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: 10/30/04

PRINCIPLE AUTHOR(S): B. LANNING, J. ARPS

DATE REPORT WAS ISSUED: OCTOBER 2004

DOE AWARD NUMBER: DE-FC26-03NT41849

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ABSTRACT

To overcome the issue of pinhole (defect) formation in membrane films over large areas, a process was developed and implemented for producing 6-12 μm-thick, Pd-Cu alloy films on thermally oxidized silicon wafer substrates. The processing parameters on silicon are such that adhesion is poor and as-deposited Pd-Cu alloy films easily release from the oxidized silicon surface.

Hydrogen permeation tests were conducted on 9 and 12 μm-thick Pd-Cu alloy films and the hydrogen flux for 9 and 12 μm-thick films were 16.8 and 8 cm^3(STP)/cm^2•min respectively. The hydrogen permeability (corrected using data in McKinnley patent) of the 9 μm-thick membrane is $7.4 \cdot 10^{-5}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$ at 350 °C and compares very well to permeability reported by McKinnley for a 62.5% Pd membrane; this permeability is ~56% of the value reported for a Pd-Cu alloy membrane with optimum 60% Pd composition. Using XRD, we confirmed the presence of a two-phase, α/β, structure and that the composition of our membrane was slightly higher than the optimum composition. We are making adjustments to the compositions of the Pd-Cu alloy target in order to produce films next quarter that match the ideal $Pd_{60}Cu_{40}$ composition.

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1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pd-Cu alloy Vacuum Deposition – As described in the previous quarterly report, Pd-Cu alloy films were magnetron sputtered onto silicon substrates in the drum coater system. Samples were affixed to the drum and held stationary during the deposition process.

H_2 Testing – A membrane foil is first sandwiched between tow circular supports, such as alumina paper, and then sealed with either a Kalrez O-ring (max. use to 315 ^{o}C) or Grafoil packing material (allowing a 650 ^{o}C 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 on Silicon

Although we have established procedures for the formation of Pd-Cu alloy films over large areas (> 75 in^2) on sacrificial polymer backing materials, such as PVA and PS, formation of Pd-Cu alloy materials on silicon wafers has helped us to address the issue of defect formation (i.e., pinholes). In general, the key factors that affect formation of a thin, dense, defect-free, Pd-Cu alloy film are surface energy, roughness, and oxygen/moisture content of the backing material. By using thermally oxidized silicon wafers, we have been able to reduce the surface roughness while at the same time, control surface chemistry, and more specifically, oxygen activity. Correspondingly, using vacuum processing conditions that have been optimized to minimize intrinsic film stress, we have produced pinhole-free Pd-Cu alloy films at thicknesses between 6 – 12 μm. Discs, 1" in diameter, were cut from the released Pd-Cu films on silicon and then tested for H_2 permeation (a photograph of the Pd-Cu alloy foil after removal of discs, is shown in Figure 1).

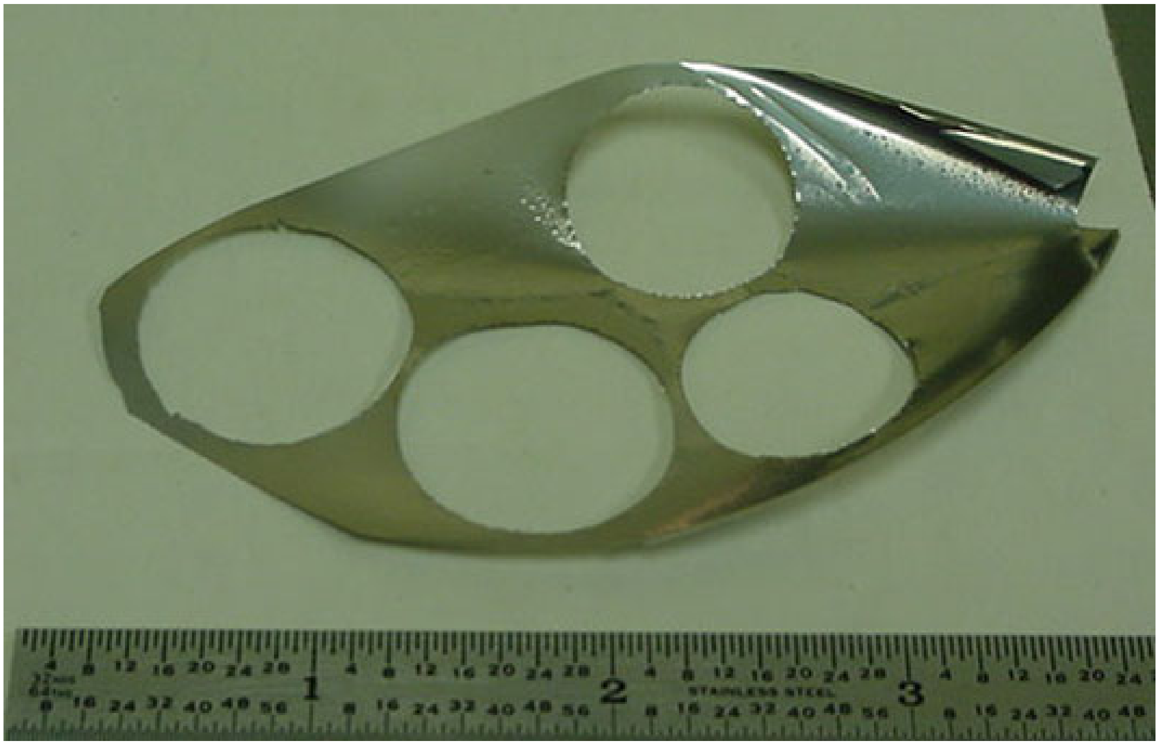

Figure 1. As-fabricated, 12 μm-thick Pd-Cu alloy film, released from thermally oxidized silicon wafer substrate, showing 1”-diameter cut-outs for H_2 permeation measurements

3.1.2 H_2 Permeation Testing

Effect of Porous Support

To insure mechanical integrity of the foil(s) at operating temperatures and pressures, the foils are supported by a porous plate (or mesh) material, typically metallic. Initially, we adopted the same Monel mesh material used in IdaTech’s commercial hydrogen production system although we have since discovered that due to the roughness of the mesh, we were unable to form a leak-tight seal in the bench-scale, Millipore test apparatus. Therefore, we are evaluating a number of alternative porous support options, such as porous stainless steel (Mott Metallurgical), porous Vycor glass (Corning), anodic porous aluminum (0.02 μm pore size from Whatman), aluminum paper (Zircar), and silver membranes (0.45 μm pore size from Millipore). Not surprisingly, there are trade-offs with each of the various options, and the goal in the upcoming quarter will be to concentrate on just one of the options.

Effect of Membrane foil Pre-treatment (25 μm-thick foil)

A control experiment was performed to investigate the effect of annealing and oxidizing the foil membranes prior to H_2 permeation experiments. A cleaned, but not annealed or oxidized, Pd-Cu foil membrane was installed in the permeation cell, heated to 400°C under inert gas and then tested under pure H_2. The volumetric flow from the permeation cell with time is shown in Figure 2. From prior experience, we expected to see the H_2 flux increase slowly with time as the foil annealed and the bulk structure changed from FCC to BCC. However, the flux increased sharply to about 60% of the flux observed in prior experiments and then decreased with longer times. The temperature was increased to 500 °C and an in-situ air purge was performed but the H_2 flux did not increase, and in fact decreased to essentially zero. We are in the process of analyzing the sample and plan to report results in the upcoming reporting period. The appearance of the metal foil was very different from those observed previously; possibly due to carbon contamination, pyrolysis of oils, introduced during fabrication of the foil. It is important to note that the foils were cleaned prior to treatment. Additional follow-on work will be conducted in the upcoming quarter in order to define the optimum parameters for pre-oxidation treatment.

Results from H_2 Permeation Testing (Commercial, 25 μm –thick foil)

Permeation testing of another 25 micron thick, $Pd_{60}Cu_{40}$ foil membrane from the Wilkinson Company was repeated with a different membrane from the same lot of film. The foil was annealed under hydrogen for 5 days at 450 °C, in order to facilitate a phase change to the higher permeability FCC β-phase, prior to being treated in air for 1 hour at the same temperature. Pure H_2 permeation tests were carried out with trans-membrane pressures between 15 and 50 psi; all at 400 °C. Figure 3 shows the same plot as presented last quarter, of pure gas permeability as a function of alloy composition at 400 °C, with the additional data point from this quarter. The H_2 permeability was determined to be $7.0 \cdot 10^{-5}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cm\ Hg^{-1/2}$. This permeability measurement was about 30% higher than the value we reported last month. Our two measurements bracket the value reported in the Juda patent (USP 6,238,645).

Results from H_2 Permeation Testing (Sputtered films on silicon)

A number of H_2 permeation tests were conducted this quarter on Pd-Cu membranes (9 and 12 μm-thick) and the results from this testing are presented below. Prior to testing the membrane in hydrogen at temperature, each membrane was tested with helium to insure a leak-tight seal.

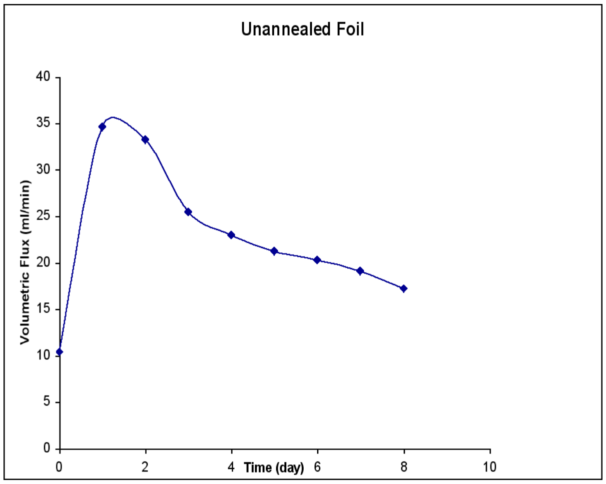

Figure 2. The influence of time on the hydrogen permeability of unannealed or oxidized Wilkinson $Pd_{60}Cu_{40}$ foil at 400 °C and 50 psig feed pressure.

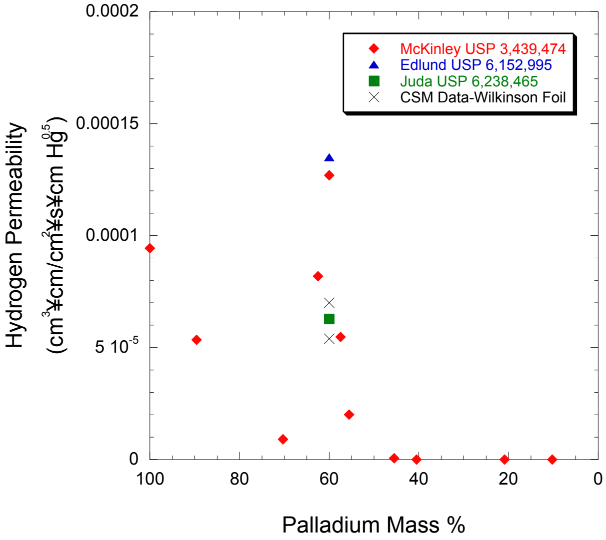

Figure 3. H_2 permeability of $Pd_{60}Cu_{40}$ foils in the patent literature at 400 °C.

The first successful membrane to be tested was a 12.7 μm-thick foil with a composition slightly off of the ideal $Pd_{60}Cu_{40}$ (i.e., slightly higher Palladium weight fraction). The membrane was heated to 250 °C, and the H_2 permeability at this temperature was determined to be $3.8 \cdot 10^{-5}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cm\ Hg^{-1/2}$ (For comparison, the permeability of a $Pd_{60}Cu_{40}$ foil at 250 °C from the patent literature (USP 3,439474) is $5.5 \cdot 10^{-5}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cm\ Hg^{-1/2}$). This is good agreement given that the palladium composition of the foil sample is higher than 60 mass %.

Figure 4 shows molar flux versus driving force for this membrane at 250 °C. The membrane was then heated up to 300 °C. The flux declined to approximately one third of the value at 250 °C. One possible reason for this could be carbon contamination from the o-ring. Upon removing the membrane from the cell, the o-ring appeared to have degraded. Another explanation could be that the membrane did not undergo a phase change to the higher permeability FCC β-phase, and that it may have moved into the mixed α and β phase.

As shown in the phase diagram of Figure 5, if the composition of the Pd-Cu membrane is greater than boundary between the pure β and α/β phase boundary (at an approximate palladium concentration (in weight percent) of 61%), then a two phase structure can exist and thereby reduce the efficiency of the membrane. For a constant composition, the membrane can transform from the single phase, β, to the two phase, α + β, structure by merely heating up the membrane and thereby crossing the phase boundary.

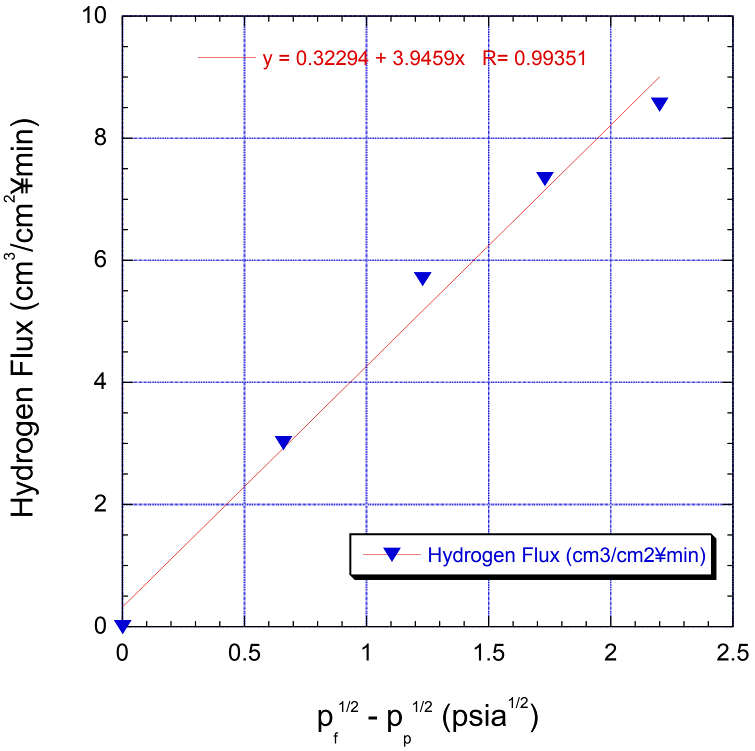

Figure 4. Pure hydrogen flux data at 250 °C for 13 µm foil prepared by IBAD on silicon wafer support. Feed pressures range from 5 to 20 psig. Atmospheric pressure is 12 psia in Golden, CO.

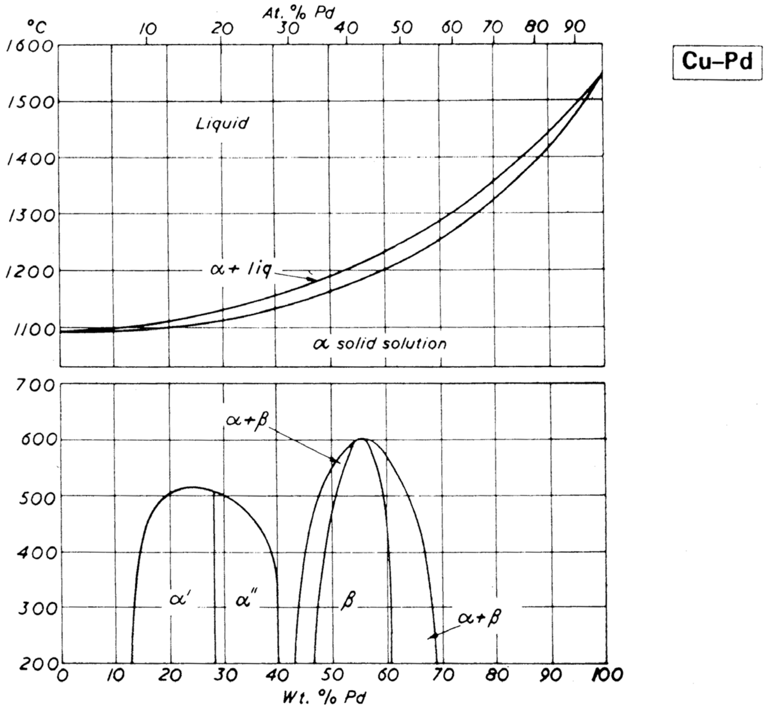

Figure 5. Pd-Cu phase diagram from Ref. 1.

XRD analysis was performed on the treated 12.7 μm-thick membrane discussed above as well as on a piece of as-received foil; the treatment consisted of: 1) exposure to H_2 at 250 °C for 24 hours, 2) 300 °C for 72 hours, 3) 250 °C for 24 hours, and finally, 4) air quench to room temperature. The XRD pattern is shown in Figure 6. Analysis indicates that the foil is in the β phase. Figure 7 shows the XRD pattern of an as received piece of foil. The pattern suggests that the material is in a mixed phase of both the α (fcc) and β (bcc) crystal structures.

Another membrane (thickness ~ 12 μm) was sealed on an anodic support in the cell using a Kalrez® o-ring. The pure H_2 flux is shows graphically in Figure 8. The drop in flux between 250 °C and 275 °C is puzzling, however it is notable that the behavior seems reversible. This could point to a phase change within the material at these temperatures.

An additional membrane, thickness assumed to be ~ 9 μm, displayed a pure hydrogen flux of 16.8 $cm^3(STP)/cm^2 \bullet min$; this is 2.2 times greater than that of the thicker membrane presented above at the same temperature and driving force. This is also shown in Figure 8. Further tests are ongoing with this membrane.

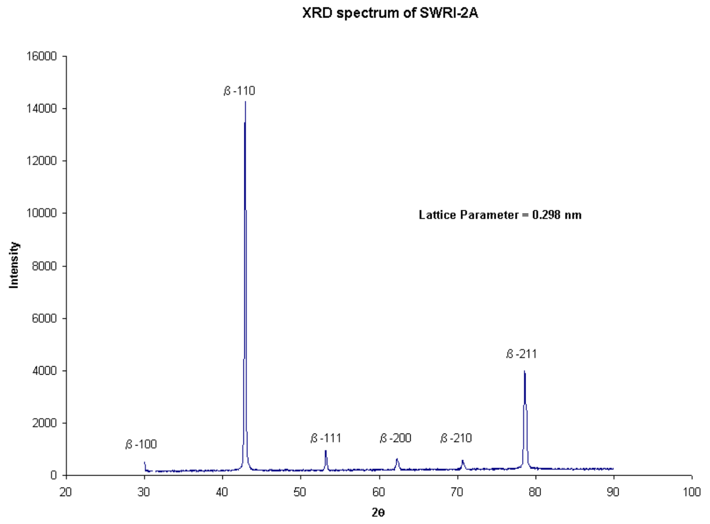

Figure 6. XRD pattern of heat treated PdCu foil

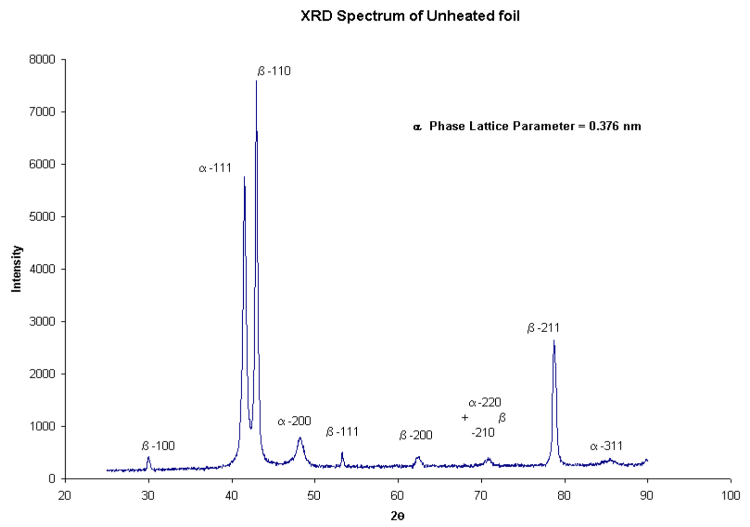

Figure 7. XRD pattern of as received PdCu foil

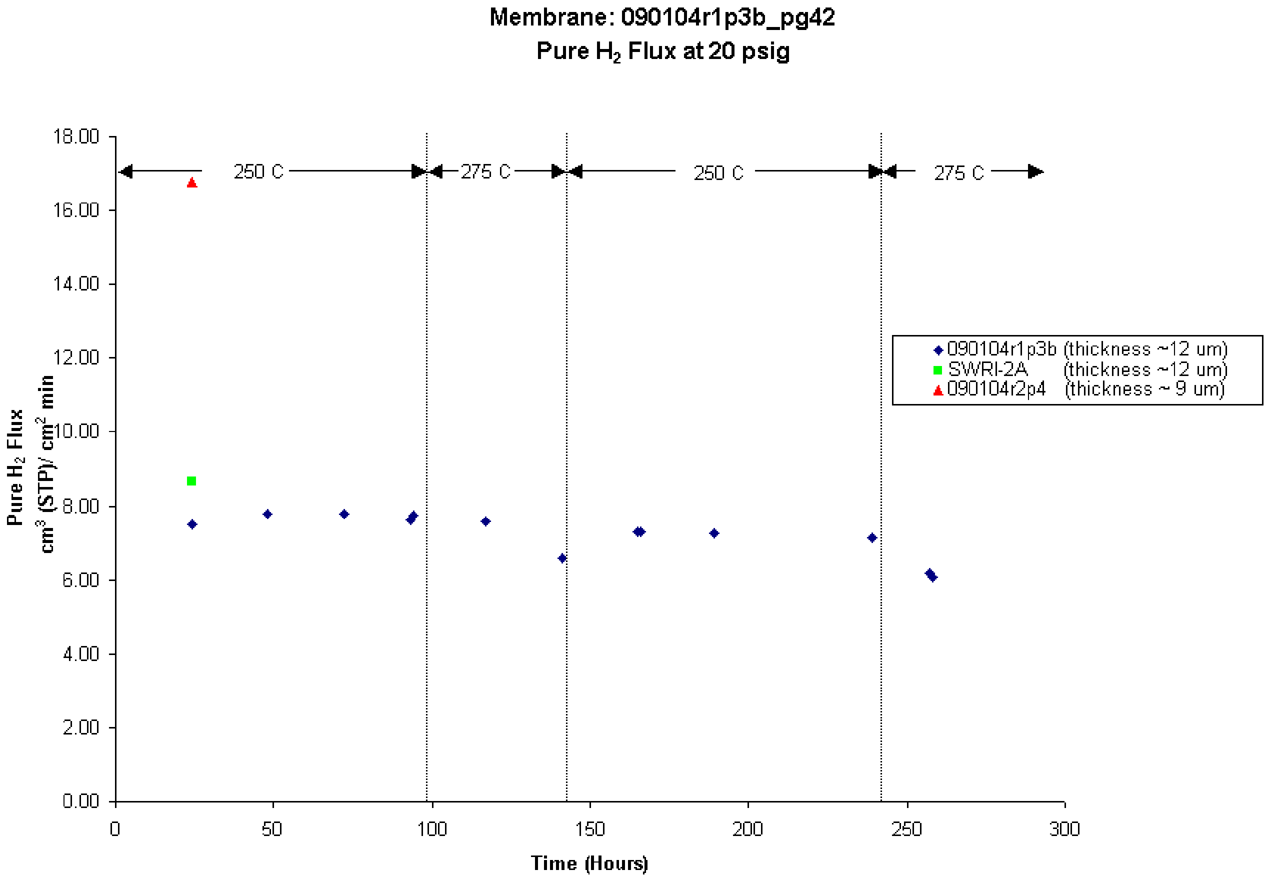

Figure 8. Pure hydrogen flux for a 20 psig feed pressure for various membranes

The H_2 permeability of the 9 μm-thick membrane above is $5.1 \bullet 10^{-5}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. Correcting the permeability value to 350 °C using the data in the McKinley patent (USP 3,439,474), we obtain a value of $7.4 \bullet 10^{-5}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. This value compares **very well** to the permeability reported by McKinley for a 62.5% Pd membrane of $7.9 \bullet 10^{-5}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. Another comparison is that the hydrogen permeability of membrane (9 μm) is 56% of the value at the same temperature reported by McKinley for a PdCu alloy membrane with the optimum 60% Pd composition. We believe that the discrepancies are due to differences in the Pd composition of our samples and the cold-rolled foils used by McKinley and Edlund.

3.2 Problems Encountered:

Other than the issue of pinhole (defect) formation in thin films over large areas, of which we are addressing with the strategies presented herein, we have no major issue or problems to report.

3.3 Plans for Next Reporting Period:

- Permeation testing with 25 cm^2, Pd-Cu membranes with thicknesses 6 μm and less,
- Complete development efforts to "functionalize" polymer surface, through plasma treatment and use of precursor wetting layers, with the goal of reducing pinholes (defects) over large areas,
- Optimization of $Pd_{60}Cu_{40}$ composition and begin efforts to improve $Pd_{60}Cu_{40}$ performance through selective alloy modifications.

4.0 CONCLUSION

To overcome the issue of pinhole (defect) formation in membrane films over large areas, a process was developed and implemented for producing 6-12 μm-thick, Pd-Cu alloy films on thermally oxidized silicon wafer substrates. The processing parameters on silicon are such that adhesion is poor and as-deposited Pd-Cu alloy films easily release from the oxidized silicon surface.

Hydrogen permeation tests were conducted on 9 and 12 μm-thick Pd-Cu alloy films. Since we are still in the process of establishing procedures for handling and testing (i.e., compressing foils in Millipore fixture) the films, we are initially testing thicker, 9-12 μm-thick, films and will progress to thinner films (6 mm and less) in the upcoming quarter. The hydrogen flux for 9 and 12 μm-thick films were 16.8 and 8 cm^3(STP)/cm^2•min respectively. The hydrogen permeability (corrected using data in McKinnley patent) of the 9 µm-thick membrane is $7.4 \cdot 10^{-5}$ cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$ at 350 °C and compares very well to permeability reported by McKinnley for a 62.5% Pd membrane; this permeability is ~56% of the value reported for a Pd-Cu alloy membrane with optimum 60% Pd composition. Using XRD, we confirmed the presence of a two-phase, α/β, structure and that the composition of our membrane was slightly higher than the optimum composition. We are making adjustments to the compositions of the Pd-Cu alloy target in order to produce films next quarter that match the ideal $Pd_{60}Cu_{40}$ composition.

5.0 REFERENCES

1) ***Smithells, Colin J.,* Smithells Metals Reference book*, Eric A. Brandes, Editor,Butterworth-Heinemann; 6th Ed, December 1983, London***