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DEVELOPMENT OF PALLADIUM COMPOSITE MEMBRANES FOR HYDROGEN SEPARATION

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Abstract

Two types of palladium composite membrane were investigated for hydrogen separation. A palladium alloy membrane was prepared by electroless plating a layer of palladium (~20 μm) and then copper onto a commercially available porous (nominal 0.2 μm pores) α-alumina substrate. The resulting multilayer metal film was annealed at 355°C for several days to promote metallic interdiffusion and alloy formation. During the heat treatment, a maximum hydrogen flux of 0.15 mol (STP)/$m^2 \cdot s$ was observed at 355°C and a pressure drop (ΔP) across the membrane of 6.8 atm. The H_2/Ar ideal separation factor was 68 at these conditions, however, the separation factor decreased upon thermal cycling. The other type of membrane fabricated was a palladium coated vanadium–copper alloy foil where the main advantage is the reduction in palladium film coating thickness to 100 nm per side. New methods are being developed for welding the thin foil into modules for testing. The hydrogen flux through a pinhole-free, 75 μm thick Pd/$VCu_{1.1}$/Pd (atomic %) composite membrane was 0.66 mol (STP)/$m^2 \cdot s$ at 350°C and $\Delta P = 3.5$ atm compared to 0.44 mol (STP)/$m^2 \cdot s$ for a 71 μm thick Pd/VCu_{10}/Pd membrane. Vanadium alloy composition was checked using Auger electron spectroscopy (AES).

Introduction

Large quantities of hydrogen are consumed by industry and hydrogen will likely become a primary energy carrier in the future necessitating safe and economical methods for its production, purification, distribution, storage, and handling. The role of hydrogen separating membranes will be to purify hydrogen for consumption in energy systems (such as fuel cells) and chemical processes at any scale. Until renewable sources of hydrogen are developed extensively or a large-scale distribution system for hydrogen is built, membrane reactors may be used to purify hydrogen from reformed fossil fuels [1]. In any case, the advantages of the membrane process should include increased energy efficiency, flexibility, pollution reduction, reliability, and decreased overall cost.

Coating a hydrogen permeable material with a Pd or Pd alloy film can 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 cheaper to manufacture because they are symmetric (same pore size throughout the membrane wall). Some research has indicated that Pd–Cu alloys (particularly 53 atomic %) are sulfur tolerant, have increased hydrogen permeability compared to pure Pd, and also resist hydrogen embrittlement [2; 3]. Group V metals such as vanadium have been considered since the 1960's as an alternative to Pd alloys for hydrogen separation membranes. These metals are still attractive due to the intrinsically lower cost compared to Pd and their high hydrogen permeabilities. For example, Nishimura et al. found that the hydrogen flux through a membrane of Pd coated V–Ni_{15} foil was twice that of $PdAg_{25}$ foil of the same thickness [4]. A Pd coating is necessary on Group V metals to protect them from oxidation and impurities found in hydrogen streams and to facilitate hydrogen entry and exit from the metal [5]. The foil serves as a solid support for Pd so that very thin coatings are effective (< 1 μm).

In systems that experience frequent thermal cycling, membrane resilience is critical and coefficient of thermal expansion must be considered. Hydriding and dehydriding also creates large stresses so alloying metals may be added to reduce the hydrogen solubility and thus embrittlement [6; 7]. Hydrogen solubility in these metals decreases with increasing temperature, generally requiring operation at temperatures in excess of 200°C to avoid the creation of hydride phases that distort the material. Although operation at higher temperatures is desirable with respect to hydrogen embrittlement, a competing problem is interdiffusion between the Pd coating and the metal foil that accelerates with increasing temperature. Therefore, while the hydrogen permeability of Group V-B metals is high, problems with hydrogen embrittlement and metallic interdiffusion impede commercial use of these materials as membranes [8-12].

Experimental

Membrane Preparation

The preparation procedure for the Pd–Cu/alumina composite membrane has been described previously [13-15]. Approximately 25 μm total of Pd and Cu were deposited sequentially by electroless plating in the lumen of a symmetric porous (nominal 0.2 μm poresize; CoorsTek, Oak Ridge, TN) tubular α-alumina tube. 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. The membrane was annealed in order to form a Pd–Cu alloy while taking hydrogen flux measurements.

High purity (99.9%) vanadium and copper were electron 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 nominal thicknesses between 40-80 μm. The foils were washed with warm 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, each side of the foil was argon ion-milled for 60-90 min. and then the chamber was evacuated again and 100 nm of Pd was evaporated onto each side of the foil. Discs were laser cut from the foil or a tubular membrane was fabricated (Figure 1) using electron beam welding and a specially designed fixture.

Hydrogen Permeability Testing

Membranes were loaded into a stainless steel permeation module that was placed in a tube furnace and the temperature was ramped at 1°C/min. while purging the membrane with argon and with vacuum on the permeate side. All gases were at least 99.999% pure and used without further purification. Hydrogen flux through the membrane was measured using either a mass flow controller or a soap film flowmeter. Hydrogen pressure on the retentate (feed) side was controlled by a back pressure regulator while vacuum was maintained on the permeate side of the membrane.

AES Analysis

The composition of the V–Cu alloy was measured by AES or XPS. X-ray photoelectron and Auger Electron spectroscopy results were obtained with a PHI 5600 System. Electron energy analysis was accomplished using a CHA with an OMNI Focus IV input lens system. The XPS results were obtained with a monochromated Al K-alpha source and the AES results were obtained with a 5 keV electron beam. Background pressure was essentially 1×10^{-10} Torr. Elemental analysis using XPS or AES was semi-quantitative (± 20%).

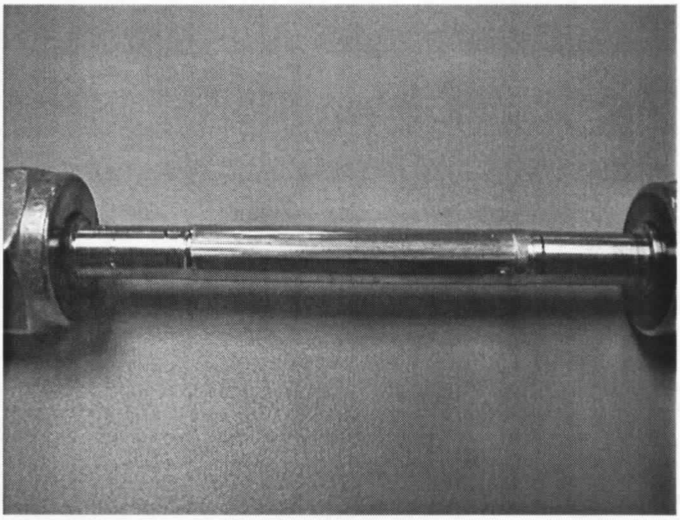

Figure 1. V–Cu foil welded into a 6 mm diameter tube and brazed to stainless steel VCR fittings.

Results and Discussion

Membrane Performance

The results of the hydrogen flux test for the Pd–Cu/alumina membrane are shown in Figure 2. From the data, 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 and leveled off, presumably due to diffusion of the Cu into the Pd. Hydrogen has a low permeability in Cu and as it interdiffused during annealing the hydrogen flux would be expected to increase. A maximum hydrogen flux of 0.15 mol (STP)/$m^2 \cdot s$ was measured at 355ºC and a transmembrane pressure differential (ΔP) of 6.8 atm across the membrane. The ideal separation factor for hydrogen over argon was 68.

The tubular membranes fabricated from V–Cu foil often fractured when exposed to hydrogen at 300ºC, probably due to thermal and hydriding stresses, therefore, foil discs of the membrane material were sealed between two 1.9 cm OD nickel gaskets in a VCR compression fitting giving 0.94 cm^2 of permeable area. A 75 μm thick Pd/$VCu_{1.1}$/Pd composite membrane gave a hydrogen flux of 0.66 mol (STP)/$m^2 \cdot s$ (88.8 cm^3 (STP)/$cm^2 \cdot min$) measured at 350ºC and a ΔP of 3.5 atm across the membrane (Figure 3). Argon did not measurably permeate through the foil. This hydrogen flux is over four times what was measured through the Pd-Cu/alumina composite membrane when it was at twice the pressure differential. At a pressure differential of 5 atm, the unsupported Pd/$VCu_{1.1}$/Pd foil membrane disentegrated. Hydrogen flux results for a 71 μm thick Pd/$VCu_{10.1}$/Pd membrane are also included in Figure 3. At 350ºC and $\Delta P = 3.5$ atm, the flux was 0.44 mol (STP)/$m^2 \cdot s$ (58.8 cm^3 (STP)/$cm^2 \cdot min$). Apparently, the additional Cu

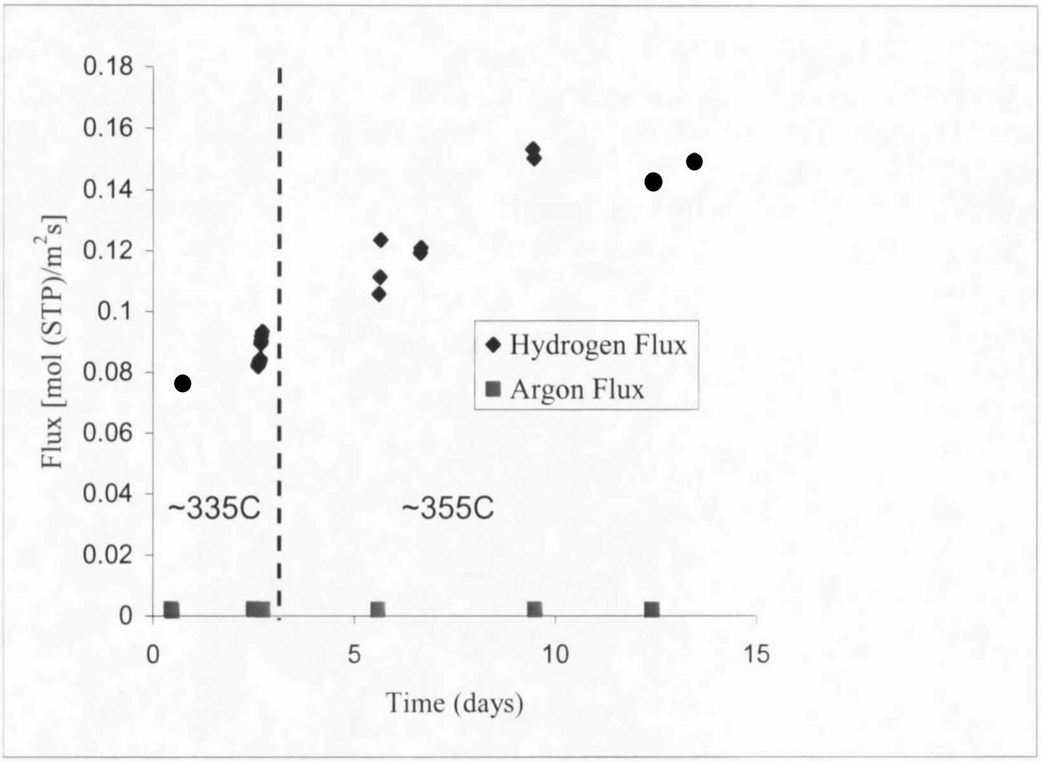

Figure 2. Hydrogen and argon flux versus time at 335 and 355ºC through a ~25 μm Pd–Cu film deposited inside a porous α-alumina tube. Transmembrane pressure differential (ΔP) = 6.8 atm.

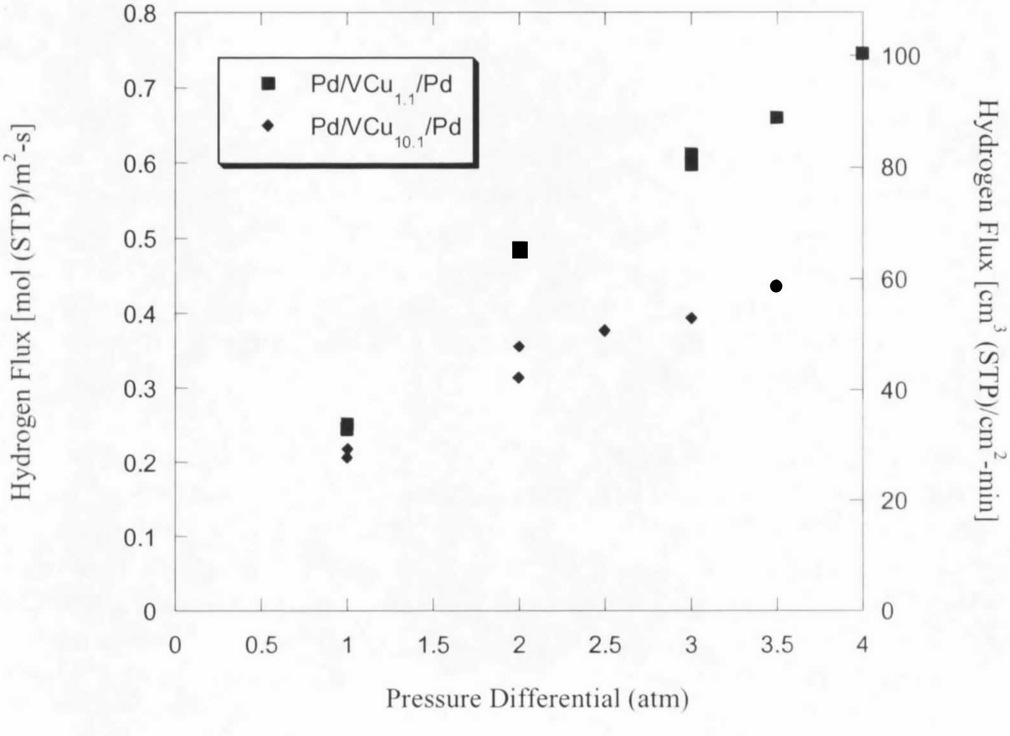

Figure 3. Hydrogen flux versus transmembrane pressure differential through Pd coated (100 nm) V–Cu foils at 350ºC. The $VCu_{1.1}$ (atomic %) foil was 75 μm thick and the $VCu_{10.1}$ foil was 71 μm thick.

content resulted in decreased permeability. However, it was anticipated that Cu would lower the hydrogen solubility of the alloy, resulting in lower permeability but greater resistance to hydrogen embrittlement.

Conclusions

The hydrogen flux through a 75 μm thick $VCu_{1.1}$ alloy coated with 100 nm Pd on each side was 0.66 mol (STP)/$m^2 \cdot s$ at 350°C and a ΔP across the membrane of 3.5 atm which compares favorably to the flux at 355°C through a ~25 μm thick Pd–Cu film supported on a porous α-alumina support (0.15 mol (STP)/$m^2 \cdot s$ at $\Delta P = 6.8$ atm). This corresponds to a factor of four higher flux through the Pd/V–Cu/Pd membrane at half of the transmembrane pressure differential, attributable to the higher permeability of vanadium to hydrogen. Although the Pd/V–Cu/Pd membrane had a higher hydrogen flux and no pinholes, it failed at a hydrogen pressure of 5 atm. Increasing the Cu content of the foil resulted in decreased hydrogen permeability.

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