Fabrication of Ternary Palladium Alloy Membranes for Hydrogen Production
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1University College Dublin, Dublin, Ireland; *Colorado School of Mines, Golden, CO USA

Conventional H2 Production

- Demand for hydrogen for use as a fuel is increasing.
- Also used in production of ammonia and fertilisers.
- 95% of all hydrogen produced in the United States is through the steam reforming of methane.
- Energy Intensive Process:
  \[ CH_4 + H_2O \rightarrow CO + 3H_2 \]
   \[ CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \]
- Only 50% conversion
- Equilibrium limited: water-gas shift
  \[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]
- Extensive, intensive separation train required

Fabrication Strategy

- Tubular Membranes
  - Pd and Au layers deposited by electroless plating
  - Ternary added by DC magnetron sputtering
  - High temperature annealing for diffusion/ alloy formation
- Objectives
  - Calibrate sputter deposition rate
  - Verify quality by XRD, 4 point probe, XRF
  - Fabricate bilayers and/or sandwich structures
  - Four elements: Mg, Zr, Ru, Mo

Membrane Reactors for H2 Production

Ideal Process

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>CO + H2</td>
</tr>
<tr>
<td>CO + H2O</td>
<td>H2 + CO2</td>
</tr>
<tr>
<td>High T H2 permeable membrane</td>
<td></td>
</tr>
</tbody>
</table>

Advantages

- Continuous H2 removal: Shifts equilibrium
- Reduce temperature, increase pressure
- High conversion, pure H2 effluent
- Concentrated CO2 for sequestration
- Challenge: Lack of suitable membrane

Molybdenum Deposition

- Delamination of Molybdenum observed at I = 1 A
- Current reduced to 0.5 A, conditioned from 0.1 A
- Pressure: 5 mTorr, Temperature: 15°C
- Deposition rate 10.93 nm/min
- Delamination of Mo on glass after 45 mins; thickness dependent
- Tube sputter length: 60 minutes
- Thickness verified using XRD and four point probe
- XRF was used to verify the thickness of this film
- May be used to measure thickness of ternary layer on tube, as profilometry will damage the membrane
- Not viable for Mg membranes; molecular weight is too low.

Zirconium Deposition

- Ignited at 0.05A, conditioned to 0.4A
- Pressure: 5 mTorr; Temperature: 17°C
- Deposition rate: 12.71 nm/min
- Tube sputter length: 240 minutes
- Film on membrane delaminated due to carbon contamination from charred parafilm
- Thickness verified using profilometer and four point probe

Palladium Membranes

- Dissociates molecular H2
- 100% selectivity in separating H2
- Becomes brittle below 300 °C
- Poisoned by H2S

Palladium Alloy Membranes

- Pd-Au reduces embrittlement at 300 °C
- Combinatorial studies identified alloys, compositions that are resilient to H2S
- Ternary candidates: Mg, Ru, Zr or Mo
- Goals: Fabricate membranes and test performance

Objective

- Plasma ignited at 0.5A, and conditioned to 0.1A
- Pressure: 5 mTorr; Temperature: 15°C
- Deposition Rate: 4.35 nm/min
- Tube sputter duration: 205 minutes
- Thickness measured and verified by profilometry and four-point probe

Conclusion and Future Works

- Targets were successfully calibrated, and their deposition rate was calculated
- Also successful in fabricating ternary palladium alloy membranes
- Membranes in process of being annealed and tested for hydrogen permeation and resistance to corrosion by hydrogen sulphide

Acknowledgements

- A. B. is grateful for support through the Pat McAdams Fellowship
- Support for materials and remaining personnel were provided by Pall through contract NETL-DE-FE0001181

Ternary Palladium Alloy Membranes

- Palladium Alloy Membranes
  - Arcing observed at 100W in beginning
  - Ignited at 50W, conditioned to 250 W
  - “Flaking off” of Ru deposit on target casing caused target to short circuit
  - Pressure: 5 mTorr, Temperature 17°C
  - Deposition Rate: 20.87 nm/min
  - Tube sputter length: 45 minutes
  - Thickness verified by profilometry and four-point probe
  - XRD confirms polycrystalline nature

XRD Analysis of Ru

<table>
<thead>
<tr>
<th>Theta (°)</th>
<th>Intensity (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°-35°</td>
<td>0-50°</td>
</tr>
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</table>

Four-Point Probe Analysis

- Voltage vs. Resistance

- Sheet Resistivity (Ω/□)

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Sheet Resistivity (Ω/□)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1000</td>
</tr>
<tr>
<td>0.2</td>
<td>1000</td>
</tr>
<tr>
<td>0.3</td>
<td>1000</td>
</tr>
<tr>
<td>0.4</td>
<td>1000</td>
</tr>
<tr>
<td>0.5</td>
<td>1000</td>
</tr>
<tr>
<td>0.6</td>
<td>1000</td>
</tr>
</tbody>
</table>

Plasma Ignited at 0.5A, and conditioned to 0.1A

- Tube sputterer length: 205 minutes
- Deposition rate: 4.35 nm/min
- Pressure: 5 mTorr, Temperature: 15°C
- Ignited at 0.05A, conditioned to 0.4A
- Film on membrane delaminated due to carbon contamination from charred parafilm

Current reduced to 0.5 A, conditioned from 0.1 A

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Carbon contamination from charred parafilm

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