Journal of Membrane Science 468 (2014) 233–241

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Perspectives of suspension plasma spraying of palladium nanoparticles for preparation of thin palladium composite membranes

Tim Boeltken [a], Dennis Soysal [b], Seungcheol Lee [c], Grazyna Straczewski [a], Uta Gerhards [a], Peter Peifer [a], Johannes Arnold [b], Roland Dittmeyer [a,c,*]

[a] Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[b] Institute of Technical Thermodynamics (TT), German Aerospace Center (DLR), Stuttgart, Germany
[c] Institute of Catalysis Research and Technology (IKFT), KIT, Germany

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form
16 April 2014
Accepted 6 June 2014
Available online 13 June 2014

Keywords:
Composite palladium membrane
Suspension plasma spraying
Thermal spraying of palladium
Diffusion barrier layer
Hydrogen separation

ABSTRACT

Suspension plasma spraying (SPS) of Pd nanoparticles was evaluated as a new method for coating of dense Pd films for H_2 separation on porous substrates. The substrates were prepared by coating porous sinter metal disks with a porous yttria stabilized zirconia (YSZ) layer acting as a barrier against intermetallic diffusion between the sinter metal and the Pd membrane (diffusion barrier layer, DBL). Before applying the Pd coating, the sinter metal substrates were characterized by N_2 permeance measurements. The maximum pore sizes before and after coating of the DBL were determined. For SPS of Pd, particles with diameters in the range between 250 nm and 550 nm were suspended in ethyl cellulose containing diethylene glycol monobutyl ether solution. A wide process parameter field was tested in the SPS. After Pd coating, the membrane morphology was characterized with scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), and the membrane performance was evaluated with N_2 and H_2 permeation measurements. The thickest Pd layer (9.5 μm) showed an ideal H_2/N_2 permselectivity of 60 at 350 °C and a H_2 permeability of $1.2 \times 10^{-7}\exp(-1392/T)$ mol m^{-1} s^{-1} $Pa^{-0.5}$. Yet rather thick Pd layers of around 10 μm were required to close the pores of the rough YSZ layers, but with further optimizations, SPS appears to be a promising new way for the fabrication of robust Pd coatings on porous substrates. A particular advantage is seen in the very quick deposition.

1. Introduction

Palladium membranes are of great industrial interest, because of their theoretically infinite selectivity to hydrogen combined with high H_2 permeability at elevated temperatures [1]. The thin Pd layer is often deposited on a porous membrane support, for example composed of a porous sinter metal coated with one or multiple additional porous ceramic layers (composite membrane). The porous sinter metal provides the mechanical strength, while the ceramic coating reduces the pore size and the surface roughness, and acts as barrier layer against intermetallic diffusion (diffusion barrier layer, DBL) between the sinter metal and the Pd layer [2,3]. On the other hand, a DBL decreases the pore size of the support surface, in turn the necessary Pd thickness to close the pores is reduced, which in turn reduces the Pd cost and increases the H_2 permeance [3,4]. This membrane configuration is a very practical approach for the integration of very thin Pd layers in technical systems, such as membrane reactors [5,6].

In literature, several preparation techniques have been reported for Pd-based membranes [7]. Electroless plating (ELP) is most frequently used for the production of laboratory scale Pd membranes [8]. However, the preparation techniques that lead to good membrane qualities in laboratory scale are not necessarily best suited for industrial application, e.g. for reasons of time consuming and expensive manufacturing processes.

Li et al. applied a flame spray pyrolysis technique for preparation of PdAg thin film membranes on the outside of porous alumina hollow fibers. Membrane thickness was in the range of 1.5–2 μm and ideal H_2/N_2 permselectivities up to 24 could be obtained [9].

Lee et al. recently developed a new fabrication method based on colloidal spray deposition of Pd particles of sizes between 100 and 300 nm that resulted in supported Pd films after subsequent sintering with controllable homogeneous thickness between 5–11 μm [10]. The best Pd membranes obtained so far showed an ideal H_2/He permselectivity of 150 at 530 °C.

Thermal spraying is a routinely applied method to prepare dense ceramic thermal barrier coatings, but so far has been rarely applied to derive dense Pd membranes. The basic idea behind the preparation of dense Pd membranes with this technique is that

* Corresponding author. Tel.: +49 721 608 2 3114; fax: +49 721 608 2 3186.
E-mail address: roland.dittmeyer@kit.edu (R. Dittmeyer).

http://dx.doi.org/10.1016/j.memsci.2014.06.003
0376-7388/

partially molten Pd particles impinging on the support cover the surface by overlapping and, given the pore size of the underlying support is small, at a certain thickness all pores of the substrate may be closed by overlaying of the solidified Pd splats. High velocity oxy-fuel flame (HVOF) spraying was used in previous works of Quicker et al. [11] and Höllein et al. [12] to prepare Pd-based composite membranes. In a different work of this group, atmospheric plasma spraying (APS) was tested [13]. Pd particles with an average diameter of 45 μm have been used in these studies. The particles were sprayed in dry state directly on the substrate. Continuous Pd films on the substrate were obtained. However, due to the large particle size, thermal spraying resulted in rather thick palladium layers above 60 μm with some residual open porosity, and the selectivity towards hydrogen was unsatisfactory. As an outlook, suggestions were given that a decrease in initial Pd particle size could result in thinner layers with improved selectivity.

Picking up these results, we report here improvements in thermal spraying of Pd to produce dense membrane layers on porous supports for application in hydrogen separation. Pd particles with a nominal size ranging from 250 to 550 nm were used. Metallic particles in this size range are pyrophoric and cannot be processed in HVOF spraying or APS, where the dry Pd powder is injected into the flame. Therefore, the Pd particles were suspended in a liquid and the suspension plasma spraying technique (SPS) was used [14–16]. One benefit of SPS is that fluctuations in particle delivery from the reservoir to the plasma torch are reduced to a minimum and much smaller particle sizes can be processed. As a consequence, more uniform layers may be obtained. The Pd particles were deposited on planar, smooth alumina sheets, and on planar porous sinter metals that were previously coated with a porous layer of yttrium-stabilized zirconia (YSZ). H_2 and N_2 separation measurements were conducted.

2. Experimental

2.1. Membrane supports

Porous stainless steel supports are frequently used due to its good availability, good chemical resistance and reasonable cost. For demanding applications, such for instance methane steam reforming, higher alloyed steels are needed. The oxide dispersion strengthened chromium-rich ferritic alloys Fe–26Cr(Mo, Ti, Y_2O_3) [6] and Crofer 22 APU are particular attractive here due to their good corrosion resistance, low creep rate under working conditions, and good compatibility in thermal expansion coefficient with the YSZ support and the Pd membrane.

Two different types of sinter metal disks (48 mm in diameter) were used in the experiments: 316L stainless steel (SS), from Nanjing Gaoq Functional Materials Co. LTD., Nanjing, China, with a thickness of 1.59 mm and a porosity of 25–28%, as well as Crofer 22 APU, from FZ Jülich, Germany, with a thickness of 0.47 mm, and a porosity of around 32%. The samples were not commercially accessible, but have been provided as test pieces upon request.

The sinter metals were cleaned in ethanol and coated at the Fraunhofer Institute for Environmental, Safety, and Energy Technology (UMSICHT), Sulzbach-Rosenberg, Germany, with an yttrium-stabilized zirconia (YSZ) layer by atmospheric plasma spraying (APS) to establish a porous ceramic diffusion barrier layer (DBL) which prevents intermetallic diffusion at high application temperature, and to decrease the pore sizes of the membrane support surface. APS as coating method for the DBL was chosen, as it is a universal technique, well suited for industrial application. APS, however, results in a rather rough surface with lower porosity compared to optimized DBLs, e.g. multi-layered DBL prepared by dip-coating of YSZ [3,6].

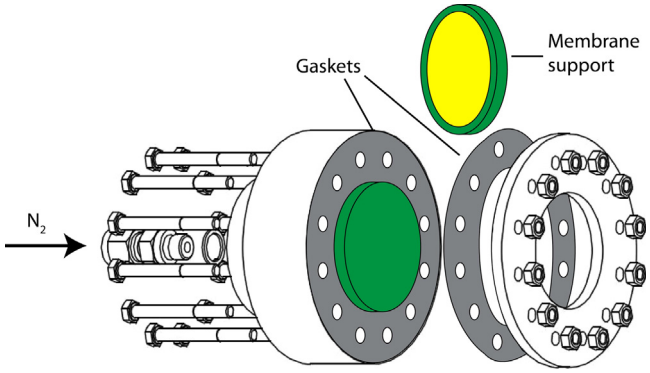

Fig. 1. Explosive view of the adapter for N_2 permeance measurements and bubble point test of the membrane supports (green: sinter metal, yellow: ceramic coating); the gaskets are schematically indicated. For bubble point test, the membrane support was installed inverted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Characterization of the porous substrates

The sinter metal substrates, both uncoated and coated with the YSZ layer, (here referred to as "membrane support") were characterized by nitrogen permeance Π_{N2} (DIN ISO 4022) and by bubble point test (DIN ISO 4003). The bubble point test is a method for the estimation of the largest pore diameter. Therefore, the membrane supports were clamped in a holder made from polyether ether ketone (PEEK) and sealed with a combination of multiple rubber and metallic gaskets, see Fig. 1.

For the determination of Π_{N2} a nitrogen flow through the membrane was adjusted and the stationary pressure difference Δp across the sample towards atmosphere was measured at room temperature. Π_{N_2} was then calculated with Eq. (1), where the nitrogen flux j_{N2} is divided by Δp.

$$\Pi_{N_2} = \frac{j_{H_2}}{\Delta p} \tag{1}$$

For the determination of the bubble point the adapter shown in Fig. 1 was completely immersed in ethanol, so that all pores of the membrane support were filled. Subsequently, the adapter was charged with a small dose of N_2 flow, while the gas pressure in the adapter was measured. As the gas pressure in the adapter exceeds the capillary pressure of the largest pore, the formation of gas bubbles is visible on the membrane support surface [17]. The Laplace equation (Eq. 2), which relates the maximum pore diameter $d_{P,max}$ to the contact angle ($\phi = 0^\circ$, complete wetting assumed), the surface tension of ethanol ($\sigma_{EtOH,20\,^\circ C} = 22.55 \times 10^{-3}$ N/m), and the pressure difference Δp at the bubble point was then applied.

$$d_{P,\,max} = \frac{4\sigma\,\cos\,\phi}{\Delta p} \tag{2}$$

Surface morphology and cross-section of the membrane supports were further analyzed with scanning electron microscopy (SEM, JEOL JXA-8530F field emission electron probe microanalyzer (EPMA)).

2.3. Suspension plasma spraying of Pd nanoparticles

Plasma spraying with liquids needs the preparation of the required suspension first. Palladium powder from Alfa Aesar (purity 99.95% (metals basis)) with an average particle size between 250 and 550 nm, the solvent diethylene glycol monobutyl