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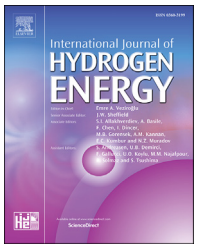

PdAg/alumina membranes prepared by high power impulse magnetron sputtering for hydrogen separation

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ABSTRACT

The development of hydrogen purification membranes that meet market demands such as high purity, dynamic hydrogen production even at small scale, and reduced costs is still an open question. With this view, the present study aims at developing, for the first time, a method based on high power impulse magnetron sputtering for the deposition of Pd77Ag23 (wt%) films onto porous alumina substrates to achieve composite membranes with high hydrogen permeability and stability. This technique allows the deposition of films also on complex geometries and can be easily scaled up, thus making this technology a potential candidate for preparing high performing membranes. Membranes made by stable and porous alumina supports and metallic, dense and crystalline $Pd_{77}Ag_{23}$ layers, from 3.5 μm to 17 μm thick, have been prepared and tested. The membranes showed good hydrogen permeability values, showing flux values up to a maximum of 0.62 mol_{H_2} m^{-2} s^{-1} at 450 °C and ΔP of 300 kPa. The resistance to hydrogen embrittlement and the chemical inertness to syngas were also demonstrated.

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Introduction

Hydrogen is a valuable energy vector and a largely consumed reagent in many industrial processes as ammonia production, hydrocarbon hydrogenation, etc. [1]. Most of hydrogen is currently produced by steam reforming of natural gas [2], although hydrogen production from biomass gasification could accelerate the H_2 utilization as a future sustainable fuel [3,4]. In both processes, an H_2-rich gas mixture is produced, and pure H_2 is obtained by some chemical processes carried out in a number of reaction units followed by separation/purification (mostly by pressure swing adsorption) [5].

The large number of steps to produce and separate hydrogen represents efficiency and cost limits of traditional reactors, that can be circumvented by using integrated systems such as membrane reactors [5], where both reaction and separation are carried out in the same device. Membrane technology is nowadays increasingly considered, thanks to several advantages including low energy consumption, ability to carry out separation continuously, and simple scaling up [6]. However, membranes will achieve commercial targets

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only when suitable hydrogen flux, cost, durability and tolerance to pollutants are optimized [7–9].

The most diffused membranes for hydrogen separation/purification are nowadays based on palladium due to its very high hydrogen diffusion and permeability, although pure palladium suffers membrane poisoning and embrittlement. The shift, upon hydrogen uptake, from α-Pd(H) to β-Pd(H) phase, with a consequent volume increase, produces internal stresses, deformation and failure of the membrane. When compared to pure palladium, Pd–Ag alloys show important advantages, such as embrittlement resistance through the avoidance of α to β phase transition, robustness during thermal cycling, high permeability, and resistance to fouling [10–12]. Among these alloys, the Pd77–Ag23 wt% composition has been largely investigated and tested due to its high permeance and resistance to hydrogen embrittlement [13].

Most commercial purification units contain conventional membranes consisting of relatively thick (>20 μm) Pd-alloy sheets or tubular membranes. However, to reduce the noble metal content, an effective strategy is needed to prepare dense membranes in the form of μm films deposited on suitable porous substrates. Various Pd– and Pd alloys-based films have been deposited onto porous alumina, nickel or stainless steel [14], but they still lack of sufficient long-term stability and selectivity to H_2. Electroless plating is commonly employed to deposit palladium-based films for this purpose. However, this technique is limited to few compositions/alloys [15]. Conversely, magnetron sputtering is effective in depositing alloys with variable compositions; it also allows the one stage deposition of multilayers in vacuum. In this work, we exploited a recent evolution of this technique, the High Power Impulse Magnetron Sputtering (HiPIMS).

HiPIMS, introduced by Kouznetsov et al., in 1999 [16], is a successful technique for improving magnetron sputtering by pulsed power technology. Its main feature is the combination of sputtering from standard magnetrons and pulsed plasma discharges, with the aim of generating highly ionized plasma with large quantities of ionized sputtered material [17]. The high degree of ionization of the sputtered species is combined to a bias voltage applied to the substrate. This leads to the growth of smooth and dense films, to a good control on composition and microstructure, and allows improving film adhesion and uniformity also on substrates of complex shapes [18]. This feature could allow the deposition of films also on tubular membranes or other geometries useful for commercial plants.

In this work, the most investigated composition, Pd 77 wt% – Ag 23 wt%, was chosen to evaluate HiPIMS influence on the preparation of membranes based on a Pd alloy widely studied in literature. Films with thickness ranging from 3 to 17 μm were deposited by a combined HiPIMS/Direct Current (DC) magnetron sputtering process onto porous alumina.

Alumina has been chosen as substrate being mechanically and chemically stable in operating conditions. Alumina substrates present also the advantage of preventing interdiffusion phenomena at high temperatures, typical of steel substrates, an issue that can reduce hydrogen permeation. A procedure was set up to achieve substrates having a fine surface porosity to allow the deposition of a dense metallic layer with no need of any interlayer, that would increase the processing time, costs and complexity.

Morphology, composition and structure of membranes were fully characterized. Hydrogen permeability was measured between 300 °C and 450 °C and at pressure difference up to 300 kPa. The resistance to hydrogen embrittlement and the chemical inertness to syngas were also investigated.

Experimental

Materials and methods

Alumina-based porous supports have been prepared by mixing 35 vol% of α-Al_2O_3 (Alfa Aesar, 99.9%) with 65 vol% of polymethyl methacrylate powders (PMMA) as pore former (Soken Chemical & Engineering, average size 1.5 μm). A wet ball milling process (absolute ethanol, Sigma Aldrich ACS reagent ≥99.8%) in zirconia jars was carried out in a planetary mill (Fritsch Pulverisette 7) at 350 RPM for a total of 2 h for each mixture. As obtained mixtures were uniaxially pressed (Nannetti Mignon SS/EA), in a 2.5 cm diameter mold by a 140 MPa load. The disks were then sintered at 1500 °C in a high temperature furnace (Nabertherm HT 04/17), with an isotherm step of 1 h at the burning temperature of PMMA (386 °C) and a very slow heating rate above 1000 °C (30 °C/h), when the shrinkage is maximum, to avoid pellet bending. The sintered disks were then polished and cleaned in an ultrasonic bath. The porosity was estimated by measuring the geometrical density and comparing it with the theoretical value of 3.98 g/cm^3 for alumina density.

The membranes were deposited by a combination of HiPIMS and DC magnetron sputtering techniques. The high vacuum chamber was preliminary evacuated to a base pressure $\leq 1 \times 10^{-4}$ Pa, while depositions were conducted in Argon atmosphere (Ar, 99.999% purity) at 1 Pa. During each sputtering run, the substrates were rotated at 5 rpm to improve homogeneity. The alloy was deposited by properly regulating the power on palladium and silver targets to achieve the Pd 77 wt % – Ag 23 wt% composition. By virtue of a deep preliminary set-up of the process, the palladium target (99.95% purity, 102 mm diameter) was driven by a HiPIMS power supply (Trueplasma HighPulse 4002, Hüttinger Electronic, Germany) at an average power of 800 W (~10 Wcm^{-2}, pulse length 50 μsec, frequency 500 Hz), while the silver target (99.99% purity, 102 mm diameter) was driven by a DC power supply (Trueplasma DC 4001, Hüttinger Electronic, Germany) at 330 W (4 Wcm^{-2}). The substrate-target distance was set at 120 mm for Pd and 150 mm for Ag to achieve the selected composition. Moreover, a 100 V negative bias (Trueplasma Bias 3018, Hüttinger Electronic, Germany) was applied to the substrates, which were heated up to 350 °C. Temperature was maintained throughout the process by *ad hoc* heaters and thermocouple monitoring. Prior to perform Pd 77 wt% – Ag 23 wt% alloy deposition, a thin PdAg film was deposited at room temperature using the sputtering parameters listed above. The aim was to produce a conductive layer for a proper bias application during the next alloy deposition by using a properly designed sample holder. Only in this way it is possible to fully exploit the combined effect of the large number of target material ions produced during HiPIMS process with a bias voltage applied to the substrate.

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