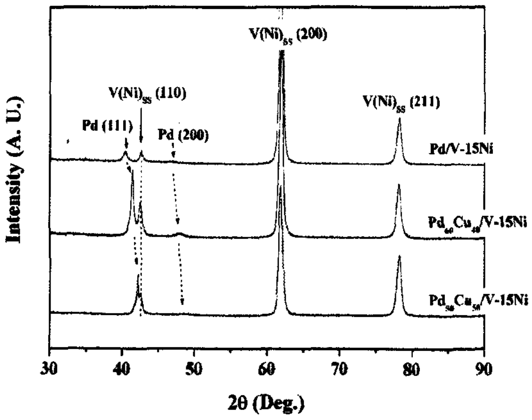

Fig. 2 XRD patterns of the composite membranes with different overlayer compositions

An AES depth profile of the $Pd_{60}Cu_{40}$/V-15Ni composite membrane, where the $Pd_{60}Cu_{40}$ overlayer was deposited for 60s, was shown in Fig.3, the sputtering rate is 20nm/min. It can be seen that both Pd and Cu intensities show very homogeneous distribution along the thickness direction. The thickness of overlayer could also be evaluated as about 200nm.

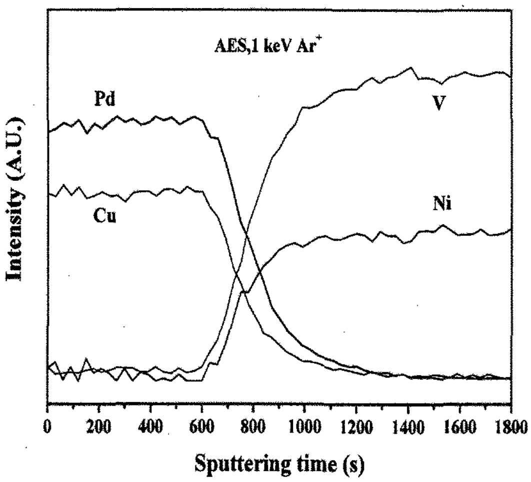

Fig. 3 AES depth profile of a $Pd_{60}Cu_{40}$/V-15Ni composite membrane with the $Pd_{60}Cu_{40}$ overlayer deposited for 60s. The sputtering rate was 20nm/min.

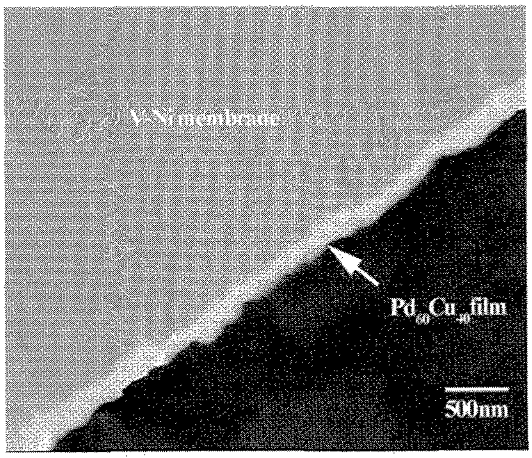

Fig.4 Cross-sectional BSE image of the $Pd_{60}Cu_{40}$/V-15Ni composite membrane deposited for 60s

For hydrogen permeable composite membrane, thinner and dense overlayer is more preferable because it means less expensive Pd metal. Therefore thickness control is very important to the Pd-Cu alloy overlayer. $Pd_{60}Cu_{40}$ films were deposited for different times and their thickness were measured by using FE-SEM, Fig.4 shows a back scattering electron image of the cross-sectional of the $Pd_{60}Cu_{40}$/V-15Ni composite membrane deposited for 60s, where the white strip corresponds to the $Pd_{60}Cu_{40}$ overlayer, the gray area is 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, which is consistent with the result shown in Fig.3. For V_{Pd} = 340V and V_{Cu} = 395V, the depositing rate is about 3.3nm/s.

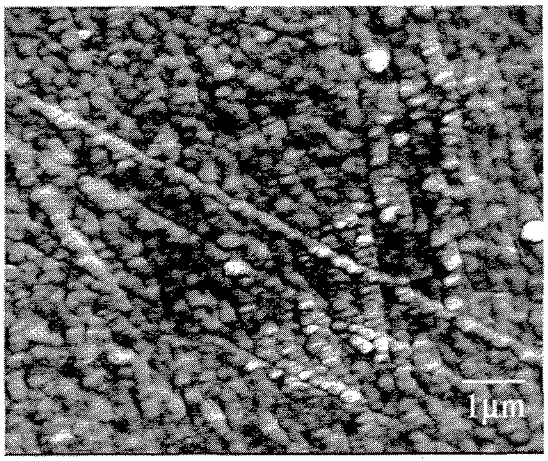

Fig.5 SEM morphology of the $Pd_{60}Cu_{40}$/V-15Ni composite membrane deposited for 60s.

Fig. 5 shows the surface morphology of the as-deposited $Pd_{60}Cu_{40}$ 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.

Hydrogen permeability of the composite membrane with about 200nm $Pd_{60}Cu_{40}$ overlayer was shown in Fig.6, and the results of $Pd_{60}Cu_{40}$ membrane reported by other researchers were also shown in the figure for comparison. The hydrogen permeability shows less temperature dependence between 523-673K and even some increase with temperature decrease, and it decreases rapidly with further temperature decreasing when the temperature is lower than 523K. In the shown temperature range, the $Pd_{60}Cu_{40}$/V-15Ni composite membrane obtained in this work shows higher hydrogen permeability than that of $Pd_{60}Cu_{40}$ membrane reported by McKinley [17] and Edlund et al [21]. It seems feasible to replace the $Pd_{60}Cu_{40}$ alloy membrane for hydrogen purification with the composite membrane developed in this work in the temperature range of 423-673K.

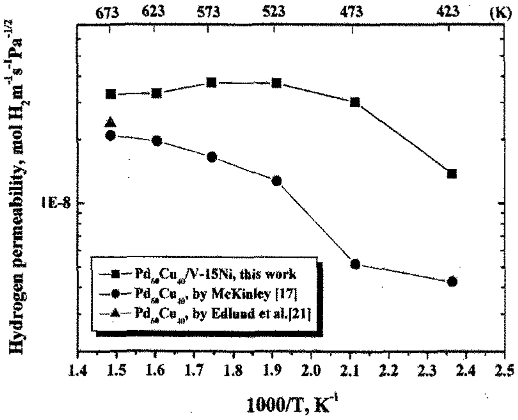

Fig.6 Temperature dependence of $Pd_{60}Cu_{40}$ and $Pd_{60}Cu_{40}$/V-15Ni composite membrane (upstream pressure: 40KPa)

4. CONCLUSIONS

Pd-Cu/V-15Ni composite membranes were deposited for the first time by co-sputtering in this paper. XRD, SEM and AES were performed to characterize the composite membrane. Cu concentration of the Pd-Cu overlayer shows a linear dependence on the Cu target sputtering voltage (V_{Cu}) when Pd target voltage is constant and $V_{Cu} > 300V$. SEM observation shows that the overlayer films have very dense and fine microstructure; XRD and AES analysis reveal that the films are well alloyed and have homogeneous composition distribution. The depositing rate is about 3.4nm/s when the Pd and Cu target voltages are set as 340V and 395V respectively. The obtained $Pd_{60}Cu_{40}$/V-15Ni composite membrane shows higher hydrogen permeability than that of $Pd_{60}Cu_{40}$ alloy membrane and presents good feasibility to replace the $Pd_{60}Cu_{40}$ alloy membrane for hydrogen purification in the temperature range of 423-673K.

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