Composite Palladium and Palladium-alloy Membranes for High Temperature Hydrogen Separations

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Introduction

As we are approaching the era of the hydrogen economy, hydrogen is not only an important industrial chemical but also becoming one of the future’s key energy resources. It is expected that the future worldwide demand for hydrogen will increase greatly. Dense composite Pd and Pd-alloy membranes supported on a porous substrate, in particular, porous stainless steel (PSS), are especially suited for high temperature hydrogen separation and membrane reactor applications.

Most early work on hydrogen permeation in palladium involved the use of palladium foils as summarized in detail by Lewis (1). However, there are a number of advantages of using composite palladium membranes supported on porous substrates, in particular, porous stainless steel, over palladium foils and tubes. These advantages include thinner membrane layer, better mechanical strength and higher hydrogen flux. Furthermore, there are additional main advantages for using porous stainless steel (PSS) supports that include the resistance to cracking and the simplicity of module construction. Composite Pd/PSS membranes, welded from both ends with non-porous stainless steel tubes, can be very easily assembled and integrated into a process. Additionally, the thermal expansion coefficient of stainless steel is very close to that of palladium, insuring good mechanical properties of the composite membrane during temperature cycling.

This paper reviews the synthesis by electroless plating and characterization of composite Pd and Pd-alloy with a special emphasis on porous stainless steel (PSS) support, and long-term thermal stability. In addition, the unique features of the controlled in-situ oxidation technique to create an intermetallic diffusion barrier are discussed.

Electroless Plating

The advantages of electroless plating include uniform deposition on complex shapes and large substrate areas, hardness of the deposited film, and very simple equipment. Electroless plating (2) generally consists of pre-treatment of the porous stainless steel (PSS) support, surface activation and plating. The pre-treatment of the PSS support includes complete removal of foreign contaminants (grease, oil, dirt, corrosion products) while surface activation consists of seeding the support surface with palladium nuclei, which during the electroless plating initiate an autocatalytic process of the reduction of a metastable Pd salt complex on the target surface. Electroless plating is carried out at constant temperature with a plating solution typically consisting of a plating agent (Pd(NH$_3$)$_2$Cl$_2$H$_2$O), stabilizing agent Na$_2$EDTA, and a reducing agent H$_2$NNH$_2$ with NH$_4$OH for pH adjustment.

One of the problems associated with electroless plating of palladium on porous metal substrates is the intermetallic diffusion of metal elements into the palladium layer at high temperatures causing deterioration of the hydrogen flux. We have developed a unique technology to create an intermediate intermetallic diffusion barrier layer by controlled in-situ oxidation prior to the plating (3).

Furthermore, there are added benefits that the intermediate barrier layer also provides surface sites for easy activation and plating as well as improved adhesion (4). Typical Pd/PSS membranes plated by the electroless plating technique with an in-situ barrier layer are shown in Fig.1. Non-porous stainless steel tubes of the same diameter were welded to the membrane tubes on both ends and the white sleeves were used to facilitate the handling of the membranes.

![Figure 1. Composite Pd/PSS membranes 1” OD (2.54 cm), Membrane area: 24.7 in$^2$ (159 cm$^2$)](image)

Hydrogen Permeation Flux as a Function of Membrane Thickness

Since the permeation of hydrogen through Pd and Pd/alloy is by the solution and diffusion mechanism and is, in most cases, controlled by the diffusion of dissociated hydrogen molecules through the Pd bulk, the hydrogen flux is proportional to the difference of the square root of the pressures, known as the Sievert’s law. A typical plot of permeance vs. the difference of the square root of pressure (Sievert’s law) is shown in Figure 2 for a membrane of thickness of 11.7 µm at 350°C. As shown in Fig. 3, these experimental

![Figure 2. The hydrogen Flux as a function of the difference of the square root of the pressure (Sievert’s law) at 350°C)](image)

thickness of 11.7 µm at 350°C. In addition, when the permeation is controlled by the diffusion of hydrogen in the bulk palladium layer, the permeation flux and thus the permeance, is inversely proportional to the membrane thickness. We have performed a systematic study of the permeation of hydrogen through composite Pd/PSS membranes with different Pd layer thickness and showed the inverse relationship between the hydrogen permeance and the Pd layer thickness at 350°C$^\circ$. As shown in Fig. 3, these experimental
Palladium Alloys for Improving Hydrogen Permeation Flux and Thermally Stability

It has long been recognized that Pd alloys may have advantages over Pd for use in hydrogen separation and membrane reactor applications. In general, Pd alloys have a reduced critical temperature over Pd for use in hydrogen separation and membrane reactor membranes will play an important and essential role in the production of pure hydrogen in the 21st century of hydrogen economy. The use of porous metal as substrates will facilitate the membrane module fabrication and process integration. Many technical issues, such as producing thin membranes with good separation characteristics and long term thermal and mechanical stability, remain to be solved. Further exploration of the use of palladium alloys to increase the hydrogen permeability and at the same time, to enhance the thermal stability can expedite the implementation of these composite membranes into hydrogen production processes.

Table 1. Improvement in hydrogen permeability of various binary Pd alloys at 350 ºC (7, 8)

<table>
<thead>
<tr>
<th>Alloy Metal</th>
<th>wt % for Maximum Permeability</th>
<th>Normalized Permeability (P_{Pd}/P_{Alloy})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>10</td>
<td>3.8</td>
</tr>
<tr>
<td>Ag</td>
<td>23</td>
<td>1.7</td>
</tr>
<tr>
<td>Ce</td>
<td>7.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Cu</td>
<td>40</td>
<td>1.1</td>
</tr>
<tr>
<td>Au</td>
<td>5</td>
<td>1.1</td>
</tr>
<tr>
<td>Ru, In</td>
<td>0.5, 6.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Ag, Ru</td>
<td>30, 2</td>
<td>2.2</td>
</tr>
<tr>
<td>Ag, Rh</td>
<td>19, 1</td>
<td>2.6</td>
</tr>
<tr>
<td>Pure Pd</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Palladium-copper alloys are attractive from the standpoint of relatively high permeabilities coupled with their enhanced sulfur resistance. In the case of Pd-Cu alloys, the formation of a solid phase with a BCC structure at 40 wt % copper, leads to an increase in the hydrogen diffusivity of two orders of magnitude, and thus a sharp maximum in permeability for this composition (6). More detailed discussion can be found in Ma et al. (12).

Conclusions

Dense composite palladium, especially palladium/alloy, membranes will play an important and essential role in the production of pure hydrogen in the 21st century of hydrogen economy. The use of porous palladium as substrates will facilitate the membrane module fabrication and process integration. Many technical issues, such as producing thin membranes with good separation characteristics and long term thermal and mechanical stability, remain to be solved. Further exploration of the use of palladium alloys to increase the hydrogen permeability and at the same time, to enhance the thermal stability can expedite the implementation of these composite membranes into hydrogen production processes.

References