TITLE: COST-EFFECTIVE METHOD FOR PRODUCING SELF SUPPORTED PALLADIUM ALLOY MEMBRANES FOR USE IN EFFICIENT PRODUCTION OF COAL DERIVED HYDROGEN

QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD START DATE:	9/09/03 (PROGRAM START)
REPORTING PERIOD END DATE:	1/31/06
PRINCIPLE AUTHOR(S):	J. ARPS
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DOE AWARD NUMBER:	DE-FC26-03NT41849
SUBMITTING ORGANIZATION:	SOUTHWEST RESEARCH INSTITUTE 6220 CULEBRA ROAD (78238-5166) P.O. BOX 28510 (78228-0510) SAN ANTONIO, TEXAS
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SUBMIT TO:	NETL AAD DOCUMENT CONTROL BLDG. 921 U.S. DEPARTMENT OF ENERGY NATIONAL ENERGY TECHNOLOGY LABORATORY P.O. BOX 10940 PITTSBURGH, PA 15236-0940

SOUTHWEST RESEARCH INSTITUTE®

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DETROIT WASHINGTON, DC

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APPROVED:

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Materials Engineering Department

DISCLAIMER

ABSTRACT

In the past quarter, significant progress has been made in optimize the deposition and release characteristics of ultrathin (less than 4 micron) membranes from rigid silicon substrates. Specifically, we have conducted a series of statistically designed experiments to examine the effects of plasma cleaning and compliant layer deposition conditions on the stress, release and pinhole density of membranes deposited on 4” and 6” round substrates. With this information we have progressed to the deposition and release of ultra-thin membranes from 12” diameter (113 sq. in.) rigid substrates, achieving a key milestone for large-area membrane fabrication.

Idatech received and is beginning preparations to test the Pd alloy membranes fabricated at SwRI the previous quarter. They are currently evaluating alternate gasketing methods and support materials that will allow for effective sealing and mounting of such thin membranes. David Edlund has also recently left Idatech and Bill Pledger (Chief Engineer) has replaced him as the primary technical point of contact. At Idetech’s request a small number of additional 16 sq. in, samples were provided in a 2 in. by 8 in. geometry for use in a new module design currently under development.

Recent work at the Colorado School of Mines has focused on developing preconditioning methods for thin Pd alloy membranes (6 microns or less) and continuing tests of thin membranes produced at SwRI. Of particular note, a 300-hour short-term durability study was completed over a range of temperatures from 300-450^{o}C on a foil that showed perfect hydrogen selectivity throughout the entire test. With a 20 psi driving force, pure hydrogen flow rates ranged from 500 to 700 cc/min. Calculated at DOE specified conditions, the H_2 fluxof this membrane exceeded the 2010 Fossil target value of 200 SCFH/ft^2.

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1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pd-Cu Membrane Deposition – A 4-factor, 16-run series of experiments was conducted to examine the effects of pre-cleaning conditions and compliant layer deposition on the stress, release, and defect density of Pd-Cu films deposited to a nominal thickness of 5 microns, on 4-inch diameter silicon wafers. The experimental design is summarized in Table 1. Two different radiofrequency plasma cleaning power settings and times were selected in addition to two different compliant layer deposition times (proportional to compliant layer thickness) and pressured. Our hypothesis was that the cleaning conditions might affect the release characteristics and pinhole density of the membrane while the compliant layer could influence the membrane intrinsic stress as well as release. In all cases, the base vacuum pressure ($7x10^{-7}$ Torr), membrane deposition conditions (500W at $8x10^{-4}$ Torr), and thickness (3 microns) were fixed.

Run #	Plasma Cln Time (min)	Plasma Cln Power (watts)	Compl Layer Time (min)	Compl Layer Press (mTorr)
1	15	18	1.5	10
2	15	18	1.5	24
3	15	18	3	10
4	15	18	3	24
5	15	38	1.5	10
6	15	38	1.5	24
7	15	38	3	10
8	15	38	3	24
9	45	18	1.5	10
10	45	18	1.5	24
11	45	18	3	10
12	45	18	3	24
13	45	38	1.5	10
14	45	38	1.5	24
15	45	38	3	10
16	45	38	3	24

Based on the results of these trials, optimal deposition conditions were selected and adapted for use in the preparation of membranes on 12-inch diameter silicon substrates. A new RF plasma cleaning apparatus was constructed to accommodate the larger samples and different methods for rotation and translation of the substrate with respect to the Pd-Cu sputter target were investigated in an effort to optimize the thickness uniformity and stress across the membrane.

H_2 Testing – Some difficulties were recently encountered with thinner membranes rupturing after heating to 300-450^{o}C. A number of membranes were assembled and found to seal acceptably at room temperature but subsequently developed significant leaks upon heating. A preconditioning procedure was developed in which the membranes were first annealed in forming gas at 400 °C for about 24 hours. The membranes were typically pressed between two flat alumina blocks to minimize curling during the annealing process. Two membranes, 100705#2 and 092805#2, showed negligible leak rates and were tested extensively this quarter.

3.0 RESULTS AND DISCUSSION

3.1 Pd-Cu Membrane Optimization

Evaluation of the membranes produced in the design of experiments yielded the following information summarized in Table 2. All membranes released completely from the silicon wafer backing regardless of the process conditions. The number of defects varied considerably from 6-150 defects per sample but no statistically significant correlation could be established between the number of defects and any of the process parameters. For membrane stress the compliant layer deposition time (related to compliant layer thickness) was correlated with statistical significance. In general, the thicker the compliant layer the more tensile stress was developed in the membrane.

Table 2. Measured number of pinhole defects, % release, and membrane stress measured for each trial.

Run #	# of Defects	% Release	Relative Stress
1	15	100	0
2	23	100	3
3	7	100	-3
4	8	100	-1
5	15	100	0
6	16	100	5
7	6	100	-3
8	7	100	-2
9	9	100	-1
10	6	100	0
11	23	100	-5
12	14	100	-3
13	14	100	5
14	29	100	1
15	150	100	-5
16	16	100	5

Based upon this information we initiated a series of trials to deposit membranes on 12" diameter silicon wafers. Figure 1 shows a Pd-Cu membrane, approximately 3-4 microns thick, prior to its release from the substrate. The chevron pattern is simply a reflection off the filter grating of the laminar flow bench where the photo was taken. While some cracking developed in the membrane as it release at the edges of the wafer, several large sheets of membrane material with near-zero internal stress were harvested for testing. Pinhole densities numbered fewer than 10 across the entire wafer in at least one instance. A small number of 2" by 8" membranes were carefully cut using a simple quilting knife (similar to a pizza cutter) with one finished example shown in Figure 2. Two samples have been provided to Idatech for incorporation into a new module design.

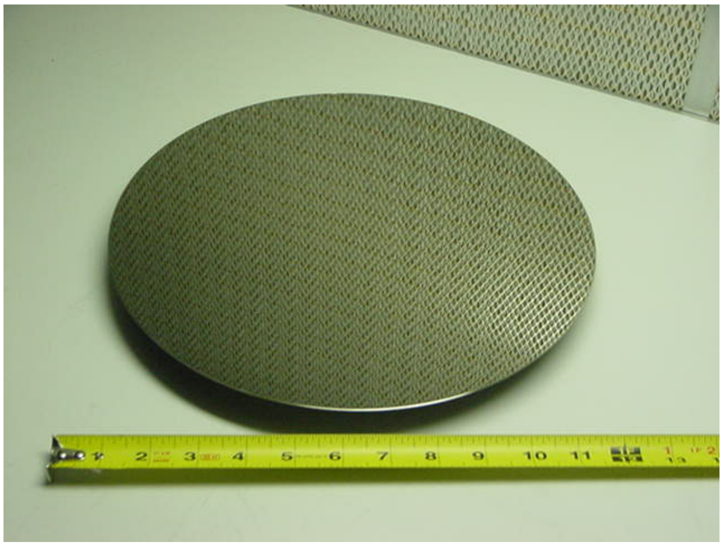

Figure 1. Pd-Cu membrane deposited on 12-inch silicon wafer

Figure 2. Rectangular membrane cut from 12-inch sample.

3.2 H_2 Permeation Testing

After pre-annealing in forming gas, one particular sample (100705#2) was tested at a driving force of 20 psi and no helium was found to leak through the membrane at room temperature. Once the furnace reached 400 °C, the helium leak rate was measured and again found to be zero. The feed was switched to hydrogen and measurements were taken periodically until the flow reached steady state. Figure 1 shows the pure hydrogen flux for a 20 psi driving force at 400 °C over a period of approximately 300 hours. This assumes 3.5 cm diameter of membrane exposed to the hydrogen flow (9.5 cm^2 area).

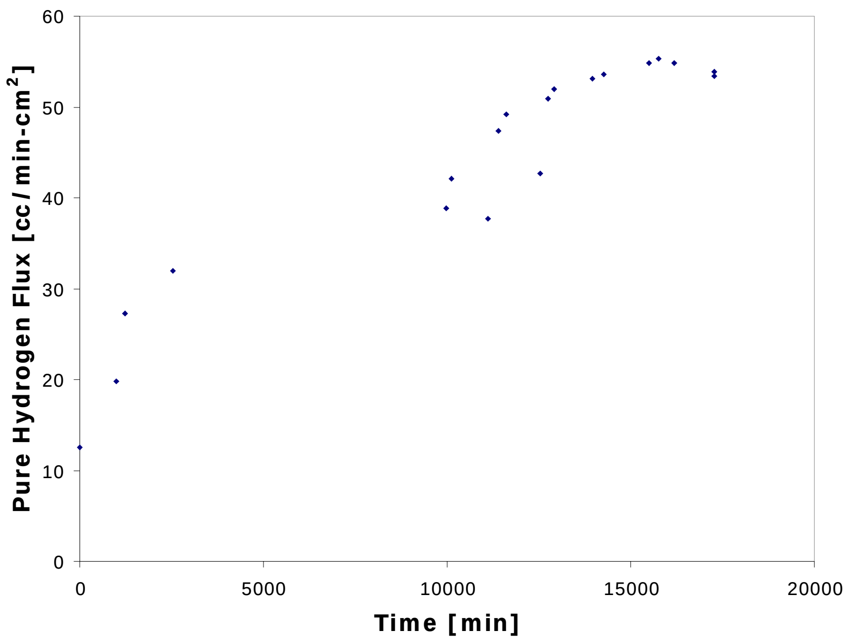

Figure 1. Membrane 100705#2 approaching steady state at 400°C and 20 psi.

The final points on the plot correspond to a hydrogen flow rate of around 700 cc/min from which value of 1.11E-4 $cm^3 \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$ was calculated at 400 °C. At steady state, the membrane permeability was calculated at 300, 350, and 450 °C using the measured thickness of 6 µm. These were then plotted with the Wilkinson and McKinley permeabilities for comparison. This plot suggests that this membrane was close to the ideal target composition of 60% Pd. The Wilkinson foils have been analyzed by EDAX using a traceable standard and the palladium weight percent is about 59.7%. Figure 2 shows the comparison of the Wilkinson membrane, McKinley patent data, and membrane 100705#2. The selectivity of this membrane was perfect throughout this extended permeation test, meaning that the flux of He was undetectable at 20 psig.

Using the measured H_2 permeability at 400 °C, we can also calculate a flux to compare with the DOE Fossil Energy targets. For a feed stream at 150 psia, the permeate stream at 50 psia, the pure H_2 flux for this membrane would be 255 SCFH/ft^2, exceeding the 2010 target of 200 SCFH/ft^2. If the thickness could be reduced from 6 μm to 5 μm with out negatively affecting the permeability, the 2015 target could be reached.

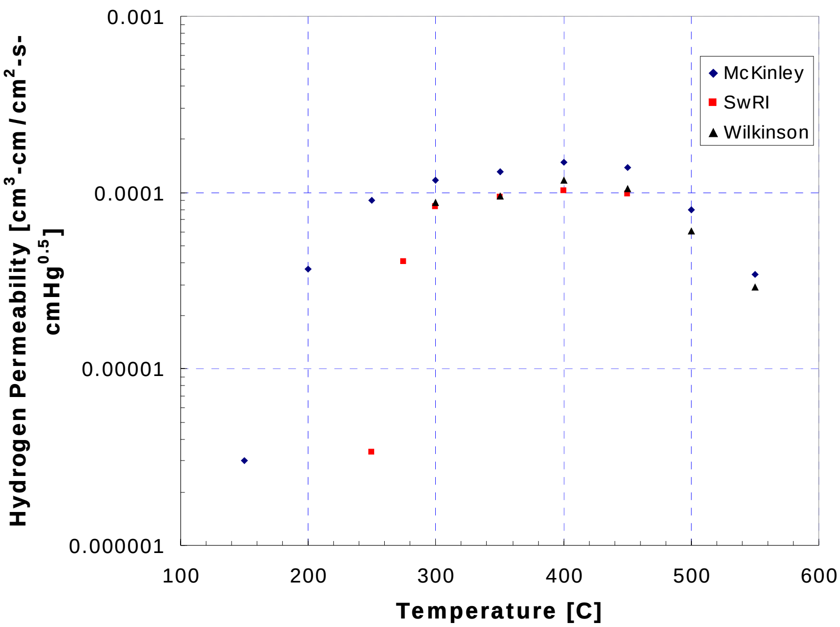

Figure 2. Permeability versus temperature plot for membrane 100705#2, Wilkinson foil, and McKinley patent data

Recently a 3.5 micron Pd-Cu foil (092805#2) was annealed in forming gas at 400°C for 12 hours, placed in the test cell, and tested for helium leaks. There was no measurable helium leak out the sides of the membrane cell and the pressure did not change over a couple minutes when the feed and retentate streams were closed. The furnace was then set to 400 °C where there was still no He leak from the cell. Figure 3 shows the membrane's approach to steady state. Overnight, the hydrogen feed flow rate is typically reduced to conserve H_2.and minimize any chance of emptying the gas bottle which is the source of the changes in flux. While the membrane seems to be slowly reaching a steady state and the total flux is significantly higher than 100705#2, it does not appear that the membrane will reach the expected flux based on the 3.5 micron thickness. We suspect that the lower concentration of palladium in this membrane, 58.49%, is the likely cause of the reduced flux.

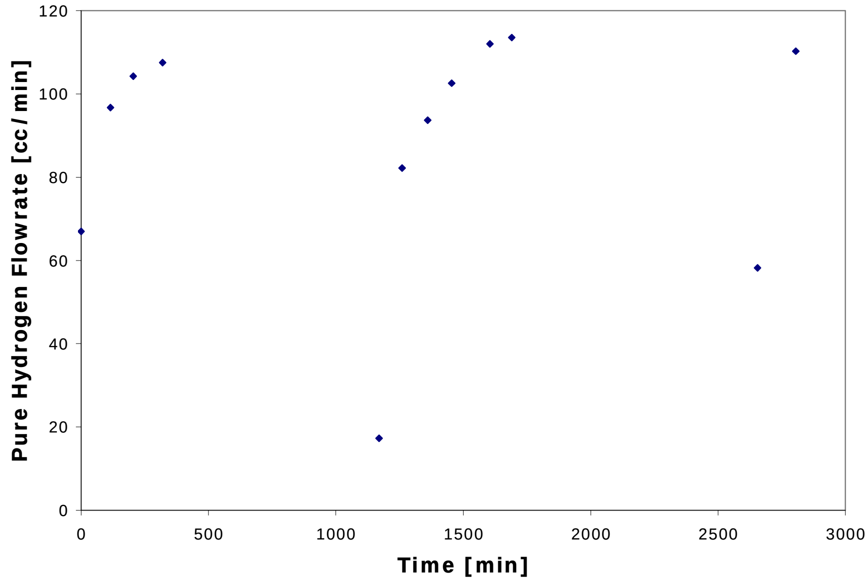

Figure 3. Membrane 092805#2 approaching steady state at 400 °C and 20 psi.

3.3 Problems Encountered:

No problems encountered this quarter.

3.4 Plans for Next Reporting Period:

- SwRI will continue process optimization for deposition of thin (<5 micron) membranes on 12” diameter Si substrates and fabricate additional samples as needed for use by Idatech.
- SwRI hopes to investigate ternary alloy additions of Rhenium and Nickel to the Pd-Cu alloy based on recent work by Kamakoti and Sholl and S-K-Ryi, et al, respectively to further enhance permeability and environmental stability. Small samples will be provided to CSM for testing.
- Prepare a simple cost analysis for manufacture of membranes using methods developed at SwRI. We believe currently even at the laboratory scale we can manufacture membranes in small quantities (few sq. ft per day) at a cost of less than $1500 per sq. ft.
- CSM has been working on a hot bonding method to fuse two thin membranes together. This method will continue to be explored experimentally as a way to “patch” large area membrane having a small number of pinholes.

- Membrane testing will continue at CSM along with surface and microstructure characterization using AFM and XRD. CSM plans to modify their test apparatus so that two membranes can be tested at one time, allowing more efficient screening studies to be carried out.
- Incorporation of SwRI membranes into prototype modules will finally begin at Idatech. We hope to have test data by the next quarterly report.

4.0 CONCLUSION

Significant progress has been made this past quarter in the fabrication of thin (<5 micron) pinhole-free membranes over areas of more than 110 sq. in. Recent test data from CSM has confirmed that SwRI membranes are capable of meeting DOE 2010 flux rate targets. We are optimistic that by the completion of the program we may be able to demonstrate small-scale (and hopefully large-scale) Pd-Cu membranes that meet DOE 2015 flux rate targets. The key remaining milestone is incorporation of these membranes into prototype modules at Idatech and we are hopeful that we will be able to report results on this effort next quarter.

5.0 REFERENCES

N/A