

**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: 01/30/04

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

DATE REPORT WAS ISSUED: JANUARY 2004

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

DETROIT

HOUSTON

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: 01/30/04
PRINCIPLE AUTHOR(S): B. LANNING, J. ARPS
DATE REPORT WAS ISSUED: JANUARY 2004
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

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness or any information, apparatus, product, or process disclose, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

ABSTRACT

Completed fabrication of an initial series of copper and palladium-copper alloy membranes in the range of 1-8 microns in thickness up to 6" x 8" in area. Films were produced using both e-beam evaporation (with and without ion assist) and magnetron sputtering from a 60%Pd/40%Cu alloy target. Pure copper and palladium-copper alloy films, with essential no intrinsic stress, were produced on both polystyrene and polyvinyl alcohol substrates. Various processing parameters and techniques were investigated in order to minimize defects and maximize uniformity in single layer films. Even though films to date are visually defect free, we are able to observe sub-micron size defects using a backlighting technique; we are currently investigating a number of methods to create a gas impermeable membrane.

At present, the metal films are effectively removed from the polymer backing material by merely immersing the film in an appropriate solvent; chloroform for the polystyrene and water for the PVA. In the future we plan to investigate alternative methods for removing the polymer backing that are more suited to large scale, low-cost manufacturing.

Table of Contents

DISCLAIMER.....	III
ABSTRACT.....	IV
TABLE OF CONTENTS	V
1.0 EXECUTIVE SUMMARY	1
2.0 EXPERIMENTAL.....	1
3.0 RESULTS AND DISCUSSION	1
3.1 PROGRESS	1
3.2 PROBLEMS ENCOUNTERED:.....	4
3.3 PLANS FOR NEXT REPORTING PERIOD:	5
4.0 CONCLUSION	5
5.0 REFERENCES.....	5

1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pure copper and copper-palladium alloy films were deposited onto polyvinyl alcohol and polystyrene films (1-3.5 mils thickness) using e-beam evaporation. Plastic films were affixed onto both flat and curved metal backing plates; the backing plates were not actively cooled or heated. A set of experiments were conducted, adjusting various deposition processing parameters, in order to optimize film properties, i.e., minimal strain, defects, composition, as a function of thickness (1-8 microns nominal thickness). An ion assist was used in conjunction with e-beam evaporation in order to control density and film stress.

In order to remove the plastic backing material, samples were immersed in an appropriate solvent; i.e., chloroform in the case of polystyrene and water in the case of polyvinyl alcohol. Once all of the plastic was removed from the metal foil, the free floating film was then “captured” with a porous metal screen to serve as a support.

Film compositions and thicknesses were verified using energy dispersive x-ray (EDX) and profilometry respectively and pinholes were qualitatively evaluated with the use of a backlighting technique similar to a light box in photography.

3.0 RESULTS AND DISCUSSION

3.1 Progress

Vacuum deposition

Initially, a number of pure copper films were vacuum deposited on PVA and polystyrene films in order to optimize processing parameters using just e-beam evaporation alone and e-beam evaporation with ion assist. An example of a 3 micron-thick film on PVA is shown in Figure 1.

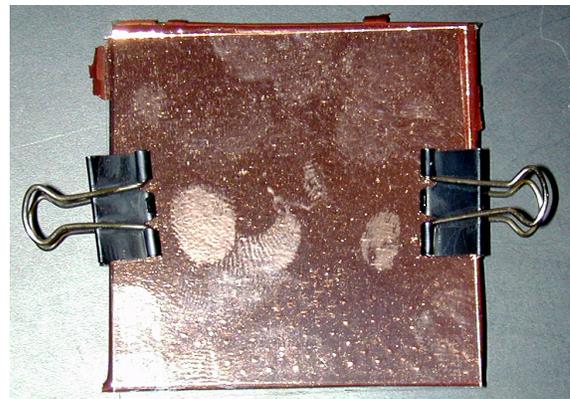


Figure 1 –Copper film (3 μm) on PVA; sample is sandwiched between two pieces of glass

Visually, the films were pinhole free although when the films were backlit, we observed a number of submicron-sized pinholes. These types of defects can originate from essentially three types of sources: 1) particles/contaminants indigenous to the plastic films (either derived from processing or storage in the ambient environment), 2) airborne particles and background contaminants residing within the deposition chamber that are subsequently activated prior to as well as during deposition, and 3) micro-arcing of the e-beam source during the deposition process; the first two sources being a function of the electrostatic charge at the film (plastic) surface.

To better quantify these effects, we prepared a number of samples using different surface preparation techniques in addition to adding a surface “pre-cleaning” step in the vacuum chamber prior to deposition. All samples were prepared in a laminar flow bench, and transported from the hood to the chamber within a ‘destat’ plastic bag to minimize possible contamination from the background environment. The results on both polystyrene and PVA substrate films are shown below.

The as-deposited copper foil on untreated, 3.5 mil polystyrene film is shown in Figure 2; it is important to note that the backlighting technique to highlight the pinholes, actually enhances the size of a pinhole in the image, i.e., these microscopic pinholes are not detectable with the unaided eye. This level of defects would be considered representative of a coating on essentially any as-received plastic substrate. When rinsed or washed (without any abrasive action) with methanol prior to deposition, the number and type of defects drops dramatically as shown in Figure 3. Subsequently, combining a methanol ‘scrub’ with a methanol rinse appears to slightly decrease the level of defects even further as shown in Figure 4.



Figure 2: *4 μm thick Cu film on Un-treated, 3.5 mil polystyrene*



Figure 3: *4 μm-thick Cu film on 3.5 mil polystyrene, rinsed in methanol*



Figure 4: 4 μm-thick Cu film on 3.5 mil Polystyrene, scrub and rinsed in methanol



Figure 5: 4 μm-thick Cu film on 4 mil polystyrene, scrub and rinse in methanol

The level of defects shown in Figure 4 is analogous to those observed on an untreated glass slide and a glass slide wiped and cleaned in methanol. Hence, this level of defect density could be representative of the background particulate level within the chamber and to a lesser extent, micro-arcing from the e-beam source. A representative defect pinhole density for a 4 μm-thick Cu film on 4 mil polystyrene (gloss finish) is shown in Figure 5. Just as in the case of a Cu film on the 3.5 mil (matte) polystyrene film, a Cu film on the 4.0 mil (gloss) polystyrene film that has been ‘scrubbed’ and rinsed exhibits a similar defect pinhole density.

Cu films were also deposited on 2 mil PVA material; the PVA had been rinsed with isopropyl alcohol prior to deposition. The defect pinhole density is much less for this type of material and although it may not be reduced to zero, it certainly can be reduced to a very low level. Other pre-treatment methods, such as plasma discharge, ionization, and surface pre-wetting layers are currently in progress to minimize defects during deposition and certain post-processing methods are also being investigated to create a gas impermeable membrane. *Un-supported, strain-free films were produced at thicknesses less than 0.5 microns.*

Having successfully produced pure copper films, we then established processing parameters for co-evaporation of palladium-copper alloy films on both polystyrene and PVA substrates. Various deposition configurations were investigated in order to optimize film uniformity and reproducibility. Co-evaporated alloy films, from 20%Cu/80%Pd to 80%Cu/20%Pd were prepared. Examples of ~60%Pd/40%Cu alloy films (3 microns thick) on polystyrene and polyvinyl alcohol substrates are shown in Figures 6(a) and 6(b) respectively. In addition to co-evaporated films, we also produced alternating layers of

palladium and copper to form multi-layer stacks of palladium-copper alloys; this method has the potential to better control the alloy composition since the control parameter is thickness (films would subsequently be heat treated in hydrogen to homogenize the alloy).

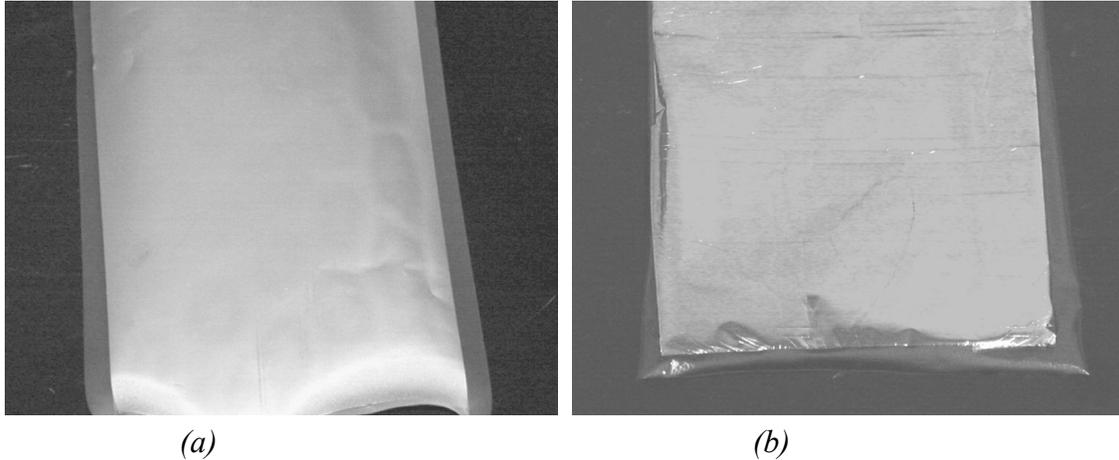


Figure 6 – Pd-Cu alloy films on a) polystyrene and b) polyvinyl alcohol films

Pd-Cu alloy films have also been fabricated using magnetron sputtering from a 60%Pd/40%Cu alloy target. Film properties are still under investigation although the preliminary film composition appears to be slightly palladium rich.

Removal of Polymer Backing Material

Using an appropriate solvent, such as chloroform in the case of polystyrene and water in the case of polyvinyl alcohol, we have been able to successfully remove the plastic backing material and create a free-standing, un-supported metal film (at thicknesses below 0.5 microns). Samples were either immersed directly into the solvent or sandwiched between two metal screens and then immersed, to dissolve the plastic. In the case of polystyrene, the chloroform solvent was unheated and in the case of the PVA, the water temperature was varied between 30° and 80° C depending on the type of PVA.

3.2 Problems Encountered:

To this point, no technical problems to report in the program; should be able to meet upcoming milestones.

3.3 Plans for Next Reporting Period:

- Formation pinhole-free, Pd-Cu alloy films (5 x 5" in² in area) using both magnetron sputtering and IBAD;
- Pd-Cu and pure copper samples to be sent to CSM for initial series of leakage and purification tests;
- Perfect backing removal methods and establish which processing methods merit further development;

4.0 CONCLUSION

Both pure copper and palladium-copper alloy films have been successfully deposited onto polymer backing materials and subsequently removed via immersion in a low temperature solvent bath. Preliminary trials with co-evaporation and sequential evaporation of palladium and copper metals have allowed us to better understand the challenges in producing a reproducible and uniform alloy composition. Although free-standing films, up to 6" x 8" in area at less than 0.5 microns in thickness, were produced, we are still in the process of developing techniques to minimize defect formation over large areas.

5.0 REFERENCES

Not applicable