Separation and Purification Technology 121 (2014) 46–53

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Composite palladium membrane prepared by introducing metallic glue and its high durability below the critical temperature

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ARTICLE INFO

Article history:
Received 2 February 2013
Received in revised form 29 April 2013
Accepted 30 May 2013
Available online 7 June 2013

Keywords:
Palladium
Composite membrane
Hydrogen
Metallic glue
Platinum

ABSTRACT

Thin palladium composite membrane suffers serious damage like cracks, peel-off, and so on from hydrogen absorption and desorption, especially below the critical temperature, 298 °C, in which $\alpha \leftrightarrow \beta$ phase transition occurs. To prevent such problems and strengthen the palladium film, it was proposed that "metallic glue" was introduced as an adhesion interlayer between porous support and palladium film. In this study, platinum was employed as the glue by taking particular note of its physical compatibility not only with palladium but also with alumina.

First, a 60–80 nm thick platinum layer was sputtered on the porous anodic oxide support, and then, 1–2 μm thick palladium film sputtered. It was found that deformation by an internal stress produced in the Pd film could be completely depressed with the platinum glue during permeation tests, which were carried out in the range of 150–350 °C including up-and-down operation with temperature.

1. Introduction

Purified hydrogen is essential for future chemical and energy industry and further hydrogen based society. Hence, expectations to palladium based membrane not only for H_2 separation but also for combined reaction and H_2 separation (or H_2 supply), etc. are as high as ever. In particular, it is desired that low temperature applications below 300 °C such as purification of hydrogen from various gaseous mixtures and efficient recovery of hydrogen from hydrogen carrier like cyclohexane [1,2], methylcyclohexane [3,4], and ammonia [5,6] are achieved. Also, from the standpoint of operating membrane separators (or reactors), it is advantageous not to need a special caution on the cool-down process. To answer such needs, a preparation method for thin and durable composite membrane, which can realize high separation rate as well as saving amount of expensive palladium metal, should be established. Although non-palladium alloys for hydrogen separable membrane like Zr–Ni [7], V–Ni–Al [8], and Ni–Nb–Zr [9] have been examined, those still need to be coated with 0.1 μm or more thick palladium layers on the both-side surfaces of the membrane plate, which are crucial for splitting hydrogen molecules to atoms on the high pressure (supply) side and for recombining hydrogen atoms to molecules on the low pressure (permeate) side. Simultaneously, the palladium coated layer has an important role of preventing oxidation of the surface of non-palladium hydrogen separation metal; this particular is serious because the stable oxides of Zr, Nb, and V are hardly reduced to their original metals.

The composite type of palladium membrane, as mentioned above, is much preferred from the viewpoint of obtaining a higher hydrogen flux for practical use, where a tight adhesion between heterologous materials, the palladium film, and the ceramic support is required to sustain not only in a wide temperature range but also in a pressurized hydrogen atmosphere. Changes in the temperature and the pressure, leading to a shape deformation in the palladium film, should be suppressed as less as possible in order to stabilize the composite membrane. Alloying of palladium layer is a well-known method of depressing the shape change; this seems imperfect and therefore still faces difficulties in the persistent adhesion between thin alloy film and support.

Many efforts so far have been made to prepare the composite types of thin palladium membranes using electroless-plating [10–17], electro-plating [18,19], chemical vapor deposition (CVD) [20–22], physical vapor deposition techniques [23–25], and the combinations. Of these techniques, the electroless-plating seems to be employed most because it can be applied regardless of support shape (flat or tube) and materials (electro-conductive or nonconductive) and do not need any special and expensive equipment. However, there are still some important unsolved problems in establishing the fabrication technique for highly durable palladium composite membrane. The most serious trouble is the fatal damages of thin palladium film on the composite membrane like peel-off and crack when the composite is exposed to hydrogen atmosphere. Such failures, particularly, are likely to occur at lower temperatures below the critical point (298 °C), where a

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http://dx.doi.org/10.1016/j.seppur.2013.05.055

comparative large volumetric change takes place according to α ↔β phase transformation. So, many attempts have been made to resolve the difficulties and increase the toughness of the composite membrane. Those can be typically categorized to the following four methods.

(1) Surface roughing of support to give an anchoring effect.
(2) Alloying to depress the β-phase formation.
(3) Thermal treatment to strengthen and stabilize the metal polycrystalline layer.
(4) Implanting palladium layer into interspace of porous support to prevent physical failure.

In particular, surface roughing of the support is the most important pretreatment for ensuring mechanically tight adherence with palladium film. According to such guidelines, both tubular and flat composite Pd membranes were prepared by sputtering with 150 W of output power in 0.7 Pa of argon for 80 min. Hydrogen permeation tests of these membranes were carried out at 300 °C. However, the nitrogen permeation rate after first hydrogen permeation test was observed to increase very much. This was found to be due to peel-off as can be seen in the photos (Fig. 1).

It has been demonstrated that completing the preparation of thin and robust membrane is insufficient only by the above treatments. Then, a way to enhance the toughness of Pd film against H_2 atmosphere has been conceived by focusing on the fact that in conventional way, Pd film is deposited directly on the support as drawn in Fig. 2a. In this structure, the interface should be the weakest part, from where peel-off may take place as in Fig. 2b. So, we reached a conclusion that a metallic interlayer should be introduced between Pd film and support (Fig. 2c). This adhesive metallic layer is called "metallic glue" in this study. When metallic glue is introduced between Pd film and support, Pd film expands or contracts according to hydrogen sorption and desorption. Deformation force generated in the Pd film works first on the metal–metal interface. Even so, the interface may not be broken because the metal–metal adhesion force should be enough large to resist these stresses. In addition, Pt, since having a lower Young' modulus, is less extensible than Pd. As the result, the stress working on the interface between glue and support may be much reduced. Thus, a large stress produced in Pd film can be relieved at the glue and support interface, and a stable contact will be established in this structure. So, it is expected that one can obtain tough composite membrane.

In this study, another idea utilizing "metallic glue" will be presented to prepare highly durable composite Pd membrane, especially at lower temperatures below the critical one.

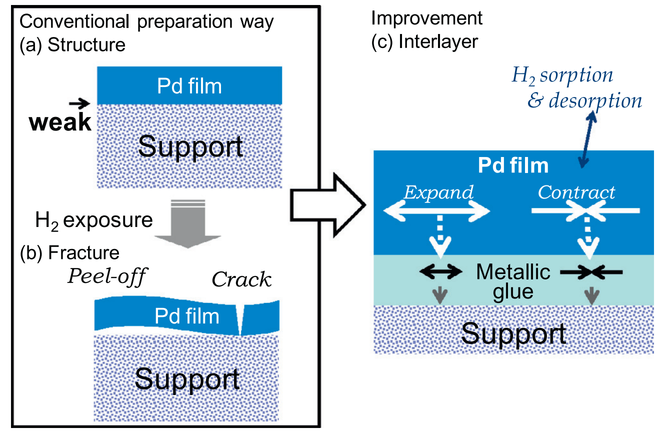

Fig. 2. An idea to introduce metallic interlayer as "metallic glue" for ensuring further toughness of composite membrane.

2. Selection of metallic glue

It is thought that the important property considered for the selection of metallic glue is physical compatibility with support material. In Table 1, three physical properties [26], i.e., thermal expansion coefficient, Vickers hardness, and Young' modulus, are compared for five metal candidates as well as alumina as support material. The reason why Ag, Au, and Pt are selected is because these are Pd's neighboring metals in the periodic table, which are assumed to have a better compatibility. Titanium is just added because titanium is known to show a better adhesion property with alumina. When the thermal expansion coefficient is arranged in descending order, Pt's coefficient is found to locate between Pd and alumina. Therefore, Pt was selected as the first option since it seemed to be the most compatible with alumina as well as Pd.

3. Experimental

3.1. Preparation of composite palladium membrane

Fig. 3 shows the whole procedure for preparing the composite membrane. Anodic alumina disk is used as support, which has straight through-pores with 60 nm in diameter and around 80 μm in thickness. Then, on the topside, 60–80 nm thick platinum glue is sputtered in Ar for 5 min. At last, by sputtering palladium for 80 min, 1–2 μm thick Pd film is deposited.

Alumina disk support was prepared by ourselves. Fig. 4 shows the procedure step by step. The detail is as follows.

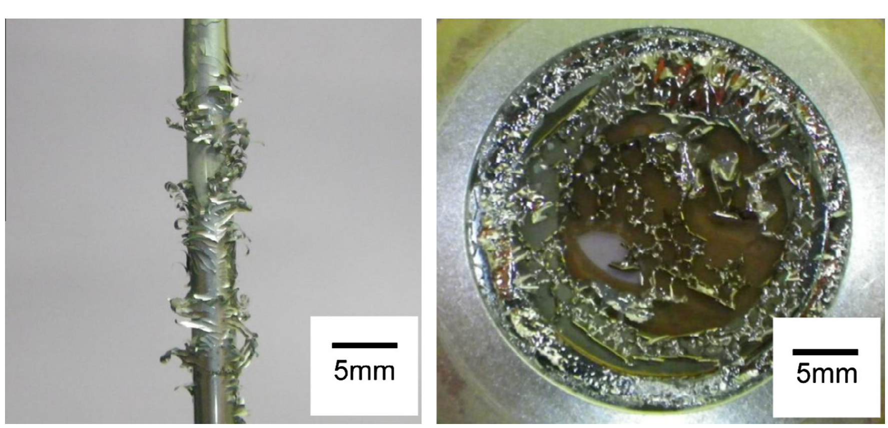

Fig. 1. Example of fatal fracture in palladium composite membrane after exposure to 0.15 MPa of hydrogen at 300 °C.