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:	9/30/05
PRINCIPLE AUTHOR(S):	B. LANNING, J. ARPS
DATE REPORT WAS ISSUED:	10/28/05
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®
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APPROVED:

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DISCLAIMER

ABSTRACT

During the last quarter, new procedures were developed and implemented to improve reliability and repeatability of release characteristics from the temporary substrate (i.e., silicon wafer) and to minimize through-thickness defects in a 6” diameter film, 3 microns in thickness. With the new procedures, we have been able to consistently produce essentially stress free films, with zero or minimal defects (less than 5) across a 6” diameter area. (It is important to note that for those films containing pinholes, a procedure has been developed to repair the pinholes to form a gas tight seal). The films are all within the identified tolerance range for composition (i.e., 60 +/- 0.2 % Pd). A number of these films have subsequently been shipped to IdaTech for evaluation and integration into their test module.

Colorado School of Mines continued their high temperature evaluation of 6 micron thick, sputtered Pd-Cu films. Pure hydrogen permeability increased up to 400 °C while the membrane was in the β-phase and dropped once the temperature increased to over 450 °C. Above this temperature, as confirmed by the binary phase diagram, the film transforms into either a mixed α/β or pure α phase. The same trend was observed for a baseline 25 micron-thick foil (from Wilkinson) where the pure hydrogen permeability increased with temperature while the membrane was in the β-phase and then decreased upon transformation to the α phase.

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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 a 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

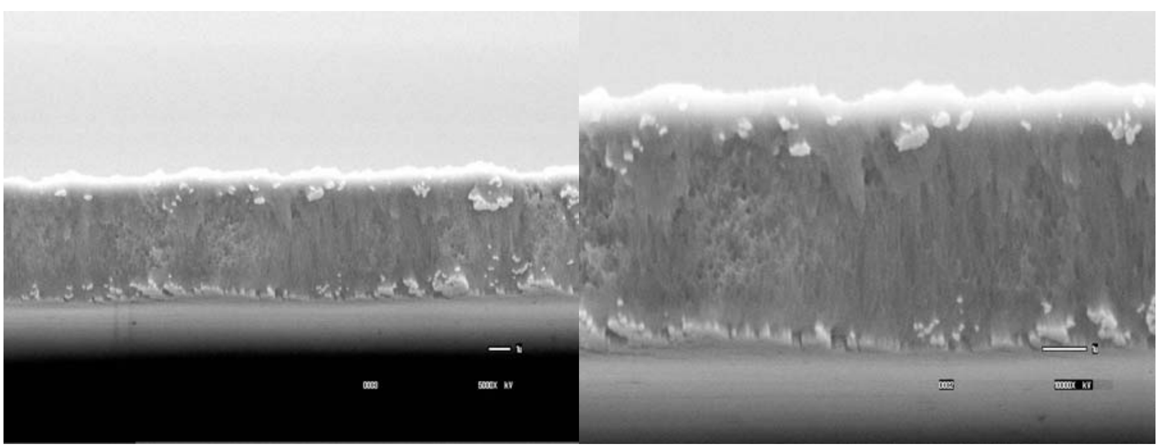
3.1 Progress

3.1.1 Optimization of Pd-Cu Membrane Formation

Rigid Substrates (silicon/glass) – Having previously established procedures for depositing a Pd-Cu film, with varying thickness and compositions, on a variety of substrates over large areas, the activity this quarter was focused on developing procedures for producing pinhole-free, free-standing films at a thickness less than 5 microns (up to 28 in2, 6" diameter surface). To produce defect-free, pinhole-free coatings less than 5 microns in thickness, the presence of micron and even sub-micron-size particulates must be minimized or through-thickness pinholes in the film membrane will develop. Although particulates can be essentially eliminated in a clean room environment, the goal for this program has been to utilize methods and procedures that do not require a class 10 or better rating.

Procedures were therefore established to clean the substrate prior to loading in the deposition chamber. Both oxidized silicon (6" diameter) and polished silica (4" diameter) substrates were coated with Pd-Cu; polished silica (optically transparent) enabled us to evaluate pinhole formation prior to and after release (since silica and oxidized silicon have essentially the same chemistry, they both yield similar release characteristics). First, the substrates are given a careful visual inspection and any visible particulates are removed using optical-grade wipes. Next, the samples are dusted off using an Ion-Air Model 7901 de-ionizing gun fed by ultrahigh purity nitrogen. This removes any remaining particulates that are electrostatically bound to the surface. The substrates are then mounted face down in the vacuum chamber and prior to sputter deposition, a radiofrequency (RF) plasma cleaning procedure was developed with the goal of removing surface contaminants and "functionalizing" the surface to enable the proper adhesion and release characteristics. The RF clean was subsequently shown to reduce surface contaminants (including particulates) to a minimum and resulted in the production of pinhole-free, 3 micron thick films.

At the beginning of the deposition, processing conditions were established to cerate a thin, <100 nm compliant layer for stress control and film release. The use of oblique angle and/or high pressure deposition conditions during magnetron sputtering are known to create porous/near amorphous structures that are compliant and therefore, this approach was incorporated into the film growth procedures. An SEM cross section of a 3 micron, Pd-Cu film is shown in Figure 1 where the 60 nm compliant layer can be seen at the bottom (released) surface of the film and a fine-grained, columnar structure is observed throughout the bulk of the film section.



a) b)

Figure 1. Cross section of magnetron sputtered, Pd-Cu film with 60 nm compliant layer at (a) 5000X and (b) 10000X magnification.

A top view of the film presented in Figure 1 is presented in Figure 2 below. A number of these films, 6" in diameter and 3 microns thick, have been prepared with essentially neutral stress in the as-deposited condition. The films release consistently, without damage, and with minimal adhesion to the substrate; it is important to note that this adhesion can be adjusted to obtain ideal release parameters.

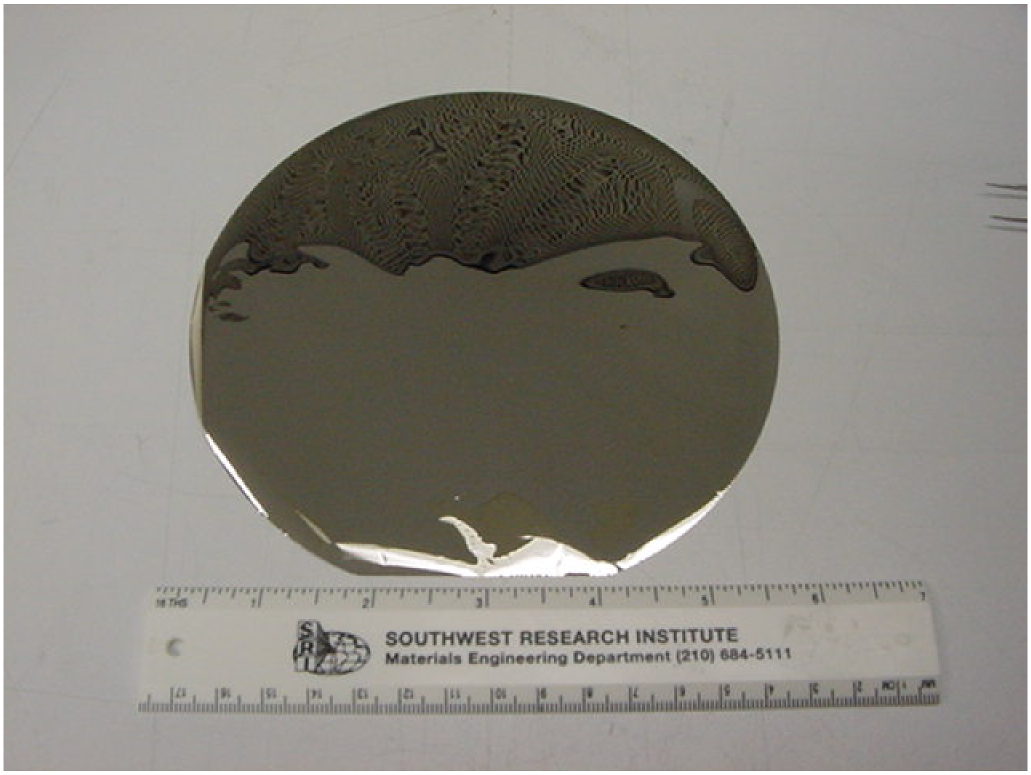


Figure 2. As-deposited (and released), 3 micron-thick, 6" diameter, Pd(60)-Cu(40), film (grown on oxidized silicon wafer).

Approximately ten 6" diameter samples were shipped to IdaTech for evaluation and testing in a small module configuration. This represents a significant internal milestone for the project. We are in the process of procuring larger, 10-inch diameter substrates which will allow us to demonstrate the fabrication of membranes 75 square inches in area.

3.1.2 H_2 Permeation Testing

Sputtered films on silicon – 6 μm-thick

Hydrogen permeation experiments were performed on a 6 micron-thick film (sample 41805SI1) in 50 °C increments from 300-600 °C. As expected, the pure hydrogen permeability increased up to 400 °C while the membrane was in the β-phase and dropped once the temperature increased to over 450 °C. According to the Pd-Cu phase diagram shown below in Figure 3, this temperature would correspond to the α and β mixed phase. Figure 4, shown below, presents the pure H_2 permeability versus temperature data.

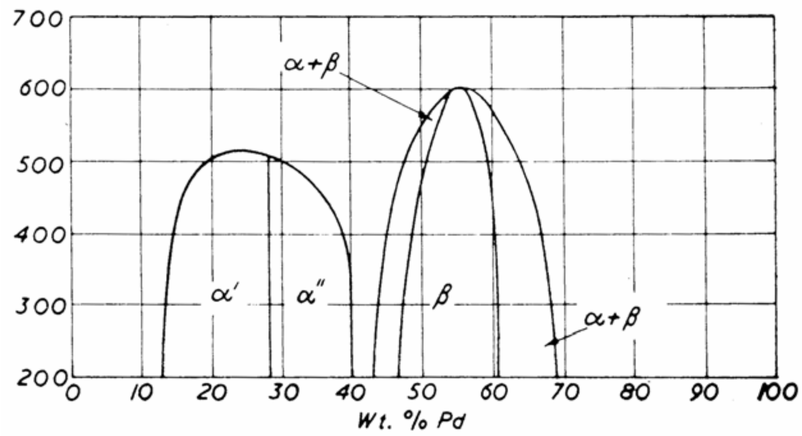


Figure 3. Low temperature section of the Pd-Cu phase diagram.

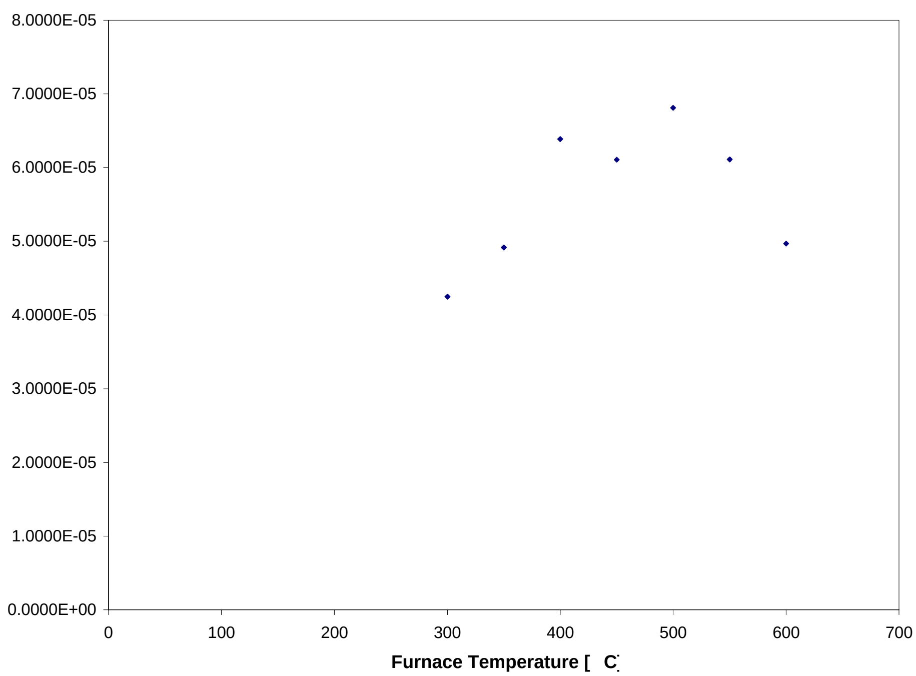
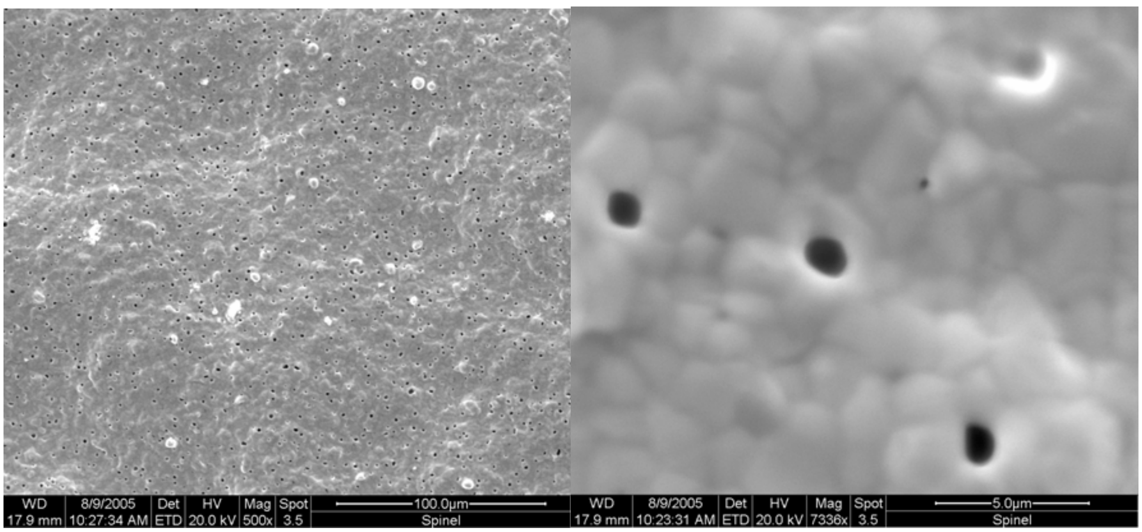


Figure 4. Pure Hydrogen Permeability versus Furnace Temperature for Wilkinson Foil.

The same trend was observed for a 25 micron-thick foil (from Wilkinson) where the pure hydrogen permeability increased with temperature while the membrane was in the β-phase (as confirmed by XRD). Between 400 and 450 °C, the membrane shifted to the α and β mixed phases, and the permeability dropped.

During testing, it appeared as though a leak formed in the 6 micron-thick, sputtered membrane as the temperature was raised above 500 °C (refer to Figure 5. This was verified through SEM imaging of the membrane surface which showed the formation of many pinholes. As was seen with the 6 micron-thick membrane, the Wilkinson foil also developed pinholes after being exposed to a temperature of 600 ^{o}C. The Wilkinson foil's H_2/He selectivity remained high even though pinholes were beginning to form.



a) **b)**

Figure 5. SEM Image of 6 micron film from a) center of film at 500X and b) close up at 7338X.

A new permeation cell for the 25 mm membranes was designed and fabricated. This cell is a scaled-down version of the one used for the 47 mm membranes. Previously, we have encountered some difficulties with sealing the smaller 25 mm cells purchased from Millipore with the Grafoil valve packing material. The new cell is shown below in Figure 6.

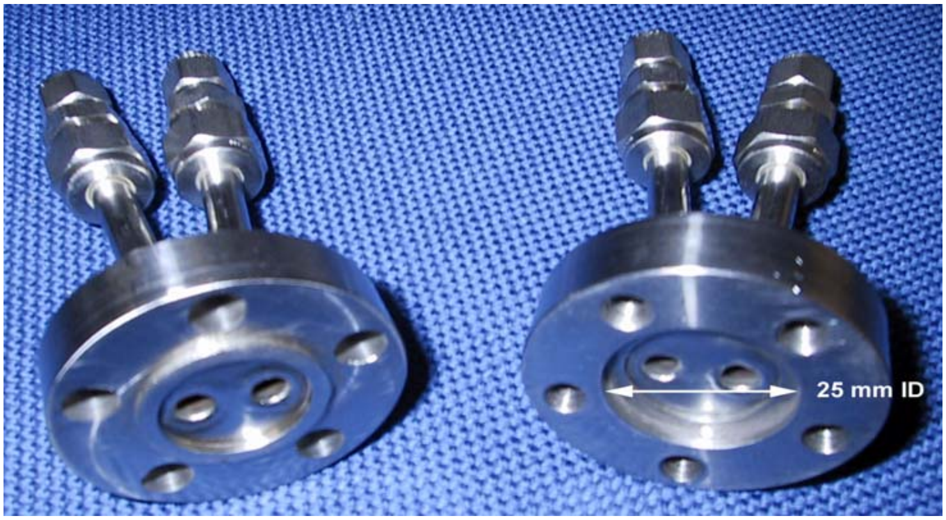


Figure 6. New stainless steel flow cell for 25 mm diameter membrane samples.

Problems Encountered:

No problems encountered this quarter.

3.2 Plans for Next Reporting Period:

- Complete a series of designed experiments to elucidate the effects of RF cleaning, compliant layer thickness, and compliant layer deposition conditions on the stress, release characteristics, and pinhole density of the Pd-Cu membranes.
- Transition process parameters, lessons learned, for the 6" diameter films to a larger, 10" diameter film and thereby produce larger area films (3 micron thickness).
- Preparation and evaluation of 3 micron-thick material in IdaTech's test module.
- Permeation testing and evaluation of recent 3-micron-thick material with 60 +/- 0.2% Pd composition.

4.0 CONCLUSION

During the last quarter, new procedures were developed and implemented to improve reliability and repeatability of release characteristics from the temporary substrate (i.e., silicon wafer) and to minimize through-thickness defects in a 6" diameter film, 3 microns in thickness. With the new procedures, we have been able to consistently produce essentially stress free films, with zero or minimal defects (less than 5) across a

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Evaluation of 6 micron thick, sputtered Pd-Cu films was continued. Pure hydrogen permeability increased up to 400 °C while the membrane was in the β-phase and dropped once the temperature increased to over 450 °C. Above this temperature, as confirmed by the binary phase diagram, the film transforms into either a mixed α/β or pure α phase. The same trend was observed for a 25 micron-thick foil (from Wilkinson) where the pure hydrogen permeability increased with temperature while the membrane was in the β-phase and then decreased upon transformation to the α phase.

5.0 REFERENCES

N/A