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Effect of adhesion of metals on deterioration of Pd and Pd alloy membranes

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ABSTRACT

Stainless-steel, Ni, Cr and Fe particles were adhered on Pd and Pd alloy membranes in order to investigate an effect of alloying of such metal components and membranes to the membrane performance. The adhesion of metal particles to Pd and Pd alloy membranes were evaluated through the thermal treatment. Cracks were observed along the metal particles on Pd and Pd–Ag membranes by alloying between the membranes and metal particles. For Ni and Cr, the crack formation was caused by the Kirkendall effect. For Fe, that should be attributed to the Kirkendall effect or the phase transition of Pd–Fe alloys. In contrast, it was found that Pd–Ni and Pd–Fe binary alloy membranes prevented the crack formation because alloying of Pd with appropriate metals could control the interdiffusion between Pd alloy membranes and adhered metal particles.

1. Introduction

Fuel cells have been extensively studied due to their high energy efficiency and low environmental load. Since the fuel cells consume hydrogen as an energy source, it has been desired to achieve the hydrogen production process with high energy efficiency. Generally, hydrogen is produced from the fossil fuels such as natural gas [1–3], LPG [4,5], kerosene [6,7] and alcohols [8,9] through the reforming. These processes have been conventionally operated at high temperature because of the thermodynamic equilibrium limitation where the composition of methane increases at relatively low temperature. To enhance the energy efficiency on these processes, it should be necessary to reduce the reaction temperature, and the membrane reformers which are the integrated reaction processes with the membrane separation have been investigated for a couple of decades. Membrane reformers, which generally consist of steam-reforming catalysts and highly permeable hydrogen separation membranes, can achieve to downsize the fuel cell units, decrease the reaction temperature and reduce their cost, because hydrogen can be separated and purified with hydrogen production simultaneously in the membrane reformers. It is well-known that Pd and Pd alloy membranes are one of the desirable materials for hydrogen separation because of their relatively high hydrogen permeability and theoretically infinite hydrogen selectivity. Numerous efforts on developing the Pd and Pd alloy membranes have resulted in preparing very thin membranes [10–12] and binary or ternary alloying [13–17], adapting various porous supports [18–20] and constructing novel membrane structures [19,21–23]. Although the durability of the Pd and Pd alloy membranes have also been investigated from the industrial viewpoints such as the effect of gaseous inpurities [24–26], a lot of issues in this field is still remaining to be further investigated. In the membrane reformers, packed catalyst pellets for steam reforming are often separated from membranes by stainless-steel mesh to avoid alloying of the catalyst metal and the membrane. However, metallic impurities such as Ni, Cr and Fe, main component elements of stainless-steel, might be possible to adhere on the Pd and Pd alloy membranes and alloy with the membranes under the reaction condition of reforming processes, resulting in deterioration of the membrane performance by the generation of pinholes and cracks. In this study, the stainless-steel and its main components were adhered with Pd and Pd–Ag alloy membranes through the thermal treatment. Changes in appearance and composition of the membrane were observed in order to evaluate the effect of alloying with these metal particles to membrane performances.

2. Experimental section

2.1. Preparation of Pd and Pd–Ag membranes

Pd membranes were prepared by electroless plating on nonporous α-alumina disk purchased from Covalent Materials Corporation (Japan). The detail of the electroless plating are described elsewhere [18]. The brief of the preparation method is shown as follow. The α-aluminum disk was washed ultrasonically by water and

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ethanol. Then, palladium nuclei were supported on the surface of the support by sensitization and activation treatments with stannous chloride and palladium chloride solutions, respectively, which was repeated several times. Pd was autocatalytically deposited on the surface of the disk support from an electrolessplating bath containing tetraammine complex of palladium, ethylenediamine tetraacetic acid, ammonium hydroxide and hydrazine. In the case of Pd–Ag membranes, a silver film was fabricated on the Pd membrane by electroless plating. Ag content was adjusted as around 20 wt% by controlling thickness of the Ag layer. Then, the Ag/Pd membranes were heated and alloyed at 973 K for 3 h in a hydrogen flow. The thickness of the Pd and Pd–Ag membranes were adjusted to approximately 5 μm.

2.2. Preparation of Ni membranes

A Ni membrane was prepared by electroless plating as well as the Pd membrane. The sensitization and activation treatments were carried out to deposit the palladium nuclei on the support and then, the Ni electroless plating was performed. The electroless plating bath containing nickel sulfate, malonic acid and dimethylamine–borane was used. The composition and electroless plating condition were shown in Table 1. After the electroless plating, the prepared membranes were washed by ethanol and deionized water, then, heated at 973 K for 3 h in a hydrogen flow to reduce a oxide layer on the surface of the Ni membrane.

2.3. Adhesion of metal particles to membrane surface

Pd, $Pd_{90}Ni_{10}$, $Pd_{95}Ni_5$ and $Pd_{67}Fe_{33}$ rolled membranes purchased from TANAKA KIKINZOKU KOGYO K.K. (Japan) were used for the adhesion experiments in addition to the Pd, Pd–Ag and Ni membranes prepared by electroless plating as mentioned above. As metal particles adhered to the membranes, Stainless-steel (SUS-304) particles (mean particle size 20 μm) were used. And, Ni, Cr and Fe particles purchased from Kojundo Chemical Laboratory Co., Ltd. (Japan) were also employed. The mean particle sizes of these metals were 10, 10 and 20 μm, respectively. Before these metal particles were used, the metal particles were washed by 10 wt% sulfuric acid to remove oxide layers on the outer surface of the metal particles. The metal particles were, then, dispersed on the surface of the membranes and these membranes with metal particles were heated at 873 or 1173 K with the rate of temperature change of 5 K/min in a hydrogen atmosphere. In the case of the Ni membranes, Pd chips were deposited on the membrane surface and heated at 1173 K for 24 h. After the thermal treatment, the membranes were analyzed by SEM–EDX.

3. Results and discussion

3.1. Adhesion of metal particles to Pd–Ag membranes

SUS-304 particles were adhered at 873 K to the Pd–Ag membrane which is often used as a hydrogen separation membrane because of its high permeability. The SEM image of a deposited SUS-304 particle after the thermal treatment for 100 h is shown in Fig. 1. The SUS-304 particle was partially alloyed with the Pd–Ag membrane and, the SEM image shows a large crack was generated along the spot where the SUS-304 particle was attached. This crack was confirmed to be gradually enlarged with the longer thermal treatment. Stainless-steel is widely employed as the main material to construct the industrial equipments. Hence, metal dust from the equipments may be possible to generate certain number of cracks with the long time operation. Caravella et al. calculated the effect of surface defects on the performance of Pd membranes. Their simulation showed defects in the nanometer size caused significant decrease of hydrogen selectivity [27]. Therefore, this crack formation must be directly limited the life time of the Pd–Ag membranes because of the degradation of hydrogen selectivity. To shorten the adhesion tests, the thermal treatment was conducted

Table 1
Composition of Ni electroless plating bath and plating condition.

	Composition
$NiSO_4 \cdot 6H_2O$ (g/l)	30
$CH_2(COOH)_2$ (g/l)	34
$(CH_3)_2NH \cdot BH_3$ (g/l)	3
	Condition
Temperature (K)	333
pH	5.3

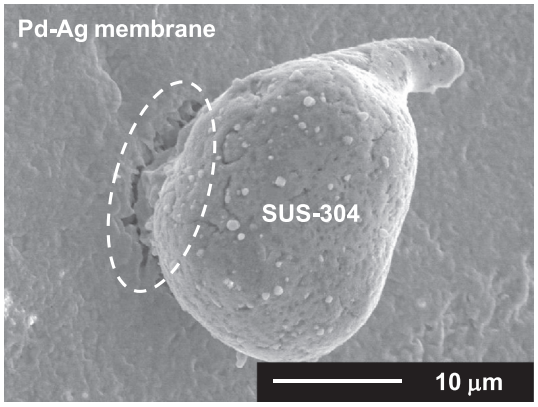

Fig. 1. SEM image of SUS-304 particle adhered to the Pd–Ag membrane at 873 K for 100 h.

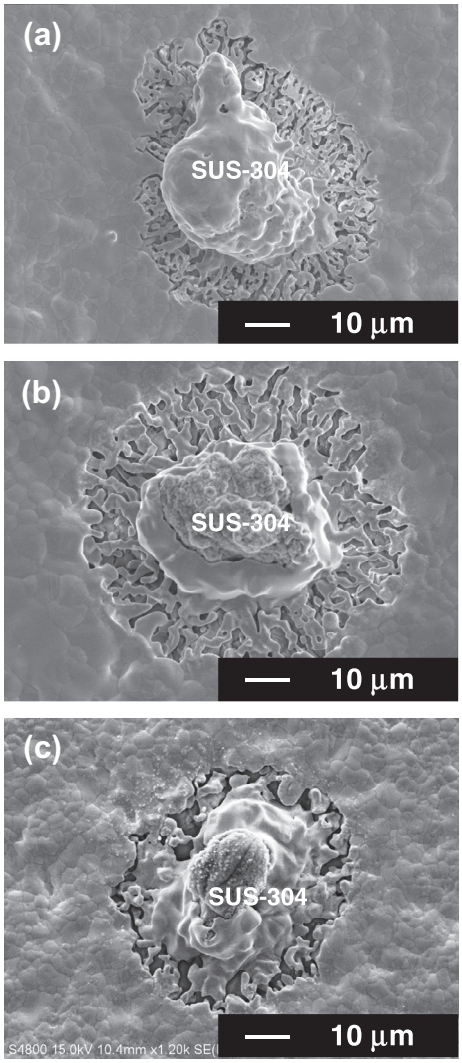

Fig. 2. SEM images of SUS-304 particles adhered to the Pd–Ag membrane at 1173 K for 24 h. (a) elevated temperature rate: 5 K/min, in a hydrogen flow, (b) elevated temperature rate: 1.5 K/min, in a hydrogen flow, and (c) elevated temperature rate: 5 K/min, in a nitrogen flow.

at the higher temperature as an acceleration test. The deposited SUS-304 particle on the Pd–Ag membrane was thermally treated at 1173 K for 24 h. The SEM image was shown in Fig. 2a. A number