Composite Membranes for Coal Gas Reforming

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Abstract

Two types of palladium (Pd) composite membranes were fabricated and tested for potential application to the water gas shift reaction in a membrane reactor. A Pd alloy membrane was prepared by electroless plating a thin (< 20 μm) layer of Pd and then copper (Cu) onto a commercially available porous (nominal 0.2 μm pores) α-alumina substrate. The resulting multilayer metal film was annealed at 360ºC for several days to promote metallic interdiffusion and alloy formation. During the heat treatment, hydrogen fluxes were measured and a maximum flux of 0.15 mol (STP)/m^2·s was observed at 360ºC and a pressure drop (ΔP) across the membrane of 100 psi. The H_2/Ar ideal separation factor was 68 at these conditions. The other type of membrane manufactured was a Pd coated refractory metal alloy. A new method of sealing the thin (40 μm) vanadium (V) foil composite into a tubular shape was developed to facilitate testing and use as a membrane reactor. The main advantage of this membrane is the reduction in Pd film coating thickness to 0.1 μm per side. However, further investigation is required to solve the problem of hydrogen embrittlement experienced by the V-Cu alloy.

Introduction

Efficient utilization of coal for chemical and electricity production may be accomplished in the context of DOE Vision 21 (see www.netl.doe.gov) through the use of membrane reactors (see Figure 1). The membrane reactor carries out the water-gas shift reaction to produce purified hydrogen from gasified coal. The pure hydrogen produces electricity in a fuel cell or chemicals in another reactor and the effluent from the membrane reactor can be further combusted to produce electricity or heat. This scheme has the further advantage of producing a high pressure CO_2-rich stream that may more easily be sequestrated. Commercialization of membrane reactor technology will require durable, cost effective, and highly hydrogen permeable membrane materials. This work examined membranes that show promise in attaining these goals.
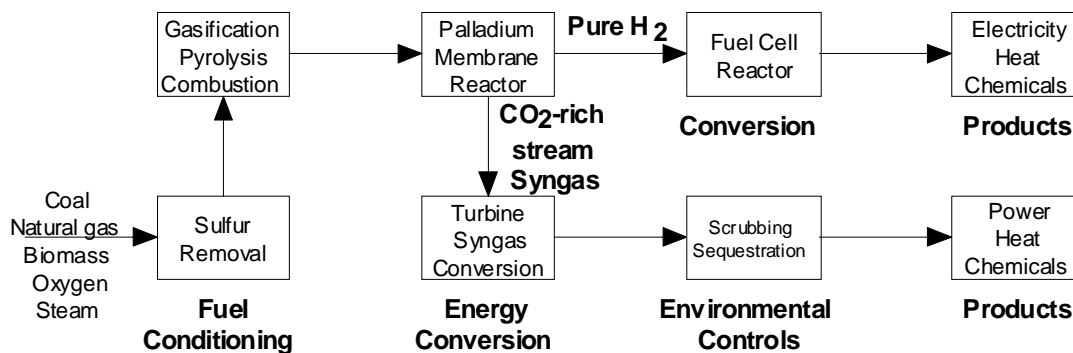

Figure 1. Schematic of Vision 21 process.

Coating a porous material with a Pd or Pd alloy film is necessary to minimize the use of costly Pd in the membrane. Porous ceramic supports, although somewhat brittle, are commercially available in a range of pore sizes. The α-alumina membranes chosen as a support material for this study are cheap to manufacture because they are symmetric (same pore size throughout the membrane wall). Pd alloy films are necessary to reduce the hydrogen embrittlement experienced by pure Pd. Some research has indicated that Pd-Cu alloys (particularly 40 weight %) are sulfur tolerant, have increased hydrogen permeability compared to pure Pd, and also resist hydrogen embrittlement [1-3]. Group V-B metals have been considered since the 1960's as alternatives to Pd alloys for hydrogen separation membranes [4]. These metals are still attractive due to the intrinsically lower cost compared to Pd and high hydrogen permeability. A Pd coating is necessary on Group V-B metals to protect them from oxidation and impurities found in hydrogen streams as well as facilitate hydrogen entry and exit from the metal. The foil serves as a solid support for Pd enabling very thin coatings (< 1 μm).

Experimental

Tubular, porous (nominally 0.2 μm pores) α-alumina membranes (CoorsTek, Oak Ridge, TN) were cut, cleaned, glazed (Figure 2a), and the lumen coated with Pd using electroless plating as described previously except that a flow through system was utilized (Figure 2b) [5]. The dimensions of the α-alumina tube were 0.6, 1.0, and 14.1 cm for the ID, OD, and length respectively giving a total lumen area of 26.6 cm^2. During plating, the membrane was immersed in 6 M sucrose/H_2O solution to create an osmotic pressure driving force across the membrane and enhance metal film formation [6]. Electroless Cu was deposited onto the Pd layer using a commercially available plating bath (EC-70, Technic Inc., Anaheim, CA) [7]. Membranes were carefully sealed into stainless steel (SS) compression fittings using graphite ferrules (Figure 2c). Membranes were checked for leaks by pressurization with nitrogen and immersion into ethanol/water. A small number of tiny bubbles emanated from the membrane surface, indicating incomplete coverage of the support by the metal film. The membrane was packed with catalyst and loaded into the furnace by attaching SS tubes and sealing into a SS shell. Figure 2d is an image of the furnace containing the membrane module.

a.

b.

c.

d.

Figure 2. (a) glazed end of α-alumina membrane (b) flow-through electroless plating system (c) SS compression fitting with graphite ferrule (d) test furnace with membrane module.

Fabrication of the V-alloy composite membranes consisted of the following steps [8-10]; melting and rolling alloy foils, cleaning, deposition of Pd, and welding into a tubular shape. High purity (99.9%) powders were mixed and electron beam (*e*-beam) melted into buttons in a vacuum furnace. The buttons were flipped and re-melted several times to ensure compositional uniformity. The alloys were cold rolled into ~5×15 cm strips with a nominal thickness of 40 μm. The foils

were washed with soap and water, rinsed with methanol, blown dry with nitrogen, mounted by clamping the ends of the foil strip, and loaded into the physical vapor deposition (PVD) chamber. After evacuation, argon was bled into the chamber to a pressure of $1.5 \cdot 10^{-4}$ Torr and the ion-gun (Ion Tech, Teddington, UK) was set to a power of 1 keV and 20-25 mA to ion-mill each side of the foil for 60-90 min. The foil was visually inspected through a window during ion-milling to ensure removal of all remaining macroscopic contaminants. After ion-milling, the chamber was evacuated to $1 \cdot 10^{-7}$ Torr and the *e*-beam (Airco-Temescal CV-14 power supply) evaporated Pd onto the foil at 3-5 Å/s. A piezoelectric device was used to determine the thickness of metal deposited. Approximately 100 nm of Pd or Pd alloy was deposited onto each side of the foil. A tubular membrane was fabricated by placing the foil in a specially designed fixture and electron beam welding the foil to itself and to stainless steel fittings. The membrane was plumbed into the SS module and the test system (Figure 2d).

Permeation tests for either type of membrane were conducted by heating at 1ºC/min under argon purge (all gases were 99.999% pure) to the desired temperature followed by introduction of pure hydrogen and measurement of the permeation flux at pressure differences across the membrane up to 100 psig. The test bench has been described previously [11].

Results and Discussion

Examples of fabricated membranes are shown in Figure 3. Before annealing, the Cu is clearly visible in the lumen of the porous α-alumina tube. Annealing of another unbroken membrane to promote interdiffusion and alloy formation between the Pd and Cu was carried out at temperatures up to 360ºC. From the data in Figure 4, it can be seen that the hydrogen flux through the membrane increased with increasing temperature. Hydrogen flux also increased with time at a given temperature, presumably due to diffusion of the Cu into Pd. Hydrogen has a low permeability in Cu and as it interdiffused with the Pd the hydrogen flux would be expected to increase. A maximum hydrogen flux of 0.15 mol (STP)/m$^2 \cdot$s was measured at 360ºC and a ΔP across the membrane of 100 psi. The hydrogen/argon ideal separation factor was 68 at these conditions. The membrane was packed with a Pt/alumina medium temperature shift catalyst, although a power disruption at day 14 precluded water gas shift testing. The membrane will be retested, although a reduction in permselectivity is anticipated due to the thermal cycling. Following testing, analysis will be performed including Auger electron spectroscopy (AES) depth profiling to determine if a uniform Pd-Cu alloy formed throughout the film thickness during annealing, scanning electron microscopy (SEM) to look at film morphology and types of defects (pores) as well as measure film thickness, and X-ray diffractometry (XRD) to determine grainsize and composition. It is anticipated that the use of other membrane supports with smoother surfaces (smaller poresizes) will enable deposition of even thinner Pd-Cu films [7].
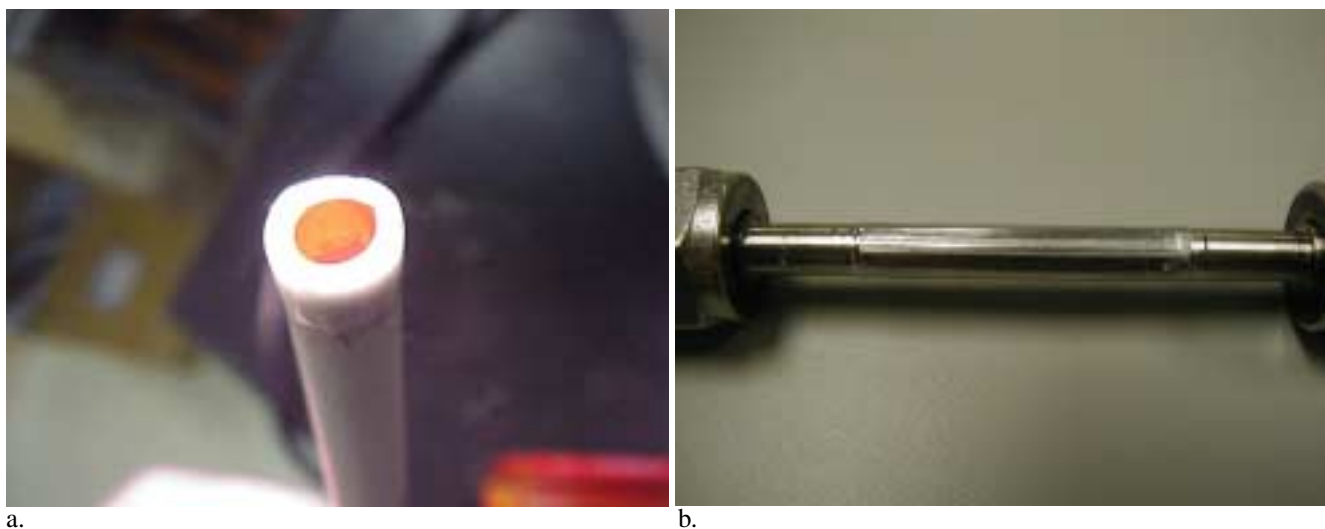

a.   b.

Figure 3. (a) unheated, broken Pd-Cu/α-alumina composite membrane showing copper layer on top of Pd (b) V foil welded into a tubular shape with fittings.

Several tubular V-Cu alloy membranes were fabricated and tested. The foil was determined to contain 2 atom % Cu by AES. This is close to the solubility limit of Cu in V [12]. The first membrane was not coated with Pd and permeated less than 1 sccm of hydrogen at 300ºC and a ΔP across the membrane of 100 psi. Argon did not measurably permeate through the membrane. The membrane survived a cool down to room temperature until it was re-pressurized with argon at ~100 psig. The next membrane tested was coated with 100 nm of Pd on each side. Soon after the introduction of hydrogen at 300ºC, a large leak formed. This suggested that failure may have occurred from a combination of stresses due to thermal expansion,
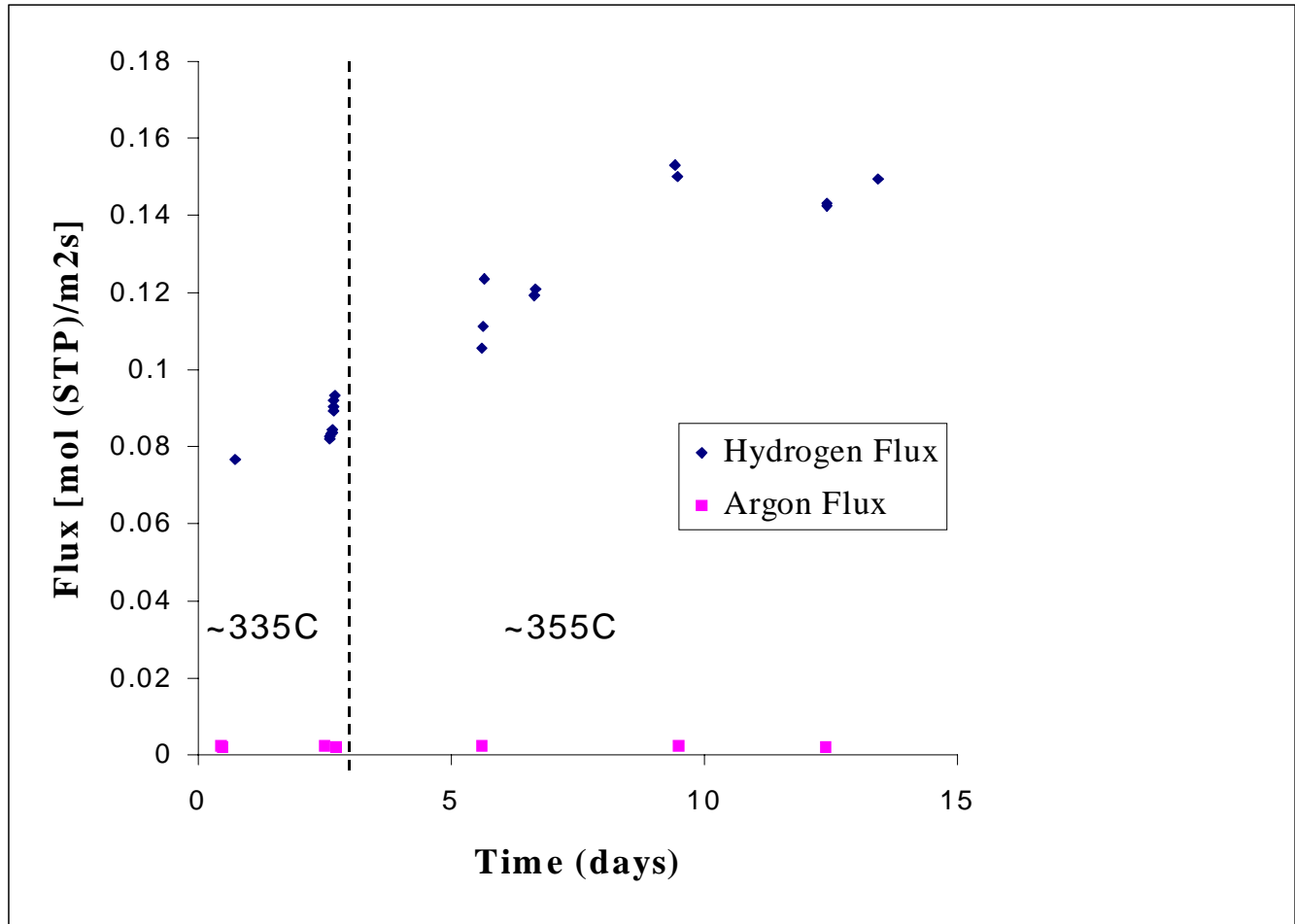
Figure 4. Flux data for Pd-Cu/α-alumina composite membrane.

hydriding expansion, and residual stress from the welding process. Therefore, the test module has been reconfigured to accommodate expansion/contraction of the membrane during heating/cooling or hydriding/dehydriding. To reduce the stress due to hydriding, other V-based alloys are presently being coated and tested for hydrogen permeability. Tested membranes are also being analyzed using AES to determine the extent of metallic interdiffusion between the Pd coating and the V-alloy foil. The weld between the V foil and the SS tube is also being studied.

Conclusions

Progress continues on the development of membrane materials to use for recovering hydrogen from coal gas. A Pd-Cu/α-alumina membrane was fabricated that had high hydrogen flux and moderate permselectivity. Further work includes determination of annealing conditions required to obtain a homogeneous Pd-Cu alloy film and development of film deposition methods to reduce the number of pinholes in the metal film. V-Cu alloy foils were coated with Pd and welded into tubes. Determination of failure mechanisms during hydrogen permeation at temperatures > 300ºC is underway.

Acknowledgements

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