Journal of Membrane Science 515 (2016) 22–28

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Hydrogen permeation through porous stainless steel for palladium-based composite porous membranes

Shahrouz Nayebossadri *, Sean Fletcher, John D. Speight, David Book

School of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, UK

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
19 May 2016
Accepted 22 May 2016
Available online 25 May 2016

Keywords:
Hydrogen separation
Palladium-based membrane
Porous stainless steel
Composite membrane
Surface modification

ABSTRACT

Surface topography and hydrogen permeation properties of Porous Stainless Steel (PSS) substrates for thin films deposition of Pd-based hydrogen separation membrane were investigated. Hydrogen permeance through the as received PSS substrates demonstrated a wide range, despite a similar average surface pore size of ~15 μm determined by SEM and confocal laser microscopy analyses. The surface pores of the PSS substrates were modified by impregnation of varying amounts of tungsten (W) powder. Maximum hydrogen flux reduction of 28% suggested that W has a limited effect on the hydrogen permeation through the PSS substrate. Therefore, it appears that hydrogen transport through PSS substrates is mainly controlled by the substrate geometrical factor ($\frac{\varepsilon}{\tau}$), that is the ratio of the porosity to tortuosity. In addition, tungsten was shown to inhibit the iron inter-diffusion between the PSS substrate and the deposited $Pd_{60}Cu_{40}$ film at temperature as high as 800 °C. Thus, tungsten layer also serves as an effective inter-diffusion barrier. The variation in the permeance between the nominally similar PSS substrates indicates the importance to independently assess the hydrogen transport characteristics of each of the components in a composite membrane.

1. Introduction

Dense palladium (Pd) metal offers excellent permeability for hydrogen, based on the solution-diffusion mechanism [1]. However, its application is limited due to the α to β phase transition during hydrogenation (at temperatures below 300 °C and pressures below 2 MPa), which involves a volume increase of 10% [2,3]. The change in volume leads to a lattice distortion, formation of high internal stresses, deformation, and ultimately failure of the membrane. The hydrogen embrittlement problem in combination with susceptibility of the pure Pd to surface poisoning by impurity gases [4,5] and the high cost of Pd have led to the exploration of a wide variety of Pd-alloy membranes [6–8].

Generally, Pd-alloy foils with a thickness of 20–100 μm are required to provide acceptable levels of mechanical strength and produce a high purity hydrogen [1,9]. On the other hand, hydrogen flux is limited by the thickness of the membranes [10–12]. Furthermore, thick membranes are associated with higher costs and efforts continue to be made to reduce the material cost. One strategy to reduce the thickness and cost is to deposit a thin Pd or Pd-alloy film on the surface of porous substrate. This approach has been practiced extensively, where thin films of Pd or Pd-alloys were deposited on the porous substrate by various techniques such as electroless plating [13–20], sputtering [11,21–26], and chemical vapour deposition [27–29]. Non-metallic and metallic porous substrates such as ceramics [17,22,27,30,31], glass [21], and Porous Stainless Steel (PSS) [13,25,32–35] are widely employed. Although, the smooth surfaces provided by ceramic and glass porous substrates can be conducive to thin film deposition, the relatively poor adhesion of the fabricated metal film to the substrates [8] limits the application of these substrates. In fact, failure of Pd or Pd-alloy films during thermal cycling and hydrogen loading was attributed to the rising shear stresses as a result of the different elongations of metallic layer and ceramic support at the interface [36]. The scale of such a shear stress was shown to be directly related to the thickness of the metallic film and therefore, thermal stability with a lower thickness of metallic film can be achieved only at the expense of reduced hydrogen selectivity.

Alternatively, PSS can be a suitable support for Pd or Pd-alloys film deposition because of the low cost, mechanical durability, and its close coefficient of thermal expansion to Pd (17.3×10^{-6} and 11.7×10^{-6} m/(m K) for 316 L stainless steel and Pd respectively). However, because of the rough surface and a wide distribution range of the surface pore size, depositing a thin and pinhole free film becomes challenging. The effect of the surface smoothness of the PSS support on the deposited Pd film was investigated by Mardilovich et al. [10]. It was shown that the surface of the PSS support greatly influence the final topology of the deposited film.

* Corresponding author.
E-mail address: s.nayebossadri@bham.ac.uk (S. Nayebossadri).

http://dx.doi.org/10.1016/j.memsci.2016.05.036
0376-7388/

This result further confirmed the initial work by Ma et al. [37] indicating the thickness of the deposited film requires to be at least three times higher than the maximum surface pore size to achieve a dense Pd film. In addition, solid state inter-diffusion at higher temperatures than Tamman temperature of stainless steel (550 °C) leads to the alloying of PSS with Pd, causing degradation of hydrogen permeability with time [8,38]. Combination of these problems highlights the requirement for the surface modification of PSS substrate before the thin film deposition.

The common method to modify the surface of the PSS is to use an intermediate layer capable of reducing the surface pore size whilst, simultaneously serving as an inter-diffusion barrier. Various intermediate layers such as Al_2O_3 (alumina) [16,32], TiN [38], ZrO_2 [33], Ni [14], W/WO_3 [39,40], and Yttria-Stabilised Zirconia (YSZ) [12,41] have been employed. In addition, Ma et al. [42] investigated the formation of an *in-situ* oxide layer on the surface of PSS as an inter-diffusion barrier. Oxide layer formed at 800 °C showed to be effective for forming a membrane with an effective inter-metallic diffusion barrier. However, further studies [43] showed that PSS substrate with *in-situ* oxide layer has a rougher surface in comparison with YSZ modified PSS substrate and therefore, it requires a larger thickness of Pd layer and has a larger permeation resistance. Other intermediate layers, such as Ag [44], and Pd–Ag [15] have been also shown to serve as an effective barrier for the diffusion of iron to the palladium layer. However, electroplating of a thin layer of Ag on PSS required a subsequent treatment with aluminium hydroxide gel to insure the evenness of the surface for the final Pd layer deposition. In contrast, Bi-Metal Multi-Layer electroless deposition (BMML) of the Pd–Ag as an intermediate layer formed a graded support without significantly changing the resistance of the PSS support, suitable for the final Pd layer deposition. Furthermore, Li et al. [45] modified PSS substrate by two layers of alumina with varying sizes and showed only a mild reduction in the permeability of hydrogen and nitrogen through the membrane at ambient temperature.

Whilst, there are ample of reports investigating the surface pore size modification by intermediate layers and their effectiveness as an inter-diffusion barrier, less attention has been paid to the gas permeability of PSS substrate itself and its relation to the surface modification. Here, surface topography and hydrogen permeation through the as received PSS substrates are investigated. PSS substrates are then modified by impregnating with sub-micron tungsten into surface pores. The extent of pore filling and the corresponding hydrogen permeation properties through the tungsten modified PSS are investigated and the main controlling factors for the hydrogen permeation through PSS are discussed. In addition, the effect of tungsten layer as a diffusion barrier once coated with Pd-Cu layer is investigated.

2. Materials and methods

Porous sintered austenitic 316L Stainless Steel (PSS) substrate discs were purchased from Mott Metallurgical Corporation. The PSS discs had a diameter of 21 mm, thickness of 1 mm and a media filtration grade of 0.1 μm. The filtration grade is calculated and defined as the minimum size of a hard spherical particle retained by the interconnected porosity [46], with 0.1 being the finest commercially available grade. All discs were cleaned with acetone in an ultrasonic bath for 15 min and dried thoroughly using a heat gun prior to use. Tungsten powder with sub-micron particles (<1 μm 99.9%) was purchased from Sigma Aldrich. 0.1 g tungsten powder was dispersed in 10 ml Industrial Methylated Spirits (IMS) to facilitate the coating of the PSS surface. A vacuum was applied to the underside of the PSS substrate and an even layer of tungsten powder was impregnated onto the surface (denoted as 1 layer). Exactly same tungsten coating process was repeated three times for some samples to triple the amount of the impregnated tungsten (denoted as 3 layers). Tungsten coated discs were then wrapped in stainless steel foil and heat treated at 900 °C for 2 h under vacuum of approximately 10^{-4} mbar and then furnace cooled for 12 h.

Stainless Steel (SS), Pd and Cu targets (99.9% purity) were obtained from Teer Coatings Ltd. Films of 316 SS of 5–20 μm thicknesses were deposited onto the as received substrates using a Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUBMSIP) system supplied by Teer Coatings Ltd. The sputtering chamber was evacuated to approximately 10^{-6} mbar prior to the depositions and refilled to $\sim 2.5\times10^{-3}$ mbar with continuous flow (25 ml min^{-1}) of ultra-high purity argon during the deposition runs. A bias voltage of 50 V was applied to the magnetron during deposition runs. Samples were deposited using pulsed DC, with a constant target to substrate distance and a sample rotation speed of 8 rpm. A target current of 2 Amps was applied for the stainless steel coatings. To investigate the effect of tungsten as an inter-diffusion barrier, a Pd-Cu alloy film was deposited onto the 3 layers tungsten modified sample using a same technique. Four test deposition runs were performed with varying target currents to adjust the deposition condition for fabricating the $Pd_{60}Cu_{40}$ alloy. A target current of 1 and 0.75 Amps for Pd and Cu were selected respectively to produce $Pd_{60}Cu_{40}$ alloy with a less than 2 wt% compositional variation. Sample was then heat treated at 800 °C (heating rate of 2 °C min^{-1}) for 6 h.

Surface morphologies were examined by a Joel 6060 Scanning Electron Microscopy (SEM) equipped with an INCA 300 Energy Dispersive Spectroscopy (EDS) for compositional analysis. The surface roughness, and pore size were also investigated by the Olympus LEXT OLS 3100 mounted on a TableStable anti vibration table. The system uses a 408 nm Class II ultraviolet laser source and has a plane resolution (X and Y) of 120 nm and a space pattern (Z resolution) of 10 nm.

Hydrogen flux was measured using a hydrogen permeation system designed and built in the School of Metallurgy and Materials Science at the University of Birmingham [47]. This system applies a controlled feed gas to the high-pressure side of a properly sealed membrane, and monitors the gas which permeates through the membrane on the downstream side (see Supporting information for the schematic of the system). All the necessary measurement devices were controlled and monitored using a PC and SpecView data logging software. The system was de-gassed under 10^{-5} mbar vacuum prior to hydrogen (99.99995%, BOC) admittance. The feed gas was controlled using Brooks 5850 S Mass Flow Controller (MFC) calibrated over a range of 6–600 ml min^{-1} with an accuracy of ± 6 ml min^{-1}. A constant upstream pressure was applied by continuous hydrogen flow and bled using another Brooks 5850S MFC. The permeated gas flow was measured by Brooks 5850S MFC placed on the low pressure side. To establish a gas tight seal, copper gaskets were used on each side of the sample.

3. Results and discussion

3.1. As received PSS substrate

The surface topography of the as-received PSS substrate is shown in Fig. 1(a). Whilst SEM images suggest an average diameter of approximately 15 μm for the surface pores, further analyses of the 3 Dimensional images obtained by confocal laser microscope (Fig. 1b) showed the both surface pore diameter and the pore depth ranged between 10 and 25 μm in a good agreement with the previously reported values by Li et al. [45]. Also, the