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Preparation of Pd-Ag/PSS Composite Membranes for Hydrogen Separation

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Preparation of Pd-Ag/PSS Composite Membranes for Hydrogen Separation

by

B. Ceylan Akis

A Thesis
Submitted to the Faculty
of the
WORCESTER POLYTECHNIC INSTITUTE
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APPROVED:

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ABSTRACT

Recent global interests in developing hydrogen economy generate substantial research and development for hydrogen production worldwide. Pd membranes are especially suited for high temperature hydrogen separation and membrane reactor applications. Alloying Pd with Ag not only suppresses hydrogen embrittlement, but also increases the permeability of the alloy membrane.

The main objective of this work was to carry out fundamental studies to understand the properties of the porous stainless steel (PSS), morphologies of Pd and Ag deposits on PSS, and the structural changes of the membrane layer upon heat treatment. Both coating and diffusion and co-plating techniques were employed in the study. The Pd-Ag membranes that had sandwiched Ag layers suffered from very low selectivity due to the voids formed because of high diffusion rate of Ag. Alloy membranes with high selectivity can be prepared by applying intermediate annealing after each Ag deposition. On the other hand, the homogeneity of the alloy depended very much on the thickness of the deposited layers and annealing temperature and time.
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B. Ceylan Akis
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CHAPTER 1
INTRODUCTION

1.1 General Background

"What if there were a form of energy that could solve our air pollution problems, would eliminate our dependence on foreign oil, could solve our balance of payments woes, would eliminate oil spills, would create domestic jobs, and could be made from unlimited, renewable, and sustainable resources? Well, there is -- it's hydrogen!" said Rick Smith, the president of Hydrogen Energy Center, September 1997.

Hydrogen is one of the key energy sources for the future. There are several ways to produce hydrogen such as from natural gas, coal, gasoline, methanol, or biomass through reforming; from bacteria or algae through photosynthesis; or by using electricity or sunlight to split water into hydrogen and oxygen.

Approximately 80 per cent of industrial hydrogen is currently generated from natural gas and other hydrocarbons through steam methane reforming (SMR). SMR systems typically include a reformer to produce a crude hydrogen stream and a gas purification unit to purify the hydrogen. Membrane reactors have the advantage of combining the reaction and the separation into one unit. Besides, the removal of the hydrogen by the membrane from the product gas stream yields a higher conversion of the reaction. Pd membranes are especially suited for high temperature hydrogen separation and membrane reactor applications.

Due to the high cost of Pd and relatively low hydrogen flux, commercially available Pd foils and tubes are not suitable for large-scale industrial applications. Composite membranes consisting of a thin Pd film supported on a porous substrate, such
as vycor glass, ceramic, stainless steel, quartz, etc., is a good alternative that provides both mechanical strength and a thin separation layer for a high hydrogen flux and reduced Pd cost. Ceramic or vycor glass supported Pd membranes are relatively difficult to assemble. PSS supported Pd membranes, on the other hand, are advantageous due to their thermal expansion coefficient close to that of Pd-based films, ease of fabrication, high mechanical strength, high resistance to corrosion and low cost. When porous metal supports are used at high temperatures, the intermetallic diffusion of metal elements in the substrate to the palladium separation layer causes the hydrogen flux to deteriorate. One way to improve the membrane stability is to create an intermediate intermetallic diffusion barrier layer, which is stable at reducing atmosphere and at high temperatures. Furthermore, among several deposition techniques, electroless plating is the most commonly used technique for Pd deposition because it provides very good uniformity on complex shapes, hardness of the deposited film, low cost as well as very simple equipment.

Pd membranes are required to have high H\textsubscript{2} permeance, good thermal and mechanical stability and perm selectivity. Pure Pd membranes, however, suffer from hydrogen embrittlement caused by the $\alpha$ to $\beta$ phase transformation when the temperature is lower than the critical temperature of $\sim$300°C. Alloying Pd with Ag not only suppresses the critical temperature for hydrogen embrittlement, but also increases the permeability of the alloy membrane.

Pd-Ag membranes can be prepared either by coating and diffusion of separate Pd and Ag layers, or by co-plating Pd and Ag simultaneously from the same plating bath followed by annealing process. Up to now, coating and diffusion treatment is the most
commonly used procedure to obtain alloys. However, a homogenous alloy formation requires temperatures as high as 700-800°C. Since the deposited Pd and Ag grains are in very close proximity, co-plating is a much more preferred way that allows the formation of homogeneous alloys at much lower temperatures. However, due to the complexity involved in the chemistry of the plating process and difficulty encountered in controlling the composition and structure of the membrane layer, up to now, there are no literature data reporting dense Pd/Ag alloy membranes prepared on PSS by the co-plating route.

1.2 Objectives

The main objective of this work was to carry out fundamental studies to understand the properties of the substrate, plating mechanisms and morphologies of Pd and Ag deposits on PSS from both single metal plating baths as well as co-plating baths, and the structural changes of the membrane layer upon heat treatment.

A native oxide barrier layer created upon in-situ controlled oxidation of the substrate prior to plating was recently developed in our laboratory. Membranes prepared by this technique were stable over 6000 hours at 350°C. The first stage of this study was to analyze the changes of the critical properties of the substrate, such as composition, porosity and pore size distribution as a function of oxidation time and temperature of the support. In addition the effect of this oxide barrier layer on the final thickness of pure Pd membranes, as well as on the H₂ permeance and stability were systematically investigated.

The second stage of the work was to understand the structures of the pure Pd and pure Ag deposits and to investigate the structural changes using the coating and diffusion
method. The effect of plating sequence on the morphology of the deposited layers and the role of Ag in the alloy formation during annealing on the final performance of the membranes provided fundamental information essential to the preparation of defect free composite homogeneous Pd-Ag/PSS membranes.
CHAPTER 2
LITERATURE REVIEW

2.1 H₂ permeable Membranes

Pd membranes are required to have high and stable H₂ permeance with high perm selectivity. This section will start with a general discussion on permeance, selectivity and stability separately. At the end, some improvements and factors affecting the membrane properties will be explained.

2.1.1 Mechanism for H₂ Permeation (Sievert’s law and n value)

The hydrogen permeation through Pd membranes include 5 steps, adsorption of hydrogen molecules on the membrane surface, dissociation into atomic hydrogen , diffusion of atomic hydrogen through the membrane layer, re-association of H₂ atoms back into H₂ molecules at the permeate side, and desorption of hydrogen molecules from surface of the membrane. Figure 2.1 shows the multi step hydrogen permeation process.

![Figure 2.1 Schematic of hydrogen permeation mechanism in palladium membranes.](image)

Figure 2.1 Schematic of hydrogen permeation mechanism in palladium membranes.
When the rate limiting step for hydrogen permeation is diffusion of hydrogen through the bulk Pd layer, the H$_2$ flux through the membrane can be obtained by integration of Fick’s Law.

$$J = -D \frac{dC}{dl} = \frac{D}{l} (C_{H_2,1} - C_{H_2,2})$$  

(2.1)

In Equation 2.1, $J$ is the hydrogen permeation flux (mol/m$^2$·s$^1$), $D$ is the diffusivity of the hydrogen in the palladium membrane (m$^2$/s$^1$), $l$ is the thickness of the membrane (m), $C_{H_2,1}$ and $C_{H_2,2}$ are the hydrogen concentrations in the inlet and outlet of the membrane, respectively (mol/m$^3$). The hydrogen concentrations can be expressed as,

$$C = \kappa \eta$$  

(2.2)

where, $\kappa$ is the hydrogen concentration constant (mol/m$^3$) and $\eta$ is the atomic $H/Pd$ ratio, the solubility of hydrogen in palladium. Figure 2.2 shows the relationship between the partial pressure of hydrogen and solubility, the ratio of H/Pd atoms, at various temperatures.
Below a critical temperature of ~300°C and a critical pressure of 2MPa, the phase diagram contains three regions; the single $\alpha$-hydride phase region (right side of the spinodal curve when $n<<1$), the single $\beta$-hydride phase region (left side of the spinodal curve) and a miscible phase region where both $\alpha$ and $\beta$-hydride phases are in equilibrium (below the spinodal curve). Above the critical point, only $\alpha$-hydride phase exits. As can be seen from the insert in Figure 2.2, at very low concentrations of hydrogen, $\eta$ is linearly dependent on the square root of partial pressure of hydrogen.

\[ P_{H}^{0.5} = K_s \cdot \eta \]  

(2.3)
In Equation 2.3, $K_s$ is the Sievert’s constant which is equivalent to Henry’s constant. Combining Equations 2.1, 2.2 and 2.3 gives,

$$J = \frac{D(\kappa/K_s)}{l}(P_{H_2}^{0.5} - P_{H_2}^{0.5})$$

(2.4)

The term $\kappa/K_s$ is the hydrogen solubility, $S$, in the palladium layer (mol/m$^3$·Pa$^{0.5}$). The product of diffusivity and solubility is termed as the permeability, $Q$, of the membrane and is a function of temperature, composition and microstructure of the membrane layer.

$$D = D_o \exp\left(\frac{-E_D}{RT}\right)$$

(2.5)

$$S = S_o \exp\left(\frac{\Delta H}{RT}\right)$$

(2.6)

In Equations 2.5 and 2.6, $E_D$ is the activation energy for hydrogen diffusion (J/mol$^1$), $\Delta H$ is the solubility enthalpy of hydrogen (J/mol$^1$), $R$ is the universal gas constant and $T$ is the absolute temperature (K). Combining Equations 2.5, 2.6 and 2.4 gives the Sievert’s law.

$$J = \frac{Q}{l}(P_{H_2}^{0.5} - P_{H_2}^{0.5}) = \frac{Q_o}{l} \exp\left(\frac{-E_Q}{RT}\right)(P_{H_2}^{0.5} - P_{H_2}^{0.5})$$

(2.7)

where,

$$Q_o = D_o \cdot S_o$$

$$E_Q = E_D + \Delta H$$

At this point it is important to remember that the Sievert’s law is only valid in certain cases;

i. For the case of dilute Pd-H solutions ($n<<1$). As seen from Figure 2.2, for each isotherm, Sievert’s law can be applied up to a certain pressure value.
ii. For the case when the rate limiting step for permeation is \( \text{H}_2 \) diffusion through the membrane. Usually when the membrane is ultra thin or when the process stream has some contaminants, the surface processes become much slower than the diffusion of \( \text{H}_2 \).

Alternatively, when Sievert’s law is not valid, an expression for the flux can be derived as being proportional to the difference of the hydrogen partial pressure raised to an exponent with a value of ‘\( n \)’ as shown in Equation 2.8.

\[
J = \frac{Q_o}{l} \exp\left(\frac{-E_o}{RT}\right)\left(P_{\text{H}_2,1}^n - P_{\text{H}_2,2}^n\right)
\]  

(2.8)

The value of the pressure dependency plays an important role in determining the rate limiting step and consequently the determination of the values of the activation energy. Hulbert and Konency (1961) reported that for palladium membranes with a thickness greater than 20 \( \mu \)m, the rate limiting step was found to be hydrogen diffusion through the palladium bulk. Ackerman and Koskinas (1972) had also reported the permeation data for deuterum and hydrogen through Pd-Ag alloy membranes at different temperatures and developed an empirical equation to show that bulk diffusion is the rate controlling step for their membranes.

Several authors, on the other hand, reported that the pressure power approaches unity when ultra thin membranes (less than 2 \( \mu \)m) were used (Nam et al., 1999; Jayaraman et al., 1995; McCool and Lin, 2001; Athayde et al., 1994). In this case the surface process of hydrogen adsorption became slower compared to the diffusion of hydrogen in the palladium layer. Ward and Dao (1999) constructed a model for \( \text{H}_2 \) permeation including all kinetic steps in the permeation step. They reported that in the absence of external mass transfer, even for membranes approaching 1\( \mu \)m thickness,
diffusion was the rate limiting step at temperatures higher than 300°C. Desorption became rate limiting at very low temperatures, whereas, adsorption was important only at very low hydrogen partial pressures.

McCool et al. (2001) reported that in lower temperature ranges the surface reaction was more likely to be the rate limiting step for hydrogen permeation through the ultra thin Pd membranes. As temperature was increased, the resistance of the surface reaction with larger activation energy became less important compared to the bulk diffusion resistance. Therefore the apparent activation energy observed for hydrogen permeation through the ultra thin Pd membranes decreased as the temperature was increased.

Mardilovich et al. (1998) reported activation energy of 16.4 kJ/mol with a hydrogen pressure dependency of 0.5 for 20 µm thick Pd membrane. Li et al. (2000) found an n value of 0.65 for a 10.3 µm pure Pd membrane deposited on α-Al2O3. The activation energy for this membrane was found to be 12.3 kJ/mol. Xomeritakis and Lin (1998) observed activation energy of 30 kJ/mol for a thin Pd film of 0.3 µm with a pressure dependency of power 1 at temperatures up to 300°C. In contrast, Roa and Way (2003) reported n-values of 0.515 for 1.5 µm thick Pd-Cu membranes at 350°C. They did not report the activation energy.

Xu et al. (2000) and Jayaraman and Lin (1995) reported a similar value of 23 kJ/mol for submicron thick Pd-Ag/γ-Al2O3 membranes at a temperature range of 400-500°C. The activation energies ranging from 29.7 to 33.2 kJ/mol were found for Pd-Ag membranes (163-325 nm thick) with Ag concentrations ranging from 10 to 18 wt% for temperatures lower than 200°C.
The permeability of hydrogen in unsupported Pd membranes (1mm thick) was determined by Morreale et al. (2003) for temperatures from 350 to 900°C and for hydrogen pressures from 1 to 27 atm. When the n-value was assumed to be 0.5, the activation energy was found to be 13.81 kJ/mol. However, for high pressures, a better fit of the data was seen when n-value was optimized to 0.62. The increase of the exponent value from 0.5 to 0.62 was attributed to a non-ideal solution of Pd-H in which the dissolved hydrogen atoms exhibited attractive forces towards one another. On the other hand there were no significant changes in the activation energy value.

The microstructure of the Pd layer, as well as the rate determining step influences the activation energies for hydrogen permeation, thus the hydrogen permeance. Compared to the lattice diffusion, the grain boundary diffusion is faster owing to the excess free volume, vacancies and imperfections in grain boundaries. Nanocrystalline materials have the benefit of a substantial grain-boundary component which acts as a network of fast diffusion pathways. The overall diffusivity of the nanocryristalline material can be as much as about ten times higher than that of conventional polycrystalline material (Gleiter, 1989).

Bryden and Ying (2002) observed an decrease in hydrogen permeance due to the grain size coarsening for Pd-Fe membranes. In contrast, McCool and Lin (2001) reported that thicker membranes with lower Ag% contents and bigger grains exhibited higher hydrogen permeance in the case of ultra thin membranes (less than 1 µm). These contradictory results might be because of compositional differences of the two systems.
2.1.2 Perm-selectivity and stability (H₂ Embrittlement)

It is important to maintain the high stability and high selectivity of the Pd membranes. Cracking of the membrane layer due to the formation of pinholes might be the result of either operation conditions or from some support and Pd layer interactions for the case of palladium membranes. When pure Pd membranes are operated below 300°C and below 2 MPa (below the spinodal curve in Figure 2.2), the instantaneous nucleation of the $\beta$-hydride phase with a larger lattice parameter from the $\alpha$-hydride phase results in severe strains in the Pd lattice. The cracking of the membrane due to this lattice distortion is termed as hydrogen embrittlement. Therefore, pure Pd membranes should be operated above this critical point, unless very dilute solutions at very low pressures are used (Grashoff et al., 1983).

Changes in the lattice parameter might also occur above the critical point due to the hydrogen loading in the system either by pressure or thermal cycling. Several authors observed a decrease in selectivity of the membranes after thermal cycling or cycling between different gasses. Even though these distortions are much gradual, the pressure and temperature changes should be handled very slowly to avoid cracking of the membrane.

The hydrogen permeation through the dense metallic film increases substantially with increasing temperature. He flux trough the pinhole, on the other hand, decreases slightly with temperature due to the Knudsen flow. As a result the separation factor increases with increasing temperature unless there is a crack formation due to cycling or hydrogen embrittlement.
Ideal separation factor is defined as the ratio of H\textsubscript{2} permeance to the permeance of a non-permeable gas, Ar, N\textsubscript{2}, He, etc. Theoretically, composite dense Pd membranes should have infinite selectivity given that they are permeable only to hydrogen. However, the presence of cracks or pinholes can permeate unwanted species, decreasing the purity of hydrogen. Important factors influencing the selectivity are the support properties, plating technique and heat treatment procedures.

2.2 Supports Used for Pd Composite Membranes

The hydrogen permeation is inversely proportional to the film thickness. Due to the high cost of Pd and relatively low hydrogen flux, commercially available Pd foils, 50 to 150 µm thick, are not suitable for industrial applications. On the other hand, thinner films have low mechanical strength and low selectivity at higher temperatures, thus they can not be reduced in thickness beyond a certain degree. Composite membranes consisting of a thin film supported on a porous substrate is an alternative that provides both the mechanical strength and thin separation layer. Vycor glass (Cheng and Yeung, 1999), ceramics (Tosti et al., 2002; O’Brian et al., 2001), porous stainless steel (Mardilovich et al., 1998; Jun and Lee, 2000; Bryden and Ying, 2002), quartz (Lu and Lin, 2000) and other metals in porous form are some alternatives for substrates.

The composition, porosity and pore size distribution of the substrate are some factors that affect the thickness of the membrane, thus the hydrogen flux, as well as the stability of the membrane at elevated temperatures.

The composition of the support is important in terms of stability. The thermal expansion coefficients between the metallic film and the substrate should be close enough
for structural stability during thermal cycling. PSS or other metal substrates are advantageous in this aspect. Ceramic supports suffer from cracking due to the thermal expansion coefficient mismatch during thermal cycling (Tosti et al., 2002). Tosti et al. (2002) also developed a model on the shear stress at the metal ceramic interface as a function of temperature and membrane thickness. Below 127°C there was very small amount of shear stress independent of thickness, however, above 127°C, the shear stress considerably increased as a function of both temperature and thickness of the film.

On the other hand, intermetallic diffusion of elements from the substrate to the metallic film causes deterioration of the hydrogen flux at high temperature; especially in the case of porous stainless steel supports (Jun and Lee, 2000). Bryden and Ying (2002) showed that the permeability of Pd-Fe alloys that contained 2.5 at.% Fe was lower than that of pure Pd membranes by a factor of 2. The permeability was very low for Pd-20 at.% Fe alloy.

Significant thermal vibration occurs in the metal lattice at the Tamman temperature that is equal to 0.5 of its melting temperature in K. The Tamman temperature of palladium and stainless steel is 640 and 550°C respectively. Therefore, the hydrogen permeance of palladium membranes prepared on PSS supports decline at temperatures above 500°C. Gryaznov et al. (1993) and Jun and Lee (1999) using XPS and EDS, reported that stainless steel components diffused into the palladium layer at temperatures above 500°C.

The final thickness of the metal layer is strongly dependent on the pore size distribution of the support. Thinner membranes can be prepared with supports that have a smaller and narrower pore size distribution. Mardilovich et al. (2002) electroless
deposited Pd on PSS supports of three different grades, 0.1, 0.2, 0.5 µm. The mercury porosimetry of the original supports showed that they had a different pore size distribution and that maximum pore size increased with higher grades. They reported that the final palladium thickness was approximately three times the diameter of the largest pore on the surface. Independent of the deposition technique, much thinner membranes can be prepared using porous glass and alumina (Huang et al., 1997; O’Brien et al., 2001) support which have very small and narrow pore size distribution compared to the PSS.

High porosity of the support means low resistance to hydrogen permeation. A one dimensional resistance model based on the electric circuit analogy was developed by Henis and Tripodi (1981) to explain how the deposited film and support layer affect the overall permeation. According to this model, when the film layer is thin enough, the permeation through the support becomes the main resistance for H₂ permeation. Despite of the thin separation layer, membranes supported on vycor glass or ceramic supports usually suffered from low H₂ permeation due to high support resistance.

At the interface between the membrane film and the non-porous part of the porous support, the flow of gas is prohibited. The H₂ travels through the film layer making a contour towards the pores of the supports. Itoh et al. (1995) showed with a three dimensional model that as the distance between the pores got bigger and as the ratio of film thickness to width of unit pore decreased, the flux through the membrane layer was reduced.

Surface roughness also contributes to the resulting coating structure. O’Brien et al. (2001) sputter coated α-alumina (50-500 nm pore size) and γ-alumina (5-20 nm pore
size) with Pd. \( \gamma \)-alumina substrates facilitated much denser coatings than \( \alpha \)-alumina on which enhanced growth encircled around pinholes were formed. The roughness and the porosity of the support also affect the quality of the Pd seeds during the activation step (section 2.3.4.1) and the adhesion of the metal to the substrate.

Considering the contribution of substrate properties to the performance of the membranes, ceramic supports are used in lab scale studies, basically on alloy formation and/or permeation characteristic of membranes as a function of microstructure. On the other hand, they suffer from sealing problems. Porous stainless steel supports are advantageous due to their thermal expansion coefficient close to that of Pd-based films, ease of fabrication, high mechanical strength, high resistance to corrosion and low cost. However, PSS composite membranes have the disadvantage of relatively large pore size distribution, yielding thicker membranes and intermetallic diffusion at high temperatures causing the deterioration of the hydrogen flux.

Several techniques, including pretreatment of supports prior to plating, are developed to improve the properties of the supports. Asymmetric supports are used to have a narrow pore size distribution on the top layer without losing the porosity of the support such as \( \gamma \)-alumina coated \( \alpha \)-alumina (Jun and Lee, 2000; Xomeritakis and Lin, 1996; Uemiya et al., 1997). Jun and Lee (2000), Nam and Lee (2000) modified the surface of the PSS (pore size 0.5\( \mu \)m) by dispersing submicron Ni granules followed by sintering at 800\( ^\circ \)C for 5 hours under vacuum. The average pore size after the treatment was 0.05\( \mu \)m.

To improve the stability at high temperatures, the same group coated the modified PSS support further with an intermediate layer of silica by sol-gel process as a diffusion
barrier between Ni and the Pd layer. The Pd-Cu alloy membrane (40 wt. % Cu) prepared on this composite support (SiO$_2$/Ni/PSS) was 2µm thick and were stable for 40 days at 450°C with H$_2$/N$_2$ selectivity higher than 10000.

An ultra thin titanium nitride intermediate layer between PSS and Pd-Ag layer is introduced by Shu et al. (1996). Titanium nitride was formed by sputtering from a Ti target in a nitrogen atmosphere. There was no intermetallic diffusion of Fe into the Pd layer at 700°C. The same group modified the surface pore size of PSS (0.5µm retention size) upon shot peening (Jemaa et al., 1996). The resulting membrane was 6µm thick which is very thin compared to that of Mardilovich et al. (1998) who used same grade support.

Edlund and McCarthy (1995) synthesized Pd/Aluminum Oxide/Vanadium membranes which were stable at 700°C for up to 2 weeks without suffering flux decline. They reported that in the absence of the intermediate layer, intermetallic diffusion occurred very rapidly, decreasing the flux. Hydrogen atmosphere was also found to be increasing the rate of intermetallic diffusion excessively when compared to Argon atmosphere.

Ma et al. (1998) used a barrier layer to prevent intermetallic diffusion from PSS to Pd layer, created by the in-situ controlled oxidation of the PSS support. The protective oxide layer inhibited the intermetallic diffusion without loosing the porosity of the support. Membranes prepared by this technique were stable for over 6000 hours at 350°C.

Checchetto et al. (2004) used a polymeric layer both as filler for the stainless steel pores ensuring a suitable surface morphology for the Pd deposition and as diffusion
barrier between sputter deposited Pd and porous stainless steel. Prior to Pd deposition, the substrates were coated with polycarbonate (PC) by spin deposition technique. 5\(\mu\)m Pd layer was deposited on a 0.5\(\mu\)m grade PSS (3.5\(\mu\)m pore size) support. Unfortunately, the membranes suffered from low hydrogen flux, mainly due to the resistance of the PC layer inside the pores of the PSS.

2.3 Synthesis of Pd Membranes

Different thin film preparation methods give thin metal membranes with a different microstructure. In this section, plating methods will be discussed in terms of film microstructure, grain size, compactness, alloy formation and how these properties influence the long term stability and selectivity of the composite membranes.

2.3.1 Physical Vapor Deposition; Thermal evaporation, Sputter Coating.

Physical Vapor deposition (PVD) is a less laborious technique, provides faster deposition rates and allows for better control of the film thickness. In contrast to CVD, the film can be obtained at relatively low temperatures, avoiding damaging the surface. PVD is the process of depositing solid material on a substrate from vapor phase. The source of the vapor phase is generally a solid “chunk” of the desired film material. This deposition technique has the advantage of depositing a desired film thickness, even in nanometer range, in the clean environment of high vacuum. The desired material is either heated until evaporation (thermal evaporation) or sputtered by ions (sputtering) on the target surface.

During sputtering, a low pressure gas with large number of ions and free electrons, referred as plasma, is created via high energy field. Bombardment of solid
(target) by high energy chemically inert (e.g. Ar) ions extracted from plasma causes ejection of atoms from the target which are then re-deposited on the surface of the substrate with the help of magnetic field generated by permanent magnets. The main advantage of this technique is that ultra thin nano-structured films with minimal impurity can be prepared with greater flexibility for synthesizing alloys. During deposition the substrate is already heated enhancing the inter diffusion of metal ions, which are in close contact, therefore no heat treatment or low annealing temperatures is needed for alloying. While sputtering an alloy film from a corresponding target, in the beginning there is a tendency to eject one atomic species in excess of the other species. But after sometime, the atoms are ejected in the same ratio as the original ratio in the target. The time required for this process is called the equilibration time (Jayaraman and Lin, 1995). Jayaraman and Lin (1995) observed that substrate temperature strongly affected the membrane gas tightness. Increasing the substrate temperature provided energy to the arriving metal atoms to orient in a certain lattice position on the growing film. Zhao et al. (2000) made similar studies on the influence of the substrate temperature on the compactness of the Pd-Ag membranes. The columnar structures of the Pd-Ag alloy films were gradually modified and disappeared when the substrate temperature was higher than 350°C. At low substrate temperatures, higher points on a growing surface received more vapor atoms than valleys, resulted in a columnar structure, i.e. shadow effect. With increasing substrate temperature diffusion of metal atoms became increasingly stronger leading to more compact Pd-Ag alloy composite membranes.
Target/substrate separation, equilibration time, substrate temperature, target current and coating pressure are some of the factors affecting the deposition rate, composition and microstructure of the thin films.

Athayde et al. (1994), sputtered Pd$_{76}$Ag$_{24}$ on micro-porous polymer supports that were coated with a suitable polymer (dimethylsiloxane). The pore free and smooth substrate did not offer any resistance to gas permeation. Membranes from 2.5 to 10 µm thick alloy layer were obtained by controlling the sputtering time.

Tosti et al. (2002), sputtered 5µm Pd-Ag layer on a ceramic support (pore size 0.5 µm). Despite the large thickness, complete selectivity was not attained. O’Brien et al. (2001) prepared Pd-Ag membranes with different sputtering bias and found that membranes sputtered at higher bias were more gas-tight, indicating denser coatings and fewer or smaller pinholes. On the other hand, a large variation in Ag content was observed with higher bias. Due to the thermal stress, cycling and H$_2$ embrittlement, the coatings peeled from the substrate. The separation factor was between 4 and 20 only.

Xomeritakis and Lin (1997) synthesized Pd-Ag membranes (0.4 µm thick) on assymetric ceramic supports (pore size 3 nm). The H$_2$ permeability and the activation energy for permeation was found to be 0.8-1.6x10$^{-6}$ m$^3$/m(²(atm$^{0.5}$)) and 28-32 kJ/mol, respectively. Very similar results were also reported by Jayaraman et al. (1995).

Recently, Gielens et al. (2002) co-sputtered a 750 nm dense layer of Pd$_{77}$Ag$_{23}$ on non-porous silicon nitride. After sputtering 0.5µm openings were created on the silicon nitride layer by etching. With 0.2 bar hydrogen partial pressure in the feed the hydrogen flux was 0.16-7.7 x 10$^{-3}$ m$^3$/m$^2$h at 350 and 450°C. The H$_2$/He selectivity was above 1500.
The vacuum thermal evaporation includes heating a material under vacuum to a temperature where a large number of atoms or molecules leave the surface of the material and deposit on a substrate by condensation. The main parameters that control the growth and structure of evaporated films are the type of the substrate, substrate and evaporation temperature, the angle of incidence of evaporant, and contamination. In thermal evaporation techniques the average energy of vapor atoms reaching the substrate surface is generally low which seriously affects the morphology of the films, often resulting in a porous and little adherent material. With respect to sputtering, evaporation results in larger grains and poorer adhesion.

Peachey et al. (1996), sputtered 1 µm of Pd on each side of tantalum sheet (13 µm). The H$_2$ permeability of this membrane was 162x10$^{-6}$ m$^3$/m$^2$/atm$^{0.5}$. Basile et al. (1996) compared three Pd-Ag membranes deposited on alumina tubes by three different techniques. When sputtering or evaporation was used for deposition on the outer surface of ceramic membranes, porous composite membranes with lots of pinholes were formed. On the other hand, co-condensation technique was used to completely cover the inner surface of ceramic tubular membranes with a uniform 0.1µm thick Pd layer; however, the stability appeared to be limited.

2.3.2 Chemical Vapor Deposition

In the chemical vapor deposition (CVD) process, the deposits are produced by a vapor-phase chemical reaction at a controlled temperature. Gaseous compounds of the materials to be deposited are transported to a substrate surface where a thermal reaction/deposition occurs. Reaction byproducts are then exhausted out of the system.
The CVD process has the advantage of depositing metallic or dielectric coatings of low and high temperature melting materials and it is very easy to control the thickness in submicron scales. On the other hand, it is difficult to deposit alloys and it requires very high purity and strict deposition conditions, making it a very uneconomical process.

Xomeritakis and Lin (1996) prepared thin and fairly gas-tight Pd membranes inside pores of a supported γ-alumina membrane by counter-diffusion CVD with PdCl₂ as precursor. On the other hand, the selectivity was fairly low due to the difficulties in sealing the ceramic substrate. They suggested that the selectivity would roughly equal to the permeance reduction ratio of the non-diffusing gas before and after CVD, which was in the range of 100-1000.

Huang et al. (1997) synthesized Pd films on top of γ-alumina coated porous α-alumina, by reducing PdCl₂ with hydrogen in a hot-wall CVD reactor. The same group prepared catalytic Pd-dispersed Al₂O₃ membranes by wet-impregnation technique (Chen et al., 2003). Wunder et al. (2002) used MOCVD to deposit finely dispersed Pd catalyst on the inner and outer surface of the γ-alumina coated porous α-alumina for hydrogenation reactions.

Jun and Lee (2000) prepared Pd and Pd-Ni membranes on γ-alumina/α-alumina and Ni/PSS support by metal organic chemical vapor deposition MOCVD. The H₂ permeabilities of Pd/Ni/PSS (1-2 μm Pd layer) and of Pd/Al₂O₃ (2 μm Pd layer) were 109-282x10⁻⁶ m³ m/(m² hatm) and 82x10⁻⁶ m³ m/(m² hatm) at 500°C, respectively. The H₂/N₂ selectivities of the membranes were 1600 and 1000. The membranes prepared on Ni/PSS showed continuous hydrogen flux reduction at 500°C due to the intermetallic
diffusion. For the alumina disks, the tests failed due to the thermal instability and sealing problems.

Kajiwara et al. (2000) deposited 3.5 µm platinum on alumina (200nm pore size). The selectivity of the membrane was 198 at 500°C. Uemiy et al. (1997) compared Pd, Ru and Pt membranes prepared by CVD and electroless plating on alumina support (200nm pore size). In the case of CVD, the penetration of the metals inside the pores was larger. Even though the pores were not completely blocked, the CVD membranes, especially platinum exhibited much higher hydrogen permeability than that of the dense electroless plated membranes. Therefore, they concluded that the permeation mechanism was different for membranes prepared by CVD and electroless plating.

Palladium-silver alloy films on quartz substrate were prepared by Lu and Lin (2000) by a hot-wall MOCVD, using a mixed inlet stream of palladium acetate and silver acetate vapors. The Ag content of the film was found to be decreasing from the surface into the film. The film resulted in two solid solutions of Pd-Ag with different compositions.

Jun and Lee (1999) synthesized Pd membranes inside the pores of stainless steel by wet impregnation technique. An organometallic precursor, Pd(C3H3)(C5H5), was reacted with hydrogen at room temperature to decompose into Pd crystallites. The H2 permeability was 282x10^-6 m^3/m^2 atm with a H2/N2 selectivity of 1600 at 450°C.

2.3.3 Electrodeposition

In electroplating, the electrodeposition of an adherent metallic coating takes place on a metallic coating electrode. Because of the electric field between the electrodes, metallic ions in the solution migrate to the cathode where they are neutralized and
included into the metal lattice. The film is affected by several parameters, such as current density, temperature of the electrolyte, migration and diffusion velocity of ions, specific weight of ions, geometric form of cathode (distribution of current lines), and the bath composition.

Nam et al. (1999) fabricated pinhole free Pd-Ni alloy membranes on Cu/Ni/PSS by electrodeposition combined with vacuum. Two membranes were prepared, first with no vacuum and second with vacuum. The resulting film thicknesses were 5 and 1µm, respectively. The H₂ permeance for the later one was between 16.4-155x10⁻⁶ m³m/(m²hatm) for temperatures of 450-550°C for a membrane containing 22 wt% Ni. The H₂/N₂ selectivity of the membrane was 500-5000. They did not report any stability data.

Pd-Cu alloy membrane was fabricated on modified PSS with intermediate silica as a diffusion barrier layer by vacuum electrodeposition (Nam and Lee, 2001). The alloy film was formed by sequential deposition of several layers of Pd and Cu followed by annealing. The resulting membrane was 2µm thick and had 37% Cu by weight. The H₂ permeance was 130x10⁻⁶ m³m/(m²hatm) and H₂/N₂ selectivity was above 70000 at 450°C. There were no decreased performance after 18 times cycling between H₂ and N₂ gas at 450°C.

Bryden and Ying (1997) used pulsed electrodeposition to prepare nano structured Pd-Fe alloys. Pyun et al. (1997) studied the hydrogen diffusion through Pd-40 at.% Au alloy electrodeposited on Pd electrode.

2.3.4 Electroless Deposition
Electroless deposition is a technique based on the controlled autocatalytic reduction of a dissolved metallic salt by reducing agents at a substrate interface. Among other techniques, electroless deposition provides strong advantages such as uniformity of deposits even on very complex shapes, very simple equipment and low cost. Not like electrodeposition, non-conductive surfaces as well as conductive surfaces can be coated easily by using electroless deposition. The deposit follows exactly all the contours of the work-piece without build-up at edges or corners.

Electroless plating is possibly the simplest means of composite membrane fabrication, although support quality, surface activation methods, electroless plating procedures and bath chemistry influence membrane selectivity, permeability and Pd/Pd-alloy film stability. Therefore electroless plating will be discussed in the following three sections; surface activation, bath chemistry and electroless plating procedures.

**2.3.4.1 Surface Activation**

Shu et al. (1993) showed that most of the substrates, including plastic and metals, needed a long induction period to start the deposition of Pd species, since they are not active enough to initiate the oxidation of the reducing agent. Therefore a pre-seeding procedure of the substrate with finely divided Pd nuclei prior to Pd deposition, so-called activation process was used by Uemiya et al. (1990). Just a short induction time was required when activated substrate was used (Shu et al., 1993). This traditional activation process consists of successive dipping of the substrate in acidic solutions of Sn\(^{+2}\) and Pd\(^{+2}\) salts respectively with gentle rinsing in de-ionized water between two baths. Sn\(^{+2}\) is absorbed on the substrate surface in hydrolytic form (sensitization step) and replaced by
Pd$^0$ through the process described by Equation 1 (catalysation step). This procedure is repeated several times to produce enough Pd particles for further deposition of palladium.

$$\text{Sn}^{2+} + \text{Pd}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pd}^0 \quad (2.1)$$

Shu et al. (1993) reported that uniform Pd particles with small amount of tin, about 500°A in diameter, were seeded on the substrate surface after the activation process. Having very small sizes and large surface areas, the Pd nuclei seeded on the surface are more active compared to the deposited Pd clusters. Therefore the activation step is repeated when the activity of the surface is depleted, e.g. after 6-8 hours of electroless plating on PSS.

Meenan et al. (1994) characterized the sensitization and activation steps by detailed XPS study and found that the Pd(0) centers were covered with a mixture of Sn(II) an Sn(IV) compounds, reducing their function as catalytic sites. They reported that residual amounts of stannic acid (Sn(OH)$_4$) and SnO formed on the metallic Pd$_x$Sn$_y$ alloy core. An acid or an alkaline accelerator solution, e.g. NaOH, HCl, H$_2$SO$_4$, NH$_4$OH, NH$_4$BF$_4$, right after activation step was added to remove tin salts and to leave active catalytic sites intact. The XPS results showed that the accelerator solution dissolved away some, but not all of the tin oxide, hydroxides. They proposed that less tin compound was removed on acceleration with rough surfaces than with smooth surfaces, due to the enhanced absorption on rough surfaces. Using transmission electron microscopy (TEM) and associated diffraction patterns, Feldstein et al. (1974) had also shown that the product was amorphous after catalysis but after the acceleration step, it was face centered cubic (fcc) with lattice parameters closely matching those of Pd$_3$Sn.
Later, Shukla et al. (2001) also made a similar XPS studies on the activation process of fly-ash cenosphere particles. They found SnCl$_2$, PdCl$_2$ and Pd(0) on the surface after catalysis step, and Sn(OH)$_4$, PdO, PdCl$_2$ and Pd(0) after DI water cleaning. However, Sn(OH)$_4$ and PdCl$_2$ were not detected after deposition in alkaline Cu plating solution.

Zhao et al. (1995), Touyeras et al. (2003) and Hihn et al. (2001) studied the influence of ultrasound and bubbling on the conventional activation step and during the initial stages of electroless Cu coatings. They showed that the mass transfer coefficient, thus the plating rate, increased continuously with transmitted power increase. When applied during the very first minutes of plating, ultrasound had a significant effect on the plating rate, whereas, no further changes were observed when applied only at the end of plating. This confirmed that the very first layers were influenced by the catalyst activity. Various tin II complexes or agglomerates of colloidal palladium were removed from the surface by agitation, leading to a greater catalyst specific area and efficiency. In addition to that, the trapping of the produced gases on the surface, which reduced the contact area of the plating solution and the substrate, was also minimized with ultrasound. Microhardness, adhesion strength, Cu-substrate bonding and resistance to welding destruction were improved.

The quality of the activated substrates, including the surface roughness, the amount, size and distribution of Pd particles has a strong effect on the quality of palladium composite membranes. The presence of tin compounds with a low melting point between the layers of metal film can cause the formation of pinholes and cracks due to melting and decomposition of the impurities at higher temperatures, thus affecting the
long term stability of the membranes. Paglieri et al. (1999) compared the long term stability of membranes prepared by using the conventional activation process and membranes activated with a new, tin free activation process. The new technique consisted of dip coating of substrates by Pd(O₂CCH₃)₂, calcination and reduction to metallic Pd in H₂ atmosphere. The membranes activated with the new method were more stable than those activated with the conventional procedure.

Li et al. (1996) and Zhao et al. (1998) avoided Sn-Pd activation all together by using a sol-gel technique in which Pd-modified boehmite sol was deposited on the surface of porous alumina, follow by calcination at 550°C and treatment with hydrogen at 400°C to reduce Pd on the surface. The sol-gel activated surface had a smoother surface and a more uniform distribution of palladium seeds compared to Sn-Pd activated substrate.

Zhang et al. (1997) used laser and ultraviolet light to decompose Pd acetate on various substrates for microcircuit fabrication. Kelly et al. (1998) deposited metal from its metal salt (palladium) or organometallic coating under exposure to an excimer lamp. Atomic force microscopy (AFM) studies revealed that the activation layer morphology and initial nucleation were influenced by the substrate roughness. Both the diameter range and average height of the Pd particles increased with higher surface roughness.

Xu et al. (2000) reported a new activation technique called photocatalytic deposition (PCD). During this process, under irradiation by UV light, electron hole pairs appeared on the porous titania ceramic substrate (2-3 nm pore size) and palladium was reduced on the surface. The thickness of the resulting membrane was about 0.3-0.4 µm.
They reported a permeability and a separation factor of $20.3 \times 10^{-6} \, \text{m}^3\text{m}/(\text{m}^2\text{atm})$ and 1140 at 500°C, respectively.

Shukla et al. (2002) recently replaced the conventional PdCl$_2$ activator with silver nitrate to reduce the overall cost of the coating process of electroless coating of cenospheres.

2.3.4.2 Bath Chemistry

The electroless plating solution generally consists of a metallic salt, a complexing agent, a reducing agent, and a stabilizing agent. Electroless plating process occurs on the solid liquid interface between support and the plating solution. It involves reduction of a metal salt on a catalytic surface. It is similar to electropolating except that a flow of electrons is not supplied by an external source. The reaction is initiated by the oxidation of reducing agent in the plating solution with simultaneous release of electrons, which reduce the metal ions on the target surface. The deposited metal catalyses the further oxidation-reduction process resulting in a uniform film on the surface, referred to as an autocatalytic reaction. An activation of the support prior to plating is necessary to initiate this autocatalytic plating process. The activation procedure will be discussed more in detail in the next section.

V, Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt and Au are some of the metals that can be plated autocatalytically. Several reductants are available for the electroless plating process, dialkyl amine bornae, borohydride, hypophosphite, formaldehyde and hydrazine. Hypophosphite is commonly used, but deposits contain phosphorus, reducing the quality of the film. Formaldehyde is not a good reducing agent, especially in the case of Pd deposition since H$_2$ gas is released during plating and cracking the membrane. Also the
reducing effect of formaldehyde is low (Ohno et al., 1985). Hydrazine is the most commonly used reducing agent.

Among several Pd metal sources, \( \text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2 \), \( \text{PdCl}_2 \), \( \text{Pd}(\text{NH}_3)_4\text{Cl}_2 \), and \( \text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2 \) were found to be the best salts to achieve high conversions. The Pd salt is stabilized by EDTA in the pH range 9-11. Hydrazine to Pd molar ratio 0.72/1, EDTA to Pd ratio 30-40/1 and pH of 11 gave 95% Pd conversion (Keuler et al., 1997).

The structural evolution of the palladium film during electroless plating, i.e. grain size, cluster size, compactness and morphology, which have significant influences on the performance of membranes, are very dependent on the bath chemistry and plating rate.

Up to now, hydrazine is the most common and suitable reducer for electroless plating of palladium. Cheng and Yeung (2001) compared the morphologies of the Pd membranes prepared from hydrazine-based and hypophosphite-based plating solutions. The hypophosphite bath had a slower but constant plating rate, providing better efficiency than the hydrazine based plating bath. However, the oxidation of hypophosphite produced hydrogen gas, leading to \( \beta \)-hydride phase at low temperatures and caused delamination of the Pd membrane. Therefore, chemical reducers that generated hydrogen were not suitable for Pd plating.

Yeung et al. (1999) developed a mathematical model to predict the rate and film thickness as a function of plating parameters for hydrazine based plating baths. With both higher palladium and higher hydrazine concentrations, the plating rate increased and resulted in larger Pd clusters. However, hydrazine was the limiting reactant. The SEM analysis showed that the cluster size varied along the thickness of the membrane as the plating rate changed during the reaction. Hydrogen permeance of a Pd membrane at
350°C were compared after step-wise annealing at three different temperatures, 350, 450, 550°C, respectively. The membrane showed a significant increase in permeance and selectivity due to enhanced sintering of Pd clusters and hydride phase formation. Similar kind of phenomena was also observed on Pd/ceramic membranes prepared by Collins and Way (1993).

The effect of the deposition rate of palladium on the compactness of palladium deposits was studied by Zhao et al. (1998). The Pd particle size decreased as the concentration of hydrazine increased. The palladium membranes composed of finer palladium particles produced at higher deposition rate of palladium were more compact.

Iliuta et al. (2003) studied the effect of metal concentration on the densification properties of the deposited film. Fast deposition from concentrated Pd solution, lead to a rapid film formation with small clusters topping the support surface. Depositions from dilute solutions lead to more efficient in depth incursions of Pd into the pores. However, large clusters made the membranes non-impervious to other gases.

Pure films can also be deposited from baths containing more than one precursor depending on the plating parameters. Chou et al. (1992) showed that Pd film microstructure could be significantly altered through addition of foreign metals such as boron to the electroless plating bath. Cheng and Young (1999) prepared pure silver membranes from plating baths containing an excess amount of ammonium hydroxide. Pure Pd membranes were obtained from plating solutions with low concentration of ammonium hydroxide and a large amount of hydrazine. The microstructures of pure Pd membranes from mixed Pd-Ag solution were very different from pure Pd plating baths.

2.3.4.3 Electroless Pd Plating Procedure
As described above, the traditional technique for preparing Pd composite membranes by means of electroless plating consists of two steps; activation of the support and plating. After activation, the supports are immersed in the plating solution. During the plating process, metal and the reducing agents in the solutions are depleted and require replacement to continue the processing. The supports are plated until the activity of the supports diminishes. The supports are reactivated for further plating. These steps are repeated until the pores on the support are fully covered with Pd and the membrane becomes gastight. Agglomerates of crystals combine to form Pd clusters on the surface (Mardilovich et al., 1998).

Many factors including the support quality, activation process and the bath chemistry, contribute to the thickness, stability and selectivity of the membranes. In addition, researchers also tried to modify the plating procedures to make thinner membranes.

Zhao et al. (1998) used vacuum-filtration during the deposition of palladium. Two kinds of Pd membranes were prepared on alumina supports, one with vacuum filtration, one without vacuum filtration. There were no texture differences on the deposited layers; however, the one prepared by vacuum became gastight easily. On the other hand, the membranes prepared by this method suffered from peeling off when annealed in inert atmosphere, which was related to the relaxation of the stresses developed during the deposition.

Uemiya et al. (2003) improved the plating rate of palladium by immersing the support into hydrazine solution prior to plating. The final thicknesses of the membranes
were almost the same but the plating time was much shorter in the case of supports pretreated with hydrazine.

Li et al. (1998) synthesized 10 µm Pd/PSS membranes by electroless plating combined with osmosis. NaCl solution was used. The membrane had H₂/N₂ selectivity higher than 1000 for temperatures above 400°C, and a permeability of 175x10⁻⁶ m³/m²/(m²h atm⁰.⁵) at 480°C. The same group used the same technique to repair Pd/α-Al₂O₃ membranes that contained defects prepared by the conventional electroless plating (Li et al., 1999; Li et al., 2000). The H₂/N₂ separation factor increased from 10 to 1000 by just adding 2 µm Pd layer.

Souleimanova et al. (2001) combined electroless plating with osmosis to effectively enhance the deposition inside the pores therefore, reduce the thickness of the membrane. The osmotic effect was generated by using aqueous sucrose solution. Vycor glass was used as a support to serve as a semi-permeable medium between sucrose and plating solution, i.e. its pore size is large enough for diffusion of water molecules, but too small for sucrose permeation. The thickness of the membranes decreased from 8 µm (regular plating) to 3 µm (plating with osmosis). Also films of finer Pd clusters and more uniform microstructures were synthesized by the use of osmosis. The membranes with smaller Pd particles exhibited higher permeabilities with lower activation energies due to the enhanced diffusion.

Itoh et al. (2000) developed a method of preparing a palladium-filled composite membrane tube using an anodic aluminum oxide tube with perforated straight pores by combining sputter and electroplating technique. A thin Pd layer was sputtered on the outer surface to provide electro-conductivity for the electroplating. Electroplating was
applied with the sputtered metal layer connected to the cathode of a direct current power and a platinum wire placed at the center inside the tube. A thin rod of palladium of several micrometers was found to be densely packed inside each pore of the anodic alumina layer. The selectivity was 1640 at 350°C.

Zheng and Wu (2000) prepared Pd/α-Al₂O₃ membranes under hydrothermal conditions. The bubble point method, which allows the detection of the available pores that are connected from one side of the membrane to the other, was used to compare the pore size shrinkage for the conventional and hydrothermal methods. The pore size decreased from 0.8 to 0.36 µm when Pd was deposited hydrothermally, whereas, the pore size of the Pd layer was 0.55 µm after regular electroless plating. They claimed that the increase in the systemic pressure forced the plating solution penetrate more deeply inside the pores yielding better pore size shrinkage.

2.4 Pd Alloy Composite Membranes

One way to reduce the hydrogen embrittlement is to alloy Pd with other metals. Among several alloying elements such as Cu, Au, Ag, Y, Ru, Pt and Ni, Pd-Ag system is the most studied alloy up to now.

2.4.1 Pd-Ag Composite Membranes

In 1956, Hunter first reported that silver addition to palladium could suppress the α-β transition. He showed that Pd alloys containing more than 20 wt% silver did not show any hydrogen embrittlement. XRD measurements showed that the dimensions of the unit cell of palladium silver alloy lattice expanded from 3.92 to 3.96°A, upon saturation with hydrogen. Under the same conditions the dimensions of the unit cell in the pure palladium lattice changed from 3.89 to 4.02°A.
Figure 2.3 shows the equilibrium isotherms of Pd-Ag alloys at 50°C taken from Brodowsky (1972). It can be seen that alloys with silver content higher than 30 wt% do not have a plateau in pressure, indicating the reduction of the miscibility gap of the α and β phases. Recently, Fazle and Sakamoto (2000) also showed that the pressure of the plateau for Pd-Ag-H system and the miscibility gap value decreased when Ag content was increased from 5 to 10 wt%.

Besides being mechanically stable, Pd-Ag membranes have a higher permeability when compared to pure Pd membranes. The solubility of hydrogen in the Pd-Ag system increases incredibly at 30 wt% silver. (Sievert 1915, 1935). The diffusion coefficient, on the other hand, decreases upon alloying (Holleck 1970). As a matter of fact the permeability which is the product of diffusivity and solubility reaches a maximum around 23 wt% Ag.

Figure 2.3 Equilibrium Isotherms of Pd-Ag-H System at 50°C (Brodowsky, 1972)
Several authors used sputtering or CVD to deposit Pd-Ag alloys as described in sections 2.3.1 and 2.3.2. In general the alloys prepared by these techniques suffered from low selectivities and very low permeabilities, even tough very thin alloy layers can be achieved. This was possibly due to the support resistance to permeation with very fine pore sizes which are preferred for these techniques.

Table 2.1 and 2.2 summarizes the performance of Pd and Pd-Ag membranes, including the pore size of the support, the final thickness of the membranes, $\text{H}_2$ permeability, activation energy of permeance and selectivity.
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
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<td>Ceramic</td>
<td>EP</td>
<td>0.2</td>
<td>4.5</td>
<td>166</td>
<td>400</td>
<td>∞</td>
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<td>Glass</td>
<td>EP</td>
<td>0.3</td>
<td>13</td>
<td>266</td>
<td>500</td>
<td>-</td>
<td>10.7</td>
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<td>Yan et al. (1994)</td>
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<td>CVD</td>
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<td>500</td>
<td>1000</td>
<td>-</td>
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<td>Jemaa et al. (1996)</td>
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<td>EP</td>
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<td>6</td>
<td>28.08</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Knapton (1977)</td>
<td>Pd Foil</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>366</td>
<td>350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Xomeritakis and Lin (1997)</td>
<td>Ceramic</td>
<td>MOCVD</td>
<td>0.003-0.006</td>
<td>1</td>
<td>0.8-1.6</td>
<td>300</td>
<td>200</td>
<td>23.8</td>
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<td>Mardilovich et al. (1998)</td>
<td>PSS</td>
<td>EP</td>
<td>0.1</td>
<td>20</td>
<td>160</td>
<td>350</td>
<td>5000</td>
<td>-</td>
</tr>
<tr>
<td>Li et al. (1998)</td>
<td>PSS</td>
<td>EP&amp;Osmosis</td>
<td>0.2</td>
<td>10</td>
<td>175</td>
<td>480</td>
<td>&gt;1000</td>
<td>-</td>
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<tr>
<td>Zhao et al. (1998)</td>
<td>Alumina</td>
<td>EP</td>
<td>-</td>
<td>87</td>
<td></td>
<td>450</td>
<td>23</td>
<td>-</td>
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<tr>
<td>Li et al. (2000)</td>
<td>Ceramic</td>
<td>EP&amp;Osmosis</td>
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<td>10.3</td>
<td>946</td>
<td>467</td>
<td>&gt;1000</td>
<td>12.3</td>
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<tr>
<td>Jun and Lee (2000)</td>
<td>Ni/PSS</td>
<td>Wet Dipping</td>
<td>0.05</td>
<td>2</td>
<td>282</td>
<td>450</td>
<td>1600</td>
<td>5</td>
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<tr>
<td>Souleimanova et al. (2002)</td>
<td>PSS</td>
<td>EP&amp;Osmosis</td>
<td>0.1</td>
<td>8</td>
<td>100</td>
<td>300</td>
<td>100000</td>
<td>-</td>
</tr>
<tr>
<td>Souleimanova et al. (2002)</td>
<td>PSS</td>
<td>EP</td>
<td>0.2</td>
<td>18</td>
<td>85</td>
<td>300</td>
<td>100000</td>
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<td>------------------------------</td>
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</tr>
<tr>
<td>Uemiya et al. (1991)</td>
<td>Glass</td>
<td>EP (Coat&amp;Dif)</td>
<td>0.3</td>
<td>21.6</td>
<td>7</td>
<td>500</td>
<td>159</td>
<td>400</td>
</tr>
<tr>
<td>Uemiya et al. (1991)</td>
<td>Ceramic</td>
<td>EP (Coat&amp;Dif)</td>
<td>0.2</td>
<td>5</td>
<td>11</td>
<td>900</td>
<td>235</td>
<td>400</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5.3</td>
<td>18</td>
<td>900</td>
<td>280</td>
<td>400</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5.8</td>
<td>23</td>
<td>900</td>
<td>310</td>
<td>400</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>5.9</td>
<td>26</td>
<td>900</td>
<td>255</td>
<td>400</td>
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<td>6.4</td>
<td>31</td>
<td>900</td>
<td>222</td>
<td>400</td>
</tr>
<tr>
<td>Jayaraman an Lin (1995)</td>
<td>Alumina</td>
<td>Sputter</td>
<td>0.003</td>
<td>0.5</td>
<td>23</td>
<td>-</td>
<td>1</td>
<td>250</td>
</tr>
<tr>
<td>Xomeritakis and Lin (1997)</td>
<td>Alumina</td>
<td>Sputter</td>
<td>0.003</td>
<td>0.4</td>
<td>25</td>
<td>-</td>
<td>0.8-1.6</td>
<td>300</td>
</tr>
<tr>
<td>Cheng and Yeung (1999)</td>
<td>Glass</td>
<td>EP (coplating)</td>
<td>0.005</td>
<td>1.2</td>
<td>12.5</td>
<td>500</td>
<td>3</td>
<td>500</td>
</tr>
<tr>
<td>Iliuta et al. (2003)</td>
<td>PSS</td>
<td>EP (Coat&amp;Dif)</td>
<td>0.2</td>
<td>20</td>
<td>28-33</td>
<td>500</td>
<td>227</td>
<td>500</td>
</tr>
</tbody>
</table>
The rest of this section, Pd-Ag alloys formed by electroless plating will be discussed. There are two possible ways to form alloys upon electroless plating: coating and diffusion method and co-plating.

2.4.1.1 Coating and Diffusion Method

Coating and diffusion treatment consists of deposition of two films sequentially followed by inter-diffusion at high temperatures. The bulk composition can be very precisely controlled by using this method. However, the homogeneity of the film, therefore permeability, strongly depends on the annealing conditions as well as the thickness and composition of the layers.

Uemiya et al. (1991), prepared a 21.6 \( \mu m \) Pd-Ag layer, 7 % Ag by weight, on a porous glass (PG) support (300 nm pore size). After heat treatment at 500°C for 12 hours, the \( H_2 \) permeability at 400°C and the activation energy of the Pd-Ag film were found to be, respectively. On the other hand, for a 10.3 \( \mu m \) thick Pd/PG membrane, they reported an activation energy of 10.7 kJ/mol and permeability of 159x10\(^{-6}\) m\(^3\)/m\(^2\)h atm\(^{0.5}\) which was higher than that of pure Pd. The membrane had a hydrogen permeability of 213x10\(^{-6}\) m\(^3\)/m\(^2\)h atm\(^{0.5}\). The lower hydrogen flux with higher activation energy was attributed to the silver-rich alloy layer in the film. The cross-sectional depth of the film showed double layers of Pd and Pd-Ag alloy. The slow diffusion of metals across the interface between the two layers resulted in a compositional gradient across the membrane and therefore reduced the permeability.

Later, the same group used porous alumina tubes (200nm pore size) that can stand higher annealing temperatures. Annealing was done at 900°C for 12 hours. Two membranes that contained 23 wt% Ag were annealed at different temperatures to see the
The effect of temperature on complete alloy formation, thus permeability. The membranes treated at 900°C, exhibited a 2.7 times greater rate of hydrogen permeation than the ones treated at 500°C. The high hydrogen permeability was attributed to the formation of a complete miscible single phase palladium-silver alloy. On the other hand, they showed that among several Pd-Ag alloys, the one that contained 23 % Ag by weight had the highest permeability, $310 \times 10^{-6} \text{ m}^3\text{/m}^2\text{hatm}^{0.5}$, which was 1.9 times that of pure Pd.

Shu et al. (1996) prepared Pd-Ag/PSS membranes. The membranes consisted of 2 µm Ag layer on top of 14.3 µm Pd layer. After annealing at 500°C for 5 hours under H$_2$ atmosphere, a non-homogeneous alloy layer with a rich silver content on the top surface was formed. A titanium nitride diffusion barrier between the PSS and the Pd-Ag layer was introduced for higher annealing temperatures. The Auger electron depth profile indicated uniform alloy formation at 700°C. However, no permeation or stability data were reported.

Keuler et al. (1999) investigated the effect of the palladium and silver deposition sequence on coating adhesion and metal distribution in the metal matrix after heating. Palladium-silver multi layers were prepared by either first depositing palladium then silver or by first depositing silver then palladium on γ-alumina. Heat treatment was done in hydrogen atmosphere at 650°C for 6 hours. When silver was first deposited, the palladium to silver ratio across the thickness of the film remained constant and a small amount of alloy penetrated inside the pores. On the other hand, when palladium was deposited first, the alloy penetrated inside the pores and the alloy composition was not homogeneous across the film thickness.
Keuler and Lorenzen (2002) synthesized Pd-Ag membranes by successive deposition of Pd and Ag, respectively, on the inside of the alumina tube (200nm pore size). The thicknesses of the membranes were between 1.4-2.13 \( \mu \)m (20-25 wt.% Ag). A pure Pd membrane and a Pd-Ag membrane of similar thicknesses were tested from 330 to 450°C. The \( \text{H}_2 \) permeance for the Pd-Ag membrane was three times lower than that of pure Pd which confirmed that separate layers of Ag could result in very poor permeance. They also developed a heating procedure with an intermediate oxidation step.

Iliuta et al. (2003) prepared 20 \( \mu \)m thick Pd-Ag membranes on PSS by coating and diffusion technique. The membrane had around 30 wt% Ag. They reported \( \text{H}_2 \) permeability values as high as \( 227 \times 10^{-6} \) and \( 315 \times 10^{-6} \text{m}^3\text{m}/(\text{m}^2\text{h} \text{atm}^{0.5}) \) at 500 and 700°C, respectively. The activation energy of this membrane was 16.8 kJ/mol. On the other hand, no stability or selectivity data were reported.

The preparation of homogeneous miscible Pd-Ag alloy films by coating and diffusion method requires high temperatures. On the other hand, the alloying temperature is limited by the collapse of the pore structure in case of glass supports or by intermetallic diffusion of elements from the PSS support to the membrane layer. Ceramic supports are the most suitable substrates for application of this method, however, difficulties existed with ceramic supports as discussed previously.

A good alternative for alloy formation is the co-deposition of two metals from the same bath simultaneously. One advantage of this technique is that lower temperatures can be used to anneal submicron Pd-Ag particles to form a homogeneous layer.
2.4.1.2 Co-deposition

Electroless co-deposition of metals is a complex process. The total metal concentration, the amount of Ag content, the amount of hydrazine, temperature of the plating bath, the substrate roughness and quality are some of the critical factors that affect the deposition properties. The control of the composition on the surface and formation of a uniform defect-free dense alloy membrane are hindered by the sensitivity of the plating bath and different plating behaviors of the two metals.

Co-deposition behavior of palladium and silver on PSS was first investigated by Shu et al. (1993). EDX and XRD analysis were performed to determine the composition of the deposited layer as a function of Ag content of the plating bath, keeping the same total metal concentration. The baths containing more than 20 at.% of Ag, resulted in the preferential deposition of silver, which passivated further Pd deposition. An effective activation of the substrate with Pd pre-deposition was developed to reduce the Ag enrichment of the support. A silver precursor was then introduced into the Pd plating bath at a later stage of the plating. Although the technique increased the Pd content of the film, the bath having 83.4% Pd to 16.6% Ag still gave a deposit with a dominant Ag phase. The co-deposited Pd and Ag were in separate phases. Annealing in H2 atmosphere at 400°C for 150 minutes lead to bi-layered membrane with a fcc Pd-Ag alloy phase and a small Pd residual phase. No permeation data or thickness were reported.

Later, Cheng and Yeung (1999) investigated the plating kinetics, film microstructure and composition during co-deposition of Pd and Ag on vycor glass and developed a mathematical model to estimate the plating rate, thickness, and composition of the layer as functions of reaction time and concentrations of the reacting species.
Plating solutions with higher hydrazine to metal ratios yielded membranes with higher palladium content. Increasing the plating temperature also lead to higher palladium composition. The average plating rate decreased with the higher Ag content confirming that the presence of silver inhibited the Pd deposition. The ratio of the initial plating rates of components yielded membranes with widely varying compositions from pure silver to pure palladium. Membranes about the same composition as the starting plating solution with a moderate composition gradient across the membrane thickness were prepared when the initial plating rate of palladium was about 2-3 times higher than that of silver. They prepared 1.2 \( \mu \)m thick 12.5 wt.% Ag membranes on vycor glass that has an average pore size of 5 nm. Single phase alloy was obtained after annealing at 500°C for 8 hours. The hydrogen flux through the Pd-Ag membrane was about 1.4-1.7 times higher than that of pure palladium. On the other hand, they report that permeability was around \( 3 \cdot 10^{-6} \) \( m^3 \cdot m/(m^2 \cdot h \cdot atm^{0.5}) \) at 500°C, which is very low mainly due to the high support resistance.

Huang et al. (2003) compared the influence of various supports on the plating rate of the Pd-Ag layer. The thickness of the film on the \( \alpha \)-Al\(_2\)O\(_3\) support (mean pore size of 95.9 nm) and the supported \( \gamma \)-Al\(_2\)O\(_3\) support (mean pore size of 8.6 nm) after 1 hour plating were 2 and 3.5 \( \mu \)m, respectively. The deposition rate increased with the number of Pd sites in the activation procedure. By applying Pd-pre deposition prior to co-plating, 20 \( \mu \)m Pd\(_{90}\)Ag\(_{10}\) film was deposited on an \( \alpha \)-Al\(_2\)O\(_3\) support in 8 hours. The selectivity factor of this membrane was 30-178 for temperatures of 200-343°C, which was very low, compared to pure Pd films of same thickness.

Most recently, Chen et al. (2003) used mixed potential theory to explain the deposition behavior of Pd and Ag during plating. The deposition rates of Pd and Ag
obtained from polarization curves followed the order as Ag/Pd > Pd/Pd > Ag/Ag. This also inferred that Ag was preferentially deposited both on Pd and on Ag sites. The difference in the deposition rates lead to the growth of dendritic structures with higher silver content than that in the plating solution. As the total metal concentration and silver content increased, the deposited layer was more dendritic and therefore more porous. No dense membrane was reported.

2.4.2 Pd-Cu Composite Membranes

Pd-Cu alloys are advantageous due to their high resistance to sulfur contamination. The permeability of Pd-Cu passes through a maximum around 40wt.% Cu (McKinley, 1967). The permeability at this composition, however, is only 1.1 times that of pure Pd.

Uemiya et al. (1991), prepared Pd-6 wt.% Cu alloy membranes on porous glass. The membrane had high selectivity at 200°C. The permeability of this membrane however, was lower than that of Pd-7 wt.% Ag and that of pure Pd. The reason for the low permeability might be due low concentration of Cu in the membrane layer.

Nam and Lee (2001) synthesized Pd-Cu alloy membrane on modified PSS with intermediate silica layer by vacuum electrodeposition. The alloy film was formed by sequential deposition of several layers of Pd and Cu followed by annealing. The resulting membrane was 2µm thick and had 37% Cu by weight. The H₂ permeance was 130x10⁻⁶ m³m/(m²hatm) and H₂/N₂ selectivity was above 70000 at 450°C. There were no decreased performance after 18 times cycling between H₂ and N₂ gas at 450°C.
Roa et al. (2002), used coating and diffusion technique to prepare Pd-Cu membranes on both α-alumina and zirconia coated α-alumina tubes. Depending on the pore size of the support, membranes with thicknesses ranging from 1 to 12 µm were synthesized. Membranes with different compositions were annealed at 350°C for 8 hours for homogenization of the layers. Membrane that contained 40 wt.% Cu had a permeability of 144x10^-6 m³/m²·h·atm^0.5) whereas, membranes with higher Cu content suffered from much lower permeabilities. This was attributed to the higher diffusivity of hydrogen in the b.c.c. structure than in the f.c.c. structure. Their data were in very good agreement with those of McKinley (1967).

2.4.3 Other Pd alloys

Gryaznov (2000) and Knapton (1977) reported that rare earth Pd-alloys have significantly higher H₂ permeabilities than Pd-Ag and Pd-Cu. Figure 2.4 and Figure 2.5 show the normalized permeability of Pd alloys as a function of alloy composition at 350 and 500°C, respectively.
Figure 2.4 Normalized H$_2$ permeabilities of different alloys at 350°C (Knapton, 1977).

Figure 2.5 Normalized H$_2$ permeabilities of different alloys at 500°C (Gryaznov 2000).
CHAPTER 3
EXPERIMENTAL

3.1 Fabrication of Composite Membranes

3.1.1 Porous Stainless Steel (PSS) Supports

Porous 316L stainless steel supports were purchased from Mott Metallurgical Corporation. Both 0.5 and 0.1 µm grade supports were used in this work. Since the supports were originally used for filtering purposes, the grade of the support was determined by the rejection particle size. The supports were called a 0.5 µm grade support, when 95% of the 0.5 µm size particles were rejected by the support during filtering. The properties of the supports are discussed in Chapter 4.

Figure 3.1 shows the schematic and the corresponding pictures of the three types of supports, used. 0.5 µm grade porous sheets, 100 cm², were cut into 1 cm² coupons (Figure 3.1a). Small holes were drilled at the corner of the coupons to hang the coupons vertically during the plating process. The coupons were used for fundamental kinetic studies and for scanning electron microscopy and energy dispersive analysis of the deposited layers.

2.5 cm long porous cylinders (Figure 3.1b) with one end sealed, referred to as cups, were used to study the plating mechanism, to monitor the compactness of the deposited Pd or Ag layer and to observe the structure of the layers without destroying the membrane. All the cup supports were 0.5 µm grade and had 1.17 cm O.D., 1.52 mm wall thickness.
Figure 3.1 Schematic and pictures of the PSS supports; [a] coupons, [b] cups and [c] tubes.
Tube supports were prepared by welding a porous cup to a long non-porous stainless steel tube (Figure 3.1c). 0.5 µm grade tube membranes had ~9 cm² porous area. 0.1 µm grade tube membranes had 22 cm² porous cylinder part with a non-porous plug sealed end. The tube membranes were used for preparing dense membranes and single gas permeation measurements.

3.1.2 Cleaning of the Supports

The surface of the PSS supports was cleaned prior to electroless deposition to remove contaminants such as oil, grease and dirt. The PSS supports were cleaned in an ultrasonic bath with alkaline solution at ~60°C for one hour. The composition of the alkaline solution is given in Table 3.1. Tap water was used to remove all the alkaline solution trapped inside the pores. The rinsing was continued until the pH of the water inside the pores was 7. The pH of the water inside the pores was measured by rubbing a pH paper on the walls of the PSS support. After that, the supports were washed thoroughly three times with deionized water in ultrasonic bath. Finally, iso-propanol was used to easily remove the water inside the pores and the supports were dried at 120°C for 3 hours.

**Table 3.1** Composition of the alkaline solution for cleaning the PSS supports.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
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<tr>
<td>Na$_3$PO$_4$·12H$_2$O</td>
<td>45 g/l</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>65 g/l</td>
</tr>
<tr>
<td>NaOH</td>
<td>45 g/l</td>
</tr>
<tr>
<td>Detergent</td>
<td>5 ml</td>
</tr>
</tbody>
</table>
3.1.3 Formation of an Oxide Barrier Layer

After cleaning, the porous stainless steel supports were oxidized in a high temperature furnace at constant temperature under air. The uniformity of the temperature in the furnace was carefully monitored and controlled. The heating and cooling rate were kept constant at 3°C/min. The supports used in this study were oxidized at several temperatures: 400, 500, 600 and 800°C for desired amount of time.

3.1.4 Electroless Plating of Pd and Ag

Electroless plating was used to deposit Pd and Ag on PSS supports. For both metals, an activation process of the support was necessary to initiate the plating process. The activation process consisted of successive immersion of the supports in the tin chloride (SnCl$_2$) solution followed by palladium chloride (PdCl$_2$) solution with rinsing in deionized water between these baths, at room temperature. The composition of the SnCl$_2$ and PdCl$_2$ is displayed in Table 3.2. 0.1 Molar hydrochloric acid (HCl) was used after each PdCl$_2$ bath to remove the remaining tin compounds on the surface. Figure 3.2 shows the schematic of the sequence and times used for each bath during one loop of the activation process. The activation process was continued until the surface became grayish brown (usually 6 loops on bare support, 3 loops on plated support).
Table 3.2 Compositions of the activation solutions.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₂·2H₂O (g/l)</td>
<td>1</td>
</tr>
<tr>
<td>HCl (37%) (ml/l)</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>PdCl₂ (g/l)</td>
<td>0.1</td>
</tr>
<tr>
<td>HCl (37%) (ml/l)</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 3.2 Schematic of one loop of the activation process.

The chemicals used in the Pd plating process were palladium (II) chloride monohydrate \(\text{Pd}({\text{NH}}_3)4\text{Cl}_2\cdot\text{H}_2\text{O}\) (Alfa Aesar, 99.9%), disodium ethylenediaminetetraacetic acid dehydrate \(\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}\) (Aldrich Chemical, 99%), ammonium hydroxide \(\text{NH}_4\text{OH}\) (Merck, 28%), anhydrous hydrazine \(\text{N}_2\text{H}_4\) (Aldrich Chemical, 98%). For the Ag plating bath, silver nitrate \(\text{AgNO}_3\) (Aldrich Chemical, 99.5%) was used instead of the palladium metal source. The compositions of the pure Pd, pure Ag plating baths are given in Table 3.3.
The plating solutions were prepared by mixing the first four compounds shown in table 3.3, at least one day prior to plating to form stable metal complexes. The hydrazine, reducing agent was added just prior to plating. The plating solution was renewed every 90 min, with rinsing with hot deionized water between each plating bath. After deposition was completed the membrane was let to cool down to room temperature in deionized water and dried at 120°C for 3 hours. After each drying, the weight and He flux were measured. The weight gain before and after the plating was used to determine the thickness of the membrane as shown in Equation 3.1. He flux at room temperature and 1 atm pressure difference was taken in a shell and tube reactor for the tube supports to monitor the densification process. The membrane is called ‘dense’, when there is no He flux at room temperature and 1 atm pressure difference. Activation, plating and drying were repeated until the membrane became dense.
### Table 3.3 Compositions of the Pd and Ag plating baths.

<table>
<thead>
<tr>
<th></th>
<th>Pd Bath</th>
<th>Ag Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NH$_3)_4$Cl$_2$·H$_2$O (g/l)</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>AgNO$_3$ (g/l)</td>
<td>-</td>
<td>0.519</td>
</tr>
<tr>
<td>Na$_2$EDTA 2H$_2$O (g/l)</td>
<td>40.1</td>
<td>40.1</td>
</tr>
<tr>
<td>NH$_4$OH (28%) (ml/l)</td>
<td>198</td>
<td>198</td>
</tr>
<tr>
<td>N$_2$H$_4$ (1 M) (ml/l)</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Total Metal Con (mM)</td>
<td>16.3</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>10-11</td>
<td>10-11</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

\[
\Delta \text{thickness(\mu m)} = \frac{\Delta \text{weight(mg) \times 10}}{\text{PlatedArea(cm}^2\text{)} \times \text{Densityoftheplatedmetal(g/cm}^3\text{)}}
\]  

(3.1)

#### 3.2 Single Gas Permeation Test of Membranes
Membrane characterization and annealing were performed in a permeator cell as shown in Figure 3.3. The temperature of the furnace was controlled using a temperature controller (Omega CN 9000A) coupled with type K Thermocouple 2 (T2 on Figure 3.3) placed between the furnace and the reactor to avoid temperature overshooting. T2 was raised until T1, temperature inside the membrane, reaches the desired value. A variable resistor was placed between the relay and the furnace to increase and decrease the temperature at low rates (1°C/min). Absolute pressures were measured at the inlet side (shell side P1) and permeate side (tube side, P2) using pressure transducers (Edwards 600AB range 10000 torr, MKS range 10000 torr). The back pressure P2, was assumed to be equal to the atmospheric pressure. P1 was accurately set using needle valves on the inlet stream and shell side flow. H₂ and He were fed to the bottom of the reactor and their volumetric flow was measured by a wet flow meter (Wet Tester GCA/precision scientific) for high flow rates, a digital bubble meter (Alltech model 4068) for medium flow rates and a bubble flow meter for very low flow rates.

Membrane characterization and annealing procedures under hydrogen required the heating of the membrane above 350°C under He atmosphere to avoid the cracking of the dense film. At the required temperature He absolute pressure was decreased to 800 torr and H₂ was slowly introduced until pressure P1 reached 1500 torr. When P1 reached 1500 torr, He flow was shut down and the pressure P1 was again adjusted to 2 atm. Switching H₂ to He was done following the same procedure. Temperature was never changed under H₂ to avoid possible embrittlement by H₂ adsorption/desorption cycles. Temperature changes were always done under He atmosphere.
Figure 3.3 Schematic of the hydrogen permeation system.
3.3 Characterization of Membranes by SEM, EDS and AFM

Surface characterization was performed using an Amray 1610 Turbo Scanning Electron Microscope (SEM) equipped with a Princeton Gamma-Tech Avalon EDS light element detector for the qualitative and quantitative analysis. The spatial resolution for SEM-EDS lies between 0.8 and 1.2 µm for the samples we investigated. SEM specimens of the metal deposited porous stainless steel supports were cut using a SiC saw blade and mounted with phenolic powder in a Smithells II mounting press. The resulting samples were ground with SiC papers with increasing grain fineness from 80 to 400 grit. Grinding was performed by using Metaserv 2000 grinder-polisher. Vibromet I automatic polisher was used to polish the sample to 1 µm overnight. Prior to SEM cross-section analysis, samples were painted with carbon ink and gold-coated to avoid charging.

Atomic force microscope studies were done with TESPA (tapping mode etched silicon probe with aluminum reflective backing layer) from Veeco Metrology Group. A paraboloid tip, which may be modeled as a sphere with radius of curvature 5-10 nm was used.
 CHAPTER 4
RESULTS AND DISCUSSION

4.1 Support and Grade Quality

The grade of the porous supports determines the pores size distribution and the porosity of the supports which greatly influence the final membrane thickness and therefore the performance of Pd membranes. In the case of PSS supports purchased from Mott, it should be kept in mind that the grade is not the average pore size of the support but is the retention particle size of the porous media as described in Section 3.1. According to the manufacturer, when 95% of the 0.5 μm particles were rejected by the porous support during filtration, that support was designated as 0.5 μm grade support. Figure 4.1 and 4.2 show the pore size distribution and the corresponding scanning electron micrographs images of 0.5 and 0.1 micron grade PSS supports used in this study. Although the average pore size was around 3.1 to 4.1 μm for the 0.5 μm grade supports and 1.6 to 2.1 μm for the 0.1 μm grade supports, much larger pores could be observed on the surface of both of the supports. Therefore, thick layers of Pd were required to close the large pores on the surface independent of the average pore size of the support. This was also consistent with the results reported by Mardilovich et al. (2002). Nevertheless, it was possible to prepare relatively thinner membranes when smaller grade supports with smaller pores were used. The final thicknesses of the dense Pd membranes were 20-25 μm on 0.1 μm grade supports and 35-40 μm on 0.5 μm grade supports.
**Figure 4.1** Pore size distribution of 0.5 and 0.1 micron grade porous stainless steel supports purchased from Mott.

**Figure 4.2** Scanning electron micrographs of 0.5 and 0.1 micron grade PSS supports after cleaning.
On the other hand, a high He flux before plating indicates low resistance to hydrogen permeation. As can be seen from Table 4.1, 0.5 µm grade supports had much higher He flux, thus lower resistance to gas permeation. 0.1 µm grade supports, were relatively more impervious to gas permeation, but they had the advantage of a thinner deposited separation layer. In this case, because of the 20 µm separation layer, the support resistance did not play a significant role in hydrogen permeation. In general, when PSS supports are considered, the effect of support resistance might be observed for membranes that have a separation layer less than 10 µm, or when the He flux of the support is much lower as a result of pretreatment of the support.

Table 4.1 Comparison of the properties of 0.5 and 0.1 µm grade PSS supports.

<table>
<thead>
<tr>
<th></th>
<th>0.5</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size (µm)</td>
<td>3.1 to 4.1</td>
<td>1.6 to 2.1</td>
</tr>
<tr>
<td>Initial He flux (m³/m²h)</td>
<td>930</td>
<td>250</td>
</tr>
<tr>
<td>Final thickness of dense Pd membrane (µm)</td>
<td>35-40</td>
<td>20-25</td>
</tr>
</tbody>
</table>

4.2 Effect of Oxidation Temperature and Time on the Properties of PSS Supports (cup study).

Ma et al. (1998) showed that one way to improve the membrane stability was to create an intermediate intermetallic diffusion barrier layer, which could be created by the in-situ controlled oxidation of the substrate prior to plating. The oxidation time and temperature might strongly influence the properties of the PSS, especially the pore size distribution and the porosity of the support.
Figure 4.3 shows the picture of the 0.5 µm grade PSS cup supports after oxidation at various temperatures. Table 4.2 summarizes the change of the properties of the cup supports including the He flux $\Delta J$ after oxidation as a percentage of the original He flux for the support and the mean pore diameter, $D_p$, from mercury porosimetry. The mass gain, $\Delta m$, was given as a percentage of the original mass. The changes in mass during oxidation were used to determine the upper and lower bounds of the oxide layer thickness based on two limiting cases for the oxide distribution. For the lower bound, the oxide layer was assumed to form a film of uniform thickness on the entire surface area, including the pore walls. This limiting case is referred to as the homogeneous oxide thickness, $t_{hom}$. The surface area for the 0.5 µm PSS was estimated to be $0.041 \text{ m}^2 \text{ g}^{-1}$ using Hg porosimetry data. This value was used with the sample mass data to determine the total oxide film area for each sample for the homogeneous oxide case. The upper bound for the oxide thickness $t_{ex}$ was estimated by assuming the oxide layer formed entirely on the exterior surface for each cup. For each case a density of 5.1 g/cc was assumed to approximate the density of our oxides based on the work of Adachi et al. (1996).

![Figure 4.3](image)

**Figure 4.3** Pictures of the cups oxidized at different temperatures.
There were no significant changes in porosity and He flux, between the unoxidized blank and the support oxidized at 400°C. Between the oxidation temperatures (T_{ox.}) of 400°C and 800°C the pore size and porosity decrease slightly with increasing T_{ox.}. However, between the oxidation temperatures of 400°C and 800°C the reduction in He flux was too drastic to be explained by the changes in porosity. This is particularly true for changes observed between 600 and 800°C. As the oxidation temperature was increased, the weight gain increased indicating the formation of more oxide at higher temperatures. The formation of greater quantities of oxide gave a larger resistance to the He permeation. In addition, the pore size distribution of the PSS supports as a function of oxidation temperature is represented in Figure 4.4.

<table>
<thead>
<tr>
<th>Cup #</th>
<th>T_{ox} (°C)</th>
<th>∆m (%)</th>
<th>D_p [µm]</th>
<th>t_{hom} (µm)</th>
<th>t_{ex} (µm)</th>
<th>∆J (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>unoxidized</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>0.03</td>
<td>4.1</td>
<td>0.002</td>
<td>0.20</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>0.56</td>
<td>3.9</td>
<td>0.027</td>
<td>3.29</td>
<td>-10.4</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>1.47</td>
<td>3.7</td>
<td>0.070</td>
<td>8.61</td>
<td>-73.5</td>
</tr>
</tbody>
</table>
Figure 4.4 Pore size distribution of 0.5 μm grade porous stainless steel supports oxidized at different temperatures for 6 hours.

As can be seen from Table 4.2, weight gains of the cups increased with the oxidation temperature indicating the formation of a thicker oxide layer at higher temperatures. However the oxidation had little effect on the mean pore size indicating that oxidation did not constrict the internal pore system even at 800°C. The estimated homogeneous oxide layer thickness values are 2 to 3 orders of magnitude smaller than the mean pore diameters indicated by Hg porosimetry (3.7 - 4.1 μm). Based on this comparison the dramatic decrease of the He flux in Table 4.2 can not be explained by the formation of a homogeneous oxide layer throughout the pore system, especially for high oxidation temperatures. However, the thickness estimates obtained by assuming oxidation only on the exterior ($t_{ex}$) were greater than the thickness estimates determined
by the cross-sectional SEM analysis that will be discussed later. This difference was less than an order of magnitude in all cases. One possible explanation for all of these observations is the predominant formation of oxide on both the exterior surface and in the pores and pore mouths near the surface. The fact that the difference in the pore size distribution between the oxidized and unoxidized support is negligible not only further substantiates this explanation but also gives a clear indication that no pore collapses occurred during the oxidation. Therefore, the mechanical strength of the support is not compromised by the oxidation.

Figure 4.5 shows the SEM micrographs of the PSS surface after oxidation at various temperatures. It can be seen that the surface of cup1, unoxidized, and cup2, oxidized at 400°C, looked smooth and similar, whereas the surfaces of cup3 and 4, oxidized at 600°C and 800°C respectively, were much rougher. For cup4, the surface was very crumblly and the roughness seemed to increase substantially compared to the unoxidized sample. The increase in the surface roughness can also be seen from the atomic force micrographs (AFM) of cup2 and cup4 shown in Figure 4.6. Another support was oxidized at 400°C for 18 h to study the effect of longer oxidation time on the surface morphology, thus the microstructure of the Pd layer. The surface morphology was almost the same as the one oxidized at 400°C for 6h. Furthermore, the weight gain and He flux decline also were essentially the same as those of cup2.
Figure 4.5 SEM micrographs (5KX) of the PSS cups after oxidation [a] un-oxidized, [b] oxidized at 400°C, [c] oxidized at 600°C [d] oxidized at 800°C.

Figure 4.6 Atomic Force Micrographs of [a] cup2, oxidized at 400°C and [b] cup4, oxidized at 800°C.
Figure 4.7 shows the EDS spectrum on the surface of the sample oxidized at 600°C. The oxygen peak observed on the left confirms the formation of an oxide layer on the support. It was also observed that the amount of oxygen on the support was increasing with higher oxidation temperatures indicating a thicker oxide layer, consistent with the weight uptakes.

Among the oxides that can be formed with the elements of stainless steel, Cr₂O₃ is the most stable oxide due to its low Gibbs free energy, the low diffusion rates of elements in the oxide scale, and its high chemical stability under a H₂ atmosphere (Samsanov, 1973). Therefore it is the most desirable oxide phase for use as a barrier layer to the intermetallic diffusion. To check the existence of a Cr-rich oxide on the surface of the samples, EDS spot scan analysis was performed. The ratio of atomic Fe to atomic Cr on the surface of the supports is shown in Figure 4.8. The ratio remained almost constant and essentially the same as the unoxidized sample for the samples oxidized at 400°C and...
600°C whereas it increased dramatically for the support oxidized at 800°C indicating a Fe-rich oxide on the outermost layer. However, it was difficult to determine the compositions of the oxide layers for samples oxidized at 400°C and 600°C because the thickness of the oxide layer was too thin to be accurately determined due to the limitation of the resolution of the EDS. Cr-oxide was likely formed on the samples at these temperatures due to its low Gibbs free energy. On the other hand, the enhancement of the diffusion of Fe at higher oxidation temperatures could have led to the growth of Fe-oxide on the Cr-oxide layer during oxidation at 800°C (Samsanov, 1973).

![Graph showing the ratio of Fe (atomic %) /Cr (atomic %) obtained from EDS spot scan analysis on the surface of the supports oxidized at various temperatures.](image)

**Figure 4.8** The ratio of Fe (atomic %) /Cr (atomic %) obtained from EDS spot scan analysis on the surface of the supports oxidized at various temperatures.

To determine the effectiveness of the oxide layer as an intermetallic diffusion barrier, the four cup samples were electroless plated with Pd and then annealed at 550°C for 10 hours under He atmosphere. Figure 4.9 and Figure 4.10 show respectively the SEM micrographs of the cross-sections and the corresponding EDS line scan data for the cup samples oxidized at 400°C and 800°C after annealing. The line scans were performed starting from inside the support, which was darker in color, and ending inside the Pd
layer which was lighter. Regions where the line scan data were taken are indicated by the arrows.

For the unoxidized cup (Figure 4.9) and the cup oxidized at 400°C (Figure 4.10) neither the SEM micrographs nor the EDS line scan data conclusively showed the oxide layer, which might have been too thin to even be detected by the EDS line scan. The diffusion of support elements into the Pd layer appeared to be similar for both samples.

From the cross-sectional SEM micrograph of cup3 (Figure 4.11), oxidized at 600°C, a dark uniform thin layer between the support and Pd layer was observed throughout the whole support. Both the EDS line scan on the cross-section and the EDS spot scan on the surface confirmed that this dark layer was actually the oxide layer. The thickness of this layer was about 0.2-0.3 µm from the secondary electron image (SEI) micrograph. This was too close to the spatial resolution of the EDS to determine an oxide-only composition.

Figure 4.12 shows the SEM micrograph and EDS line scan data for cup 4, which was oxidized at 800°C. A thicker dark region with a very non-uniform thickness was observed throughout the whole cup. It could also be observed that the surface of this oxide layer was very crumbly (Figure 4.5d). In the cross section of this sample the Pd penetrated deeply into all the cavities of the oxide layer, therefore, the adhesion of the Pd layer might also be enhanced by the formation of this oxide layer. The thickness of the dark region varied from 1 µm to 6 µm from spot to spot. Since the oxide layer was relatively thick in this case, it was possible to determine the composition by EDS analysis. It can be seen that there existed a Fe-rich oxide on the outermost layer whereas there was a Fe-depleted and a Cr enriched mixed oxide on the inner layer. These data
Figure 4.9 [a] The SEM micrograph of the cross section of cup1, unoxidized and annealed at 550°C under helium atmosphere. [b] The EDS composition profile along the length of the arrow indicated in Figure 4.9a.
Figure 4.10 [a] The SEM micrograph of the cross section of cup2, oxidized at 400°C and annealed at 550°C under helium atmosphere. [b] The EDS composition profile along the length of the arrow indicated in Figure 4.10a.
Figure 4.11 [a] The SEM micrograph of the cross section of cup3, oxidized at 600°C and annealed at 550°C under helium atmosphere. [b] The EDS composition profile along the length of the arrow indicated in Figure 4.11a.
Figure 4.12 [a] The SEM micrograph of the cross section of cup4, oxidized at 800°C and annealed at 550°C under helium atmosphere. [b] The EDS composition profile along the length of the arrow indicated in Figure 4.12a.
agree well with the results reported by Tanabe and Imoto (1979) and are consistent with our determined mass gains and spot scans on the surface.

In general, the oxidation process consists of two main steps, surface oxidation and then the oxide scale formation. During the oxide scale formation there are several mechanisms including the diffusion of elements along their respective gradients, the diffusion of oxygen and oxidation at the metal-oxide interface. All these mechanisms may affect the composition and the thickness of the formed oxide layer (Shackelford, 1996). Considering the fact that the Tamman temperature of 316L stainless steel, above which the elements become mobile, is about 550°C, for relatively low oxidation temperatures like 400°C, it is most likely that only surface oxidation step takes place. For the sample oxidized at 400°C, the very low mass gain after oxidation, the similarity of the surface morphology to that of the unoxidized sample, and the cross-sectional SEM and EDS results all suggest that the oxide layer formed was very thin. For this case where the oxidation temperature was well below the Tamman temperature, the oxide was probably in the nm scale, and therefore could not be detected by using SEM or EDS. This was consistent with Shibagaki et al. (1997), who using µAES, reported a 16 nm thick oxide layer on 316L stainless steel after oxidation at 427°C under air. The existence of an oxide layer and the growth of this oxide layer with increasing oxidation temperatures have been reported by many authors (Tanabe and Imoto, 1979; Shibagaki et al., 1997). For high oxidation temperatures such as 800°C, the thick oxide layer consisted of an Fe-rich oxide layer on top followed by a mixed Cr and Fe oxide layer. Tanabe and Imoto (1979) used SEM to show the lava like Fe-oxide on SUS 316 type stainless steel after oxidation at 800°C in air. Their SEM micrographs of Fe-oxide on the surface were very similar to
what we observed. However, for lower oxidation temperatures there were different results reported by different authors in the literature. For example, Sivaraman et al. (1984) reported that the oxide layer consisted of Cr$_2$O$_3$ after oxidation at 700°C in air whereas, Shibagaki et al. (1997) reported Fe-rich top layer after oxidation at 427°C in air. These differences might have arisen from the difficulty in the analysis of the thin oxide layer.

Independent of the composition, the most important feature for the oxide layer to be used as a barrier layer for Pd/PSS membranes is its stability under H$_2$ atmosphere. It is known that most of the oxides are reduced to metallic state under H$_2$ atmosphere. No reduction will occur on the oxide-metal interface if the inner oxide layer consists of Cr-rich phase which has a high resistance to reduction under H$_2$ atmosphere even at high temperatures (Samsanov, 1973). In this case, even if the inner oxide layer is a Fe-rich phase and reduction occurs, the effectiveness of the barrier layer will not be compromised because of the presence of the stable Cr-oxide phase. The line scan results shown in Figures 4.9 and 4.10 appear to, at least, qualitatively substantiate the fact that the intermetallic diffusion between the substrate metals and Pd layer has been minimized with the presence of the oxide barrier layer.
4.3 Synthesis of Pd Membranes

4.3.1 The effect of oxide barrier layer on the morphology of the deposited Pd layer and final thickness of Pd membranes (tube study).

The fundamental understandings of the properties of the oxide barrier layer were used to investigate the influence of the oxide barrier on the morphology of the deposited Pd layer and the final thickness of membranes. PSS tubes were used to prepare dense membranes.

Figure 4.13 and 4.14 shows the scanning electron micrographs of the oxidized tubes (0.5 µm grade) after 1 hour and 3 hour Pd deposition, respectively. The size of the Pd clusters was bigger on the supports oxidized at higher temperatures. Aggressive oxidation caused enhanced formation of a porous oxide layer which provided more surface area. Furthermore, the oxidized surface appeared to enhance the absorption of SnCl₂ and nucleation of Pd seeds during activation and increased the surface roughness for easy attachment of Pd ions during plating.
Figure 4.13 Scanning electron micrographs of oxidized tubes after 1 hour Pd plating: [a] unoxidized (1.8µm), [b] 400°C (2.7µm), [c] 600°C (2.8µm) and [d] 800°C (2.54µm). Note: Numbers in the parentheses indicate the Pd layer thickness at the end of one hour plating.
Figure 4.14 Scanning electron micrographs of oxidized tubes after 3 hour Pd plating: [a] unoxidized (7.24µm), [b] 400°C (7.55µm), [c] 600°C (7.62µm) and [d] 800°C (7.95µm). Note: Numbers in the parentheses indicate the Pd layer thickness at the end of 3 hour plating.

The He flux was used to check if the Pd layer was dense. The membrane is deemed ‘dense’ when there was no He flux at room temperature under a pressure difference of 1 atm. One unoxidized tube and three tubes oxidized at three different temperatures, 400°C, 600°C, 800°C, were electroless plated with Pd until they were dense. As shown in Figure 4.10, the He flux declines after oxidation showed similar behavior as the cups shown in Table 4.2. The final thicknesses of the dense Pd layers were about the same for the supports oxidized at 600 and 800°C and appeared independent of the oxidation temperature as shown in Table 4.3. The slightly thicker Pd layer for the support oxidized at 400°C and for the unoxidized support appeared to be due
to the lower extent of oxidation that provided less active oxide area for absorption and plating.

**Table 4.3** Thickness of dense Pd layer on PSS tubes oxidized at different temperatures.

<table>
<thead>
<tr>
<th>Membrane #</th>
<th>Grade [µm]</th>
<th>Oxidation Temp. [°C]</th>
<th>Oxidation Time [h]</th>
<th>He Flux Change ΔJ[%]</th>
<th>Thickness l [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>no oxidation</td>
<td>-</td>
<td>0.0</td>
<td>37.7</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>400</td>
<td>6</td>
<td>0.0</td>
<td>40.0</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>600</td>
<td>6</td>
<td>-12.2</td>
<td>35.5</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>800</td>
<td>6</td>
<td>-52.2</td>
<td>36.6</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>no oxidation</td>
<td>-</td>
<td>0.0</td>
<td>40.2</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>800</td>
<td>4</td>
<td>-66.7</td>
<td>33.8</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>800</td>
<td>4</td>
<td>-89.9</td>
<td>33.2</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>800</td>
<td>4</td>
<td>-99.2</td>
<td>15.5</td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>600</td>
<td>5</td>
<td>-31.9</td>
<td>26.7</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>400</td>
<td>6</td>
<td>-1.8</td>
<td>18.1</td>
</tr>
</tbody>
</table>

**Figure 4.15** He flux at 1 atm difference as a function of Pd layer thickness for membranes 1-4, that have different support oxidation temperatures.
The typical behavior of the He flux as a function of the Pd layer thickness is shown in Figure 4.15 for tube membranes #1-4. The curves can be divided into two parts. The first part is the linear decline of He flux with the plated Pd thickness, where all the small pores were being plugged. All membranes had different initial He fluxes as a result of the oxidation at different temperatures, however they intersected the abscissa at essentially the same point. This point essentially indicates the thickness when the membranes become liquid dense. When the supports did not permeate liquid anymore, they were called liquid dense. The second part of the curves is the exponential decline of the He flux with the thickness, where the largest pores were being plugged. The fact that the exponential decline starts at similar Pd layer thickness for all oxidation conditions indicates that the pores being blocked in this portion of the curve are too large to be significantly affected by the oxidation conditions. These pores may be regarded as defect pores for the purpose of Pd membrane fabrication. Previous works also showed that the dense Pd layer thickness was dependent on the largest pore size (Mardilovich et al., 1998). Therefore, for large grade supports, the oxidation temperature will not affect the size of the pore enough to cause a significant reduction of the plated Pd layer thickness.
4.3.2 Characterization of Pure Pd Membranes

Figure 4.16 shows the hydrogen flux of the membranes #2-4 at 500°C and 1 atm pressure difference. The membranes were heated under He at 1°C/min up to 500°C. At time zero in Figure 4.16, hydrogen is fed to the system at 500°C. As seen from the figure, membrane #4, which had a thicker oxide layer, had a stable hydrogen flux, whereas membrane #3 and #2, which had a thinner oxide layers, were not stable. The decline in the hydrogen flux was possibly due to intermetallic diffusion.

![Graph showing hydrogen fluxes of Pd membranes #2, #3, and #4](image)

**Figure 4.16** Hydrogen fluxes of Pd membranes #2, #3, and #4 at 500°C and 1 atm pressure difference.

The oxidation of PSS supports of smaller grades resulted in higher declines in the He flux after oxidation. Table 4.4 shows the summary of the membranes prepared in our lab, including the grade (µm) and the oxidation temperature of the support (°C), final thickness of the dense membrane prepared on that support. With a 0.2 µm grade support
over 99% reduction in He flux was observed after oxidizing at 800°C for 4h. Despite the very low flux, 15.5 µm thick Pd layer were deposited to make the membrane dense. The characterization of this membrane showed that the maximum H₂ flux that could be achieved was limited by the reduced support porosity (Figure 4.17) (Mardilovich, 2004).

![Graph](image)

**Figure 4.17** Hydrogen flux of the membrane #8 (15.5 µm thick Pd layer) at 350°C.

Although the oxide layer was used as a barrier for the intermetallic diffusion, it could also act as a barrier for hydrogen diffusion through the pores if the oxide layer were too thick. Therefore, the thickness of the oxide layer should be thick enough to prevent intermetallic diffusion, thereby increasing the thermal stability of the membrane but thin enough not to block the flow of hydrogen through the pores of the PSS support.
4.3.3 Hydrogen Permeance, Permeability and Activation Energy of Pure Pd Membranes.

Having shown very stable hydrogen flux at 500°C, Pd membrane #4 was used to study the hydrogen permeance at several temperatures and to calculate the activation energy for permeation. Figure 4.18 shows the hydrogen permeance at several temperatures for Pd membrane #4 and Table 4.4 summarizes the hydrogen permeance and the corresponding permeability of this membrane.

![Graph showing hydrogen permeance over time and temperature](image)

**Figure 4.18** Hydrogen permeance of Pd membrane #4 at several temperatures as a function of time.
Table 4.4 Summary of hydrogen permeance and permeability of Pd membrane #4 as a function of temperature.

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>H₂ Permeance [m³/m²·atm⁰.⁵]</th>
<th>H₂ Permeability [m³/m²·atm⁰.⁵]x10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.47</td>
<td>127.002</td>
</tr>
<tr>
<td>400</td>
<td>5.97</td>
<td>218.502</td>
</tr>
<tr>
<td>500</td>
<td>8.38</td>
<td>306.708</td>
</tr>
</tbody>
</table>

The experimental values of hydrogen permeances at different temperatures (Table 4.4) were used to estimate the activation energy for hydrogen permeation. Equation 4.1 and 4.2 represent the temperature dependence of hydrogen permeance through the Arrhenius relation.

\[
F = F₀ \cdot \exp\left(-\frac{E₀}{RT}\right) \quad (4.1)
\]

\[
\ln(F) = \ln(F₀) - \left(\frac{E₀}{R}\right)\left(\frac{1}{T}\right) \quad (4.2)
\]

Figure 4.19 shows the Arrhenius relation between the permeance and the temperature based on Equation 4.2. A linear fit of the data was used with a 0.9996 regression coefficient to calculate the activation energy for permeation. The activation energy of the Pd membrane #4 was found to be 14.24 kJ/mol, which was close to the previously reported values for pure Pd membranes (Mardilovich et al., 1996; Collins and Way, 1993, see Table 2.2).
Figure 4.19 Arrhenius relation between the hydrogen permeance and temperature.

Figure 4.20 shows the SEM picture and the corresponding EDS line scan data through the skin layer of the Pd membrane #4 after testing. The oxygen peak in the line scan belongs to the oxide layer existing between the support and the Pd layer. When compared to cup4 (Figure 4.12) which was annealed at 550°C for 10 hours under He, the Pd membrane #4, which was tested at 500°C for 250 hour under H₂ atmosphere, had much thinner oxide layer. The oxide layer might have been reduced due to the hydrogen atmosphere. But nevertheless, the Pd membrane #4 (support oxidized at 800°C) was stable at 500°C for 250 hours and no intermetallic diffusion could be detected using EDS.
Figure 4.20 The SEM micrograph of the cross section of Pd membrane #4 (support oxidized at 800°C) after characterization. [b] The EDS composition profile along the length of the arrow indicated in Figure 4.20a.
4.4 Synthesis of Pd-Ag Membranes

4.4.1 Characteristics of the deposited Pd-Ag layers

Understanding the structure of the plated film was of key importance when preparing dense membranes. Figure 4.21 shows the typical scanning electron micrograph of the PSS coupons (0.5 µm grade) that were oxidized at 600°C, after 30 min plating with pure Pd (a-b) and with pure Ag (c-d). The pores of the substrate can clearly be seen due to the very thin layers of Pd and Ag. When supports were plated with palladium (Figure 4.21 a-b), the round clusters of Pd uniformly covered the substrate following all the features of the support. With further deposition, the uniformly growing Pd layer covered the pores on the surface, making a compact dense layer on the substrate.

Unlike Pd, Ag deposits had very unique structure on the surface. The faceted Ag clusters tended to deposit on the hills of the rough surfaces without totally covering the surface (Figure 4.21 c-d). With further plating, the Ag clusters started to grow on top of each other, forming islands rising perpendicular to the surface forming dendritic structures. Apparently, the relationship between the structure and the plating bath appeared to be more complex in the case of Ag.

Electroless deposition of Pd is an autocatalytic process where the deposited palladium catalyzes the oxidation of hydrazine. Compared to palladium, silver has relatively low activity in catalyzing the oxidation of hydrazine. Thus, electroless deposition of Ag was also initiated by foreign nuclei like Pd. On the other hand, the complexing ability of EDTA for Ag⁺ was weak and thus Ag was likely to have deposited immediately upon reaching an active site without diffusing inside the valleys.
This unique property of Ag deposition was further studied by using PSS coupons oxidized at different temperatures, to observe the influence of surface roughness on the microstructure. Figure 4.22 and 4.23 show respectively the SEM pictures of pure Pd and pure Ag on PSS coupons with different oxidation temperatures. Figure 4.24 shows the PSS coupons that were first plated with Pd and then with Ag.
Figure 4.22 SEM pictures of electroless plated Pd on PSS coupons [a] unoxidized, [b] oxidized at 400°C, [c] oxidized at 600°C, [d] oxidized at 800°C.
Figure 4.23 SEM pictures of electroless plated Ag on PSS coupons [a] unoxidized, [b] oxidized at 400°C, [c] oxidized at 600°C, [d] oxidized at 800°C.
Figure 4.24 SEM pictures of Ag on Pd on PSS coupons [a] unoxidized, [b] oxidized at 400°C, [c] oxidized at 600°C, [d] oxidized at 800°C.

Earlier results (Figure 4.13 and 4.14) showed that the size of the Pd clusters on PSS cups during plating were bigger on the supports oxidized at higher temperatures. However, in the case of PSS coupons there did not appear to have a strong correlation between the morphology of the deposited Pd and the surface roughness as shown in Figure 4.21. The difference was, possibly, due to the different ways the supports were produced as well as the geometric shape (flat surface for coupons versus curved surface for cup samples).
From Figure 4.23, Ag seemed to deposit uniformly covering the unoxidized surface when the surface was smooth. However, when the surface was not smooth, Ag deposited on the first active site forming islands growing perpendicular to the surface. Therefore Ag tended to deposit on the hills of the rough surface without totally covering the surface even if the surface was completely activated. As the surface became rougher with higher oxidation temperatures, more island formation was observed. Moreover, the supports oxidized at higher temperatures had Ag islands growing perpendicular to the walls of some of the larger pores, as indicated by SEM. This indicates that Ag could diffuse inside these larger pores during plating forming bridges and reducing the effective pore size. Further evidence of this phenomenon was observed during studies of effective strategies for Ag and Pd deposition on actual cup membranes, as discussed later. As a matter of fact, the compactness and coverage of the Ag layer were very weak compared to those of the Pd layer.

% weight uptake of the samples over 30 min of plating was used to infer the effect of surface roughness on the initial metal deposition rates for Pd and Ag separately. Increasing oxidation temperature, the plating rate of Ag on PSS decreased. On the other hand, the plating rate of Pd on PSS did not depend on the oxidation temperature of the support. For Pd, the highest plating rate was achieved with support oxidized at 800 °C and for Ag with unoxidized support. The rate of Ag deposition on Ag was believed to be less than the rate Ag deposition on the Pd seeds that were nucleated during activation, since Ag was not as good a catalyst as Pd for the reduction of Ag ions. Therefore, as the island formation increased with higher oxidation temperature, the ratio of Ag deposition
on Ag covered surface versus Ag deposition on the bare Pd activated surface could increase and thus the deposition rate of Ag on PSS decreased.

Figure 4.25 shows the scanning electron micrograph of a PSS coupon oxidized at 400 °C, activated and plated for 30 min with Pd, dried, then activated and plated for 30 min with Ag. When Ag was deposited on the sample that was first plated with Pd, we observed behavior similar to Ag deposition on the PSS substrate. Figure 4.20 shows that the island formation was increasing with increasing oxidation temperature of the support. However less bridge formation was observed since the Pd plating decreased the surface roughness slightly. From Figure 4.22, it can be seen that during plating, the Ag deposited on the surface without diffusing into the pores. It can also be seen that inside the pores, the morphology is almost the same as pure Pd. EDX analysis also shows that the amount of Ag decreases substantially inside the pores.

Figure 4.25 Scanning electron micrograph of support oxidized at 400°C, then plated with Pd and Ag sequentially.
4.4.2 Effect of Ag Plating Sequence on the Final Thickness of Dense Pd-Ag Membranes

As mentioned above, the bridge formation as a result of Ag growing perpendicular to pore walls of the substrate could be observed in the initial stages of plating when the pores were big enough for Ag plating solution to diffuse inside. For this purpose 0.5 µm grade PSS tubes were used to prepare three Pd-Ag membranes. For each Pd-Ag membrane 1 to 3, the Ag deposition was applied at different stages of plating, during final, middle and initial stages, respectively.

Figures 4.26 shows the He flux as a function of the membrane thicknesses for the tube membranes prepared to study the effect of Ag plating. All of the tube supports were oxidized at 400 °C for 6 hours. All the membranes were plated until the He flux at room temperature was less than 0.001 m³/m²h. The first Pd-Ag membrane (Pd-Ag membrane #1) was Pd plated until it was almost dense and then plated with Ag to make it dense. A typical 0.5 µm grade support became liquid dense around a thickness of 15-20 µm independent of the oxidation temperature of the support (Figure 4.26). From then on, the size of the largest pores determined the final membrane layer thickness causing a long tail in He flux. Therefore for the second Pd-Ag membrane, Ag was deposited after 16 µm of pure Pd layer. The third membrane, however, was prepared using Ag at the very initial stages.
As seen from Figure 4.26, when Ag was applied at the final stages (Pd-Ag membrane #1), it did not have any effect on further reducing the He flux, thus not closing the very small pores resulting originally from the big pores on the initial as received support. That could be because Ag grew islands perpendicular to the surface rather than diffusing inside the pores. Since the pores were small at this stage of the plating, Ag had no effect on reducing the size of the pores.

The second Pd-Ag membrane (Pd-Ag membrane #2) became dense at around 42 µm, which was slightly thicker than the thickness of pure Pd membranes on 0.5 µm grade supports. Therefore, the Ag plating was not effective in closing the pores. In contrary, the addition of Ag layer resulted in thicker separation layers.
The third membrane (Pd-Ag membrane #3), which was prepared using Ag in the early stages of the plating, on the other hand, became dense with a 15 µm separation layer. Pd-Ag membrane #1 and #2 were barely liquid dense at this thickness. Since the Ag deposition was used at the initial stages of the plating when the pores were large enough for Ag to diffuse inside the pores to form bridges, the time required for plugging large pores was much shorter, thus the final thickness was much thinner. Therefore, by forming bridges, when applied at the very initial stages, Ag could reduce the size of the large pores which had been shown to determine the thickness of the dense membrane layer.

Up to now, no membrane has been prepared using Ag as the first layer on the support. However, with higher oxidation temperature and thus enhanced roughness, using Ag as an initial layer on PSS may also affect the membrane layer thickness, due to the enhanced bridge formation.

4.4.3 Structural Changes of the Pd-Ag Layer during High Temperature Annealing (Coupon Study)

PSS coupons were used to investigate the structural changes during annealing. For this purpose two coupons were plated with Pd and Ag by using different sequences. The first coupon was plated with Ag for 9 hours and Pd for 3 hours respectively, whereas the second coupon was plated with Pd for 3 hours and Ag for 9 hours. Activation step was used prior to each metal deposition. After plating was completed, both of the coupons were cut into 3 pieces. One piece from the first coupon and one piece from the second coupon were annealed at 600°C for 10 hours under He atmosphere. Another pair
was annealed at the same conditions but under H$_2$ atmosphere. The third pair was kept untouched to observe the morphology right after plating. Table 4.5 summarizes the plating and heating procedures for all the coupons.

**Table 4.5** Summary of plating sequences and heat treatments for the coupons.

<table>
<thead>
<tr>
<th>Coupon No</th>
<th>1$^{\text{st}}$ Layer</th>
<th>2$^{\text{nd}}$ Layer</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Ag</td>
<td>Pd</td>
<td>none</td>
</tr>
<tr>
<td>1b</td>
<td>Ag</td>
<td>Pd</td>
<td>600°C for 10h under He</td>
</tr>
<tr>
<td>1c</td>
<td>Ag</td>
<td>Pd</td>
<td>600°C for 10h under H$_2$</td>
</tr>
<tr>
<td>2a</td>
<td>Pd</td>
<td>Ag</td>
<td>none</td>
</tr>
<tr>
<td>2b</td>
<td>Pd</td>
<td>Ag</td>
<td>600°C for 10h under He</td>
</tr>
<tr>
<td>2c</td>
<td>Pd</td>
<td>Ag</td>
<td>600°C for 10h under H$_2$</td>
</tr>
</tbody>
</table>

Table 4.6 shows the thicknesses of the metal layers and the overall compositions for the coupons after plating. The thicknesses were calculated by using the weight uptakes, plating areas, the densities of the deposited metals, assuming that the deposited metal layers were homogeneously covering the surface. It can be seen that the deposition rates of both Pd and Ag were not the same for the two coupons even if same amount of plating times were used. This was mainly because of the fact that the structure of the Pd deposits was not the same as that of the Ag deposits. Ag was deposited on PSS for the first coupon, and on Pd layer for the second coupon. The two substrates might have different catalytic activities for Ag plating. Considering the non-uniform deposition of Ag and the fact that Ag was plated on different substrates, the differences in the plating rate of Ag and Pd were not surprising.
Table 4.6 Thicknesses of the deposited layers and overall compositions of the coupons after plating.

<table>
<thead>
<tr>
<th>Coupon</th>
<th>1st Layer</th>
<th>2nd Layer</th>
<th>Overall Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.3 µm Ag</td>
<td>10 µm Pd</td>
<td>30 wt % Ag</td>
</tr>
<tr>
<td>2</td>
<td>6.25 µm Pd</td>
<td>6.75 µm Ag</td>
<td>50 wt % Ag</td>
</tr>
</tbody>
</table>

Figure 4.27 and 4.28 show the SEM micrographs of the surfaces and the cross-sections of coupon 1 and 2 respectively, including after deposition and after heat treatment procedures. When the support was first plated with Ag and then Pd, the plating resulted in a porous (dendritic) structure without the formation of a dense membrane layer. These dendritic structures consisted of a skeleton of silver, covered very uniformly with Pd (Figure 4.27 a-b). When these dendritic structures were observed more closely, EDS map scans showed that they consisted of a skeleton of silver, covered very uniformly with Pd.

Figure 4.29 shows the EDS maps on coupon 1a and 1b. The iron coming from the support (blue), the deposited Ag (green) and the deposited Pd (red) are displayed in the EDS map.
Figure 4.27 SEM micrographs of [a] top view of coupon 1a, [b] cross section of coupon 1a, [c] top view of coupon 1b, [d] cross section of coupon 1b, [e] top view of coupon 1c, [f] cross section of coupon 1c.

Figure 4.28 SEM micrographs of [a] top view of coupon 2a, [b] cross section of coupon 2a, [c] top view of coupon 2b, [d] cross section of coupon 2b, [e] top view of coupon 2c, [f] cross section of coupon 2c.
Independent of the annealing atmosphere, after annealing at 600°C for 10 hours, there were voids appearing in the middle of these structures, where Ag was before (Figure 4.27 d-e). Considering the fact that Ag was very mobile at 600°C which was much higher than its Tamman temperature and that Pd, having a Tamman temperature of 640°C, was almost stationary, the diffusion rate of Ag into the Pd layer was much faster than that of Pd into the Ag layer. Having high mobility, and being covered uniformly with Pd, Ag diffused into the Pd layer in all directions. Since Pd was relatively motionless at these temperatures, the Pd atoms were incapable of replacing the vacancies formed inside the Ag layer. This effect is called Kirkendall effect and seen in many diffusing metal couples whose diffusion rates differ by a considerable amount. The annealing temperature and time, the thickness of the layers and the composition might all have effects on the formation of these voids.

When the surface morphology of coupon1 was compared to that of coupon 2 immediately after plating (Figure 4.27a and 4.28a), coupon 2 seemed to have much denser structure, most probably, because of the uniform Pd layer underneath the non-uniform Ag. Pd was incapable of densifying coupon 1, because it perfectly repeated the non-uniform Ag structures that grew perpendicular to the surface. The EDS map of coupon 2 after plating, shown in Figure 4.29 c-d, showed that the uniform layer on the support was Pd and that the non-uniform structures on the top were Ag. After annealing under He or under H₂, all the Ag on the top surface penetrated into the Pd layer making a smooth alloy layer that uniformly covered the surface. Diffusion of Ag only occurred in one direction until all the Ag on the surface penetrated into the Pd layer. Although the dendritic structure completely diminished after the heat treatment, the formation of a
dense Pd-Ag alloy depended on the thickness of deposited layers, as well as the annealing temperature and times.

Figure 4.30 shows the EDS line scans performed along the cross-sections of coupon 2b, annealed under hydrogen and coupon 2c, annealed under helium. The line scan results, qualitatively substantiate the fact that uniform alloy was achieved around 47 wt % Ag which was very close to the alloy composition determined gravimetrically.

![Figure 4.29](image-url) [a] SEM micrograph of coupon 1 after plating, [b] EDS map of figure 4a, iron (blue), palladium (red) and silver (green), [c] SEM micrograph of coupon 1 after plating, [d] EDS map of figure 4c, iron (blue), palladium (red) and silver (green).
For both coupons, there were no significant differences observed on the structures of the layers and the effectiveness of alloy formation resulting from different annealing atmospheres. The plated layers looked similar after annealing under He or under H₂. In addition, considering the resolution of the SEM, there was no observable intermetallic diffusion to the Pd-Ag layer in spite of the high annealing temperature. This could be due to the protective oxide barrier layer or penetration of Ag towards the Pd layer and the high mobility of Ag could hinder the diffusion of Fe into the Pd layer. Also the effect of H₂ as a reducing atmosphere for most of the oxides on the thin protective oxide layer was not very clear since the membrane layers were not dense. It could be seen from Figure 4.30c that there was still a dark thin oxide layer in between the alloy layer and the PSS.
substrate even after annealing under H₂. However, this oxide layer was not as clear as it could be seen after annealing under He and it was too thin to be detected by EDS. Since the coupons were not dense when they were annealed, some parts of the oxide layer might be reduced since water could easily leave the system, whereas for the dense parts, since there was no place for the water to escape from the system, the reduction in the oxide layer might have been prevented.

### 4.4.4 The Effect of Sequence of Ag Deposition and Annealing on the Performance of Composite Pd-Ag Alloy/Porous Stainless Steel Membranes (Tube Study)

Based on the results obtained from the PSS coupons, porous tubes were used to synthesize two Pd-Ag membranes by using different procedures. The first membrane (Pd-Ag Membrane #2 in Figure 4.26) was prepared by sequential Pd and Ag plating with intermediate annealing after each Ag deposition (the coating and diffusion technique). The plating and annealing steps were repeated until the membrane became gastight. The resulting membrane was 42 µm thick and had 18 wt% Ag. The second membrane (Pd-Ag Membrane #3 in Figure 4.26), however, consisted of several sandwiched layers of Pd and Ag with no intermediate heat treatment. The membrane was finally annealed after it was dense. The final thickness of the membrane was about 15 µm and contained around 10 wt % Ag.

The practical application for these membranes is illustrated by the hydrogen permeation data, shown in Figure 4.31. The figure includes the H₂ flux of the two membranes (Pd-Ag #2 and #3) at 350°C and at 500°C. The increase in the He flux of Pd-
Ag Membrane #3 for both temperatures corresponds to a leak development during annealing, yielding a very low H₂/He selectivity. Table 4.7 shows the heat treatment history with corresponding hydrogen permeance and selectivity for both of the membranes. The leak development increased incredibly as the temperature increased, indicating formation of pinholes or cracks. This phenomenon can also be seen from the increase of slope of the hydrogen flux of Pd-Ag #3 with increasing temperature (Figure 4.31). Therefore, despite of the much thinner separation layer, Pd-Ag #3 suffered from very low stability and very poor separation factor.

On the other hand, Pd-Ag Membrane #2 had a stable hydrogen permeance of 6 m³/m²·h·atm⁰.⁵ at 500°C. The H₂ permeance of Pd-Ag Membrane #2 at 500°C was lower than that of pure Pd membranes that had similar thicknesses (see Table 4.4 for Pd Membrane #4). This was possibly due to the non-homogeneous alloy formation with layers that contained higher Ag content than the desired composition. Since thick Pd and Ag layers were used, the annealing temperature was not high enough for complete alloy formation. Since this membrane showed stable hydrogen flux at 500°C, it was heated to 550°C for further homogenization of the non-uniform alloy layers. Unfortunately, the oxide layer formed at 400°C was not thick enough to minimize the intermetallic diffusion from the support to the separation layer at 550°C and the hydrogen flux started to decline as shown in Figure 4.32. The activation energy was 16.7 kJ/mol for temperatures from 350 to 500°C.
Table 4.7 Summary of the hydrogen permeance of Pd-Ag membranes at different temperatures.

<table>
<thead>
<tr>
<th>Pd-Ag Membrane</th>
<th>Temp. [°C]</th>
<th>H₂ Flux ( [m^3/m^2h] )</th>
<th>H₂ Permeance ( [m^3/m^2hatm^{0.5}] )</th>
<th>Selectivity [H₂/He]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>350</td>
<td>1.30</td>
<td>3.13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.64</td>
<td>3.95</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>2.05</td>
<td>4.94</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2.51</td>
<td>6.02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>2.54-1.9</td>
<td>6.35-4.75</td>
<td>660</td>
</tr>
<tr>
<td>#3</td>
<td>350</td>
<td>3.12</td>
<td>7.96</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>4.15</td>
<td>10.49</td>
<td>278</td>
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<tr>
<td></td>
<td>450</td>
<td>4.69</td>
<td>12.10</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>9.91</td>
<td>23.92</td>
<td>9.4</td>
</tr>
</tbody>
</table>

After the characterization was completed, both membranes were cut for cross-sectional analysis. Figure 4.33 and 4.34 shows the SEM images of the cross sections and the EDS analysis performed through the separation layer of the Pd-Ag membranes #2 and #3, respectively.

It was observed that there were several layers of cracks and voids all around the Pd-Ag membrane #3, due to the initial pure Ag layers sandwiched between the Pd layers prior to annealing and the faster diffusion of Ag during annealing (Figure 3.34). These cracks and voids caused the membrane to have very low selectivity and poor stability. The formation of larger voids, therefore increasing leak rate, could be explained by the faster diffusion rate of Ag into the Pd layers with increasing temperature. In addition, from the EDS analysis (Figure 4.34 c-d), the diffusion of Fe from the support into the Pd-
Ag layer can clearly be seen. After testing Pd-Ag #3 (oxidation temperature of the support was 400°C) at 500°C for 350 hours, the extent of intermetallic diffusion was around 7\(\mu\)m.

On the other hand, Pd-Ag membrane #2, which was annealed after each Ag deposition, did not contain voids all around the membrane (Figure 4.33), unlike Pd-Ag #3. There were only few voids at some spots which might be resulting from the Ag which did not diffuse completely into the Pd layer before further Pd deposition.
Figure 4.31 Hydrogen flux at 1 atm pressure difference as a function of time for Pd-Ag membrane #2 and #3 [a] at 350°C, [b] at 500°C.
Figure 4.32 Hydrogen flux at 1 atm pressure difference as a function of time for Pd-Ag membrane #2 and #3 at 550°C.
**Figure 4.33** SEM micrographs of the cross section of Pd-Ag Membrane #2 after testing. [a, b, c] Different portions of the membrane, [d] EDS analysis through the arrow indicated in [c].
Figure 4.34 SEM micrographs of the cross section of Pd-Ag Membrane #3 after testing. [a, b, c] Different portions of the membrane, [d] EDS analysis through the arrow indicated in [c].
Semi-infinite slab model (Equation 4.3) was used to estimate roughly, the temperatures \((T)\) and times \((t)\) required to diffuse Ag completely into the Pd layer at a given thickness of Pd layer. Ag concentration at the Pd-Ag interface \((C_s)\) was assumed to remain equal to 100 wt.% and the diffusion coefficient of Ag in the Pd layer \((D\) in m\(^2/s\)) was assumed not to change. In Equation 4.3, \(C_x\) represents the Ag concentration at a distance from the Pd-Ag interface which is set to 20 wt% (the desired alloy composition) and \(x\) is the distance from the interface which is equal to Pd layer thickness in this case. The diffusion coefficient of Ag in the Pd \((D)\) at each temperature \((T\) in K) was calculated through the Arrhenius relation shown in equation 4.4. R is the universal gas constant.

\[
\frac{C_x}{C_s} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) 
\]

\[
D = 7.4 \cdot 10^{-10} \exp\left(-\frac{103000}{RT}\right) 
\]

Table 4.8 summarizes the annealing temperatures and times as a function of the Pd layer thickness calculated using Equations 4.3 and 4.4. As seen from Table 4.8 as the thickness of the Pd layer decreases, lower temperatures and shorter times could be used for uniform alloy formation. Pd layers thicker than 5 micron are not suitable for alloy formation since temperatures higher than 500°C are required at reasonable times or very long times are needed for temperatures less than 500°C. Considering both the ease of control of deposition and the limitations in the annealing process, the most practicable and reasonable condition for alloy formation is proposed to deposit Pd layer between 3 to 5 \(\mu m\), and then deposit Ag as much as 20 wt% of deposited Pd and use 500 or 450°C for
the required amount of time as shown in Table 4.8. By repeating this procedure a uniform alloy membrane, which does not suffer from leaks like Pd-Ag #3, could be achieved after 3-5 annealing on a 0.1 µm grade PSS support.

Table 4.8 Annealing temperatures and times as a function of the Pd layer thickness to achieve 20 wt.% Ag, calculated using equations 4.3 and 4.4.

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>D [m²/s]</th>
<th>Time [h] for Ag to diffuse completely into Pd layer of thickness x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x= 5 µm</td>
</tr>
<tr>
<td>350</td>
<td>1.71E-18</td>
<td>1253</td>
</tr>
<tr>
<td>400</td>
<td>7.49E-18</td>
<td>286</td>
</tr>
<tr>
<td>450</td>
<td>2.68E-17</td>
<td>80</td>
</tr>
<tr>
<td>500</td>
<td>8.11E-17</td>
<td>26</td>
</tr>
<tr>
<td>550</td>
<td>2.15E-16</td>
<td>10</td>
</tr>
<tr>
<td>600</td>
<td>5.08E-16</td>
<td>4</td>
</tr>
<tr>
<td>650</td>
<td>1.10E-15</td>
<td>2</td>
</tr>
</tbody>
</table>
CHAPTER 5

CONCLUSIONS

1. The oxidation of PSS supports should have an optimum time and temperature at which stable, uniform oxide layer is formed without plugging pores, thus without producing a hydrogen diffusion barrier, yet sufficient to prevent intermetallic diffusion. For relatively low oxidation temperatures, the time of oxidation does not affect the He flux appreciably.

2. Higher oxidation temperatures cause a larger reduction of the He flux resulting possibly from either the pores been blocked or the formation of a thicker oxide layer. Although the final thickness of the dense palladium layer does not appear to be affected appreciably by the oxidation temperature, the oxide layer not only acts as a diffusion barrier but also provides surface sites for easy activation and plating and improved adhesion.

3. Although for relatively low oxidation temperatures, the oxide layer was too thin to be detected by SEM or EDS, both mass uptakes and cross sectional SEM and EDS analyses showed a uniform thin oxide layer at intermediate temperatures around 600°C and a crumbly, thick oxide layer at high temperatures such as 800°C. The composition of the oxide layer was found to contain higher Fe content on the outer surface and higher Cr content closer to the interface between stainless steel and the oxide layer.
4. Surface roughness of the PSS substrate increases with higher temperature oxidation. The increase in surface roughness enhances Pd attachment to the surface and causes the formation of larger Pd clusters. On the other hand, surface roughness enhances Ag deposition as islands growing perpendicular to the surface with non-uniform deposition. However, this non-uniform deposition, island and bridge formation reduced the size of large pores when the pores are large enough for Ag solution to diffuse inside. Thus, Ag plating in the initial stages reduces the thickness of the dense membrane layer.

5. Membranes which contain intermediate layers of Ag trapped in between Pd layers, suffer from leaks due to fast diffusion rate of Ag, resulting in very poor selectivity and stability at high temperatures. On the other hand, when Ag is not used as an intermediate layer, an alloy without any voids can be achieved. One way to prepare homogeneous alloy membranes is either to use coating and diffusion method (annealing after each Ag deposition and let Ag penetrate fully into the Pd layer) or to try co-deposition of the metals from the same bath and use lower temperatures and shorter times for annealing which do not cause intermetallic diffusion or which reduces the Kirkendall effect for crack formation.
CHAPTER 6
RECOMMENDATIONS

1. Considering the fact that the intermetallic diffusion less than 2 µm is hardly detectible by using EDS due to the spatial resolution of the EDS, annealing experiments to investigate intermetallic diffusion should be run with more aggressive annealing conditions, either using higher temperatures or longer times which would enhance the extent of intermetallic diffusion. By this way, the cross-sectional EDS analysis can be used to study the effectiveness of the different oxide barrier layers in terms of minimizing the intermetallic diffusion.

2. A support that has a protective oxide layer can be used to prepare a new Pd-Ag membrane with the same technique as Pd-Ag #2, but which has thinner Pd-Ag layers. Table 4.8 can be used to estimate the ideal thickness of the deposited layers with corresponding annealing temperatures.

3. In this study, no improvement of the hydrogen permeance could be observed with the Pd-Ag membranes relative to pure Pd membranes. On the other hand, there is very few reported literature on the permeability of Pd-Ag system. Therefore, several alloy disks which have different Ag compositions could be used to predict how the H$_2$ permeability changes as a function of Ag content and temperature, as well as the activation energy for hydrogen permeation. The obtained data can be used to predict the behavior of Pd-Ag membranes prepared in our lab.
REFERENCES


Chou M.L., Manning N., Chen H. “Deposition and characterization of thin electroless palladium films from newly developed baths” Thin Solid Films, 213, 1992, 64.


