

Preparation and characterization of Ni–P amorphous alloy/ceramic composite membrane

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Abstract

The Ni–P amorphous alloy/ceramic composite membrane of high selectivity and permeability for hydrogen was prepared by a new technique of partial electroless plating. Its permeability and ideal separation factor for H₂/Ar were investigated. The results demonstrated that the permeability of the Ni–P amorphous alloy membrane was almost the same as that of a porous inorganic membrane, but the separation factor for H₂/Ar through the Ni–P membrane was obviously higher than that through a porous inorganic one. The morphology and microstructure of Ni–P amorphous alloy/ceramic composite membrane were characterized by SEM and XRD.

Keywords: Partial electroless plating; Ni–P amorphous alloy; Ceramic composite membranes; Gas separations

1. Introduction

Inorganic membranes can be classified into dense and porous membranes according to their pore structures. Some dense metal membranes have been reported [1–3] to be of high selectivity for some gases. For example, a palladium membrane is highly selective for hydrogen permeation and can be applied to a membrane reactor for dehydrogenation. A silver membrane is highly selective for oxygen permeation and can be applied to a membrane reactor for methane oxidizing. But except for a few higher permeability materials [4] such as iron, nickel and steel, dense membranes are costly and their permeability is extre-

mely small, in general. Although porous membranes have relatively high gas permeability, their separation selectivity is low, in general. At high temperature, the conventional mesoporous inorganic membranes could not be used in the practical separation for most gas because of low separation selectivity due to the Knudsen diffusion mechanism. In order to improve their properties, Itoh et al. prepared a palladium-based catalytic membrane used for hydrogenation of phenol [5] and acetylene [6]. In addition, Kikuchi et al. [7–11] prepared a palladium/ceramic composite membrane which was successfully applied to the membrane reactor [10,11] of catalytic dehydrogenation. However, for the conventional electroless plating Pd technique [12], there was a necessary preceding process including 10 repetitions of successive sensitization and activation. This process is strenuous and even

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introduced some impurities of tin into the composite membrane. Recently, Xiong et al. [13] dispersed activation metal to an alumina membrane by means of a sol–gel technique and then deposited a layer of palladium on the surface of an alumina/ceramic substrate with Kikuchi's method. This membrane, furthermore, improved the thickness and gas permeability of the palladium layer. But this process depended on the quality of the alumina membrane to a great extent and still needed very expensive palladium.

The studies of the Ni–P amorphous electroless plating composite membrane used as a membrane for gas separation have not been reported yet. A new partial electroless plating Ni technique with activation paste containing metal ions have been developed in this paper. The effect of Ni–P amorphous alloy/ceramic composite membranes on gas separation has been studied, and satisfactory results have been obtained.

2. Experimental

2.1. Preparation of activated metal paste

0.0825 g PdCl₂ was dissolved in 0.5 ml 1 : 1 HCl and then mixed with 14.30 ml ethylene glycol diethyl ether to prepare a varnish, and its viscosity was adjusted with ethyl cellulose.

2.2. Preparation of Ni–P amorphous alloy/ceramic composite membrane

The porous ceramic tubes (98.5 wt% SiO₂, 1.0 wt% Al₂O₃ and some trace additives, O.D. 12 mm, I.D. 8 mm, average porous size 1.1~1.2 μm, porosity 0.45, made in ZhiBo special ceramic factory, Shangdong, P.R. China) after being abraded with sandpaper were cleaned with deionized water and 0.1 M nitric acid and dried at 150°C. In order to improve the porous size of substrate ceramic tubes, pre-treated ceramic tubes were dipped into boehmite sol (γ-Al₂O₃) as previously reported [14] for 10 s, then dried at room temperature for 20 h, and calcined at 500°C for 16 h. This dipping–drying–calcining process was repeated four times in order to avoid the effect of the γ-Al₂O₃ layer formed by the adherence of electroless plating layer. The γ-Al₂O₃ membrane tubes obtained were carefully

Table 1
Composition for electroless plating Ni solution [15]

Nickel chloride	A.R	30~45 g/l
Sodium citrate	A.R	60~100 g/l
Triethenolamine	A.R.	70~90 ml/l
Ammonia chloride	A.R.	40~45 g/l
Sodium hypophosphite	A.R	5~25 g/l
pH	—	9~10
Temperature	—	50~60°C
Opening load	—	150 cm ² /l

abraded with fine sandpaper again, and cleaned with deionized water and dried at 150°C. Then activated metal paste was arbitrarily brushed on to the desired electroless plating outer surface of the ceramic tube, the thickness of which was several microns, and then dried at room temperature. The dried ceramic tube was activated at 550°C in air. During the activated process, the organic carrier was removed and PdCl₂ in the top layer of the ceramic tubes was decomposed into fine metallic palladium particles. The post-treated ceramic tube was plated in the electroless nickel bath with the composition listed in Table 1.

After a given time, the ceramic tube with deposited Ni–P amorphous alloy membranes was washed with deionized water and dried at 80°C. The thickness of the coating layer was estimated by its weight and density. A Ni–P amorphous alloy membrane with only a single layer on the outer tube was prepared in this way.

The Ni–P amorphous alloy membrane could also be obtained without the activated paste, known as the conventional method, in which the ceramic tube was sensitized by stannous salt and activated by a PdCl₂ solution alternatively more than 10 times before electroless plating. However, both the outer and the inner tubes were coated with the membrane by the above-mentioned method.

2.3. The characterization of Ni–P amorphous alloy/ceramic composite membranes

The Ni–P amorphous alloy/ceramic composite membranes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Meanwhile, the separation efficiency of Ni–P amorphous alloy/ceramic composite membranes was evaluated by the separation factor of H₂/Ar.

3. Results and discussion

3.1. The relation between deposition content and electroless plating time

As shown in Fig. 1, the amount of deposited Ni–P amorphous alloy increases proportionally with plating time, and then becomes stable gradually. As is known, electroless Ni plating is itself a catalytic process. At the beginning, the rate of deposited Ni–P amorphous alloy membrane is linearly related to electroless plating time. However, with the increase of electroless plating time the rate of deposition gradually becomes slow. The thickness of Ni–P amorphous coating membrane is 8–15 μm in general.

3.2. Structure and morphology of the Ni–P amorphous alloy membrane

The XRD patterns of the as-prepared Ni–P amorphous alloy/ceramic composite membrane is shown in Fig. 2(b). By subtracting the peaks generated from the substrate, as shown in Fig. 2(a), only one broad peak around 45° is observed, indicating the existence of the amorphous structure in the above sample. Fig. 2(c) is the XRD patterns of the Ni–P amorphous alloy membrane after being crystallized at 337°C for 2 h. The result shows that only slight crystallized peaks are observed.

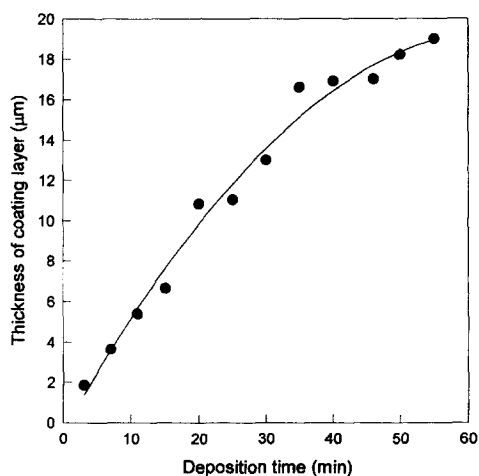


Fig. 1. The relation between thickness of coating layer and deposition time.

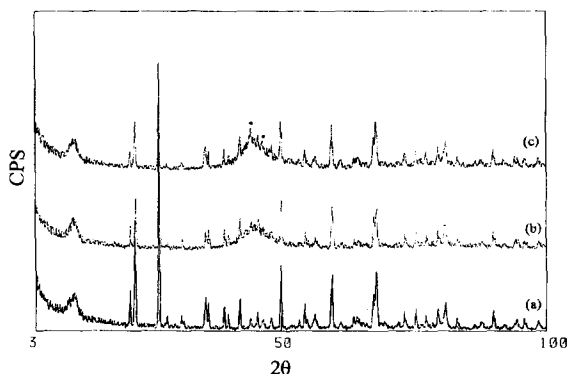


Fig. 2. XRD of the Ni–P amorphous alloy/ceramic composite membrane: (a) ceramic substrate, (b) Ni–P amorphous alloy/ceramic composite membrane, (c) Ni–P amorphous alloy/ceramic composite membrane after being crystallized at 337°C for 2 h.



Fig. 3. SEM of the Ni–P amorphous alloy/ceramic composite membrane: (a) top surface, (b) cross-section.

The surface morphologies of the Ni–P amorphous alloy/ceramic composite membrane on the top layer and interface can be observed from Fig. 3. The results show that the amorphous Ni–P particles exist in a

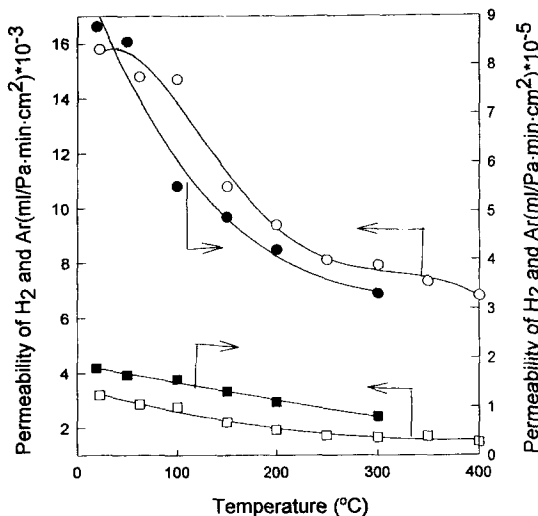


Fig. 4. The permeability of H₂ (○ ●) and Ar (□ ■) through Ni-P amorphous alloy/ceramic composite membrane prepared by a new technique (○ □) and the conventional method (● ■).

cluster, and that no significant crystallization and aggregation occur on the surface of the Ni-P amorphous alloy/ceramic composite membrane. As shown in Fig. 3(b), the thickness of the membrane is in the range of 14~20 μm, which is similar to that estimated by weight.

3.3. The gas permeability of the Ni-P amorphous alloy/ceramic composite membrane

A gas permeation test was carried out in a membrane reactor without a catalyst bed. The pure sample gas, such as H₂ or Ar, was introduced into the outer tube and permeated through the membrane into the inner tube. The pressure difference between outer and inner tubes was about 20.265 KPa. The amount of permeated gas was measured by a soap film flow meter or a wet flow meter. Fig. 4 shows the permeability of H₂ and Ar through Ni-P amorphous alloy/ceramic composite membranes prepared by two different methods. The results show that the permeability of H₂ and Ar through two different membranes decreased with an increase of temperature, but the permeability of H₂ and Ar through the membrane prepared by the new technique is 100 times more than that of H₂ and Ar through the membrane prepared by the conventional method, and is 10 times greater than the results

obtained by Kikuchi et al. [16]. Kikuchi had reported that the rate of hydrogen permeation at 500°C through the Pd/porous glass composite membrane was 2.5×10^{-4} cm³ (STP)/Pa cm² min, and it was more than 10 times greater than that through commercial palladium alloy membrane [17]. These experimental results showed that the permeability of hydrogen through Ni-P amorphous alloy/ceramic composite membrane prepared by the new technique was obviously higher. It was because hydrogen permeates through Ni-P amorphous alloy/ceramic composite membrane, not only via the surface diffusion mechanism, but also via the Knudsen diffusion mechanism due to its structure of 'cluster' and interstitial space available for hydrogen diffusion. According to Knudsen's diffusion law, gas permeation was related to the thickness and the porous structure of the membrane under the same conditions of temperature and composition of gas. Thus, the difference of gas permeability through two kinds of Ni-P amorphous alloy membrane can be understood by considering the following factors:

(1) Since a double layer existed in the membrane obtained by the conventional method, the thickness of the membrane was calculated to be 37 μm, which is much thicker than that of the membrane prepared by the new technique. Gas permeability through the membrane decreased with increasing thickness, as shown in Fig. 5.

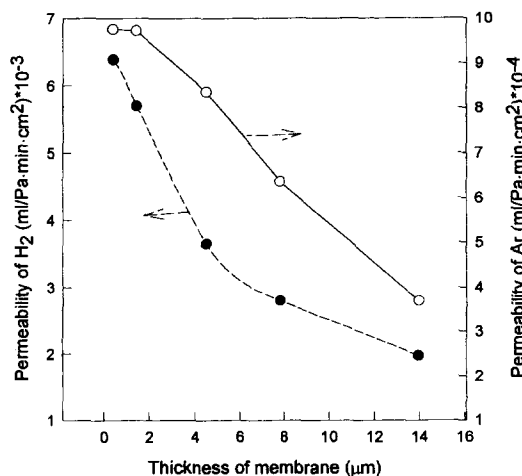


Fig. 5. Permeability of H₂ and Ar vs. thickness of membrane.

(2) Knudsen diffusion and surface diffusion occurred during gas permeation through the membrane with a single layer obtained by the new technique. However, the double processes of Knudsen and surface diffusion were essential in the membrane with a double layer obtained by the conventional method. As the diffusion processes caused by the porous structure of the double layer membrane increased, the gas permeability decreased.

(3) As the average pore size of the support ceramic tubes used in the study is larger, slight pinhole defects are formed in the electroless plating process due to deposition for a short time. Thus we consider that the increased gas permeability may be partly attributed the formation of pinhole defects. Fig. 5 presents the results obtained by the electroless Ni-plating on the substrate tubes which are modified more than 6 times by boehmite sol indicating that the pinhole formation is related to the pore structure of substrates to a great extent.

3.4. Effect of the difference in pressure on the surface diffusion of gas

The relationship between the permeability of H₂ and Ar through amorphous Ni–P alloy/ceramic composite membrane and the pressure difference are

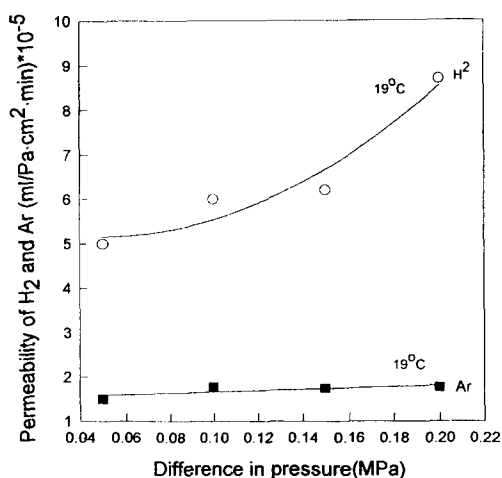


Fig. 6. The permeability of H₂ (○) and Ar (■) vs. the difference in pressure.

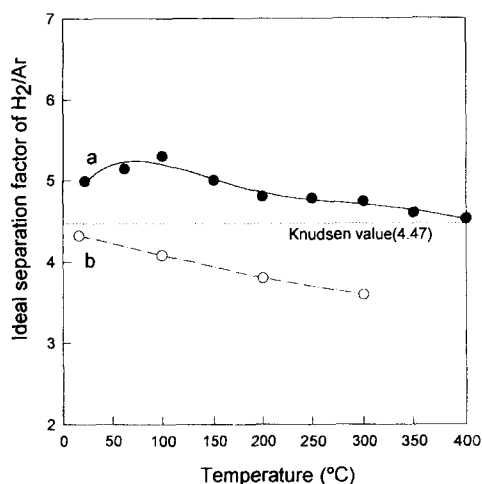


Fig. 7. The relation of ideal separation factor of H₂/Ar with temperature: (a) Ni–P amorphous alloy/ceramic composite membrane, (b) γ -Al₂O₃ membrane.

shown in Fig. 6. The permeability of Ar does not change with increase in the pressure difference, indicating that Ar permeation is carried out mainly by the mechanism of Knudsen diffusion. However, H₂ permeability is quite different since it increases dramatically with increasing pressure difference. This observation is in agreement with the results of Itoh et al. [18] on Pd_xSi_x amorphous membrane.

3.5. Ideal separation factor of Ni–P amorphous alloy/ceramic composite membrane

The separation efficiency of the membrane is evaluated by the separation factor. The ideal separation factor of H₂/Ar through porous γ -Al₂O₃ membranes and the Ni–P amorphous membranes prepared by the new technique with change of temperature is shown in Fig. 7. For the pure γ -Al₂O₃ membrane, the separation factor approaches Knudsen diffusion theoretical value (4.47) at room temperature and then decreases slowly with the increase in temperature. For the Ni–P amorphous alloy/ceramic composite membranes prepared with a new technique, the separation factor of H₂/Ar is higher than that of the γ -Al₂O₃ membrane, and also exceeds the Knudsen diffusion theoretical value in the range of 400°C, and reaches maximum value at about 100°C. These results show that Ni–P amorphous alloy membrane increases the permeability of hydrogen

indicating that Knudsen diffusion is no longer the dominant diffusion mechanism in the Ni–P amorphous alloy/ceramic composite membrane. Surface diffusion can be proposed to explain such a high separation factor. In other words, this has been proved by TPD [19] spectra of hydrogen. As previously reported, there is a peak of hydrogen desorption at 70°C and more than 300°C respectively, for amorphous Ni–P–SiO₂, and a peak of hydrogen desorption at 110°C and 280°C respectively, for crystalline Ni–P–SiO₂. Therefore, it may be speculated that the maximum separation factor at about 100°C in Fig. 7 may be related to hydrogen desorption at a low temperature (70°C and 110°C), and that the terraced area around 300°C may be related to spill-over hydrogen on ceramic supports. But with the increase of temperature, cracks on the surface of Ni–P amorphous alloy membrane may be formed due to hydrogen embrittlement or a slight crystallization, which has been proved by XRD (Fig. 2 (c)), and consequently the separation factor of H₂/Ar declines.

4. Conclusion

By means of a new technique of partial electroless plating with metal activated paste, the palladium nuclei only existed in the top layer on the ceramic support; and therefore, a Ni–P amorphous alloy membrane was only formed on the top layer. There was no Ni–P amorphous alloy existing inside the pore channel nor on the other side even if the two sides were exposed to the electroless plating bath. In contrast, it was very difficult to avoid nickel depositing on the undesired side by the technique of conventional electroless plating.

The membranes prepared by the new technique enhanced the permeability of H₂ and Ar, and furthermore improved the separation factor of H₂/Ar. We therefore solved the problem [20] that the content of metal loading in sol–gel was too low, and provided a new way for the preparation of porous inorganic membranes.

The other properties of the Ni–P amorphous alloy/ceramic composite membrane, such as, pore size distribution, catalytic performance etc, will be reported in other papers.

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