

A POROUS IRON ALUMINIDE MEMBRANE FOR HYDROGEN SEPARATION

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ABSTRACT

Porous membranes were fabricated from Fe-16Al-2Cr (wt.%) microparticles $\leq 3\text{-}\mu\text{m}$ diameter. Membrane surface morphology was characterized using optical profilometry. A slurry of Fe-16Al-2Cr particles was applied onto porous stainless steel supports (40- μm particle cut off grade) and sintered at 975°C for 1 h. The membrane had high hydrogen and argon permeability during testing at temperatures up to 600°C, but the gas permselectivities were characteristic of Knudsen diffusion. After heat treatment at 800°C for 24 h in UHP argon, X-ray photoelectron spectroscopy (XPS) showed that the porous iron aluminide membrane was covered with a layer of alumina that should serve as an effective barrier to metallic interdiffusion between the porous support and a thin palladium film on its surface.

INTRODUCTION

Ultra-pure hydrogen can be conveniently produced using metal membranes. Palladium alloy membranes are frequently used to purify hydrogen for compound semiconductor manufacturing, and in laboratories. It is also advantageous to use membranes reactors to perform chemical reactions more efficiently¹. Unfortunately, the high cost of palladium prevents metal membrane technology from replacing large-scale hydrogen purification methods such as pressure swing adsorption. Filters for hot gas cleanup have been fabricated using iron-aluminide particles that resist oxidation and degradation by gaseous impurities commonly present in coal gas². Extruding the molten metal through a nozzle and shearing the stream with high-velocity gas such as helium produces microparticles with a narrow size distribution². Alloys with extra aluminum such as Fe-16Al-2Cr can form a thermally grown aluminum oxide layer on the surface that protects the metal from further degradation. An advantage of thermally grown layers compared to coatings is more uniform surface coverage with fewer defects. For example, chrome-containing alloys have been shown to form a continuous nitride layer at 1373 K that resists leaching in the acidic environment of a proton exchange membrane fuel cell (PEMFC)³.

Porous metal as a palladium membrane support has the advantages of similar coefficient of thermal expansion to palladium, increased strength compared to porous ceramic or glass, and the potential to more easily seal into a module⁴. Porous metal tubes and sheet are commercially available in poresizes as small as 0.1 μm particle retention. However, the as-received surface roughness and poresize is too great to successfully deposit a thin ($< 10\ \mu\text{m}$), pinhole-free palladium or palladium alloy film⁵. The deposition of a palladium film without defects depends on the ability to span all of the pores in the support membrane⁶. Therefore, the critical qualities of a palladium membrane support are low surface roughness and small poresize⁷. Metallic atoms

from stainless steel such as chromium are also known to diffuse through into palladium and cause a decrease in membrane permeability. Metallic interdiffusion that occurs between palladium and porous stainless steel at temperatures $\geq 450^{\circ}\text{C}$ has been reduced by thin layers of oxide, nitride, or refractory metal^{5; 8-12}. Of course, membrane stability then depends on the stability of the intermediate layer. The ability to operate at higher temperatures will improve efficiency and enable more flexibility in membrane applications.

EXPERIMENTAL

The iron-aluminide microparticles were prepared by a high-velocity gas jet extrusion method described in detail elsewhere². The Fe-16Al-2Cr particles were nominally $\leq 3\ \mu\text{m}$. A slurry of particles was prepared and applied to a porous stainless steel (Mott Metallurgical) frit that was press fit into the ends of a 0.95 cm ID Inconel tube that had been drilled out to form a lip inside. A 1 mm gap was left between the porous frit and the end of the tube for the microparticle slurry. The top of the particle film was smoothed off evenly with a razor blade and the membrane was fired in a vacuum furnace at 975°C for 1 h. Single gas hydrogen and argon permeation tests were performed using a flow-through system. Retentate pressure was controlled using a back-pressure regulator and permeate flowrate was measured using a calibrated flowmeter. Overall system control and datalogging was carried out using National Instruments Labview software and Fieldpoint modules. XPS was performed in a Kratos Axis-Ultra surface analysis system. Optical profilometry was performed using a WYKO NT2000 Profiler that uses vertical scanning interferometry.

RESULTS AND DISCUSSION

MEMBRANE PERFORMANCE

Permeation measurements were conducted on the composite membrane consisting of porous stainless steel (nominal $40\ \mu\text{m}$ poresize) coated with a layer of the $3\text{-}\mu\text{m}$ particles. The flowrate versus pressure drop through the composite membrane is shown in Figure 1. From SEM micrographs of cross sections of a similarly prepared membrane, the layer consisting of the $3\ \mu\text{m}$ Fe-16Al-2Cr particles was $\sim 0.1\text{-mm}$ thick. The effective surface area of the membrane was $0.625\ \text{cm}^2$.

For Knudsen flow, where the interaction of gaseous atoms or molecules with the pore wall becomes more prevalent because of the small poresize, the separation factor is determined by the inverse ratio of square root of molecular weights of the gases¹³:

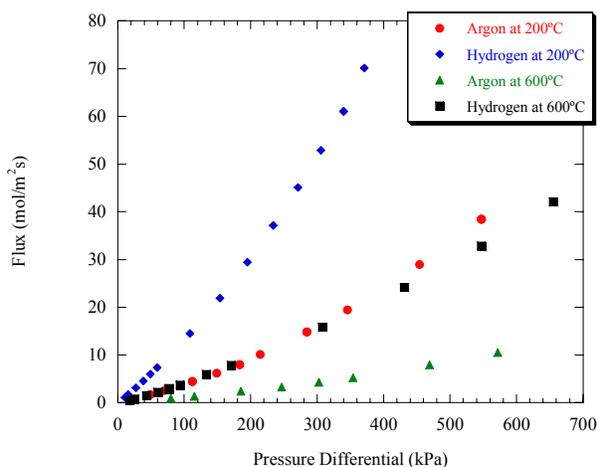


Figure 1: H_2 and Ar flowrates through a $0.625\ \text{cm}^2$, porous Fe-16Al-2Cr ($3\text{-}\mu\text{m}$ particle) membrane at 200 and 600°C and $\Delta P = 0\text{-}656\ \text{kPa}$

$$\alpha_{Knudsen} = \sqrt{\frac{MW_{Ar}}{MW_{H_2}}} = 4.45$$

The ideal gas permselectivities ($\alpha_{H_2/Ar}$) calculated from the data in Figure 1 were between 2.7 and 3.1. Therefore, the gas permeation mechanism through the porous membrane had contributions from both Knudsen and viscous flow.

MEMBRANE CHARACTERIZATION

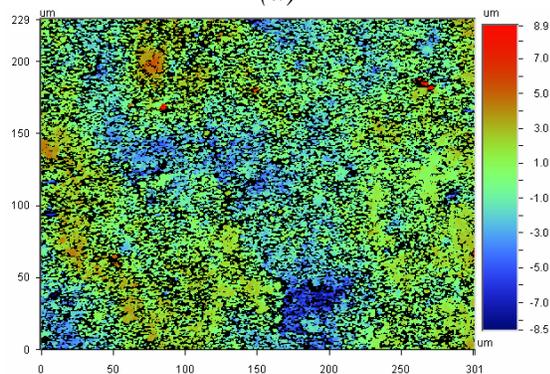
After heat treatment at 800°C for 24 h in UHP Ar, the surface of the Fe-16Al-2Cr membrane was analyzed using AES (Table 1). As shown in Table 1, aluminum, oxygen, some iron and chrome, and significant amounts of carbon and nitrogen were detected. The surface consists mostly of alumina. These results are in agreement with similar XPS analysis

Table 1. Results of XPS analysis of Fe-16Al-2Cr surface, heat-treated at 800°C for 24 h in UHP Ar.

Element	Atomic %
carbon	25
nitrogen	6
oxygen	29
aluminum	36
chrome	1
iron	3



(a)



(b)

Figure 2. (a) surface of Fe-16Al-2Cr membrane. (b) optical profilometry of membrane surface ($R_a = 1.51 \mu\text{m}$)

conducted at Ames Laboratory. Carbon is a commonly seen contaminant, and some of the carbon present is undoubtedly a result of air exposure.

When depositing a palladium film onto a porous membrane support, low surface roughness of the substrate is essential for depositing a thin, defect-free film. Optical profilometry of surface of the iron aluminide membrane gave a root mean square roughness, $R_a = 1.51 \mu\text{m}$, as shown in Figure 2.

CONCLUSIONS

Porous membranes fabricated from Fe-16Al-2Cr (wt.%) particles $\leq 3\text{-}\mu\text{m}$ diameter were characterized for hydrogen and argon permeability, surface chemistry, and surface structure. The membrane was tested up to 600°C and had high hydrogen and argon permeability, but the gas permselectivities were indicative of Knudsen diffusion. XPS showed that the membrane was covered with a thin layer of alumina that could serve as an effective barrier to metallic interdiffusion for a thin palladium film deposited onto the surface. The membrane also had a low surface roughness, $R_a = 1.51 \mu\text{m}$, determined by optical profilometry.

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