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# Surface characterization of Pd–Ag composite membranes after annealing at various temperatures

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#### ABSTRACT

Pd–Ag films (~24% Ag, 20–26  $\mu$ m thick) were deposited by sequential electroless plating onto porous tubular stainless steel substrates. Intermediate  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> oxide layers were employed to modify the support pore size and to prevent intermetallic diffusion of the stainless steel components into the Pd–Ag layer. The aluminum oxides were applied to the substrate porous system by a vacuum assisted-coating method. Composite membranes annealed at temperatures between 500 and 600 °C were characterized for film structure (XRD), morphology (SEM), bulk and surface component distribution (EDS, XPS), and hydrogen permeance. Pd–Ag alloy formation progressed as annealing temperature was increased to 600 °C. Composition measurements within the Pd–Ag layer revealed preferential segregation of the Ag component to the top surface; this result is consistent with Ag's lower surface free energy. No diffusion of stainless steel components into the Pd–Ag layer was observed, demonstrating the effectiveness of the oxide interdiffusion barrier. Hydrogen permeation tests of membranes annealed at 500 °C. Permeabilities were higher but selectivities were lower for membranes annealed at 550 °C. This performance deterioration may be related to defects within the Pd–Ag layer caused by growth of dendritic Ag deposits.

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#### 1. Introduction

Composite palladium alloy membranes have been used to purify hydrogen or to enhance the conversion of thermodynamically limited reactions. Several recent articles have described membrane reactors for the hydrogen production from methane and alcohols reforming reactions, showing the potential application of the Pd–Ag membranes [1,2].

Several methods have been investigated for fabrication of composite membranes [3]. When electroless plating is used for sequential deposition of Pd and a second metal, high temperature treatments are needed to promote atomic inter-diffusion of metals and alloy formation. Membrane systems supported by porous stainless steel are often configured as multi-layers to prevent inter-diffusion of the Pd layer and the support and to minimize defect formation in the Pd layer. Several authors [4–7] have proposed application of a micro porous diffusion barrier onto the macro porous substrate prior to deposition of the thin Pd film. Ayturk et al. [8] reported that, without effective diffusion barriers to prevent

the formation of undesired Pd/Fe alloys at the interface between the support metal and the membrane layer, both the thermal stabilities of the supports and the measured hydrogen permeances deteriorated significantly.

Alumina has been reported as diffusion barrier and substrate modifier in the literature [9–11]. We have previously reported how the introduction of thin layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Pd activated  $\gamma$ -alumina on the support affects the hydrogen permeation flux and hydrogen selectivity of Pd–Ag composite membranes [12]. Tong et al. [9] used aluminum hydroxide gel as modification material for the fabrication of thin Pd membranes on macroporous tubular stainless steel substrates. They introduced an aluminum hydroxide sol into the tube from vacuum suction along with Pd seeds. This modification resulted in the formation of a pinhole-free, stable, pure Pd membrane. Broglia et al. [10] recently reported their synthesis of Pd membranes on alumina-modified PSS supports. Two  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers, 3–4 µm thick, were deposited by dip coating of a colloidal dispersion of  $\gamma$ -alumina particles.

Understanding the impact of component segregation at the alloy surface is critical to the development of alloys for various applications [13,14]. It is well established that differences between the surface and bulk compositions of Pd alloy membrane materials can influence their hydrogen permeabilities and catalytic activities [3].

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The surface properties of Pd–Ag bimetallic alloys have been studied using both single-crystalline bimetallic bulk alloy surfaces and surface alloys as model systems [15]. Ag growth on Pd(1 1 1), surface segregation of Ag in bulk PdAg alloys and the electronic structure of PdAg alloys have been studied both experimentally and theoretically [16]. Surface enrichment of silver has been reported for Pd–Ag alloys both in vacuum and in an inert atmosphere. This situation may change when adsorbates are in contact with the alloy surface leading to adsorbate-induced segregation or desegregation of binary metal alloys [16,17].

Few articles have been published concerning surface segregation on Pd-Ag membranes [18,19]. In a pioneering work, Kaliaguine and coworkers [18] concluded that hydrogen chemisorption induces palladium segregation on the surface of a dense Pd-Ag commercial membrane which was cold-worked to a thickness of 100 or 50 micrometers. Recently, Peters et al. [19] performed a surface analysis after long-term testing of Pd–23%Ag/stainless steel composite membranes prepared by wrapping stainless steel substrates with Pd–Ag films that were first sputter co-deposited onto silicon substrates. Both XPS results and AES depth profiling data gave evidence for segregation of silver to the membrane surfaces.

The aim of this contribution is to study the surface features of the synthesized Pd–Ag alloy membranes after annealing at different temperatures. The Pd–Ag alloy films were deposited by electroless plating on an alumina modified stainless steel support. The aluminum oxide was applied inside the substrate porous system employing a vacuum assisted-coating method.

#### 2. Experimental

#### 2.1. Composite membrane synthesis

Composite Pd–Ag/PSS membranes were prepared by the electroless plating method. Porous stainless steel (PSS) supports were purchased from Mott Metallurgical Corporation ( $0.2 \mu$ m grade, 6.4 mm i.d., 9.5 mm o.d.). Before deposition, one end of the PSS support was welded to a non-porous stainless steel tube and the other one, to a non-porous SS plug. The supports were cleaned in an alkaline solution based on Guazzone et al. [20] to remove the dirt and grease (NaOH, 74 g/l; NaHCO<sub>3</sub>, 5.1 g/l; Na<sub>2</sub>HPO<sub>4</sub>, 17 g/l). The cleaning process was performed in an ultrasonic bath at 60 °C, followed by rinsing with deionized water and isopropanol [21]. Then the supports were oxidized in stagnant air at 500 °C for 12 h.

After oxidation, the surface of the porous metal supports was modified by sequentially depositing pre-activated  $Al_2O_3$  particles with intermediate short Pd deposition by electroless plating [22]. The aluminum oxide was forced to penetrate somewhat inside the substrate porous system through a vacuum assisted-coating method.

 $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Buehler, 1 µm) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Buehler, 50 nm) aluminas were pre-activated through immersion in 125 ml of a SnCl<sub>2</sub> solution (1 g/l, pH 2). Then, 125 ml of a PdCl<sub>2</sub> solution (1 g/l, pH 2) were added. This process was carried out in an ultrasonic bath, at 60 °C during 20 min. The activated powder was filtered and dried at 120 °C during 2 h. Three different slurries (A–C) were prepared. Slurry A was prepared by dispersing 1 g of non-preactivated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in 80 ml of 0.01 M HCl (pH 2). Slurry B was obtained by dispersing the pre-activated mixture (60 wt.%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 40 wt.%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) in 80 ml of water. Pre-activated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was employed for slurry C.

During the dip coating, the porous stainless steel tube was connected to a vacuum system. The first step involved immersion for 1 min in a cylindrical vessel containing slurry A in an ultrasonic bath followed by rinsing. This process was repeated with slurry B

#### Table 1

Composition of Pd and Ag plating solutions.

	Pd bath	Ag bath
$PdCl_2$ (g/l)	3.6	4.9
Na <sub>2</sub> EDTA (g/l)	67	33.6
NH4OH (28%) (ml/l)	650	650
HCl (37%) (ml/l)	5	-
N <sub>2</sub> H <sub>4</sub> (1 M) (ml/l)	10	10
рН	~11	$\sim 11$
Temperature (°C)	50	45

followed by a Pd electroless plating for 5-10 min at  $50 \,^{\circ}\text{C}$ , without vacuum. Then, the last immersion was performed with slurry C followed by a short Pd deposition. The modified support was rinsed and dried at  $120 \,^{\circ}\text{C}$  overnight.

Modified substrates were activated using a conventional twostep SnCl<sub>2</sub>/PdCl<sub>2</sub> procedure [20]. Substrates were immersed in solutions of 1 g/l of SnCl<sub>2</sub>.2H<sub>2</sub>O (pH 2) and then 0.1 of PdCl<sub>2</sub> (pH 2); this sequence was repeated six times. Electroless plating (ELP) was used to coat the PSS composite with a continuous palladium-silver laver. The ELP bath compositions for Pd and Ag are shown in Table 1. The non-porous stainless steel parts were covered with Teflon, and then the modified substrates were immersed in the plating baths for 90 min. The as-deposited membranes were carefully rinsed with deionized water between each plating step, and the plating bath was renewed. The Ag was deposited sequentially after two or three palladium depositions; then the membranes were rinsed with water and finally dried at 120 °C overnight. After the silver deposition and drying, the membrane was re-activated before the next plating step. When the membrane became impermeable to liquid, the plating was performed with vacuum in order to block the last remaining large pores [22]. The activation-plating procedure was repeated until the composite Pd-Ag membrane became impermeable to N<sub>2</sub> at room temperature and at a pressure difference of 10 kPa. The thickness was estimated from the weight gain after palladium-silver deposition and checked by SEM; the number in the name of each membrane represents its thickness in microns. The membranes were heated in a nitrogen flow at a rate of 0.5 °C/min. A final annealing treatment was performed at 500, 550 and 600 °C during 100 or 200 h in H<sub>2</sub> atmosphere.

#### 2.2. Bulk characterization

The XRD patterns of the films were obtained with an XD-D1 Shimadzu instrument, using Cu K $\alpha$  radiation at 30 kV and 40 mA. The scan rate was  $1-2^{\circ}$ /min in the range  $2\theta = 30-100^{\circ}$ .

The outer surface and cross-section images were obtained using a JEOL scanning electron microscope, model JSM-35C, equipped with an energy dispersive analytical system (EDS, EDAX<sup>TM</sup>). For the cross-section views, tubular pieces with a length of ~12 mm were placed in a plastic tube; then epoxy resin was added. After hardening, they were cut. The grinding was carried out with waterproof abrasive paper of 180, 280, 500, 800 and 1200 grit. The polishing was done with a ~1  $\mu$ m-grade paste, and finally with a suspension of  $\gamma$ -alumina (50 nm). The grinding and the polishing cycles lasted 5 min; after each cycle, it was necessary to clean the samples with ethyl alcohol in ultrasonic bath.

#### 2.3. Surface characterization

X-ray photoelectron spectroscopy (XPS) analyses were performed in a multi-technique system (SPECS) equipped with a monochromatic Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and the Al-K $\alpha$  X-ray source was operated at 200 W and 12 kV. The working



Fig. 1. SEM images of the α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS. Top views (a, b) and cross-sectional view (c) at different magnifications (1500× and 5400×). The EDS results for points b and c are given in Table 2.

pressure in the analyzing chamber was less than  $5 \times 10^{-10}$  kPa. The XPS analyses were performed on the used Pd-membranes after being exposed to ambient conditions. Prior to the XPS measurements, the Pd–Ag membranes were heated in flowing H<sub>2</sub>/Ar at 400 °C. This treatment was performed at atmospheric pressure with a flow rate of 60 mL min<sup>-1</sup> in the load lock chamber of the spectrometer and then, the samples were transferred to the XPS analysis chamber without exposure to air. The treatment temperature was chosen taking into account the temperature employed during the permeation measurements (400–450 °C).

The spectral Pd 3d, Pd 3p, Ag 3d, O 1s, C 1s, Si 2p, Na 1s, Fe 2p and Al 2p were recorded for each sample. The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK). The peak areas were determined by integration employing a Shirleytype background. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

XPS depth profiles were acquired on a ThermoFisher Theta Probe instrument, with a base working pressure of ~ $1.0 \times 10^{-10}$  kPa. A monochromated Al K $\alpha$  X-ray source and 50 eV analyzer pass energy were used for the analyses. These analyses were performed on the used Pd-membranes after being exposed to air. For each sample, spectra were recorded for Pd 3d, Pd 3p, Ag 3d, Ag 3p, O 1s, C 1s, Fe 2p and Cr 2p photoelectrons. Elemental concentrations were calculated from peak areas, using sensitivity factors and software provided by the instrument manufacturer. Elemental depth profiles were performed using argon ion sputtering. The differentially pumped ion gun was operated at  $1.5 \times 10^{-8}$  kPa and 3 kV, conditions which deliver a sputtering rate of approximately 5–10 nm/min. The sputtering was performed in 5 steps of 10 s, followed by 20 steps of 60 s and 1 step of 600 s to examine the top ~100 to 200 nm of the membrane surfaces.

#### 2.4. Thermal treatments and gas permeation measurements

Thermal treatments and gas permeation measurements were conducted in a shell-and-tube membrane module [7]. The open end of the membrane was sealed to the permeator wall with Teflon ferrules. The permeator was placed in an electrical furnace and heated to the desired temperatures. A thermocouple inserted within the membrane tube monitored and controlled the temperature during the experiments. All the gases were fed to the permeator using calibrated mass-flow controllers. Feed gases flowed along the outside of the membrane while the permeated gases flow rates were measured in the inner side of the membrane. A N<sub>2</sub> sweep gas stream was fed in the permeate side only during the heating and cooling periods. The membranes were tested with pure hydrogen or nitrogen, the unit was operated without sweep gas and the fluxes were measured as a function of the retentate pressure. Pressure differences across the membranes were controlled using a back-pressure regulator. The upstream was varied from 110 to 200 kPa while keeping the downstream pressure constant at 100 kPa. The gas permeation flow rates of either  $H_2$  or  $N_2$  were measured using two bubble flow meters at room temperature and atmospheric pressure. All the membranes were tested over a period of more than 100 h. The experiments were carried out to evaluate the hydrogen permeability and selectivity of the membranes using single gases. The ideal selectivity, given by the ratio of the hydrogen flux versus the nitrogen flux at the same temperature and driving force, was used to gauge the separation capability of the membranes.

#### 3. Results and discussion

#### 3.1. Modified support

The oxidized porous stainless steel support was modified by vacuum assisted dip coating of an  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mixture followed by short Pd depositions. The diffractogram obtained after the modification shows the reflection peaks of both austenite and pure palladium (not shown here), indicating that the metallic deposition is <1  $\mu$ m. The oxidized PSS substrate displays the diffraction features assigned to the  $\gamma$ -phase (austenite), suggesting that the oxides were produced at the surface level [23].

The morphologic features of the modified support were characterized by SEM. The top (a and b) and cross-sectional view (c) with different magnifications are shown in Fig. 1. Fig. 1a shows evidence of alumina deposition inside the pores, but without formation of a continuous alumina layer. The short Pd depositions led to a thin Pd layer covering the external surface. This effect could improve the adherence of the alloy film. The cross-section view (Fig. 1c) clearly shows the penetration of the alumina to ~30  $\mu$ m, likely due to the vacuum applied during the dip coating. EDS analyses were performed at points b.1, b.2 and b.3 in the top view (Fig. 1b) and at points c.1–c.4 (Fig. 1c) in the cross-sectional image. The calculated compositions are presented in Table 2. The Pd content on the surface of the support was 94 wt.%; it decreased to 3 wt.% at point c.4, located ~20  $\mu$ m from the external surface.

These results indicate that the modification of the support with dip coating and short Pd depositions allows penetration of Pd

#### Table 2

Compositions (%) determined by EDS (Fig. 2b and c) for  $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS.

View	Point	Pd	Al	Fe
External surface	b.1	36	60	3
	D.2	81	2	12
	b.3	94	-	4
Cross-section	c.1	28	4	46
	c.2	30	32	25
	c.3	52	17	21
	c.4	3	24	51

Sn was not detected.

into the pores of the support. The nitrogen permeances of the unmodified supports were  $2-4 \times 10^{-5}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> at room temperature, consistent with previous measurements of the same support [24]. The alumina modification led to a 20–25% decrease of the initial N<sub>2</sub> permeance.

#### 3.2. Pd-Ag alloy membranes

Pd and Ag were sequentially deposited by electroless plating on the alumina modified support. The composite membranes were annealed at 500, 550 and 600 °C; these temperatures were chosen for comparison with previous studies on Pd–Ag alloys [25] and for the potential application of the composite membranes in reactors for hydrogen production.

The formation of a bulk PdAg alloy was followed by XRD, SEM and EDS techniques. Fig. 2a and c shows the XRD patterns of the PdAg- $26/\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane before and after annealing at 500 °C. Before annealing, the diffractograms show the expected (1 1 1); (2 0 0); (2 2 0); (3 1 1); (2 2 2) reflections from the Pd and Ag face-centered cubic (fcc) structure. Upon annealing at 500 °C, the Ag reflections disappear and new features, located between the Pd and Ag reflections, develop. The new features are characteristic of the lattice spacing of the fcc Pd–Ag alloy. However, low intensity Pd peaks are still detected, suggesting that the alloy formation is not complete.

Fig. 2b and d shows the XRD patterns of the PdAg- $20/\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane after annealing at 550 and 600 °C. At the highest temperature, the intensity of the remaining Pd peaks significantly decreased.

The average lattice constant for the Pd–Ag alloy is 3.9398 Å. This value is between the Pd lattice (a = 3.8930 Å) and the Ag lattice (a = 4.0870 Å) constants. The Ag content in the metallic layer, for the sample PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at 600 °C, was calculated from the lattice constant [8,26,27]. The Pd-Ag solid phase forms a continuous solid solution. These Pd-Ag alloys, which have the face-centered cubic (fcc) phase, vary only in composition but not in crystal structure. Ayrtuk et al. [8] discussed that the only effect of a change in the composition is the shift in the diffraction line positions in accordance with the change in the lattice parameter, which varies continuously from that of pure Ag to that of pure Pd. Therefore, it is possible to assume a linear relationship between the lattice constant of the alloy and the Pd content. From the lattice constant of the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane, a Pd content of 76 wt.% Pd was determined. Note that this concentration is representative of only a few microns in depth. Ayturk et al. [8] estimated that the information recorded on the diffraction pattern comes from the X-rays which penetrate  $2.0-2.2 \,\mu\text{m}$  deep for Pd and Ag and 2.8–3.0  $\mu$ m for PSS when Cu K $\alpha$  X-rays are used.

Fig. 3 displays the SEM images corresponding to the top views of Pd–Ag membranes annealed at 500, 550 and 600 °C. All images show a uniform deposition with a "cauliflower-like" morphology. After annealing at 500 °C, the Pd–Ag clusters are between 30 and 60  $\mu$ m in size with well-defined borders. When the annealing temperature is increased, the cluster borders seem less defined, and the structure is more compact (Fig. 3b and c). There is, however, no evidence of through-hole formation in these samples.

The cross-section SEM images (Fig. 3d–f) show the metallic deposition on the external surface of the porous support, as well as in the outer-most pores. The film thickness was not homogeneous and, in some regions, was larger than the one determined by the gravimetric technique ( $26 \,\mu$ m). Bhandari and Ma [11] have reported that the Ag electroless deposits could present dendritic and highly non-uniform growth with tendency to grow more in the perpendicular direction to the substrate surface with poor lateral growth or pore coverage. The small voids observed in the cross-section images (Fig. 3) could be related to the formation of

Table 3

Elemental compositions (%	) determined	by EDS for the Pd-	Ag membranes (Fig. 4).
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Membranes <sup>a</sup>	Point	Pd	Ag	Al	Si	Fe <sup>b</sup>
PdAg-26/α-γ-Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	a.0	68	32			
Annealed at 500 °C	a.1	92		4		3
	a.2	53		30		12
	a.3	29		40		21
	a.4	3	1	25		50
PdAg-20/α-γ-Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	b.0	77	23			
	b.1	63		1	1	20
Annealed at 550 °C	b.2	65	9	6	1	13
	b.3	47	4	1	<1	26
PdAg-20/α-γ-Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	c.0	68	32			
	c.1	70	7	3		14
	c.2	70	2	1		20
Annealed at 600 °C	c.3	7	<1	19		52
	c.4	42	<1	1		40

Sn was not detected.

<sup>a</sup> The number in the name of each membrane represents its thickness in microns. <sup>b</sup> The % to reach 100% corresponds to Cr, Ni and Mo.

non-uniform, dendritic silver deposits [11,28]. The voids are larger at higher annealing temperatures and likely contribute to the deterioration of the membrane.

Film composition profiles were determined by EDS; results are presented in Fig. 4. They show that, at all three annealing temperatures, the metal composition is not uniform throughout the film. The average percentages of silver are lower than the expected value of 25 wt.%. The EDS average values through the total thickness were 11% (Fig. 4a, 500 °C), 16% (Fig. 4b, 550 °C) and 13% (Fig. 4c, 600 °C). However, a higher Ag concentration is observed in the external part of the Pd-Ag film, (close to 1  $\mu$ m). This behavior was confirmed through the measurement of metal concentration of the outer-surface sample (Top-view images, Fig. 3d,e and f and at points "x.0" shown in SEM Fig. 4, Table 3). Significantly, the absence of Fe, Cr or Ni in the EDS profiles demonstrates that diffusion of components from the PSS support into the Pd–Ag matrix did not occur upon annealing at 500, 550 or 600 °C.

The EDS results of the modified substrate regions are summarized in Table 3. These results show that palladium enters the porous system and reaches concentrations higher than 50 wt.%, at a.2 and b.2 points, which are distant from the support external surface. Ag was only detected in some points (a.4, b.3 and c.1); however, its concentration was always below 10 wt.%. This observation suggests that palladium probably penetrated inside the porous system during the support modification step. In this process, the second and third dip coatings were performed with pre-activated alumina. On the other hand, aluminum was detected at several points (a.2, b.2 and others) with concentrations higher than 30 wt.%.

#### 3.3. Surface characterization

To characterize the surface features of the Pd–Ag composite membranes annealed at different temperatures and after the permeation measurements, the membranes were analyzed by XPS. Prior to the analysis, the samples were heated in H<sub>2</sub>/Ar mixture during 10 min at 400 °C in the pretreatment chamber attached to the spectrometer.

Fig. 5 shows the Pd and Ag 3d core level spectra of the membranes after the permeation measurements. Gaussian/Lorentzian product GL(p) line shapes modified by an asymmetric form were used for fitting the spectra. The asymptotic form and the shape of the asymmetric tail were considered employing an appropriate software [29]. The same fitting parameters were used for all Pd-Ag alloy samples.



Fig. 2. XRD pattern of the PdAg-26/α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS and PdAg-20/α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes before and after annealing at 500, 550 and 600 °C.



Fig. 3. SEM images of top views (a-c) and cross-section views (d-f) of the PdAg/a-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes after annealing at (a, d) 500, (b, e) 550 and (c, d) 600 °C.





Fig. 4. EDS measurements along line *a* for the Pd-Ag/α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes after annealing at (a) 500, (b) 550 and (c) 600 °C. The elemental compositions for points a, b and c are given in Table 3.

Table 4 summarizes the binding energies (BE) of the PdAg-26/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS and PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes after annealing and permeation measurements. Values reported by other authors for the Pd–Ag alloys are included for comparison [31]. The binding energy of Ag 3d<sub>5/2</sub> level is lower than that corresponding to pure silver (Table 4). Ag 3d BE shift is in agreement with the one reported for Pd–Ag alloys [31,32] and suggests formation of the surface alloy in our samples. This observation is consistent with our XRD characterizations of the annealed membranes, which also suggested formation of the Ag–Pd alloy.

Table 4 shows that the atomic concentrations of Ag at the surfaces of our samples (XPS) decrease with increasing annealing temperature, but they are always higher than "bulk" compositions (EDS). These data indicate the segregation of Ag to the alloy surface. Surface segregation has been shown in a number of binary Pd-alloys of relevance to hydrogen purification, including PdAg [33,34] and PdCu [14]. In many cases, the difference in component surface free energy (surface tension) is the primary driving force for surface segregation. The surface tensions of Pd and Ag are  $1.7 \times 10^{-3}$  and  $1.12 \times 10^{-3}$  kJ m<sup>-2</sup>, respectively [34]; with a lower surface tension, Ag would be expected to be preferentially exposed at the top surface layer of the alloy.

#### 3.4. XPS depth profile

XPS depth profile data for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane obtained after annealing at 550 and 600 °C in the permeator system and subsequent permeation measurements are presented in Figs. 6 and 7. These samples were measured after being exposed to air; no treatment was performed in the reaction chamber attached to the spectrometer. During the experiment, the spectra of C 1s, O 1s, Fe 2p and Cr 2p were also measured. No signal from either Fe or Cr was observed; C was observed only in the first scan, before sputtering started. On the other hand, Sn was not detected, although this element was employed during the activation procedure. Fig. 6 shows that, for the sample annealed at 550 °C, there is a single Pd  $3d_{5/2}$  peak, located at  $335.05 \pm 0.1$  eV. However, for the sample annealed at 600 °C, the feature can be fit by two components, one at 335.80 and a second at 335.10 eV. After sputtering this sample for several minutes, only the low-binding energy contribution remained. The Ag  $3d_{5/2}$  spectra showed only one peak for both samples. The high-binding energy contribution to the Pd 3d<sub>5/2</sub> signal in the 600 °C membrane could originate from the PdO<sub>x</sub> formation at the surface level. However, to confirm this assignment, a complete analysis of the Pd 3p-O 1s region is required.

а



**Fig. 5.** XP spectra of Pd and Ag 3d obtained from membranes annealed at different temperatures after permeation measurements. All samples were heated for tem minutes in flowing  $H_2/Ar$  at 400 °C in the reaction chamber of the spectrometer.

Fig. 7 shows the evolution of the Pd 3p XPS region with sputtering time for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes annealed at 550 and 600 °C. Three features are observed: Ag 3p<sub>3/2</sub> at 573 eV, Pd 3p<sub>1/2</sub> at 560 eV, and an overlap between the O 1s and the Pd 3p<sub>3/2</sub> at ~532 eV. Through curve fitting of the spectra, taking into account the theoretical ratio for the spin-orbital splitting of Pd 3p core level, it is possible to confirm the presence or absence of O on the surface. Analysis of the spectra in this manner reveals that both samples contain a similar proportion of oxygen on the surface (15–20%), which is no longer detectable after 60 s of Ar sputtering.

A binding energy of 530.5 eV and a Pd  $3d_{5/2}$  signal at 337 eV were reported for a uniform Pd oxide layer by Peuckert [35]. By using atomic sensitivity factors and curve fitting of the overlapping Pd  $3p_{3/2}$  and O 1s peaks, they calculated an elemental ratio O-to-Pd of  $1.0 \pm 0.1$ . This analysis quantitatively confirmed that the oxide layer grown on a palladium surface in oxygen atmosphere consists of PdO. In our PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membranes annealed at 600 °C, the O/Pd surface ratio was equal to 0.25 and the O 1s binding energy was 532.0 eV. An XPS O 1s chemical shift to higher binding energies than in the oxide was previously attributed to molecularly adsorbed oxygen [36].

Then, the high O 1s binding energy (532 eV) suggests the presence of adsorbed oxygen on the PdAg membranes after exposure to air.



Fig. 6. Evolution of Pd 3d XPS spectra with sputtering time for the PdAg-20/α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at (a) 550 °C and (b) 600 °C in the permeation system.



Fig. 7. Evolution of Pd 3p-Ag 3p<sub>5/2</sub> XPS spectra with sputtering time for the PdAg-20/α-γ-Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at (a) 550 °C and (b) 600 °C in the permeation system.

	מווכז ח במוכח זון נוור שלהכם מוווכוכו זכי									
Membrane	Annealing temperature (° C)	Ag 3d <sub>5/2</sub> (eV)	FWHM (eV)	GL(p) <sup>d</sup>	Pd 3d <sub>5/2</sub> (eV)	FWHM (eV)	GL(p)	Atomic surfa	ice concentration	s
								Pd % XPS	Ag % XPS	Ag % EDS e
PdAg-26/ $\alpha$ - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	500	367.7	1.03	GL(40)	335.0	1.02	GL(10)	50.6	49.4	32
PdAg-20/ $\alpha$ - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	550	367.6	0.96	GL(50)	335.1	1.07	GL(20)	57.1	42.9	23
PdAg-20/ $\alpha$ - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -Pd/PSS	600	367.6	0.94	GL(60)	335.1	1.05	GL(20)	61.6	38.6	32
$Pd/\alpha - Al_2 O_3 - Pd/PSS$	1	I			335.1			100		
Pure Ag foil <sup>a</sup>		368.3								
Pure Pd foil <sup>b</sup>		I			335.4			100		
Pd49Ag51/C <sup>c</sup>		367.9			335.2			51		
Pd60Ag40/C <sup>c</sup>		367.85			335.35			60		
Pd65Ag35/C <sup>c</sup>		367.85			335.40			65		

Value measured in point "x.0" shown in SEM Fig. 4.

Gaussian/Lorentzian product GL(p) line shapes.

Measured in the Specs instrument

Ref. [30]. Ref. [31].

U. / Ar flow

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Ramachandran et al. [37] studied the effects of different heat treatments in N<sub>2</sub>/Ar mixtures or in air on Pd-Ag membranes with thicknesses from 1.5 to 10 µm. Their investigations were focused on changes in surface topography, surface segregation and hydrogen flux. They showed the XPS Pd 3d<sub>5/2</sub> spectrum for the as-grown film, with a binding energy shift of  $0.61 \pm 0.03 \,\text{eV}$  relative to the bulk Pd contribution. They assigned the high BE peak to the initial oxide formation (PdO<sub>x</sub> sub-oxide with x < 1) due to the exposure to air during transfer between the sputter deposition chamber and the XPS system. In comparison, the Pd 3d<sub>5/2</sub> spectrum obtained for a membrane where no hydrogen permeation measurements have been performed after an oxygen treatment at 300 °C, showed a strong palladium oxide (PdO) contribution with a chemical shift of 1.9 eV compared to bulk Pd. In the case of our sample annealed at 600 °C, based on the changes in the Pd spectra with sputtering time and on the analysis of the Pd 3p-O 1s region, the high-BE Pd  $3d_{5/2}$ peak might be assigned to Pd near the top surface of the Ag-Pd layer and the low-BE peak to Pd in the binary Pd-Ag alloy.

A Pd-rich phase has been reported to segregate on the surface of PdAg alloys under the influence of 500 eV Ar<sup>+</sup> and N<sub>2</sub><sup>+</sup> bombardment. By examining the XP spectra of these surfaces, Slusserand and Winograd [38] observed changes in the structure of the Pd 3d peaks which were specifically linked to this phase. Studies of the spectral changes with Ar<sup>+</sup> dose showed that one peak arises from electrons originated at the altered overlayer and a second peak arises from the underlying alloy with a binding energy dependent on the underlying concentration.

Ag/(Ag+Pd) and Pd/(Ag+Pd) ratios as functions of sputtering time after annealing at 550 and 600 °C are shown in Fig. 8. After 30 min of sputtering, both samples present a homogeneous composition. The relative composition of Pd and Ag with the sputtering time is affected by the different sputtering yield for silver and palladium. However, a more significant silver enrichment is observed near the surface of the sample annealed at 550 °C (Fig. 8a and Table 4).

#### 3.5. Permeation measurements

To evaluate the performance of the membranes annealed at 500 and 550 °C in reducing atmospheres, permeation measurements were performed at 400 and 450 °C, with pressure differences between 10 and 100 kPa. The PdAg-26/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS and PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS were annealed for periods of 125 h and 130 h, respectively. The total time including the tested period was ca. 420 h for both membranes.

Fig. 9 shows the hydrogen fluxes vs  $(P_{H_2ret}^{0,5} - P_{H_2per}^{0,5})$ . Note that the hydrogen flux increases linearly with  $(P_{H_2ret}^{0,5} - P_{H_2per}^{0,5})$  for all membranes and temperatures. This trend is consistent with the solution-diffusion mechanism of pure hydrogen through a palladium–silver membrane, when the rate determining step is the diffusion of H in the metallic film. In these cases, the hydrogen flux through the membrane can be described in terms of Sievert's law (Eq. (5)):

$$J = \frac{Q_0}{L} \exp\left[-\frac{E_p}{RT}\right] \left(P_{\rm H_2 ret}^{0,5} - P_{\rm H_2 per}^{0,5}\right)$$
(5)

where *J* is the hydrogen flux (mol m<sup>-2</sup> s<sup>-1</sup>), *L* the membrane thickness (m),  $Q_0$  the pre-exponential factor (mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup>),  $E_p$  the activation energy of permeability (J mol<sup>-1</sup>),  $P_{\text{H2ret}}$  and  $P_{\text{H2per}}$  the partial hydrogen pressures in the retentate and permeate, respectively, *T* (K), and *R* the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). The apparent activation energy in the 400–450 °C temperature range was determined for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane annealed at 500 °C. A value of 9.7 kJ mol<sup>-1</sup> was obtained, which is within the range of values previously reported for



**Fig. 8.** XPS Ag/(Ag + Pd) ratio as a function of the sputtering time for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at (a) 550 °C and (b) 600 °C in the permeation system.



**Fig. 9.** Sievert's law plots measured at 400 °C (empty symbols) and 450 °C (full symbols) for the PdAg-26/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS ( $\bullet$ ) membrane annealed at 550 °C and for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at 500 °C ( $\blacksquare$ ) and 550 °C ( $\blacktriangle$ ).



**Fig. 10.** Effect of the pressure difference upon  $H_2/N_2$  ideal selectivity measured at 400 °C (empty symbols) and 450 °C (full symbols) for the PdAg-26/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS ( $\bullet$ ) membrane annealed at 500 °C and for the PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS annealed at 500 °C ( $\bullet$ ).

Pd–Ag alloy membranes [11,40]. The permeability was equal to  $3.1 \times 10^{-4}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-0.5</sup> at 450 °C and 100 kPa, in agreement with the reported data for Pd based membranes [11,20].

The ideal selectivities  $(H_2/N_2)$ , defined as the ratio of the fluxes of two pure gases, under the same trans-membrane pressure difference and temperature, are shown in Fig. 10. PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS, with thickness of 20  $\mu$ m, is the most selective membrane and presents H<sub>2</sub> fluxes lower than the membrane of 26  $\mu$ m. This behavior could be attributed to the higher Knudsen contribution to the hydrogen permeation of the latter membrane. Note that for this membrane the nitrogen flux was detected only at 100 kPa, the H<sub>2</sub>/N<sub>2</sub> selectivity being equal to 954 at 450 °C.

After the permeation measurements, the PdAg- $20/\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane was annealed at 550 °C in hydrogen flux, for a period of 120 h. Annealing at 550 °C produced an increase of hydrogen fluxes and a decrease of ideal selectivities, while the apparent activation energy decreased to 8.5 kJ mol<sup>-1</sup>. These results suggest that this treatment produced a deterioration of the metallic layer, developing defects through which all gases can permeate. The dendritic growth of silver deposits shown in Fig. 3 could favor the appearance of pin-holes or other defects upon high temperature treatment [11]. The low selectivity of the PdAg membrane was previously assigned to a microstructural difference between electroless plated Pd and electroless coplated PdAg films [3].

Several features have been reported that affect the permeation behavior of the Pd based membranes, such us surface roughness, alloy composition, surface segregation, microstructure differences between Pd and its alloys, grain sizes, surface area, presence of defects, that could be discussed taking into account the hydrogen transport limiting step. For thin Pd membranes where surface processes are dominant, the activation energies are usually high (>15 kJ mol<sup>-1</sup>), while the values for sputtered thin films are larger than the electroless plated ones [39]. In this case, several factors may affect the permeation, including microstructure, grain sizes, surface area and composition and grain boundary composition.

For electroless plated or cold rolled Pd membranes, the activation energy lies between 8 and  $15 \text{ kJ} \text{ mol}^{-1}$  if bulk diffusion is the rate-limiting step, or both bulk diffusion and surface process are responsible for controlling the permeation process [39]. The activation energy obtained in our work is in good agreement with the reported values.

#### 4. Conclusions

Membranes for hydrogen separation were prepared by deposition of Pd–Ag films onto  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified porous stainless steel substrates. The aluminum oxides were applied to the substrate porous system by a vacuum assisted-coating method. A PdAg-20/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Pd/PSS membrane annealed at 500 °C displayed very high selectivity; at 100 kPa and 450 °C, the ideal H<sub>2</sub>/N<sub>2</sub> selectivity was 954. However, the treatment of the membrane at higher temperatures resulted in deterioration of the metallic layer, creating defects that caused increased permeability and decreased selectivity.

Characterization of the membrane surfaces by XRD and XPS provided convincing evidence of PdAg alloy formation in the bimetallic film. Both SEM/EDX cross sectioning and XPS confirmed preferential segregation of Ag to the top surface of the film at all conditions studied, consistent with the lower surface free energy of Ag.

Significantly, neither SEM/EDS cross sectioning nor XPS depth profiling identified stainless steel components (Fe, Cr or Ni) in the Pd-Ag/ $\alpha$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers, even after annealing at temperatures as high as 600 °C. These results demonstrate the ability of Al<sub>2</sub>O<sub>3</sub> applied by vacuum assisted dip-coating to effectively block intermetallic diffusion of support components under these conditions.

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