High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

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REB Research & Consulting
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Overview

Timeline

• October 1, 2005-September 30, 2008
• 50% complete

Budget

• Total project: $2,919,857
  – DoE: $2,334,646
  – REB+ ISU: $585,211
• DoE funds ‘06: $474,505
  – Non DoE ‘06: $85,929
• DoE funds ‘07: $886,206

H₂ Barrier addressed

• Lowering the cost/flux H₂ permeation membranes. This lowers the cost of H₂.
  – Replace palladium with base metals: $100/ft² vs $3000/ft²
  – 100% selectivity like Pd
  – 50 scfh/ft² UHP H₂ at ΔP=200psi
  – 15+ life, no embrittlement

Partners

• Iowa State U.: Helps pick alloys, x-rays
• Ames Lab: Makes alloy samples
• LANL: Coats, welds alloys, some tests
• NETL: Permeation and life tests
• G&S Titanium Co.: Fabricate membranes
• REB Research: Management and assembly
Who Does What?

- Allan Russell, Iowa State, helps REB pick the alloy; does x-ray analysis, Instron tests.
- Larry Jones, Ames Lab - Materials Preparation Center makes up the alloys in disc and striker form; manufacturability.
- Robert Buxbaum, REB Research embrittles the alloys; Charpy test of embrittlement; braze tests; assembly of bundles, flux test; management, commercialization.
- Steve Paglieri, LANL, coats the alloys, does some permeation tests, and oversees welding into tubes, life analysis.
- Mike Ciocco, NETL, oversees most permeation tests and basic life tests.
- Rodger Geiser, G+S Titanium, draws the welded tubes into membranes.
We aim to make hydrogen so cheaply that only the very rich will use bottled gas

• REB Research is the only company making commercial membrane reactors.
• This membrane reactor unit reforms CH₄OH + H₂O and outputs 3.5 slpm of ultra-pure hydrogen for laboratory use.
• Our generator design was developed in a phase 1 SBIR grant.
Project Objective:

- Find a base metal replacement for palladium ($470/oz) and for our own sandwich membranes for use in hydrogen purifiers and membrane reactors.
  - Stable at 350-400°C
  - 100% selectivity like Pd
  - $100/ft² vs $3000/ft²
  - 50 scfh/ft² UHP H₂ at ΔP=200psi
  - 15+ life, no embrittlement
**Approach: make sandwich membranes**

REB’s US Patents 5,108,724; 5,149,420; and 6,576,350.

Pd alloy coat; 0.5µ thick

\[\text{B2 intermetallic}\]

Pd alloy coat; 0.5µ thick

With some alloys, the coat is not needed

US Patent applied for
Accomplishments: Pick B2 alloys

At left, note that several metals: V, Nb, and Ta have 100 times higher permeabilities than Pd at 350-400°C. They cost only 1/100 as much as Pd. Unfortunately they embrittle in H₂.

Our approach is to try B2 intermetallic alloys, like NiTi (above). So far we’ve tried about 60. We’d previously noted high interdiffusion and embrittlement in B1, random BCC alloys.

Allan Russell (ISU) a key helper here

Ames Lab makes the alloys
We aim for stable, ductile B2 alloys that we think will pass H$_2$
Roll and cut into discs (Ames Lab)
Coat with a thin Pd layer (LANL)
Measure mechanical properties (REB Res., ISU)
Hydride and then measure mechanical properties (REB Res)

Two newly discovered, ductile B2 alloys
Al 3105 shown for comparison.
Alloys are ductile to over 20% strain
Charpy Mechanical Tests

Hit it with an instrumented Charpy hammer. If it breaks it’s brittle.

• Determine stress-strain curve before and after hydriding
X-ray pictures

Random BCC structure

B2 cubic structure
Alloy A, slightly embrittling
Vanadium, embrittling
Alloy B, Low cost, non-embrittling

Result of Hydrogen Permeability Measurements

Permeability at 400 °C and 8psig, mol/m/s/Pa^{0.5}
We met the target flux at 1/5 the target pressure, suggesting 3 or 4x the target flux at 200 psi.

Accelerated lifespan measured, as we planned, with a thinner Pd coat. Life meets project targets.

- Price of this membrane about $95/ft² meets targets
- Membrane broke when temperature lowered below 200°C under pressure. Not robust enough for most industrial uses. OK for nuclear use at low P.
For the alloy to be worthwhile, it must be possible to fabricate hydrogen purifiers from it: should braze to stainless steel.

• Try lots of brazes connecting SS to alloys in tube and sheet form.
• Two successful brazes shown below.
## Accomplishments, year by year

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
<th>2005</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>Pick first alloys, mostly B2. Use base metals so $100/ft^2$ is likely</td>
<td>Done</td>
<td>Exceeded: 82 alloys 51 scfh/ft^2, 44 psi</td>
</tr>
<tr>
<td></td>
<td>Buy equipment</td>
<td>Done</td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>Test for manufacturability and embrittlement of first 50 alloys using Charpy hammer</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Test flux: want 50 scfh/ft^2 at 400°C, 200 psi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>Test life accelerated aging: want 15 years</td>
<td>40% done</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Make another 50, better alloys</td>
<td>70% along</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Test for permeation and embrittlement</td>
<td>30% along</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Test brazing and welding; make first tubes</td>
<td>30% along</td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>Make tubes of best 2 alloys</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Make and test membrane reactor</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Final report, begin commercialization</td>
<td>5% along</td>
<td></td>
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</tbody>
</table>
Technical Accomplishments:

We found several “almost” alloys

Among our “misses” are alloys with other valuable properties: one that seems like Pt; another like aircraft Ti, but 20% lighter; another like aircraft Ti, but with a 200°C higher creep temperature. These may be good for catalysis, aircraft, 4th generation nuclear, or prosthetics.

• We have 2 publications, and more in works and we keep working on alloys for the next 18 months.

• Lowering the cost/flux H₂ permeation membrane lowers the cost of H₂
  – Replace palladium with base metals: $100/ft² vs $3000/ft² √
  – 100% selectivity like Pd √
  – 50 scfh/ft² UHP H₂ at ΔP=200psi √
  – 15+ life √
  – no embrittlement (1/2 - not for high flux)
  – Welding + manufacturing (1/2 done)
Future Work (2007)

• “Tweaked” alloys: for high flux, no embrittlement (ISU, Ames)
• Continue to make welded tubes (LANL)
• Draw tubes into membranes (G+S)
• Continue braze tests (REB)
• Fabricate and test as purifier, membrane reactor (REB)
• Confirm that behavior matches flux, cost, and durability goals (REB, LANL)
Summary

We aim to make hydrogen so cheaply that only the very rich will use bottled gas

Make hydrogen, $250/MMBtu, from methanol, $16MMBtu,

- Lowering the cost/flux H₂ permeation membrane lowers the cost of H₂
  - Replace palladium with base metals: $100/ft² vs $3000/ft² ✓
  - 400°C Operation
  - 100% selectivity like Pd ✓
  - 50 scfh/ft² UHP H₂ at ΔP=200psi ✓
  - 15+ life ✓
  - no embrittlement + high flux not yet

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Additional Slides
Questions?

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Thank you for your support!
NETL permeation setup
REB’s View of Hydrogen and the Energy Picture
Comparison of Metals, Intermetallics and Ceramics

<table>
<thead>
<tr>
<th>Metals</th>
<th>Intermetallic Compounds</th>
<th>Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>high densities</td>
<td>Intermediate densities</td>
<td>low densities</td>
</tr>
<tr>
<td>intermediate elastic moduli</td>
<td>fairly high elastic moduli</td>
<td>high elastic moduli</td>
</tr>
<tr>
<td>extensive ductility@RT</td>
<td>little ductility@RT</td>
<td>no ductility@RT</td>
</tr>
<tr>
<td>moderately high tensile and compressive strength @RT</td>
<td>variable tensile strength, fairly high compressive strength @RT</td>
<td>variable tensile strength, high compressive strength @RT</td>
</tr>
<tr>
<td>fairly low hot strength</td>
<td>high hot strength</td>
<td>very high hot strength</td>
</tr>
<tr>
<td>mediocre/low hot oxidation resistance</td>
<td>fairly high hot oxidation resistance</td>
<td>high hot oxidation resistance</td>
</tr>
<tr>
<td>high electrical conductivity</td>
<td>moderately high electrical conductivity</td>
<td>very low electrical conductivity</td>
</tr>
<tr>
<td>high RT fracture toughness</td>
<td>low RT fracture toughness</td>
<td>low RT fracture toughness</td>
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</tbody>
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