



Development of PVD-deposited Pd-Ag functional thin film membranes on ceramic supports for hydrogen purification/separation

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1 Introduction

Palladium (Pd)-based membranes have been studied for many years, regarding applications in production and purification of hydrogen. The reaction of water gas shift ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$), for example, can advantageously be conducted in a Pd-based membrane reactor, where hydrogen produced selectively permeates the membrane [1]. When hydrogen permeates with an infinite selectivity, its passage is governed by sorption-diffusion mechanism through the atomic structure.

Among all metals, palladium is the material that exhibits the highest atomic hydrogen permeability, resulting from the high capability in the catalytic dissociation of H_2 molecules in its metallic structure [2]. However, the use of pure palladium membranes has some limitations [3]. When palladium alloys such as Pd-Ag are used, the result is a homogeneous solid solution with a fcc structure [4,5]. This alloy prevents the formation of hybrid phases, allowing higher hydrogen permeation along with chemical and mechanical stability, reducing also the overall cost of raw material [2].

Structurally, membranes can be classified in two groups: composite and self-supported. In order to obtain thin metal films, porous supports are used to increase mechanical strength and thermal stability [2,6,7], being the most commonly used made of porous stainless steel, ceramics and glass [6]. However, a porous support inevitably offers a higher superficial roughness and hosts imperfections due to porosity, leading to formation of pin-holes and imperfections in the thin film membrane [2].

Alumina ($\alpha\text{-Al}_2\text{O}_3$) has been reported as one of the most used membrane supports. Upon preparation of the composite porous support, the introduction of thin layers of $\gamma\text{-Al}_2\text{O}_3$ by dip coating affects the hydrogen permeation flux and selectivity. This modification results in a pinhole-free and stable membrane [8,9]. Recently, Tanaka et al. reported the doping of $\gamma\text{-Al}_2\text{O}_3$ with yttria-stabilized zirconia (YSZ), prepared by dip coating [10].

The synthesis of membranes by magnetron sputtering, with optimized processing parameters, originates a thin film with good quality, mostly free of voids and pin-holes with a high coverage on the substrate in order to prevent any leakage [11, 12]. Furthermore, it has the important advantage of allowing producing very thin films, of the order of hundreds of nanometers, decreasing the membrane cost while increasing hydrogen permeation flux. However, if the support

has initially a very high roughness the coating would not guarantee a uniform deposition over the support, leading to different microstructural morphologies in the membrane that hinder densification of the microstructure [13, 14].

In this study, Pd-Ag based membranes were produced on alumina porous supports (previously doped with yttria-stabilized zirconia) by magnetron sputtering technique. The deposition parameters were optimized concerning the membrane selectivity towards H_2/N_2 and the materials subsequently characterized. Permeation tests were endured to assess the selectivity and hydrogen permeation of the membrane. The membrane cross-section microstructure, surface morphology and thickness were analyzed by Scanning Electron Microscopy (SEM); by coupling SEM with Energy Dispersive X-Ray Spectroscopy (EDX) enabled the chemical assessment of its composition, which is very important for membrane quality control and reproducibility. X-ray Diffraction (XRD) was used to characterize the membrane crystallinity.

2 Experimental

A porous $\alpha\text{-Al}_2\text{O}_3$ (99.9%) tube with an average pore size of 200 nm was used as membrane support. The $\gamma\text{-Al}_2\text{O}_3$ with yttria-stabilized zirconia layer (YSZ- $\gamma\text{-Al}_2\text{O}_3$) was produced by a sol-gel technique with sol synthesis, deposited by dip-coating onto the $\alpha\text{-Al}_2\text{O}_3$ porous support, then subsequently dried at 40 °C and calcinated at 550 °C, as described in detail elsewhere [13]. This layer was added to create a smoother surface that allows an enhanced adhesion of the Pd-Ag film membrane, which was due to the pores dimension reduction upon doping (from 200 to ca. 5 nm).

Palladium and silver were deposited onto the YSZ- $\gamma\text{-Al}_2\text{O}_3$ layer by Magnetron Sputtering (MS). MS is a type of Physical Vapor Deposition (PVD) technique, using high vacuum and metal target-loaded magnetrons. This method consists in bombarding both Pd and Ag targets with energetic argon ions and subsequent ejection of the neutral metal atoms species, which will then condense as a growing thin film on the support. The process parameters were: base pressure $\approx 10^{-4}$ Pa; working pressure = 0.37 to 3 Pa; target current density (Pd) = 7.6 to 10 mA/cm²; target current density (Ag) = 1.6 mA/cm²; bias voltage applied to support holder = -60 V, working gas flow (Ar) = 35 to 50 sccm. Table I shows more details for each sample. Prior to deposition the supports were etched in argon plasma at 1 Pa for a maximum of 15 min. During deposition, the support was heated



to ~200 °C and rotated vertically with a speed of 19 rpm between both inclined magnetrons.

Gas-permeation measurements were performed to determine the permeation to nitrogen and to hydrogen. First, the membranes were tested only with nitrogen to evaluate the ability to stanch other gases than hydrogen. If the permeance towards nitrogen proves to be low, which in our case was set to a lower limit of $0.1 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 300 kPa, the experimental procedure evolved to selectivity (α) test, where nitrogen and hydrogen gas-permeation were measured. The permeation tests were performed at room temperature and flow rates converted to NTP conditions. The pressure difference, $\Delta P = (P_{\text{feed}} - P_{\text{permeate}})$, in the membrane varied between 100 and 500 kPa. The permeate flow rate was measured by a bubble meter *Horiba STEC VP-3*.

SEM and EDX were used to observe the surface and cross section of the PVD-deposited Pd-Ag thin film membranes, and YSZ- γ -Al₂O₃ interfacial layer, supported on the α -Al₂O₃ tube. A FEI Nova 200 (FEG / SEM) apparatus coupled with EDAX Pegasus-X4M (EDX) was used for this purpose. For X-ray diffraction experiments, a Bruker AXS D8 Discover diffractometer with Cu K α radiation in the θ -2 θ geometry was used to analyze the crystalline structure.

3 Results

Table I. Selected samples and respective PVD process parameters for deposition of the Pd-Ag thin films, including thickness and wt.% of Ag.

Sample	Dep. time [min]	Thick. [μm]	$J_{\text{Pd}}/J_{\text{Ag}}$ [mA/cm^2]	%wt. (Ag)	Argon [sccm]	Dep. pressure [Pa]
A1	20	0.73	9.2/1.6	14.8	50	0.43
A3	20	1.41		19.8		3
B1	20	0.71	8.1/1.6	18.1		0.43

Table I shows more details for each sample used in this work. The morphology of the PVD-deposited Pd-Ag thin films can be observed in the SEM micrographs of Figure 1,

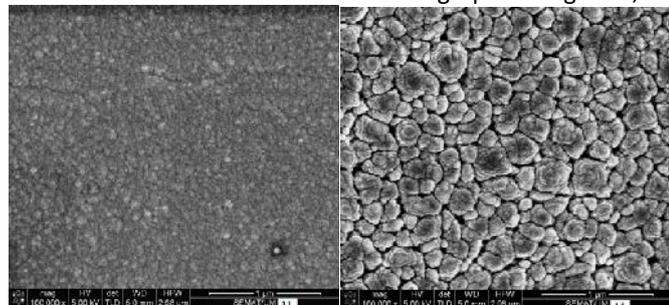


Fig. 1 SEM micrographs of the surface topography of the thin film onto the porous support for samples: a) A1 b) A3.

taken for a series of sample membranes A1 and A3 (see Table I). In this series, the process parameters remained constant, except for the sputtering pressure. Albeit the sputtering gas (argon) flow rate was kept constant at 50 sccm, resulting in a sputtering pressure of 0.43 Pa (for A1), in order to increase the pressure (for sample A3) the gate-valve con-

ductance between the sputtering chamber and the turbomolecular pump was reduced accordingly. Thus, from the SEM micrographs in Figure 4, it is obvious that upon increasing the sputtering pressure from 0.43 Pa to 3 Pa the morphology resulting from the top of the columnar structure becomes rougher, especially for A3, with wider grains surrounded by larger voids, in contrast to the more dense structure seen for membrane A1. Membrane A1 has a morphology characteristic of Zone T in Thornton's model, while A3 clearly resembles zone 1 [14]. As the deposition pressure increased from 0.43 to 3 Pa in this series of membranes, the measured silver content in the Pd-Ag film also increased, due to the concomitant increase in silver sputtering yield. One would expect a decrease in film thickness with this variation in pressure; however, it can be seen in Table I that in fact the sputtering yield increase escalates the film thickness, minimizing the reduction in mean free path of the sputtered atoms and reduced adatom mobility on the growing film surface. Thus, from Figure 1 it should be expected for membrane A1 an ideal microstructure for hydrogen selectivity.

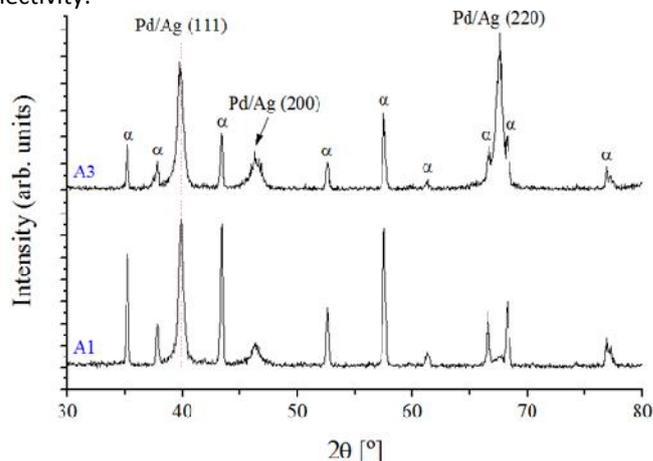


Fig.2 X-ray diffraction patterns for samples A1 and A3, α denotes diffraction peaks from the α -alumina porous support.

Figure 2 shows the XRD patterns of membrane samples A1 and A3, deposited with the minimum (0.43 Pa) and maximum (3 Pa) sputtering pressure. It can be observed that the stress state and crystalline texture changes from sample A1 to sample A3. While A1 shows a prominent reflection associated with a face-centered cubic (fcc) lattice plane (111), a (220) texture is favored for higher deposition pressures (A3), competing with the former. These diffractions correspond to a solid-solution of Pd-Ag with an fcc lattice. In this type of fcc structure, the {111} family of crystallographic planes have the densest atomic packing. Moreover, these crystallographic planes possess the lowest surface energy, thus providing a stronger adatom mobility and tighter microstructure, as seen in Figure 1 a) for the A1 membrane. It has been reported by other authors that atomic hydrogen permeates more efficiently across palladium fcc (111) planes [5], hence we expected that process conditions leading to larger (111) facets will enhance the hydrogen selectivity.

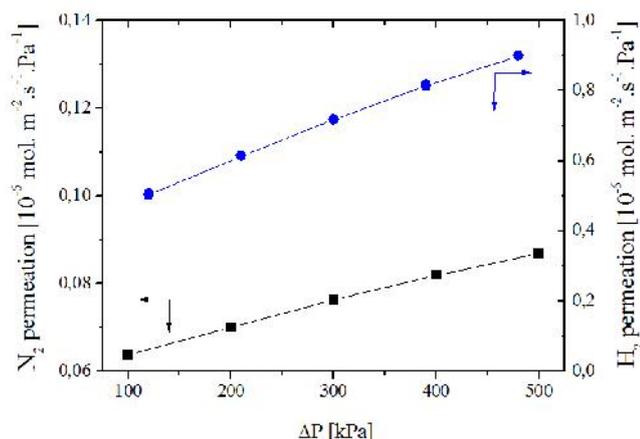


Fig. 3 Membrane permeance towards nitrogen and hydrogen as a function of pressure difference through the membrane B1; permeate pressure is the ambient pressure.

Figure 3 shows the membrane permeance to H_2 and N_2 as a function of the average pressure for sample membrane B1. The permeate flow of hydrogen is larger than that of nitrogen, which yields evidence that this Pd-Ag membrane has a selectivity towards H_2 with respect to N_2 . Hydrogen permeates by two mechanisms: sorption-diffusion of atomic hydrogen, which is intended; and by Knudsen diffusion, which is characteristic of N_2 . From Figure 3 it was found that for an pressure difference of 300 kPa the H_2 -flux is $0.21 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, which corresponds to a permeance of $0.71 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, yielding a selectivity factor $\alpha (H_2/N_2)=10$. This value is only moderate; hence, further optimization must be endured.

4 Conclusions

In future work, it will be necessary to perform additional permeance tests at higher temperatures in order to activate the mechanism of sorption-diffusion and hence will increase membrane selectivity towards hydrogen and also H_2 flux. Furthermore, the porous ceramic supports should be monitored in order to avoid micro cracks that can significantly induce a replication of the defect structure in the thin film.

The friendly welcoming nature of the Portuguese people, highly professional and cost-effective services are a guarantee of a successful sojourn and will give you something more than pictures and memories to cherish.

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