Selection and Production of a Suitable Support for Palladium Membranes

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Abstract – The present work focuses on establishing an actual manufacturing strategy that is suitable for the viable production of a substrate support for a palladium membrane; one that will lower production costs and be utilised to gain a competitive edge within the industry. Porous stainless steel supports for palladium membranes were produced using various types of stainless steel powders and methods. Observations indicate that SS powder 410L type Chengdu Huarui with particle sizes 1-5 µm, sintered in the HPT induction furnace at temperatures between 930-950°C for a period of 8 minutes, in the presence of argon flow and vacuum, creates a first-class Pd membrane substrate. Notwithstanding that this result is the most economical method. The results of the study were based on the: roughness test, first bubble point test, and scanning electron microscope (SEM). The Chengdu Huarui powder type 410 L – 1-5 µm, which achieved the best results, produced a roughness test result of Ra 0.614 µm, and a bubble point pore size is 1.992 µm.

Index Terms: **Porous Stainless Steel, Palladium Membrane, Roughness Test and Porolux.**

I. INTRODUCTION

Among readily available alternatives for hydrogen purification, the use of membranes for hydrogen separation applications has been proposed and used in practice [1]. palladium membranes (Pd) have a number of advantages : high purity hydrogen can be prepared in a single step and that the process can be carried out at high temperatures [2]. Palladium is an excellent H_2 permeable material because of its relatively high atomic hydrogen solubility in its face centered cubic (FCC) lattice structure, and its ability to efficiently dissociate H_2 into atomic hydrogen [3]. However, due to the high cost of Pd membranes as well as their low durability; unsupported membranes are not suitable for manufacturing applications [4]. The important support characteristics for Pd membranes are: thermal and chemical stability, small pore size, smooth surface, appropriate mechanical strength, resistance to cracking; and ease of sealing [5].

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A porous stainless steel (PSS) support provides a suitable surface for the deposition of Pd or Pd-alloy films. PSS is mechanically durable; reasonably priced and its thermal expansion is like that of Pd [6]. For these reasons and with the aim of producing a usable Pd membrane, PSS was selected as the substrate for the deposition of a Pd or Pd alloy film. There are more than 250 different SS types. These various grades of stainless are divided into five major classes. The general classes and types depend on their chemical and mechanical properties; martensitic stainless steels, ferritic stainless steels, austenitic stainless steels, duplex and precipitation hardening [7]. Porous metals are fabricated by sintering either milled or atomised metal powders, with various grades of stainless steel. Inconel, aluminium and titanium all available commercially [8].

II. EXPERIMENTAL

Porous stainless steel (PSS) support are widely used for composite palladium membranes as they are relatively cheap, offer low mass transfer resistance, possess similar thermal expansion properties to palladium and, with careful surface preparation, provide excellent adhesion to the Pd alloy film when compared to non-metallic substrates.

Stainless steel type 410L is a ferritic steel (L refers to a carbon content below 3% to avoid carbide precipitation)[9]. Ferritic steel is a magnetic stainless steel, which is resistant to corrosion and stress corrosion cracking. Type 410L has been chosen as a suitable support for the Pd membrane due to its high corrosion resistance, strength, hardness, ductility and heat strength. It makes an excellent support owing to its high cryogenic toughness and high-temperature oxidation resistance [10]. The present work focuses on establishing an actual fabrication strategy that is suitable for the viable production of a substrate support for a Pd membrane; one that will lower production costs and be utilised to gain a competitive edge within the industry, the previous studies do not have demonstrated reproducible fabrication techniques that could be applied to the lower cost supports. Palladium membrane supports should have a smooth surface, chemical resistance, similar thermal expansion coefficient to that of palladium, and great porosity with a narrow distribution of small pore sizes.

II.1. MATERIALS USED

Various grades type 410L stainless steel powders were used with different particles size; Höganäs SS powder 410 LHD standard particles sizes 150 µm, Höganäs SS powder 410L particles sizes 20-53 µm, Chengdu Huarui SS powder 410L particles sizes 1-5 µm and US Research Nanomaterials SS powder 410L particles sizes 10 µm.

II.2. EQUIPMENT USED

The following Equipment and devices were used to aid the process of producing a good support for palladium membranes: an induction furnace (Hot Platinum OPC 400), a tubular furnace (Brother XD-1600MT), a hydraulic press automatic machine, SS rings type 430, ceramic (Alumina), SS type 316 plate, a circle mold template, Porolux™ 1000 capillary flow instrument to determine bobble point and pore size, Tesa Rugosurf 20, scanning electron microscope (SEM) with magnification 500X and EHT of SEM= 20.00KV, WD= 13mm, scale 100µm

II.3. EXPERIMENTAL PROCEDURE

The annealing and sintering method was used to fabricate different-sized PSS discs by varying the input parameters and specific conditions. Each type of the powders (as shown in table 1) were placed in the SS ring or plate then sintered at 920°C, 950°C, 1000°C, 1100°C, and also at 1200°C in an induction furnace or tubular furnace under vacuum and gas flow (hydrogen, nitrogen or argon).

Table 1. Powder and Parameters

Sample No	Stainless steel powder suppliers	SS powder particle sizes (µM)	Powder weight (G)	Type of sintering ring	Size of sintering ring (mm)	Type of coverage disc
1	Höganäs	SS 410L – 20-53	15	SS type 430	47 OD, ID15	Ceramic (Alumina)
2	Höganäs	SS 410L – 53-150	15	SS type 430	47 OD, ID15	Ceramic (Alumina)
3	Höganäs	SS 410L – 53-150	15	SS type 430	47 OD, ID 15	Ceramic (Alumina)
4	Höganäs	SS 410L – 20-53	20	SS 410 pressed ring	30 OD, ID 26	Ceramic (Alumina)
5	Höganäs	SS 410L – 20-53	20	SS 410 pressed ring	30 OD, ID26	Ceramic (Alumina)
6	Chengdu Huarui China	SS 410L – 1-5	23	SS 410 pressed ring	30 OD, ID26	Ceramic (Alumina)
7	Chengdu Huarui China	SS 410L – 1-5	22	SS type 316 Plate	27	Ceramic (Alumina)
8	Chengdu Huarui China	SS 410L – 1-5	23	SS type 316 Plate	27	Ceramic (Alumina)
9	US Research		15	SS type 430	47 OD, ID15	Ceramic (Alumina)

The stainless steel (SS) powder has been sintered at different temperatures, varying from 900°C to 1200°C, depending on the particle sizes of the powder. The sintering processes were administered using various parameters as shown in table 2. For particle sizes 1-5 µm the sintering temperature is 930-950°C, and for particle sizes 50-150 µm the sintering temperature is 1100-1200°C as small particles sinter significantly faster than large particles. The sintering processes were regulated using various parameters. The goal of sintering is to increase powder compact strength. Powder compact parameters include: shape, shape distribution, degree of agglomeration, presence of impurities, and chemical composition. Sintering condition parameters include: temperature, pressure, atmosphere, heating and cooling rate.

Table 2. The Sintering Parameters

SS powder particle sizes (µM)	Type of the used furnace	Sintering temp (°c)	Sintering time (minutes)	Gas flow	Gas flow rate (l/min)	Pressure (bars)
1- SS 410L – 20-53	Tubular furnace	1100	60	Argon	2.5L	110
2-SS 410L – 53-150	Tubular furnace	1100	60	Argon	2.4	110
3-SS 410L – 53-150	Tubular furnace	1200	60	Argon	2.2L	100
4-SS 410L – 20-53	Tubular furnace	1100	90	Nitrogen	1.1	100
5-SS 410L – 20-53	Tubular furnace	1100	90	Hydrogen	1.1	100
6-SS 410L – 1-5	HPT induction furnace	1200	8	Argon	1	80
7-SS 410L – 1-5	HPT induction furnace	1000	8	Argon	1	80
8-SS 410L – 1-5	HPT induction furnace	950	8	Argon	1	80

In order to determine an appropriate technique for producing suitable substrates, as well as good substrate fabrication; the investigations were administered on a PSS support. The following tests were done after the cooling period:

- Measurement of first bubble point (FBP), porosity, maximum pore size, mean flow pore size, minimum pore size, average pore size distribution of uniform materials and air permeability using a Porolux™ 1000 capillary flow instrument.

- A roughness test was administered using a Tesa Rugosurf 20. Rugosurf 20 is robust and easy to use. The powerful and reliable probe drive mechanism is housed in an aluminum alloy base used to determine roughness values; the diamond tip provides excellent wear resistance. Rough surfaces often wear out more quickly than smoother surfaces. Rougher surfaces are normally more vulnerable to corrosion and cracks [11]. A roughness tester shows the measured roughness depth (Rz) as well as the mean roughness value (Ra) in micrometers or microns (µm). Measuring the roughness of a surface involves applying a roughness filter. Different international standards and surface texture or surface finish specifications recommend the use of different roughness filters. For example, a Gaussian filter often is recommended in ISO standards.
- An investigation of the surface topography and composition of the sample with a scanning electron microscope (SEM).
- An investigation of the chemical composition of the sample by energy dispersive spectroscopy (EDS).

III. SUMMERY AND RESULTS

The purpose of the investigation (bubble point, roughness, SEM and EDS) is to produce a cost-effective substrate support for Pd membranes with the outcome of a procured competitive industrial advantage over market rivals. Three factors that should be considered because they affect the end result are: the type of powder used the size of its particles, as well as the sintering parameters. The sintering disks results obtained are shown in table 3.

Table 3. The Results of the Samples after Sintering.

Sample	Disc thickness (mm)	Shrinkage	Sample appearance	Surface roughness Ra (µm)	Bubble point pore size (µm)
1 SS 410L – 20-53µm 1100°C Ar	2	None	No oxidation	11.359	10.07
2 SS 410L – 53-150 µm 1100°C Ar	2	None	No oxidation	15.067	20.76
3 SS 410L – 53-150µm 1200°C Ar	2	None	Good	16.56	22.27
4 SS 410L – 20-53µm 1100°C N_2	3	None	Green colour. Oxidation	5.6	/
5 SS 410L – 20-53µm 1100°C H_2	3	None	Green colour. Oxidation	6.56	/
6 410L – 1-5 µm 1200°C Ar	2	Yes	Good appearance. No oxidation	3.1	4.95
7 410L – 1-5 µm 1000°C Ar	3	No	Good appearance. No oxidation	1.01	3.456
8 410L – 1-5 µm 950°C Ar	3	No	Good appearance. No oxidation	0.614	1.922

By using Porolux 100 the cumulative filter flow and pore size flow distribution is illustrated in Figure 1. The pore size flow distribution (calculated by comparing the flows on the wet with the dry run) is the highest value at approximately 10.97 µm at the disc diameter 3.49 µm and is zero at a diameter of 26.05 µm.

Figure 3 represent scanning electron microscope image for sample 3 which made from Höganäs stainless steel powder 410L- 53- 150µm was sintered using the tubular furnace at 1200°C for 60 minutes in the presence of an argon flow. it shows the big holes and large spherical particles sizes of about 111 µm. The roughness test for this sample was Ra 16.56 µm, and the bubble point was at 28.27 µm. The high sintering temperature (1200°C) was used to explore what effect the increasing temperature had on the quality of the disc fabrication.

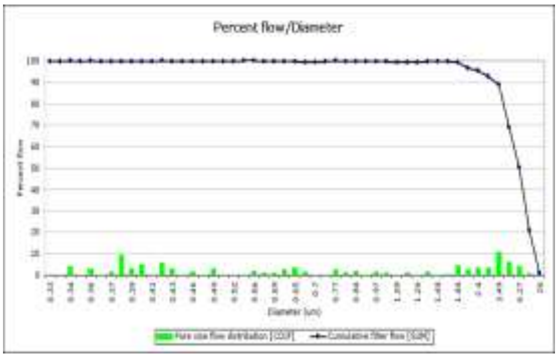

Figure 1. Sample 1 Porolux Test Showing Pore Size Flow Distribution

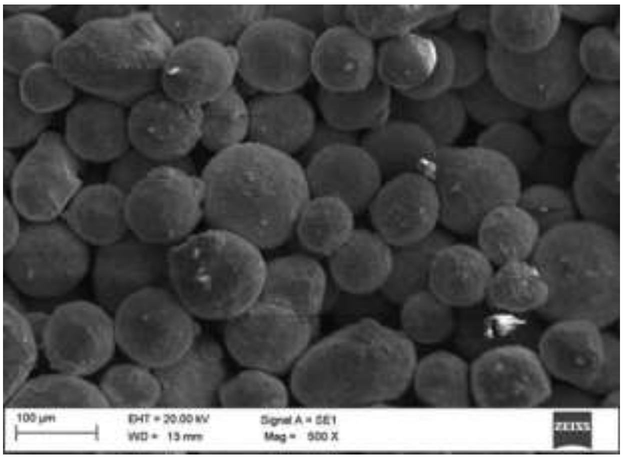

Figure 2. Sample 3 SEM Showing Large Particle Sizes and Outsized Holes

Sample 4 is made of Höganäs powder type SS 410L – 20-53 µm. The sample was sintered using a XD-1600 MT Tubular Furnace at a temperature of 1100°C and with a vacuum and nitrogen flow for a period of 90 minutes. The resulting sample was oxidised (evident in the yellowish-green colour), due to the mixture of powder and water as well as poor furnace efficiency. While sample 5 is made of Höganäs powder type SS 410L – 20-53 µm and was sintered a XD-1600 MT Tubular Furnace at 1100°C with a hydrogen flow for 90 minutes, it also oxidised.

Sample 7 is made of Chengdu Huarui powder type 410L – 1-5 µm and was sintered in the HPT Induction Furnace at 1000°C with an argon flow for 8 minutes. A shrinkage rate of 10% occurs, with the roughness test showing Ra 1.01 µm (Figure 3) and the bubble point is 3.456 µm.

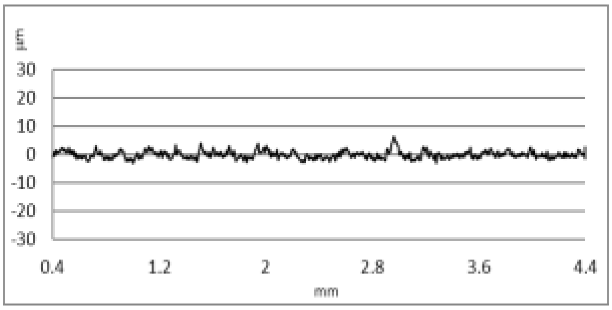

Figure 3. Sample 7 Roughness Test, Showing a Result of Ra 1.01 µm

Sample 8 was made by using Chengdu Huarui powder type 410 L – 1-5 µm and sintered in the HPT Induction Furnace at 950°C with argon flow for 8 minutes. The sample shows good appearances without oxidation or any shrinkage. To obtain a smooth disc surface, powder particle sizes 1-5 µm need to sinter at 930-950°C. The roughness test produces a result of Ra 0.614 µm (as shown in Figure 4) and the bubble point pore size is 1.992 µm.

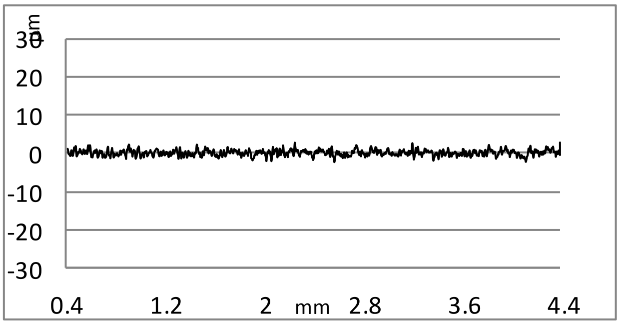

Figure 4. Sample 8 Roughness Test Showing a Result of Ra 0.614 µm

Figure 5 shows a comparison of the test results that were carried out on the samples 1, 2, 3, 6, 7 and 8. These samples were manufactured using several techniques under different conditions. Samples 4 and 5 are not included in the comparison due to the evidence of green body (which indicates oxidation) and because the oxidised samples cause a block in the Porolux 1000. The oxidised samples cause the blockage because of the contents in the sample rust and also due to the fact that the small powder particles are not solid [12] when being inserted into the sample holder. The sample should be solid without any loose powder or rust when being inserted into the Porolux.

Figure 5. Comparison of the Roughness and Bubble Point Results of Samples

CONCLUSION

In order to prevent the occurrence of oxidation and/or cracks, the present work made a paste of SS powder 1-5 µm, without adding water or PVA, and spread the paste on to a SS430 plate. The plate was covered with a ceramic disc. The disc was then sintered in the induction tubular furnace at a temperature of 950°C in the presence of argon gas flow 8 MPa for a period of 8 minutes. The induction furnace produces a better-quality substrate in less time, and consequently it is a commercially-viable and more economical option.

REFERENCES

[1] D. Alique, D. Martinez-Diaz, R. Sanz, and J. A. Calles, *Review of supported pd-based membranes preparation by electroless plating for ultra-pure hydrogen production*, vol. 8, no. 1. 2018.

[2] G. S. Burkhanov, N. B. Gorina, N. B. Kolchugina, N. R. Roshan, D. I. Slovetsky, and E. M. Chistov, "*Palladium-based alloy membranes for separation of high purity hydrogen from hydrogen-containing gas mixtures*," *Platin. Met. Rev.*, vol. 55, no. 1, pp. 3–12, 2011.

[3] D. A. Cooney, J. D. Way, and C. A. Wolden, "*A comparison of the performance and stability of Pd/BCC metal composite membranes for hydrogen purification,*" *Int. J. Hydrogen Energy*, vol. 39, no. 33, pp. 19009–19017, 2014.

[4] J. J. Conde, M. Maroño, and J. M. Sánchez-Hervás, "*Pd-Based Membranes for Hydrogen Separation: Review of Alloying Elements and Their Influence on Membrane Properties,*" *Sep. Purif. Rev.*, vol. 46, no. 2, pp. 152–177, 2017.

[5] K. Zhang, H. Gao, Z. Rui, P. Liu, Y. Li, and Y. S. Lin, "*High-temperature stability of palladium membranes on porous metal supports with different intermediate layer*s," *Ind. Eng. Chem. Res.*, vol. 48, no. 4, pp. 1880–1886, 2009.

[6] S. Nayebossadri, S. Fletcher, D. John, and D. Book, *"Hydrogen permeation through porous stainless steel for palladium–based composite porous membranes*," *J. Memb. Sci.*, pp. 1–25, 2016.

[7] R. A. Covert and A. H. Tuthill, "*Stainless Steels : An Introduction to Their Metallurgy and Corrosion Resistance*," *Dairy, Food Environ. Sanit.*, vol. 20, no. 7, pp. 506–517, 2000.

[8] S. Fletcher, "*Thin film Palladium-Ytrium membranes for hydrogen separation*," University of Birmingham, 2010.

[9] M. Seitovirta, *Handbook of Stainless Steel*, 1st ed. Avesta: Outokumpu Oyj, 2013, 2013.

[10] D. S. Kothari, "*CORROSION STUDIES OF STAINLESS STEEL BLADES*," the Faculty of New Jersey, 2017.

[11] B. Sahoo, B. Nayak, and R. R. Panda, "Fabrication and Characterisation of Aluminium Based Silicon Carbide Composite," *Vandana*, vol. 8, no. 2, pp. 66–73, 2018.

[12] International Stainless Steel Forum, "*The Stainless Steel Family,*" *www.worldstainless.org*, vol. 32, no. 0, pp. 1–5, 2013.