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PALLADIUM-COATED VANADIUM-ALLOY MEMBRANES FOR HYDROGEN SEPARATION

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ABSTRACT

Hydrogen-separating membranes have the potential to generate pure hydrogen from abundant fossil fuel supplies such as coal, for use in fuel cells. Foils of $V_{0.95}Ti_{0.05}$ and $V_{0.88}Cu_{0.12}$ (at. %) coated with thin films of Pd or Pd alloy (Pd–Ag) were fabricated and tested for hydrogen permeability and stability during operation at temperatures from 320-450ºC. Vanadium-alloy foils were ion-milled and coatings between 50 and 200 nm thick were applied to both sides *in-situ*, via electron beam evaporation PVD. The membranes were completely permselective for hydrogen. Hydrogen flux stability was dependent on palladium coating thickness, with constant flux observed during tests at 350ºC, and slow decline observed at 400ºC that accelerated at higher temperatures.

INTRODUCTION

With increasing pressure on energy supplies and the threat of global climate change, more efficient and less polluting ways of utilizing fossil fuels are being explored. Near-zero emission coal power plants of the future could use hydrogen separating membranes to facilitate the recovery and utilization of pure hydrogen [1-3]. Metals such as vanadium, niobium, and tantalum have been considered since the 1960's as cheaper alternatives to palladium alloys for hydrogen separating membranes [4]. A catalytic coating is necessary on these metals to facilitate hydrogen entry and exit from the metal [5]. Metallic interdiffusion between Pd coatings and membrane supports has been recognized to cause a decrease in the hydrogen permeability of composite membranes around 400ºC [6-9], while hydrogen embrittlement is known to cause premature failure of metal membranes [10]. Addition of alloying elements to reduce the solubility of hydrogen and prevent the formation of brittle hydrides can increase membrane strength [11]. Therefore, alloys of vanadium with titanium or copper were investigated for hydrogen permeability and increased resilience, while various surface coatings were studied for resistance to metallic interdiffusion.

EXPERIMENTAL PROCEDURES

High purity (99.9%) metals were electron beam (*e*-beam) melted into buttons in a vacuum furnace. The buttons were flipped and re-melted several times to ensure compositional uniformity. Buttons of roughly 250 g were sliced and cold rolled into ~5×15 cm strips with nominal thicknesses of 40 μm (V–Ti) or 75 ±5 μm (V–Cu). 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,

argon was bled into the chamber to a pressure of $1.5 \cdot 10^{-4}$ torr and the ion-gun was used 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 again to $1 \cdot 10^{-7}$ torr and palladium was *e*-beam evaporated onto the foil to the desired thickness at 3-5 Å/s. A quartz crystal was used to monitor the thickness of metal deposited. The Pd–Ag films were deposited by sputtering from a $Pd_{0.50}Ag_{0.50}$ target. In all cases, the same metal coating was deposited onto both sides of each foil.

Samples were handled using gloves and forceps. Discs (2 cm diameter) were laser cut from the foil or cut by hand from larger foil samples using clean scissors. The membrane foil was sandwiched between two Ni VCR gaskets (12.7 mm OD) and positioned in the fixture, a stainless steel VCR fitting adapted with an impinging flow design. A final helium pressurization test was performed to confirm the absence of leaks. The membrane module was placed in a heater and connected to a gas plumbing and measurement system. Mass flow controllers metered the gas while 0-10,000 or 0-100 torr pressure transducers measured upstream and downstream pressures, respectively. All gases used were at least 99.999% pure and used without further purification. The membrane module was heated in the absence of hydrogen (vacuum or argon purge at the feed and permeate sides). The inlet hydrogen flowrate was maintained in excess of twice the permeate flowrate during all tests. The feed pressure was set at 760 torr and the retentate pressure ranged from 700 to 750 torr. The permeate pressure was typically between 10 and 25 torr. Sweep gas was not used during the permeation experiments.

RESULTS & DISCUSSION

The hydrogen flux vs. time at 1 atm pressure differential through 40-μm thick $V_{0.95}Ti_{0.05}$ membranes with 90 or 100 nm thick $Pd_{50}Ag_{50}$ coatings is shown in Fig. 1. Interestingly, the hydrogen flux was higher through the membranes coated with a thinner palladium layer. There appeared to be more variation in membrane flux than can be explained by the slight difference in $Pd_{50}Ag_{50}$ coating thickness. Perhaps, although it was thinner, the 90-nm thick coating was more continuous due to variation in the deposition process, allowing more hydrogen to pass into and out of the membrane surfaces. Any difference in alloy composition of the coating would also be expected to significantly impact permeability. In the case of one of the membranes coated with 90 nm of $Pd_{50}Ag_{50}$, the flux dropped substantially faster when the temperature was increased to 450°C. Coating the V–Ti foil with $Pd_{0.50}Ag_{0.50}$ resulted in higher initial flux than for $Pd_{0.47}Cu_{0.53}$ coated membranes (not shown) [12], however, more rapid flux decline with time at 450°C was observed compared to membranes with either $Pd_{0.47}Cu_{0.53}$ or pure palladium surface coatings.

Hydrogen flux results for $V_{0.88}Cu_{0.12}$ membranes with 200-nm thick Pd coatings are displayed in Fig. 2. Initial hydrogen flux at 400°C (and a transmembrane pressure differential of one atmosphere) was the highest observed during the test (> 0.5 mol[STP]/m^2•s), dropping quickly when the temperature was reduced to 350°C. A constant hydrogen flux (~0.2 mol[STP]/m^2•s) was observed at 350°C for a period of >150 h, followed by a moderate increase in flux upon increasing the temperature to 400°C. The hydrogen flux leveled off again at 400°C, to the same value observed at 350°C. After 100 h at 400°C, the flux began to decline noticeably. Increasing the temperature to 450°C again resulted in a temporary flux increase, followed by fast decline in flux to a fraction of its value. Apparently, hydrogen flux decrease is accelerated at higher temperatures. This is consistent with a mechanism based on metallic interdiffusion between the palladium surface coating and the vanadium alloy foil, as has been studied previously [12].

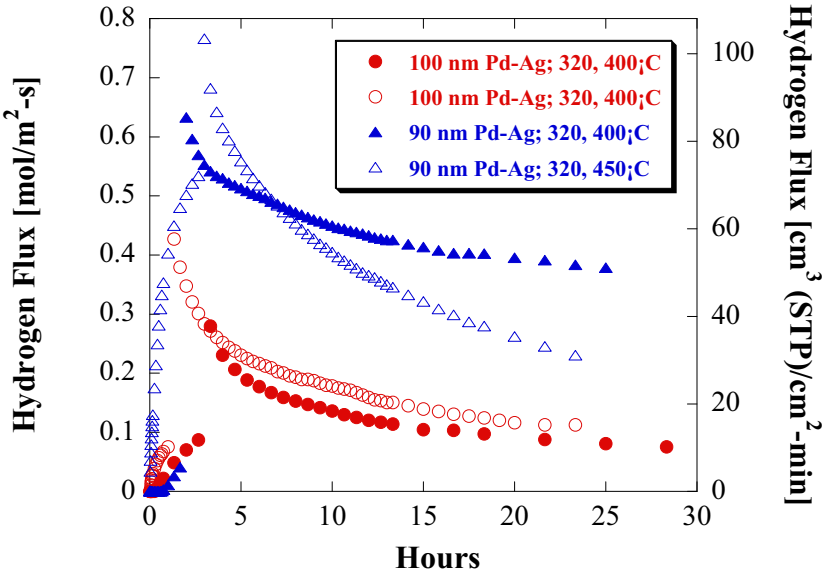

Figure 1. Hydrogen flux through 40-µm thick $V_{0.95}Ti_{0.05}$ membranes coated with 90 or 100 nm of $Pd_{0.50}Ag_{0.50}$ and tested at 320˚C, and 400 or 450˚C. The transmembrane pressure differential was 1 atm.

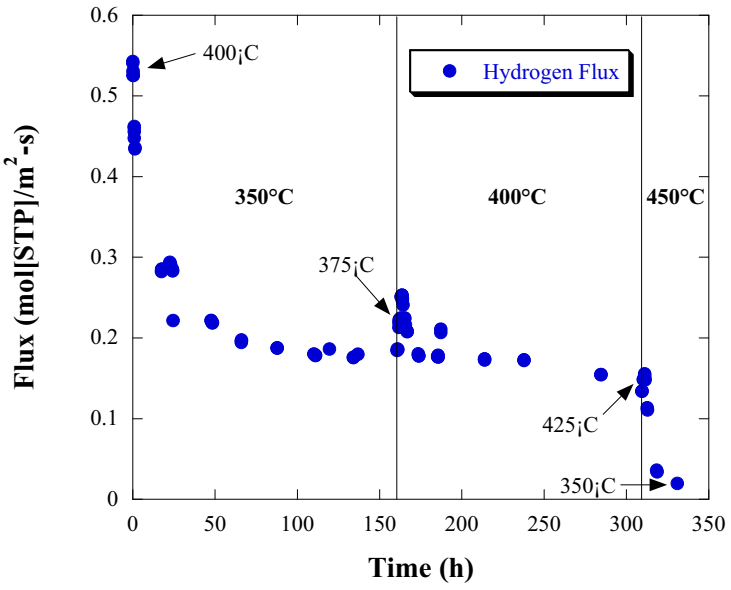

Figure 2. Hydrogen flux through a 75-µm thick $V_{0.88}Cu_{0.12}$ membrane (with 200 nm Pd per side) at 350-450ºC and ΔP = 1 atm.

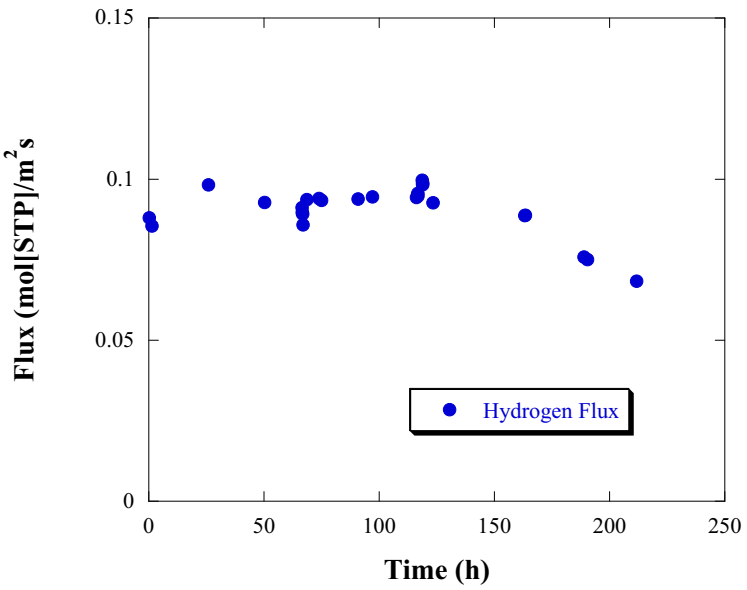

Figure 3. Hydrogen flux through a 75-µm thick $V_{0.88}Cu_{0.12}$ membrane (with 50 nm Pd per side) at 400ºC and ΔP = 1 atm.

Long-term testing was also conducted on a 75-µm thick $V_{0.88}Cu_{0.12}$ foil coated with 50 nm of palladium for comparison. At the same testing conditions (400ºC and ΔP = 1 atm) the hydrogen flux was substantially lower than the flux through the membrane with a 200-nm thick palladium coating (about 0.1 vs. 0.2 mol[STP]/m^2•s). Since palladium is less permeable than the base metal at these conditions, a thicker palladium layer should offer increased resistance to flux. However, more continuous surface coverage by the thicker palladium coating could result in increased flux through the composite membrane. After about 150 hours, the flux began to decline slowly. Further testing is necessary to determine the ultimate steady state that the hydrogen flux will reach.

CONCLUSIONS

The hydrogen flux and flux stability through $V_{0.95}Ti_{0.05}$ and $V_{0.88}Cu_{0.12}$ foils coated with various thicknesses and compositions of palladium alloy was investigated at 320-450°C. Coating 40-µm thick $V_{0.95}Ti_{0.05}$ with 90 or 100 nm of $Pd_{0.50}Ag_{0.50}$ did not result in increased stability, although high initial hydrogen fluxes were obtained. Fairly large discrepancies in flux between membranes with similar coating thicknesses will require further work to explain, although behavior (flux decline with time) was qualitatively similar. $V_{0.88}Cu_{0.12}$ alloy foils coated with either 50 or 200 nm of palladium exhibited stable hydrogen fluxes with time at 350°C, slow decline in hydrogen flux at 400°C, and rapid decline at 450°C. The flux through a $V_{0.88}Cu_{0.12}$ foil with 200 nm of palladium was twice that through a membrane with only 50 nm of palladium. The higher flux was attributed to more thorough coverage of the vanadium foil surface by the thicker palladium coating.

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REFERENCES

1. Ruth, L.A., *Advanced clean coal technology in the USA.* Mater. High Temp, 2003. **20**(1): p. 7-14.
2. Rutkowski, M., et al., *Coal Processing Plants For Hydrogen Production With CO_2 Capture.* J. The Franklin Institute, 2002. **8**: p. 149-158.
3. Paglieri, S. and J.D. Way, *Innovations in Palladium Membrane Research.* Sep. Purif. Meth., 2002. **31**(1): p. 1-169.
4. Makrides, A.C., M.A. Wright, and D.N. Jewett, *Separation of hydrogen by permeation*. 1967: US Patent 3,350,846.
5. Boes, N. and H. Züchner, *Secondary ion mass spectrometry and Auger electron spectroscopy investigations of Vb metal foils prepared for hydrogen permeation measurements.* Surf. Tech., 1978. **7**: p. 401-11.
6. Edlund, D.J., *Composite hydrogen separation metal membrane*. 1995: US Patent 5,393,325.
7. Peachey, N.M., R.C. Snow, and R.C. Dye, *Composite Pd/Ta metal membranes for hydrogen separation.* J. Membr. Sci., 1996. **111**: p. 123-133.
8. Moss, T.S., et al., *Multilayer metal membranes for hydrogen separation.* Int. J. Hydrogen Energy, 1998. **23**(2): p. 99-106.
9. Mardilovich, P.P., et al., *Defect-Free Palladium Membranes on Porous Stainless-Steel Support.* AIChE J., 1998. **44**(2): p. 310-22.
10. Buxbaum, R.E. and A.B. Kinney, *Hydrogen Transport through Tubular Membranes of Palladium-Coated Tantalum and Niobium.* Ind. Eng. Chem. Res., 1996. **35**: p. 530-37.
11. Nishimura, C., et al., *Hydrogen permeation and transmission electron microscope observations of V–Al alloys.* J. Alloys Cmpds., 2003. **356-357**: p. 295-299.
12. Paglieri, S.N., et al. *Influence of surface coating on the performance of V–Cu, V–Ti, and Ta membranes for hydrogen separation*. in *18th Annual. Conf. Fossil Energy Mater.* June 2-4, 2004. Knoxville, Tennessee, U.S.A.: Oak Ridge Natl. Lab.