High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

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REB Research & Consulting

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Hydrogen Separations and Membrane Reactors

PD43

Overview

Timeline

- Oct. 1, 2005- Mar. 31, 2008
- 70% complete

Budget

- Total project: $2,919,857.
  - DoE: $2,334,646.
  - Non DoE $ 585,211.
- DoE thru '07: $1,240,388.
- DoE '08, est. : $ 700,000.

H_2 Barrier addressed

- **Lowering the cost/flux H_2 permeation membranes. This lowers the cost of H_2.**
  - Replace palladium with B2 base metals: $100/ft^2 vs $3000/ft^2
  - 100% selectivity like Pd
  - 50 scfh/ft2 UHP H_2 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 $CH_4OH + H_2O$ and outputs 3.5 slpm of ultra-pure hydrogen for laboratory use.
- Our generator design was developed in a phase 1 SBIR grant.
- B2 alloys should allow us to extend the life of the separator, and thus, cut the effective cost

Project Objective
plus 2007, 2008 milestones:

- **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/ft^2 vs $3000/ft^2
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi
  - 15+ life, no embrittlement

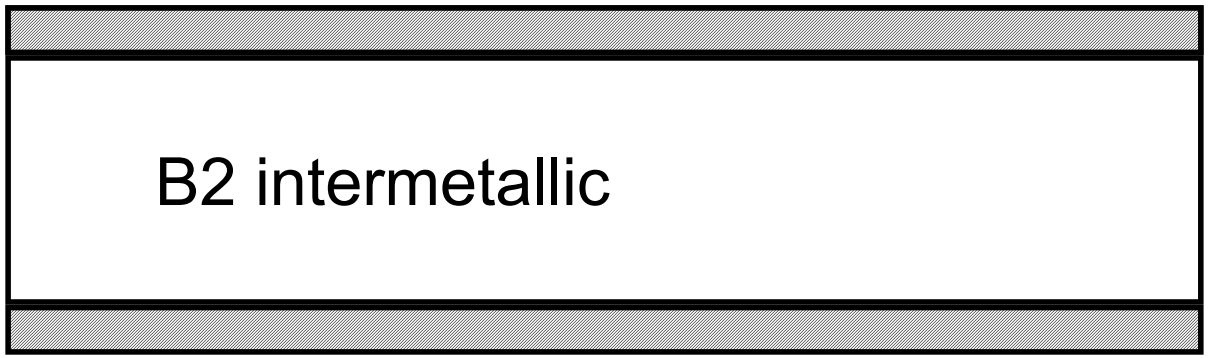
2008 Milestones:

- Good manufacturing with current tweak
- Repeat demonstration of long life tests
- Manufacture reactor purifier discs

Approach: make sandwich membranes

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

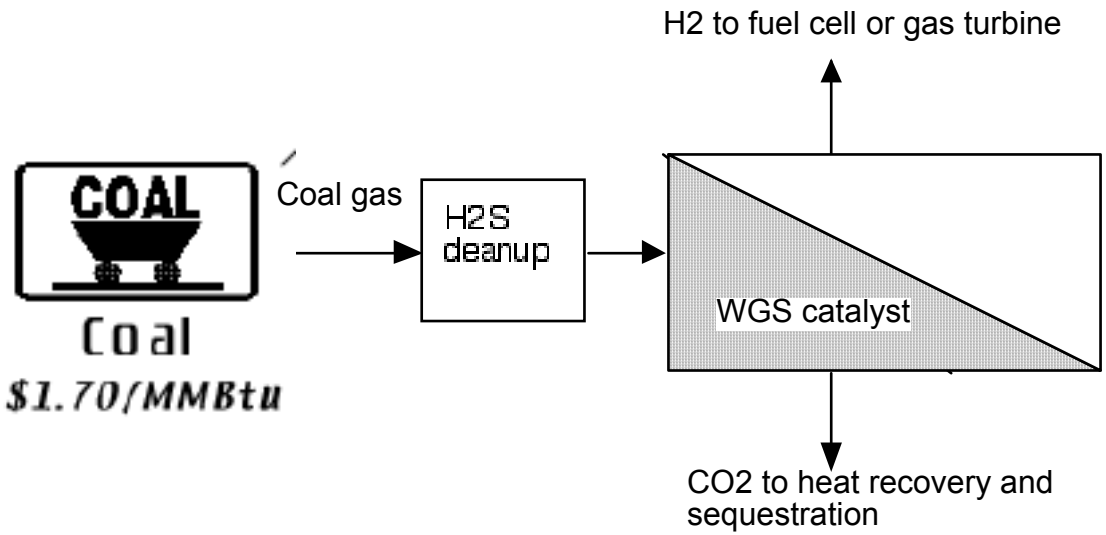
Pd alloy coat; 0.5μ thick



Pd alloy coat; 0.5μ thick

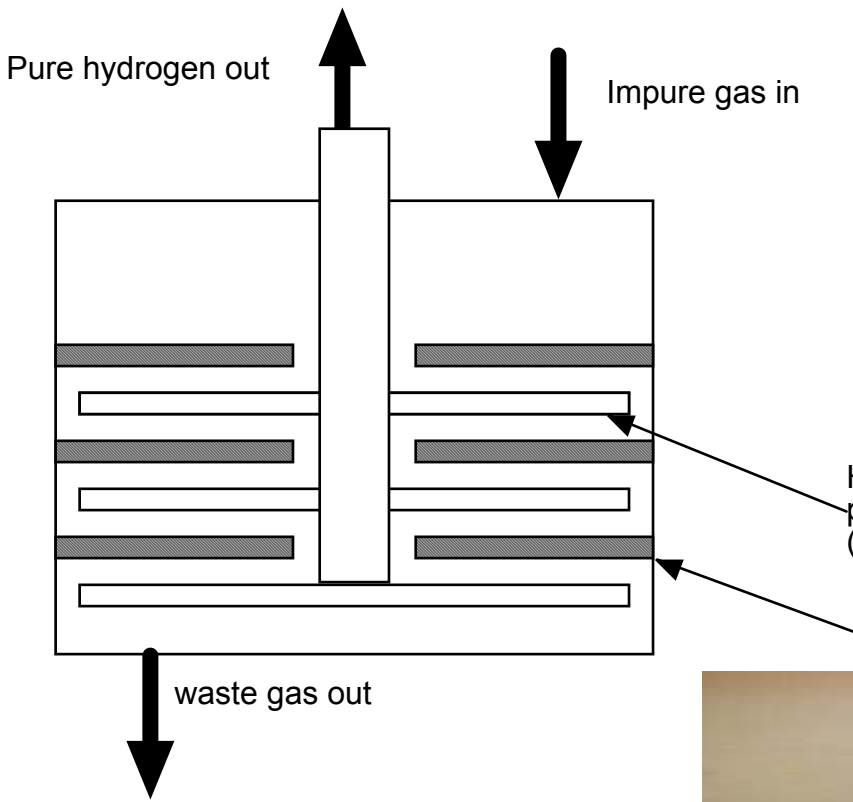
With some alloys, the coat is not needed

Coal to H2 process
(BuxGen)



- Most of our products to date use tube membranes: lots of surface/volume
- Purity of our H2, excessive for FutureGen, good for electronics, fuel cells

Technical accomplishment: B2 alloys require a new design



- Each Disk expected to deliver 20 scfh H2 for synthesis gas (50% H2) at 250 psi ΔP w/coal impurities
- Reactor delivered to WRI for tests May 22, 2008

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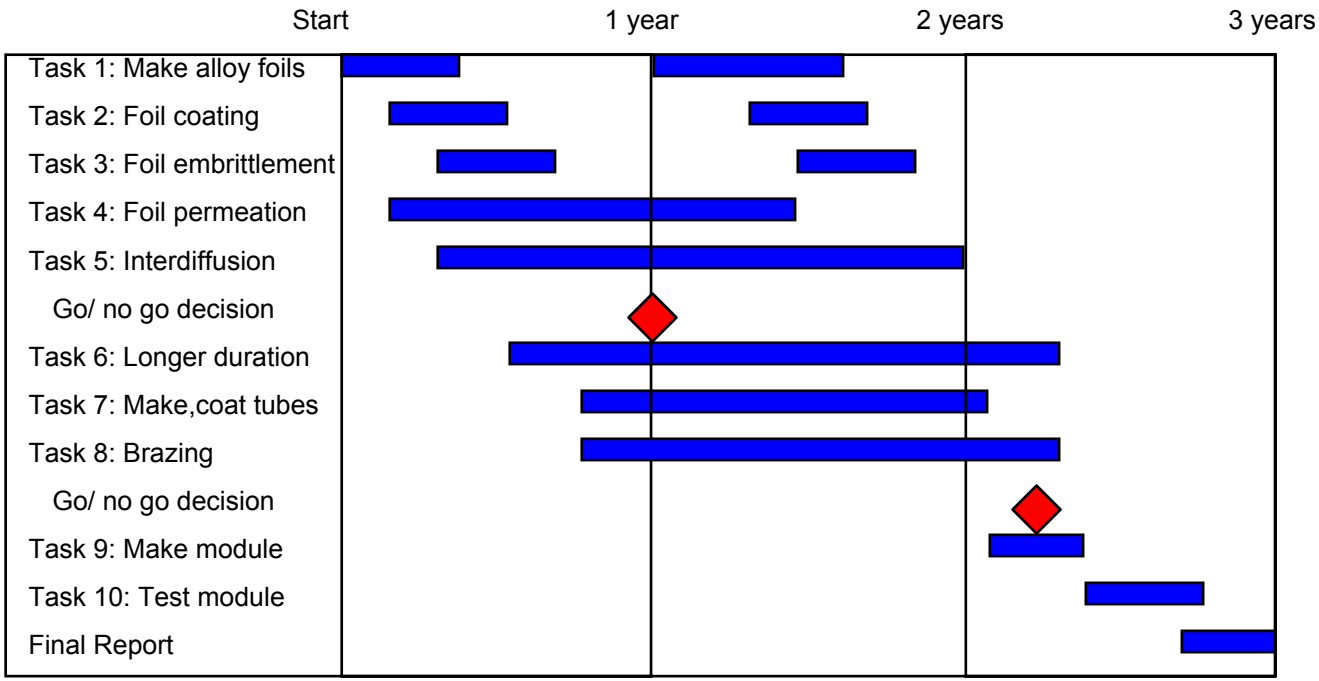
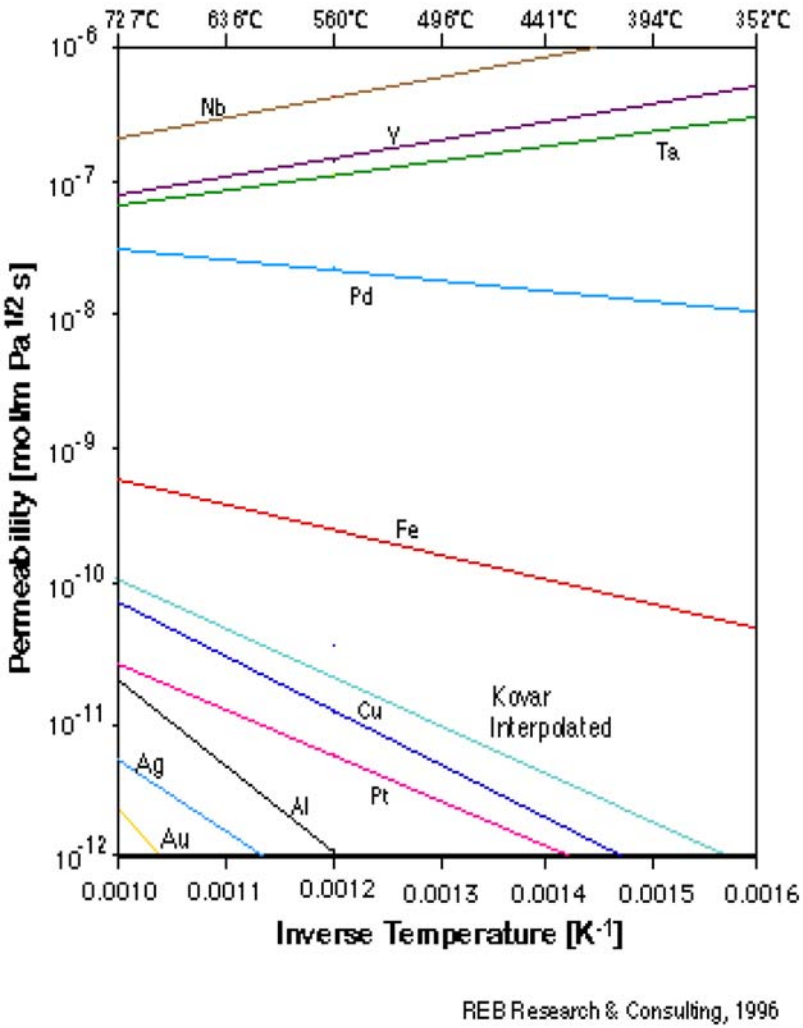
Original Schedule

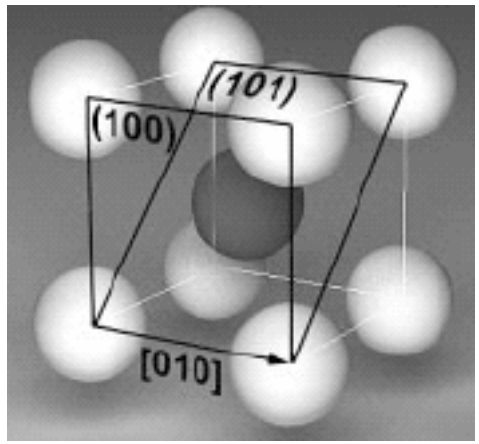
Figure 7: Gantt Chart of Project Schedule by Task



On Schedule except for 6 months due to manufacturing problems - it's hard to work B2 alloys

Accomplishment: Picked B2 alloys

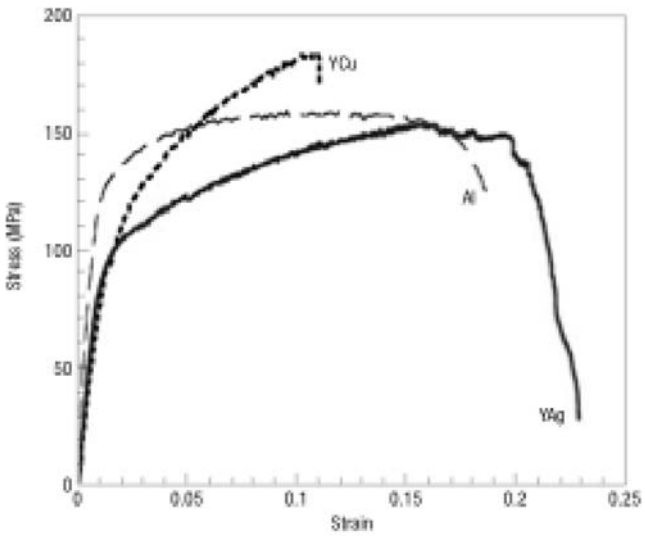


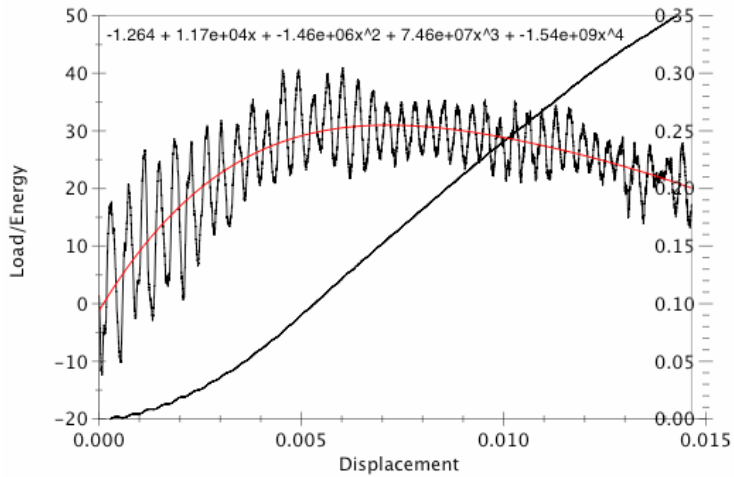


- At left, note that several metals: V, Nb, and Ta have 100 times higher permeabilities than Pd at 350-400°C They cost only 1/100 as much as Pd. Unfortunately they embrittle in H_2.
- Our approach is to try B2 intermetallic alloys, like NiTi (above). So far we've tried about 60. We'd previously noted 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)



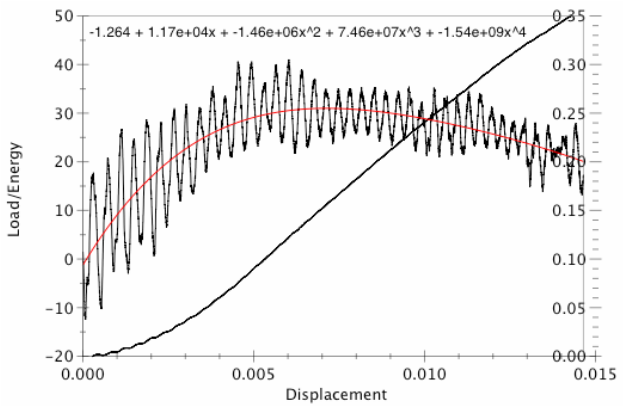


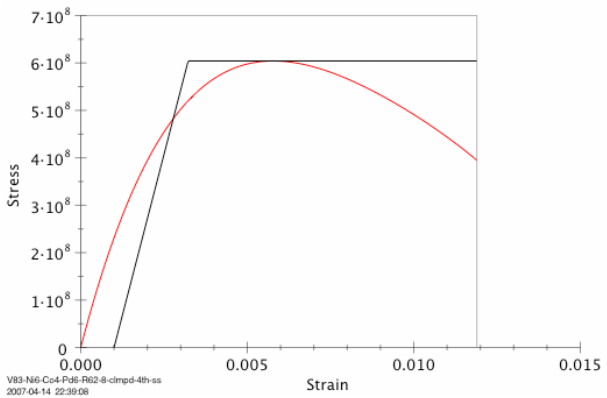
Two ISU- discovered, ductile B2 alloys
Al 3105 shown for comparison.
Alloys are ductile to over 20% strain

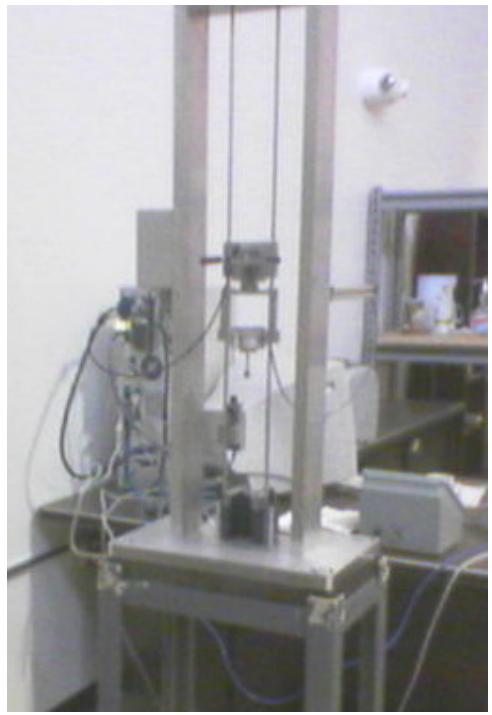
Charpy Mechanical Tests

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

•Determine stress-strain curve before and after hydriding

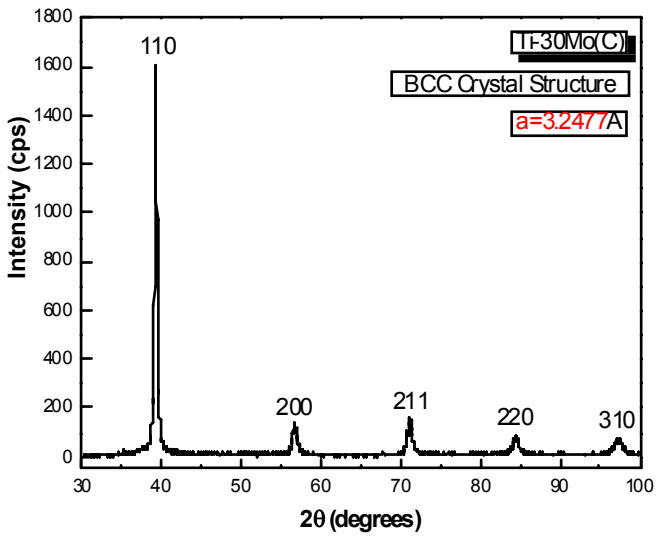




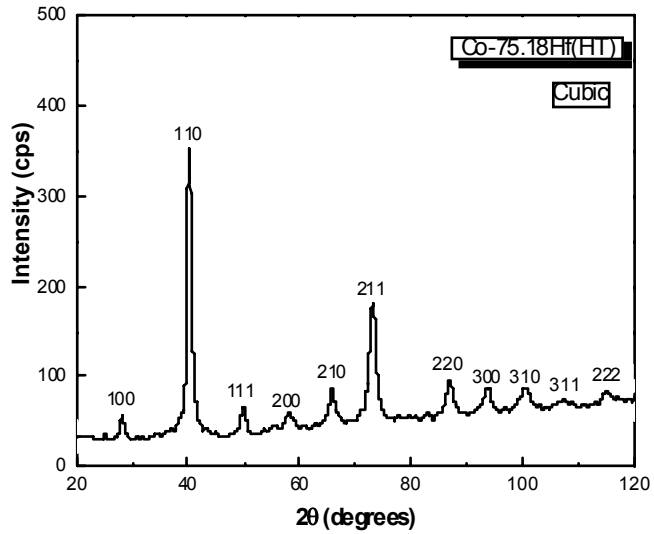


X-ray pictures

- Work continues at ISU as we tweak the alloys

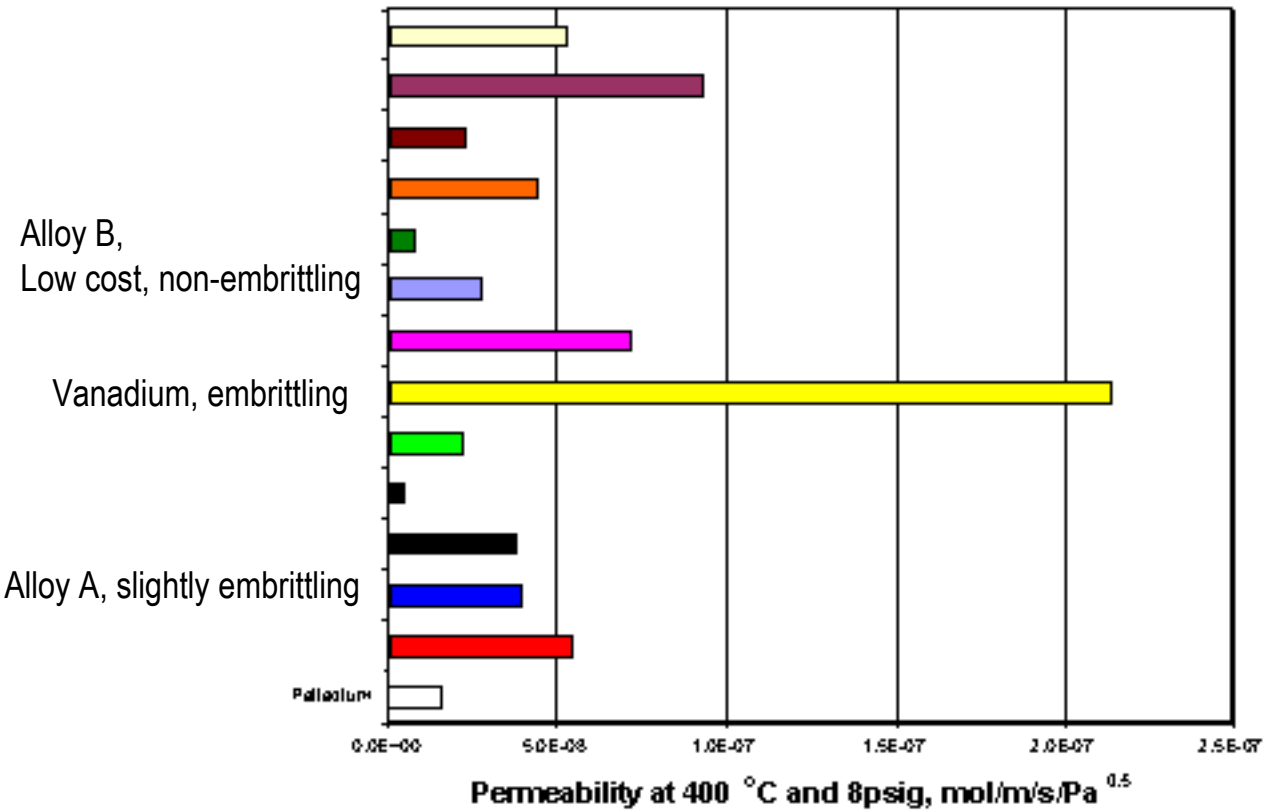


Random BCC structure

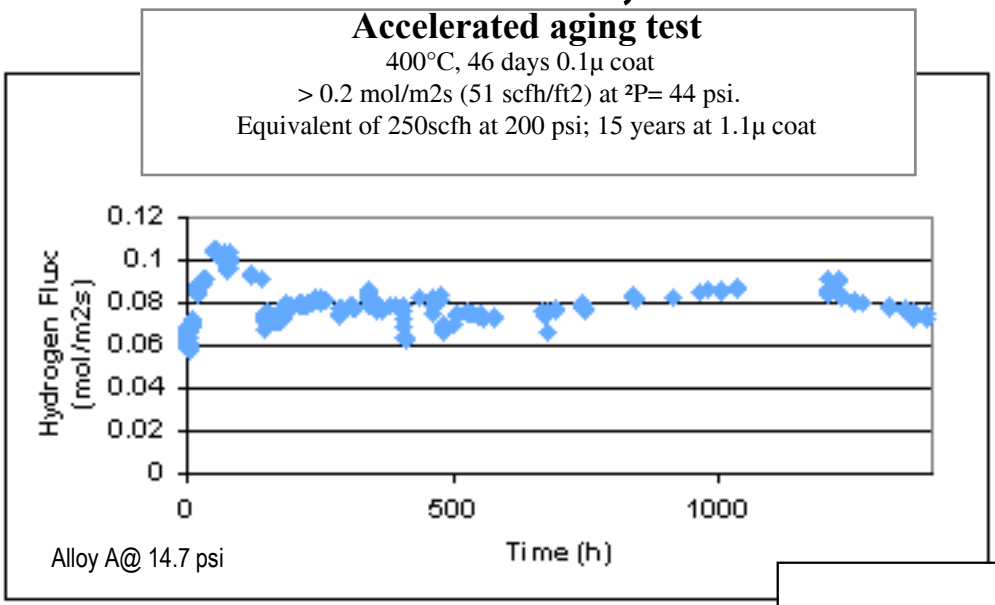


B2 cubic structure

Result of Hydrogen Permeability Measurements

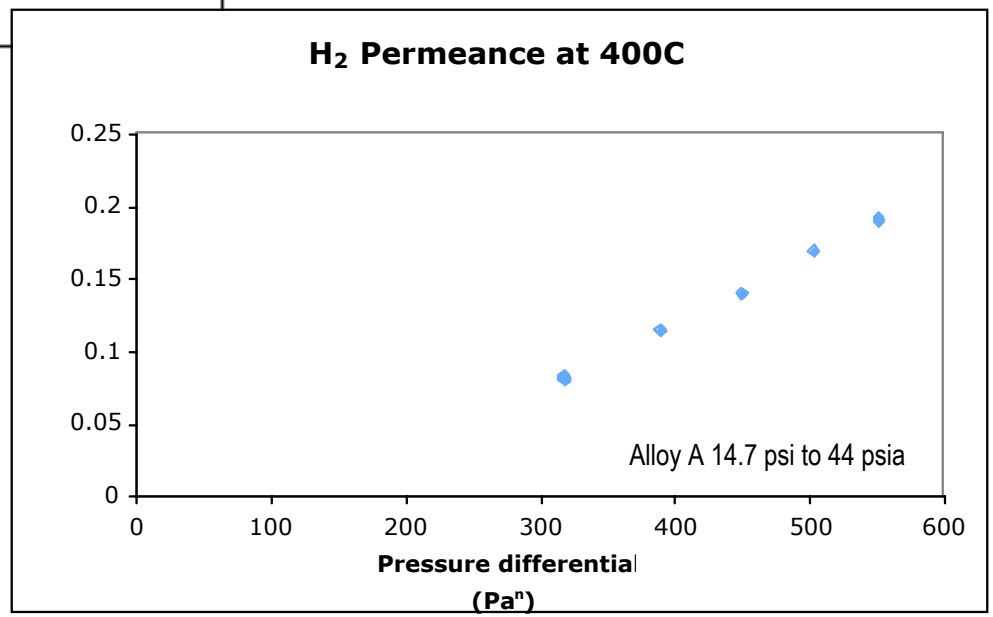


Technical accomplishment: Demonstrated suitable life in accelerated tests, and suitable flux at target costs



- We met the target flux at 1/5 the target pressure, suggesting 3 or 4x the target flux at 200psi
- Accelerated lifespan measured, as we planned, with a thinner Pd coat. Life meets project targets.
- Alloy B is more robust; doing life tests. Robust is a key hurtle

- Price of A or B ≤ $95/ft^2 meets targets
- Alloy B survived below 80°C under pressure. Nearly robust enough for FutureGen. OK for nuclear use at low P.



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Technical accomplishment: Demonstrated acceptable brazing behavior:

For the alloy to be worthwhile, it must be possible to fabricate hydrogen purifiers from it: should braze to stainless steel.

- We tried lots of brazes connecting SS to alloys in tube and sheet form.
- Two successful brazes shown below.
- Found that brazing in H2 was much better than brazing in vacuum for these alloys

Technical Accomplishments:

- **Lowered the cost/flux H_2 permeation membranes to lower the cost of H_2.**
  - Replace palladium with base metals: \$100/ft^2 vs \$3000/ft^2 √
  - 100% selectivity like Pd √
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi √
  - 15+ life projected √
  - low embrittlement √
  - Welding + manufacturing (1/2 done)
- **Side benefit: found several new B2 alloys with useful properties**
  - One of these seemed good for Advanced Nuclear
  - Got DoE SBIR to test alloy in that application

Last years' Future Work statement (2007)

- "Tweaked" alloys: for high flux, no embrittlement (ISU, Ames) --- Done
- Continue to make welded tubes (LANL) --- Still trying, but moved to discs
- Draw tubes into membranes (G+S) --- Discs OK, tubes were not good
- Continue braze tests (REB) --- Done
- Fabricate, test a purifier, membrane reactor (REB) -- Fabricated using earlier membrane
- Confirm that behavior matches flux, cost, and durability goals (REB, LANL) ---Done

Future Work (2008)

- Make larger non-porous membranes (Great Western, REB)
- Higher pressure tests, sulfur tests with current, tweaked alloy (NETL)
- Test membranes, purifier w/coal gas (REB, WRI)
- Continue life tests with new tweaked alloy (LANL)
- Make disc-membrane membrane reactor with new alloy membranes (REB)
- Confirm that behavior matches flux, cost, and durability goals (REB, ISU)

Future Work (Jan. - Mar. 2009)

- Test disc membrane reactor made with new alloy membranes (REB, WRI)
- Write up results
- Marketing study (if DoE allows us)
- Start to market the product

Summary

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

Figure 9: Membrane reactor hydrogen generator made by REB Research. Only two other companies make similar products: Tokyo Gas and Idatech; Idatech licenced from REB.

Hydrogen sells @ $250/MMBTU,
Methanol sells @ $16 MMBTU,
Coal sells @ $1.70/MMBTU

- **Lowering the cost/flux H_2 permeation membrane lowers the cost of H_2**
  - Replace palladium with base metals: $100/ft^2 vs $3000/ft^2 √
  - 400°C Operation
  - 100% selectivity like Pd √
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi √
  - 15+ life, low embrittlement √
  - Manufacture/works not yet

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