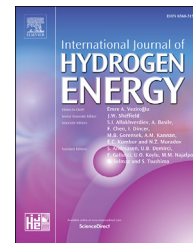




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Hydrogen separation by thin vanadium-based multi-layered membranes

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ABSTRACT

Thanks to their high hydrogen permeability, vanadium based alloys can be a valuable and sustainable alternative to palladium alloys, commonly employed in commercial membranes for hydrogen purification/separation. In this work, the unprecedented deposition of micrometric vanadium-based multilayers and their investigation as hydrogen selective membranes have been reported. In particular, this work describes the use of High Power Impulse Magnetron Sputtering, a technique easily scalable also for complex geometries, for the deposition of dense and crystalline Pd/V₉₃Pd₇/Pd multilayers with total thickness <7 μm onto porous alumina. These membranes showed high hydrogen fluxes in the 300–400 °C range, up to 0.26 mol m⁻² s⁻¹ at 300 kPa pressure difference and 375 °C, as well as an unexpected and significant resistance to hydrogen embrittlement and to syngas in operating conditions.

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Introduction

Hydrogen-based energy systems are an attractive strategy for a future replacement of the current fossil fuel-based systems. In fact, H₂, with its high energy density (33 kWh/kg), is a valuable energy vector that can increase penetration of renewable and intermittent sources [1].

At industrial scale, 95% of hydrogen is currently produced in the United States by steam reforming of natural gas [2], but hydrogen production from biomass gasification can still accelerate the utilization of H₂ as a sustainable fuel for the

future [3,4]. In steam reforming or biomass gasification reactors, an H₂-rich gas mixture containing CO, CO₂ and other by-products such as H₂S and NH₃ is obtained. Therefore, to produce pure H₂ some chemical processes are 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 affects the whole process in terms of system efficiency and costs, but the specific limits of traditional reactors can be circumvented by using integrated systems such as membrane reactors [5], in which both reaction and separation

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are carried out in the same device. In fact, membrane technology is nowadays increasingly considered as a candidate for substituting conventional purification systems, thanks to several advantages including low energy consumption, ability to carry out separation continuously, and simple scaling up [6]. However, this technology will become attractive only when membranes will achieve some targets as suitable hydrogen flux, cost, durability and tolerance to pollutants [7–9].

Since most of commercial membranes are based on palladium and its alloys, a cost reduction and an increase in membrane sustainability can be fulfilled only by using an alternative metal to Pd, or by limiting the use of Pd to few % or to very thin surface layers. Several metals belonging to the groups IV and V and not included among critical elements show high hydrogen permeability and have been studied as possible alternatives to Pd [8–14]. In particular, the rate of hydrogen transport through the lattice of group V metals is typically an order of magnitude higher than through any other metallic lattice including palladium [15].

Among the group V metals, the high hydrogen solubility of vanadium at pressures of practical interest may affect its mechanical stability due to embrittlement. For limiting the hydrogen solubility, various binary and ternary alloys of vanadium have been tested, and Pd was identified as one of the most efficient alloying element in substitutional alloys [8–17]. In particular, $V_{90}Pd_{10}$ and $V_{92.7}Pd_{7.3}$ resulted promising, demonstrating an optimal permeability to hydrogen and relatively good ductility [16–18]. In fact, alloying with Pd reduces the hydrogen solubility of pure vanadium to ranges of pressure and concentration that are more advantageous for practice ($P > 0.1$ MPa and $[H]/[M]$ between 0.1 and 0.2) [17]. Since the phase diagram of the V–Pd system shows several intermetallics, the amount of Pd should not exceed 18 at% to guarantee a solid solution.

Most commercial purification units contain conventional metal membranes consisting of relatively thick (>20 μm) Pd-alloy sheets or tubular membranes. However, to further reduce the noble metal content, an effective strategy is to reduce dense membranes to few μm films deposited on suitable porous substrates. Various Pd- and Pd alloys-based membranes have been produced and tested as few μm films deposited onto porous alumina, nickel or stainless steel [19], but they still lack of sufficient long-term stability and selectivity. Conversely, to the best of our knowledge, so far vanadium or vanadium alloys membranes have been tested only as sheets or tubes with thicknesses ≥ 40 μm [16,20], showing problems due to hydrogen embrittlement. These membranes need a protective coating against oxidation and palladium is typically used with the further function of catalytic layer for hydrogen absorption/desorption [8,16]. The Pd films, electroless deposited onto these membranes, showed some failures due to their delamination or Pd interdiffusion with the underlying alloy [16,21,22].

Conversely to electroless plating, magnetron sputtering is effective in depositing alloys with variable compositions [23]; it also allows the sequential deposition of protective and catalytic Pd layers and of non-noble alloys in one stage in vacuum, thus avoiding the oxidation at the interface. In this work, we exploited for the first time a recent evolution of this

technique, the High Power Impulse Magnetron Sputtering (HiPIMS), for the deposition of a hydrogen-selective membrane film.

HiPIMS, introduced by Kouznetsov et al., in 1999 [24], is a successful technique for improving magnetron sputtering by pulsed power technology. Its main feature is the combination of sputtering from standard magnetrons using pulsed plasma discharges, with the aim of generating highly ionized plasma with large quantities of ionized sputtered material [25]. The high degree of ionization of the sputtered species, combined to a bias voltage applied to the substrate, has been shown to lead to the growth of smooth and dense films, to enable a good control on composition and microstructure, and to improve film adhesion and uniformity also on complex shapes [26].

In this work, the $V_{93}Pd_7$ composition was chosen to limit the Pd content, to avoid intermetallics formation and since a similar alloy exhibited hydrogen permeability higher than a typical commercial Pd–Ag alloy [18]. Pd/ $V_{93}Pd_7$ /Pd multilayer films, with total thickness <7 μm , were deposited by a combined HiPIMS/Direct Current (DC) magnetron sputtering process onto porous alumina.

Since porous substrates can significantly affect the final cost of membranes, alumina has been chosen being an inexpensive material, 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. Therefore, a proper procedure has been set up to achieve substrates having a controlled porosity to allow the deposition of a dense metallic layer with no need of an interlayer.

The morphology, composition and structure of membranes were characterized and the hydrogen permeability was measured. Moreover, considering that still good result for V_xPd_y membranes in terms of resistance to hydrogen embrittlement and syngas have not been demonstrated so far, these aspects were deeply investigated.

Experimental section

Materials and methods

Alumina-based porous supports have been prepared by mixing different ratios of $\alpha\text{-Al}_2\text{O}_3$ powder (Alfa Aesar, 99.9% metal basis) and a pore former. Poly-methyl methacrylate powders (PMMA) with spherical shape and different average particle dimension (Soken Chemical & Engineering - average size 1.5 μm , 3 μm or 7 μm) were tested as pore former. A wet ball milling process (absolute ethanol, Sigma Aldrich ACS reagent $\geq 99.8\%$) in zirconia jars with proper amount of zirconia balls were carried out in a planetary mill (Fritsch Pulverisette 7) at 350 rpm for a total of 2 h for each mixture. Various ratios between Al_2O_3 and pore former were tested (20, 40, 50 and 65 vol% of PMMA).

As obtained mixtures were uniaxially pressed (Nannetti Mignon SS/EA) in a 2.5 cm diameter mold by a 140 MPa load. Thermogravimetric (SDT Q 600, TA Instrument) and dilatometric analyses (Netzsch DIL 402PC) were performed to develop the sintering process and to help in choosing ramps

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