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:	04/30/05
PRINCIPLE AUTHOR(S):	B. LANNING, J. ARPS
DATE REPORT WAS ISSUED:	APRIL 2005
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
OTHER TEAM MEMBERS:	COLORADO SCHOOL OF MINES IDATECH
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®
SAN ANTONIO HOUSTON
DETROIT WASHINGTON, DC

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:	04/30/05
PRINCIPLE AUTHOR(S):	B. LANNING, J. ARPS
DATE REPORT WAS ISSUED:	APRIL 2005
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
OTHER TEAM MEMBERS:	COLORADO SCHOOL OF MINES IDATECH
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

APPROVED:

James H. Arps, Manager
Surface Engineering Section

DISCLAIMER

ABSTRACT

Over the last quarter, we continued to optimize procedures for producing free-standing, defect free films using rigid silicon and glass substrates. A strong correlation was observed between sputter power and formation of defects (pinholes) in the film; i.e., lower power, and correspondingly lower deposition rate, results in a lower defect density. Films less than 1 μm-thick have been successfully released from both silicon and glass substrates although the minimum thickness for pinhole-free films over a 4-inch diameter disc is still on the order of 3-4 μm.

Results from hydrogen permeation testing over the last quarter have shown a marked increase in membrane performance primarily due to proper alloy composition and pre-treatment procedures. As an example, the hydrogen flux at 400 °C and 20 psi trans-membrane pressure, for a 5 μm-thick membrane, was 120 cm^3 (STP)/cm^2 min. The productivity of this membrane exceeds the 2015 DOE Fossil Energy targets. Hydrogen permeability was calculated to be $2.0 \cdot 10^{-4}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. Permeation tests were then repeated on a sibling membrane sample and the measured hydrogen flow rate at 400 °C and 20 psi was 58 cm^3 (STP)/min. Although lower than the flow rate of the first sample, the hydrogen flow rate increased to 175 cm^3 (STP)/min after two oxidation treatments.

Finally, with the attendance of John Shen and the rest of the program team members at the IdaTech facility in Bend, OR, we presented an overview of program activities. Subsequently, we prepared detailed written responses to John Shen's questions with regard to technical feasibility, maturity, scale-up and commercialization potential in comparison to competing hydrogen separation methods such as pressure swing absorption and ionic conducting membranes.

Table of Contents

1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pd-Cu alloy Vacuum Deposition –

Rigid substrates – Based on procedures reported previously for depositing and releasing Pd-Cu films from rigid silicon substrates, we extended this development to include larger silicon and glass substrates. In brief, processing parameters were optimized to produce films with poor adhesion and minimal electrostatic interaction forces using magnetron sputtering from an alloy target.

H_2 Testing – A membrane foil is first sandwiched between two circular supports, such as alumina paper, and then sealed with either a Kalrez O-ring (max. use to 315 ^oC) or Grafoil packing material (allowing a 650 ^oC upper use temperature in oxygen-free environments) in the 25 mm Millipore membrane cell. The membrane is then checked with helium to confirm a tight seal and that the membrane is defect (pinhole) free. Subsequently, the membrane is heated to operating temperature to begin permeation testing.

3.0 RESULTS AND DISCUSSION

3.1 Progress

3.1.1 Optimization of Pd-Cu Membrane Formation

Rigid Substrates (silicon/glass)

We have established processing procedures that will enable reliable and consistent (with greater than a 95% level of confidence) release of Pd-Cu alloy films (currently 4” diameter rounds) from rigid support materials such as silicon and glass. We have also observed a strong correlation between sputter deposition power and the formation of defects (pinholes); namely, the higher the power, the greater the probability of pinhole formation assuming everything else remains constant (invariant). However, optimum release does not always coincide with low power and therefore, we are continuing to investigate processing conditions that will reduce defect formation while maintaining adequate release characteristics.

3.1.2 H_2 Permeation Testing

Results from H_2 Permeation Testing (Sputtered films on silicon)

Membrane SwRI-pg168 was prepared in accordance with the procedures outlined in the experimental section and then tested for permeation with pure hydrogen. See Figure 1 for the hydrogen flux behavior with time at 400 °C and 20 psi trans-membrane pressure.

A helium leak of 1.1 cm^3 (STP)/ cm^2 min was observed at time, t ~ 51 hours indicating that a leak may have developed during testing. The data in Figure 1 have been corrected for this leak.

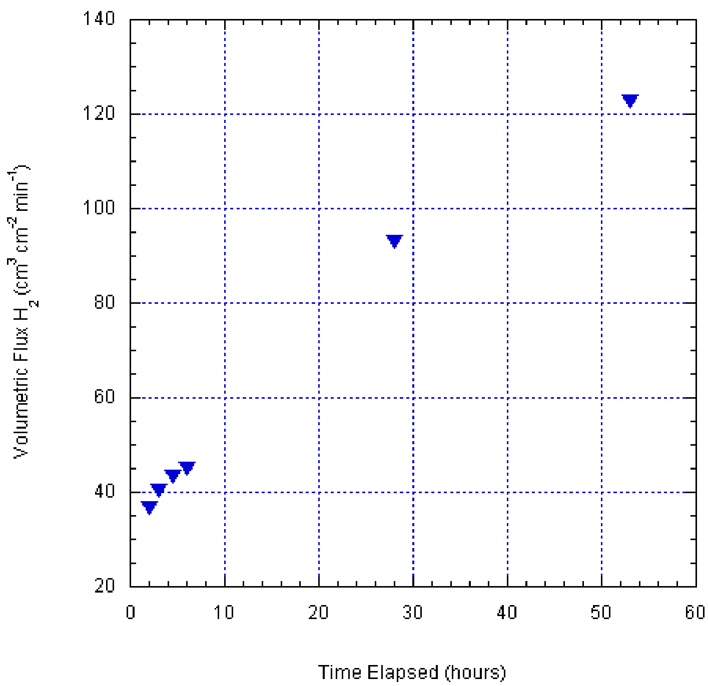

Figure 1. Influence of time on hydrogen permeation of membrane SwRI-pg168 at 400 °C with a hydrogen feed pressure of 20 psig.

Table 1 shows the how the hydrogen flux of membrane SwRI-pg168 compares to the targets established by the Office of Fossil Energy Hydrogen from Coal RD&D plan. The hydrogen flux at the target conditions is calculated based on the results at 20 psig. This foil exceeds the 2015 target.

Table 1. Calculated H_2 flux of membrane SwRI-pg168 and Office of Fossil Energy performance targets

Performance Criteria	**Membrane SwRI-pg168**	**2007 Target**	**2010 Target**	**2015 Target**
Flux scf/h/ft2 @ 100 psi ΔP H_2 partial pressure & 50 psia permeate side pressure	564	100	200	300

The thickness of membrane SwRI-pg168 was measured after testing in order to minimize handling of the film before hydrogen permeation could be studied and was measured with a micrometer to be 5 µm. The hydrogen permeability was then determined to be $2.0 \cdot 10^{-4}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$.

A separate sibling membrane, labeled SwRI-pg176, was also tested this quarter and is still under test at 400 °C. This membrane was mounted as received using the same arrangement as SwRI-pg168. Hydrogen flow rates will be reported here rather than flux until the experiment is concluded and the area available for permeation can be measured. At 400 °C and 20 psi, a helium leak of 7.4 cm^3(STP)/min is observed. The hydrogen flow rates have been corrected for this leak. The hydrogen flow rate at 20 psi achieved a steady state of approximately 58 cm^3(STP)/min relatively quickly. An in-situ air oxidation was performed at 20 psig and 400 °C for 1 hour, upon which the hydrogen flow rate doubled to a steady value of approximately 121 cm^3(STP)/min. A second air oxidation was then performed where air was supplied to the foil at 20 psig and 400 °C for a period of 2 days. A jump in the hydrogen flow rate was observed followed by a gradual decrease to a higher steady state. Figure 2 shows the hydrogen flux behavior with time at 400 °C and 20 psi trans-membrane pressure and the influence of air oxidation treatments. This foil exhibited dramatic enhancements in hydrogen flux as a result of air oxidation similar to the 25 µm foil reported during the March project review meeting in Oregon.

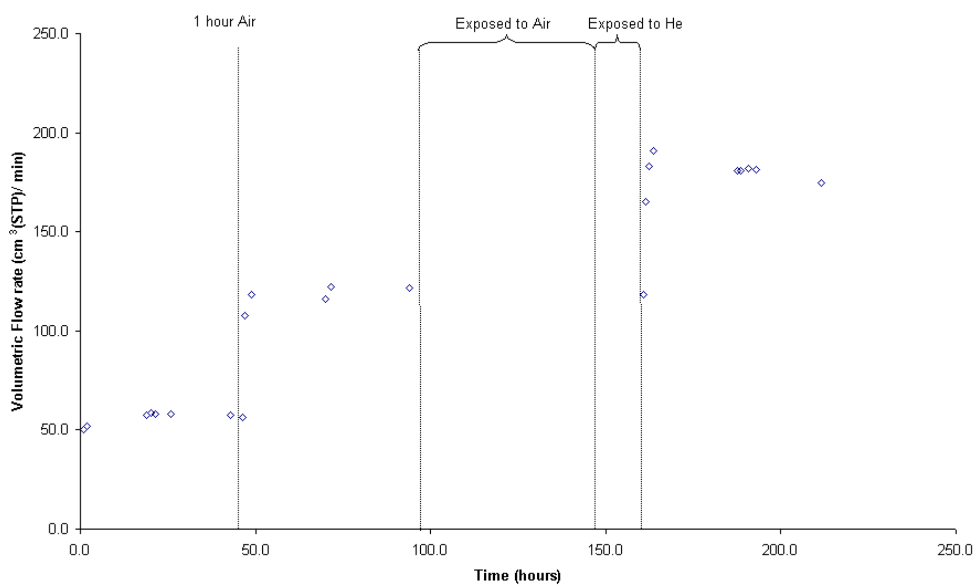

Figure 2. Influence of time and air oxidation on hydrogen permeation of membrane SwRI-pg176 at 400 °C with a hydrogen feed pressure of 20 psig.

Permeation experiments with membrane SwRI-pg176 will continue. Analysis of the surface using SEM will be performed in addition to structure and composition analysis.

3.2 Problems Encountered:

As we have concentrated this last quarter on establishing procedures for producing thin, less than 5 μm-thick membranes without any pinholes, we have delayed fabrication of membranes to be delivered to IdaTech. We are currently scheduled to produce these films and will deliver to IdaTech upon completion.

3.3 Plans for Next Reporting Period:

- Complete fabrication of 4" diameter membranes for delivery to IdaTech for incorporation into test module.
- Continue to develop procedures, such as oxygen pre-treatment, and develop processes for the incorporation of alloy additions, that will enhance hydrogen permeation.

4.0 CONCLUSION

Continued to optimize procedures for producing free-standing, defect free films using rigid silicon and glass substrates. A strong correlation was observed between sputter power and formation of defects (pinholes) in the film; i.e., lower power, and correspondingly lower deposition rate, results in a lower defect density. Films less than 1 μm-thick have been successfully released from both silicon and glass substrates although the minimum thickness for pinhole-free films over a 4-inch diameter disc is still on the order of 3-4 μm.

Results from hydrogen permeation testing over the last quarter have shown a marked increase in membrane performance primarily due to proper alloy composition and pre-treatment procedures. As an example, the hydrogen flux at 400 °C and 20 psi trans-membrane pressure, for a 5 μm-thick membrane, was 120 cm^3 (STP)/cm^2 min. The productivity of this membrane exceeds the 2015 DOE Fossil Energy targets. Hydrogen permeability was calculated to be $2.0 \bullet 10^{-4}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. Permeation tests were then repeated on a sibling membrane sample and the measured hydrogen flow rate at 400 °C and 20 psi was 58 cm^3 (STP)/min. Although lower than the flow rate of the first sample, the hydrogen flow rate increased to 175 cm^3 (STP)/min after two oxidation treatments.

Finally, with the attendance of John Shen and the rest of the program team members at the IdaTech facility in Bend, OR, we presented an overview of program activities. Subsequently, we prepared detailed written responses to John Shen's questions with regard to technical feasibility, maturity, scale-up and commercialization potential in comparison to competing hydrogen separation methods such as pressure swing absorption and ionic conducting membranes.

5.0 REFERENCES

N/A