

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: 10/31/06

PRINCIPLE AUTHOR(S): J. ARPS, K. COULTER

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ABSTRACT

In the past quarter, we have conducted additional characterization and permeation tests on different Pd alloy membranes including PdCuTa ternary alloy materials. We attempted to address some discrepancies between SwRI® and CSM relating to PdCu stoichiometry by preparing a range of PdCu membranes with compositions from ~58-65 at% Pd (bal. Cu). While some difficulties in cutting and sealing these thin membranes at CSM continue, some progress has been made in identifying improved membrane support materials. We have also completed an initial cost analysis for large-scale vacuum deposition and fabrication of thin Pd ally membranes and project that the process can meet DOE cost targets.

Minimal progress was made in the past quarter relating to the testing of prototype membrane modules at Idatech. In the past quarter Idatech was acquired by a UK investment firm, which we believe may have impacted the ability of key technical personnel to devote sufficient time to support this effort. We are hopeful their work can be completed by the end of the calendar year.

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1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 MEMBRANE TESTING AND CHARACTERIZATION

CSM has continued hydrogen permeation testing of SwRI fabricated membranes while investigating methods to anneal samples and bond samples together to seal pinholes. A list of samples that CSM attempted to test over the past three months are listed in Table 1. Selected samples were also characterized at SwRI and CSM XRD, SEM, and EDS in the past quarter.

Table 1. Samples tested at CSM in past quarter, N/A indicates the sample tore or developed a leak during testing

Sample Number	Date	Marker Pd %	EDAX Pd %	Max Flux @ 400C & 20psi [cm ³ /cm ² min]	CSM Thickness [microns]	Source	Marker Thickness	Permeance @ 400C [cm ³ (STP)/cm ² s cmHg ^{0.5}]	Permeability @ 400C [cm ³ (STP)cm/cm ² s cmHg ^{0.5}]
051206#1	07/25/2002	---	57.00	17.9	8.80	SEM	---	5.98E-02	5.26E-05
051206#1	07/25/2002	---	57.00	30	8.80	SEM	---	1.00E-01	8.83E-05
072806#1	08/06/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
072806#1	08/27/2002	62.00	---	22.21	4.40	SwRI	4.40	5.14E-02	2.26E-05
073106#1	08/06/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	08/07/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	08/07/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	09/10/2002	62.00	---	19.3	4.40	SwRI	4.40	6.46E-02	2.84E-05

3.0 RESULTS AND DISCUSSION

3.1 Pd-Cu Membrane Testing and Characterization

Two membranes from batch 051206#1 were tested. One of the membranes was annealed in argon gas at SwRI and the other was tested as-received. The annealed membrane leaked helium at room temperature, but once it reached 400 °C the helium leak disappeared. The as-received membrane did not leak helium at room temperature or 400 °C. The steady state permeabilities at 400 °C were 2.54×10^{-5} and 1.17×10^{-5} cm³(STP)cm/cm²s cmHg^{0.5} for the as-received and annealed samples, respectively. An air purge was then done for 90 minutes on each membrane. The final steady state permeabilities at 400 °C and were 8.83×10^{-5} cm³(STP)cm/cm²s cmHg^{0.5} for the as received membrane and 5.26×10^{-5} cm³(STP)cm/cm²s cmHg^{0.5} for the annealed sample. Please note that the pure H₂ permeability of 8.83×10^{-5} cm³(STP)cm/cm²s cmHg^{0.5} is very comparable to that measured for the highest flux membrane that Omar tested. The Idatech permeability for the Pd₆₀Cu₄₀ alloy is about 1.2×10^{-5} cm³(STP)cm/cm²s cmHg^{0.5} at 400 °C.

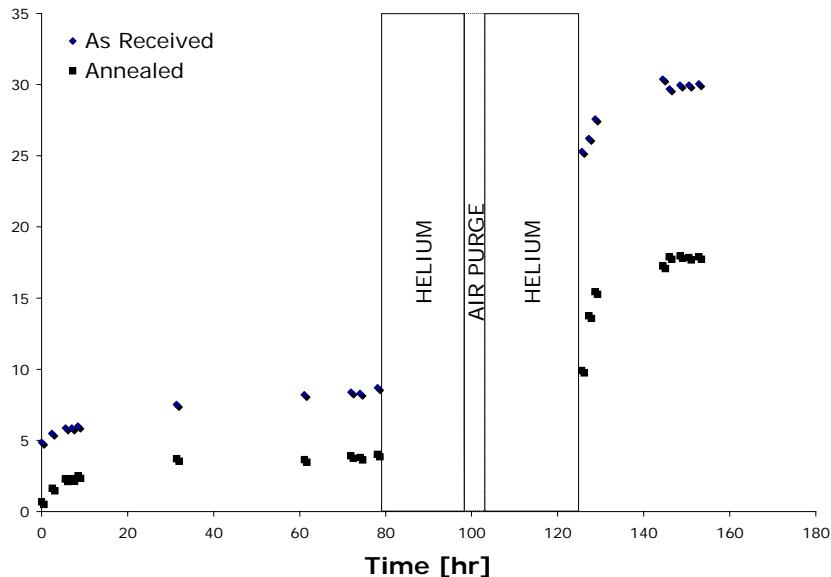


Figure 1. Pure hydrogen flux versus time for annealed and as received samples 051206#1

Although the permeability of the as-received material was not double the annealed sample, the fact that the permeability is higher for the as-received sample is consistent with previous samples from this batch. Figure 1 shows the flux versus time for both membranes. The air purge significantly increased the flux for both samples. For this reason, the remaining membranes to be tested will be purged once the furnace reaches 400 °C. This should decrease the time it takes for the membrane to reach steady state. The permeability values are higher than previously reported for this same sample. The previous permeabilities were 6×10^{-5} and 3×10^{-5} $\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}^{0.5}$ for the as-received and annealed samples respectively. The higher permeabilities are probably due to composition differences in the samples. A slightly higher palladium composition would result in a significant difference in the permeability (see last quarterly report). Further analysis of these samples will be done to determine the composition.

Two samples from batch 032406#1 were annealed for 8 hours at 400 °C in forming gas to reduce the stress in the membranes. These samples were loaded and had helium leaks of 0.64 and 19.0 cm^3/min at room temperature. They were heated to 400 °C where the leak rates dropped to 0.30 and 7.50 cm^3/min , respectively. A 120-minute air purge was performed on each membrane the morning after the furnace reached temperature. After the air purge, the leak rates were 1.55 and 6.10 cm^3/min . These leak rates are accounted for in calculating the fluxes. At 400 °C and 20 psid, the fluxes were 14.5 and 17.3 $\text{cm}^3/\text{cm}^2\cdot\text{min}$ before an air purge and 20 and 21 $\text{cm}^3/\text{cm}^2\cdot\text{min}$ after a 120-minute air purge. The permeabilities will be calculated after SEM imaging is done to find the thickness of the membranes.

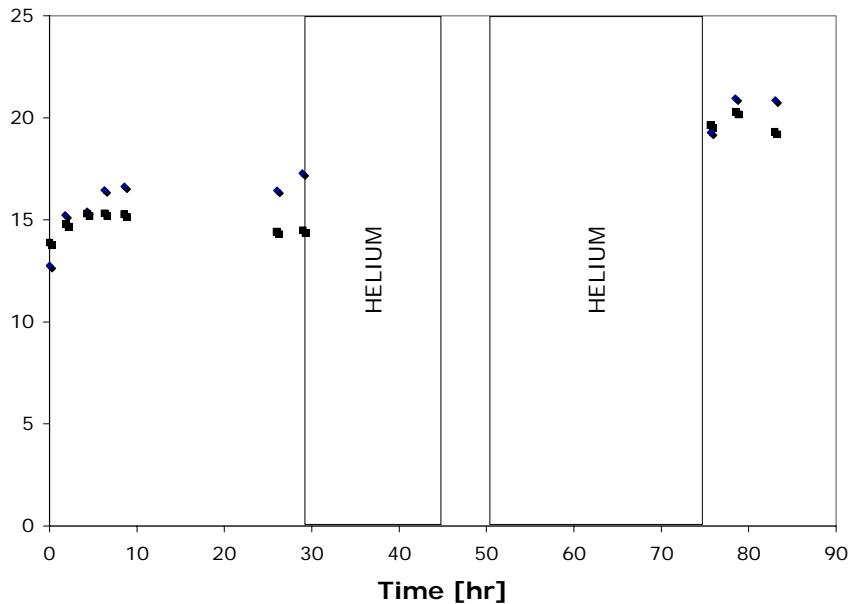


Figure 2. Pure hydrogen flux versus time for batch 032406#1

The effects of performing an air purge once the membrane reaches temperature can be seen by comparing Figures 1 and 2. The samples from batch 051206#1 took about 80 hours to reach steady state (Figure 1) while batch 032406#1 took about 28 hours (Figure 2). An air purge will be performed on the remaining membranes once the furnace reaches 400 °C. This will speed the testing process along and should allow for more tests to be completed.

Finally, four samples with an estimated composition of 62% palladium (batches 072806#1 and 073106#1) tore during preparation for testing. Two of the samples tore while being cut and the other two tore when pressure was applied during sealing. Two more samples, 072806#1 and 073106#1, were annealed in forming gas at 400 °C for 24 hours. The membranes appeared to be more brittle than before, but cutting should be easier since the membranes lay flat.



Figure 3. Sample 073106#1 after 24 hours at 400 °C in forming gas

As can be seen in Figure 3, a significant amount of wrinkling occurred during annealing. Although it can not be seen in Figure 3, there is also portions of the membrane that are copper colored. These sections are found in the more wrinkled part of the membrane (left side of membrane in Figure 3). For this reason, the membrane will be cut from the right hand side of the membrane pictured in Figure 3 and the remaining pieces will be examined with SEM and XRD. Sample 072806#1 did not show the same effects as 073106#1, but both membranes seem to be extremely brittle.

The final ternary membrane (PdCuTa) was tested for 5 days at 400 °C. The sample was heated to 400 °C in helium where a 1 hour 30 minute air purge was performed. The sample had a helium leak and the H₂/He selectivity was about 17. The permeability, corrected for the helium leak using Knudsen diffusion, reached a maximum value of $9.85 \times 10^{-6} \text{ cm}^3(\text{STP})\text{cm/cm}^2\text{s}\text{cmHg}^{0.5}$ at 400 °C and 20 psid but was decreasing as the test continued. After approximately 5 days the feed was switched to helium so an air purge could be performed. The membrane tore when the feed was switched to helium, therefore, the air purge was never completed.

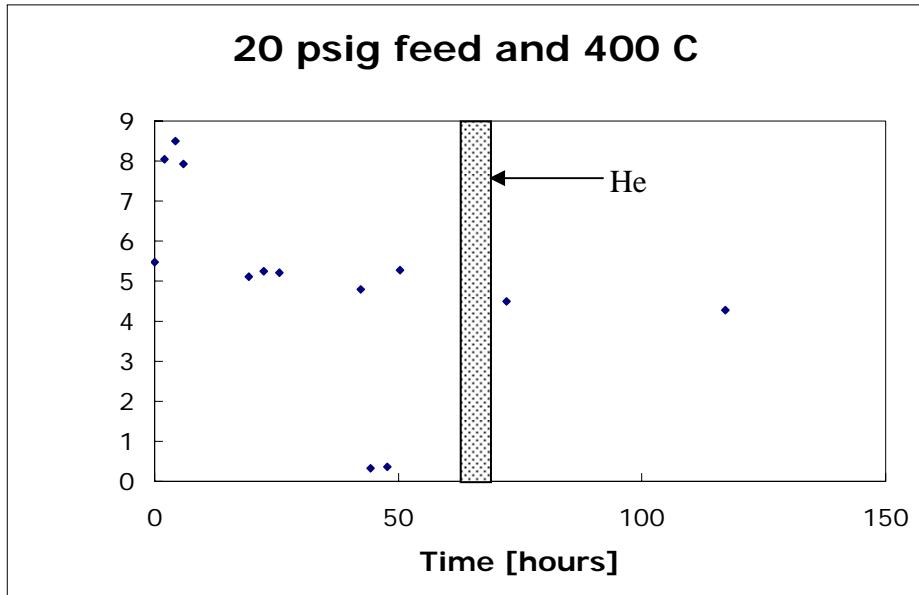
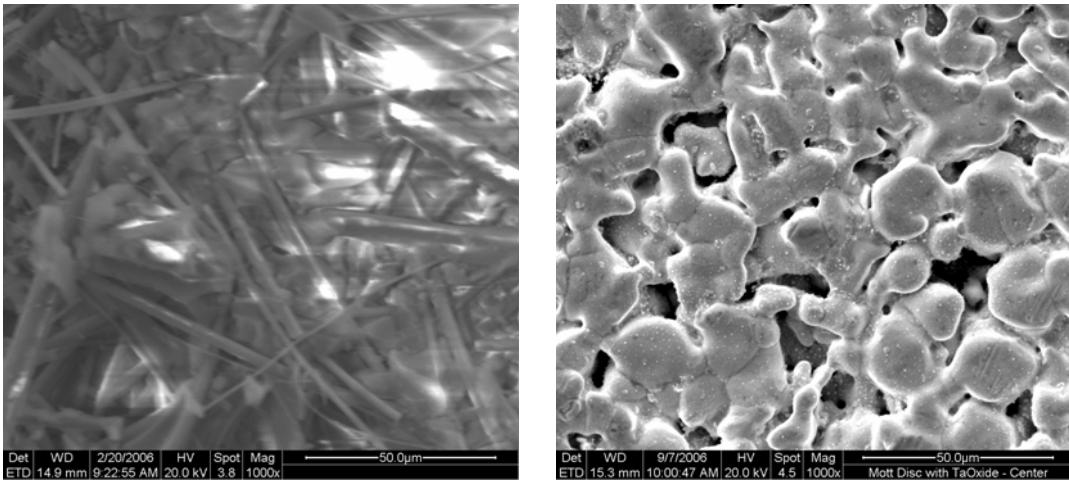


Figure 4. Pure hydrogen flux versus time for ternary sample 032006#1

The final value of the permeability was $4.95 \times 10^{-6} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s}\text{cmHg}^{0.5}$. This value is much closer to the values obtained for the other ternary alloys, PdCuRh (2.46×10^{-6}) and PdCuRu (3.52×10^{-6}). Figure 4 shows the pure hydrogen flux versus time for sample 032006#1.

Membrane 072806#1 was tested for 5 days. The selectivity of the membrane was poor, 4.3, since the membrane had a few pinholes. More importantly was the test of the new diffusion barrier. A 50 nm coat of tantalum oxide was deposited onto the surface of the porous stainless steel support disc. The layer did not hinder the flow through the disc so sample 072806#1 was placed in the test fixture on the coated support. After 5 days the test was stopped and the sample removed. The membrane came off the stainless disc without any force. The membrane not sticking to the disc shows that the tantalum oxide layer provided resistance against diffusion bonding. Another significant result was the lack of tearing in the sample.



Figures 5a,b. SEM images of ceramic paper and tantalum oxide coated stainless steel

As can be seen in Figures 5a and 5b, the surface of the tantalum oxide does not have any sharp points. The thinner membranes, this batch especially, tear when sealed into the test apparatus. The tear is around the outside where the fixture applies a pressure to the graphite seal. The ceramic paper pokes through the membrane causing a defect. When the membrane is introduced to gas at any pressure, the defect from sealing opens and ruins the membrane. Batch 072806#1 tore in this manner before, however, when used with the tantalum oxide coated disc the membrane sealed and no tears were present after testing. The tantalum oxide layer shows promise as a diffusion barrier in that EDAX measurements on the surface of the stainless steel disc show no palladium or copper. Also, the surface of the oxide layer is more spherical which gives more area for contact between the layer and the membrane. This will reduce the amount of tearing in the membrane and allow for testing of thin (<5 μm) membranes.

Finally, membrane 073106#1 was tested for 6 days. The membrane had a slight helium leak, $0.80\text{ cm}^3/\text{min}$, but the Knudsen corrected hydrogen flux was about $19\text{ cm}^3/\text{min}$. The membrane was heated to 400°C in helium and then air purged once at temperature.

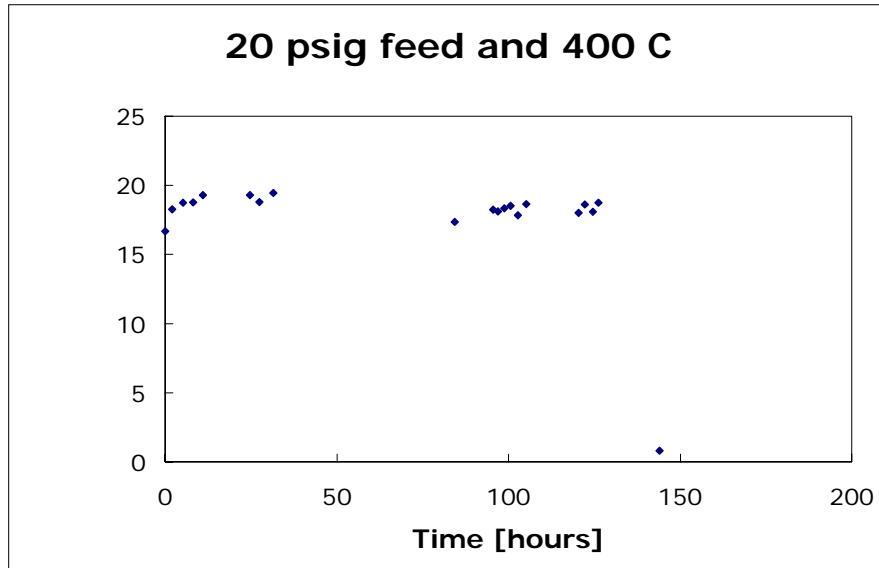


Figure 6. Hydrogen flux versus time for membrane 073106#1

As can be seen in Figure 6, once the membrane was exposed to hydrogen after the air purge it reached a steady value within a day. This membrane had a Knudsen corrected permeability of $2.84 \times 10^{-5} \text{ cm}^3(\text{STP})\text{cm/cm}^2\text{s}\cdot\text{cmHg}^{0.5}$ at 400 °C and 20 psid. This value is low and probably due to the composition. This was the 62%Pd sample and the membrane is probably high in palladium putting us on the opposite side of the peak in permeability versus alloy composition as the previous samples.

3.2 Process cost analysis

Of the elements that comprise a hydrogen purification module, the membrane is presumed to be by far the most significant cost contributor. Analogous to a computer's central microprocessor, the membrane lies at the heart of the purification system and is the key element defining system performance. The DOE has set aggressive performance and cost targets for several membrane properties in 2005 and 2010 including flux, cost per square foot, hydrogen purity, and differential pressure.

Vacuum deposition methods for rolled products, commonly referred to as "web coating," have been applied for more than 20 years in the manufacture of thin film capacitors and batteries, magnetic media, and packaging for food products. Metal films, typically only a few hundred Angstroms thick, can be deposited onto film up to several meters wide with a uniformity of better than 10%. Typical costs for manufacture of metallized plastic (e.g., aluminum on PET) can be less than a penny per square meter of material while production volumes for a single production web coater can exceed 100 million square meters a year (assuming round-the-clock operation). The fixed cost invested for this

technology; however, can be considerable, with production machines costing several millions of dollars to design and construct. Figure 7 shows the relative cost contribution of several key factors to the operating cost for a typical aluminum metallizer as estimated by Broomfield¹ (cost does not include substrate material).

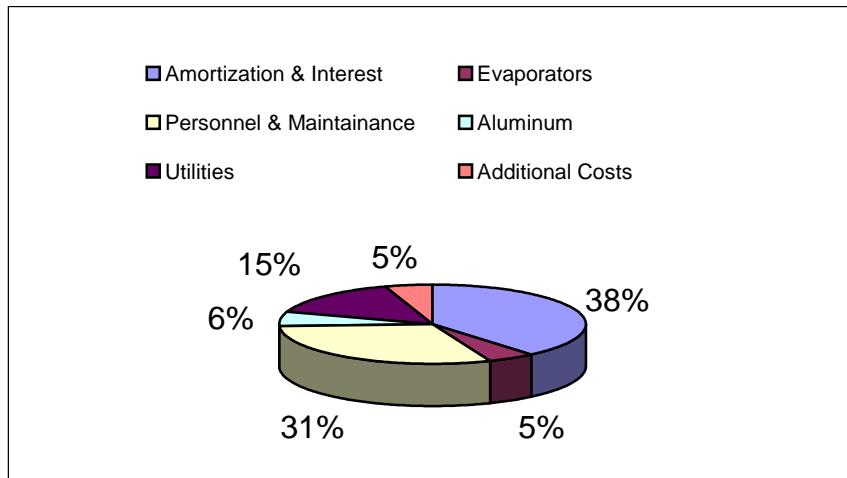


Figure 7. Relative cost contributions to operation of a conventional web coating system

For Pd alloy membrane fabrication the materials cost is expected to be higher relative to other fixed costs. Another key element impacting the cost is material throughput. If a greater square footage of material can be produced over a given time, the labor and capital equipment costs can be substantially reduced. This has been verified for vacuum-based sputter deposition processes used in the semiconductor industry². In fact, we believe that it is highly likely a semiconductor process tool can be adapted to produce full-size Pd alloy membranes up to 12 inches in diameter. An example of a multi-station sputter deposition tool made by Novellus is shown in Figure 8. The membrane throughput for such a system can be estimated to first order using the following empirical equation.

$$\# \text{ ft}^2/\text{min} = 0.785 \text{ N D / d}$$

Where N is the number of process stations, D is the deposition rate (nm/min) and d is the target membrane thickness in nm. A typical system can allow up to 5 12-inch wafers to be processed simultaneously and deposition rates of 600nm/min are possible. So for a membrane thickness of 4 microns (4000nm), 0.59 sq. ft. of membrane per minute can be

¹ A. A. Broomfield, Society of Vacuum Coaters, Annual Technical Conference Proceedings (1992), p. 21.

² S. Edelstein, R. Davenport, and J. Nulman, Proc. SPIE Vol. 2336, p. 162-168, *Manufacturing Process Control for Microelectronic Devices and Circuits*, Anant G. Sabinis; Ed, 1994.

produced. Obviously, this estimate neglects the contributions of cycle time and downtime due to maintenance although these may be included by altering the above equation in the following manner

$$\# \text{ ft}^2/\text{min}, P = 0.785 \text{ N D U (1-C) / d}$$

Where U is the average uptime percentage and C is the percentage of time in each cycle where material is not being deposited. Assuming 75% uptime and 25% coating cycle idle time, then 0.33 sq ft/min of membrane will be produced on average.

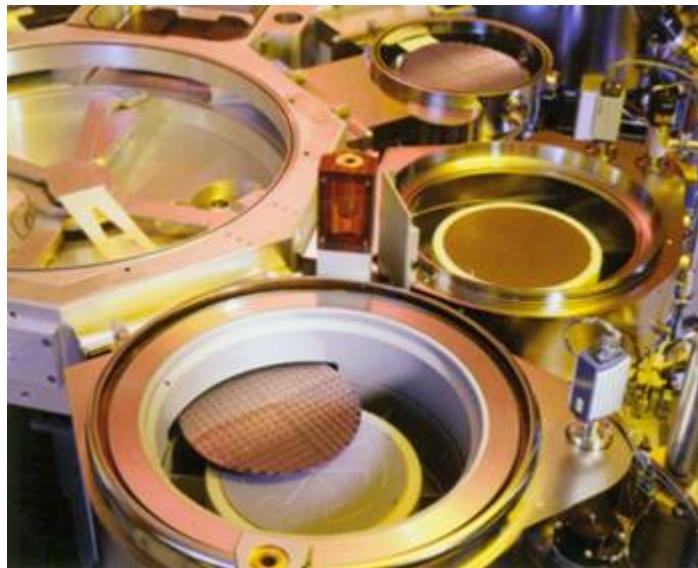


Figure 8. Photograph of INOVA xT of multi-station sputter deposition tool made by Novellus (San Jose, CA)

The next issue to consider is raw materials cost. The cost of palladium greatly exceeds that of copper so we can reasonably omit the latter from consideration. Sputter deposition processes are highly efficient with more than 95% of sputtered material typically deposited on the support material in a production system. The balance of the material can be recovered as scrap and recycled. The other cost consideration is fabrication of the PdCu alloy target. This is usually done by taking powders of each material in appropriate quantity to make the desired alloy composition then hot pressing the powder in vacuum or inert atmosphere to make a plate, typically 0.5 inches thick. For this calculation we add an additional 25% to the cost of palladium for target manufacturing and material recovery. Based on this as well as the composition, density, and thickness of the membrane and market price of Pd, we can calculate the membrane raw materials cost per square foot using the following empirical equation

$$\text{Raw materials cost/ft}^2, R = 1.2 \times 10^{-2} P W (W+3) T$$

Where P is the market price (\$/oz), W is the weight percentage, and T is the membrane thickness in microns. Hence a 4 micron thick, 60 wt% Pd alloy membrane with a market price of \$330/oz, will have approximately \$35/ft² of Pd in it. Combine this information with the projected material throughput we can arrive at a total cost for manufacturing based on the following factors

$$\text{Total Cost/ft}^2 = (F + L + E) / (P \cdot S \cdot 1.75 \times 10^5) + R$$

Where F is the annual equipment depreciation, L is the fully burdened annual labor costs, E is the annual cost of utilities and maintenance, P is the throughput per minute, and S is the number of 8 hour shifts per day. If we assume a \$1.5M piece of equipment with level amortization over 3 years, four full time personnel (three technicians and one engineer) working a total of two shifts at \$0.50M/yr, and \$0.20M/yr in utilities and maintenance, and the above estimates for productivity and raw materials, we get a total cost of \$45.40 per square foot. Even if we have significantly underestimated the throughput, equipment, or labor costs, this cost estimate is still more than an order of magnitude lower than the DOE 2010 target, which gives us great confidence that the process will be cost effective.

3.3 Project Extension

A no-cost time extension was approved by DOE, the new date of completion for the project is 12/31/06.

3.4 Plans for Next Reporting Period:

- We hope that Idatech will be able to complete pressure and purification testing of at least one SwRI-manufactured membrane and test it in a prototype module assembly.
- CSM will complete testing of remaining membranes fabricated at SwRI
- SwRI will analyze any additional data and prepare a final report.

4.0 CONCLUSION

We are continuing our efforts with CSM to produce and test thin Pd alloy membranes develop and establish more reliable sealing methods. We have completed an initial study of ternary alloys (Pd-Cu-X) and have demonstrated to ability to produce novel compositions which may hold promise for improved stability and performance. A more detailed cost analysis of the membrane production process has been prepared and projected costs appear to be well within long term DOE targets.