High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

Robert E. Buxbaum
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:
  - DoE: $2,334,646.
  - Non DoE: $ 585,211.
- To-date:
  - DoE $1,160,593.
  - Non DoE $ 342,031.

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

Partner s

- 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

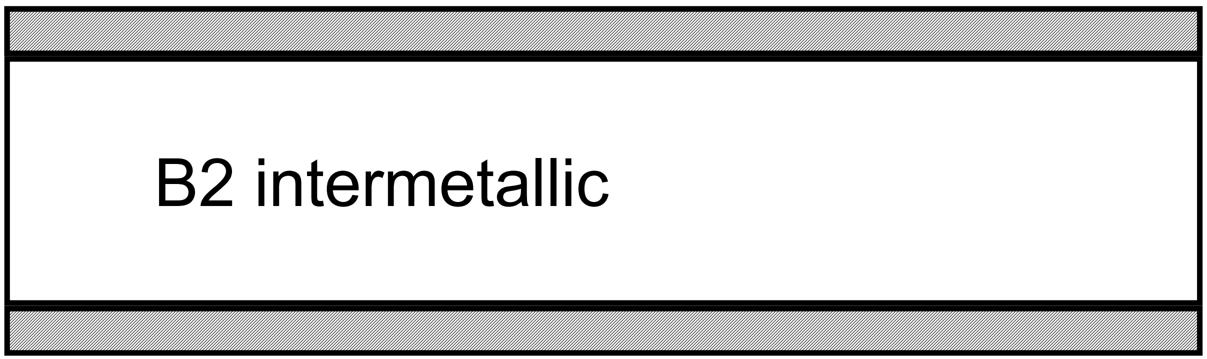
We aim to make hydrogen so cheaply that only the very rich will use bottled gas

- 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

Approach: make sandwich membranes

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

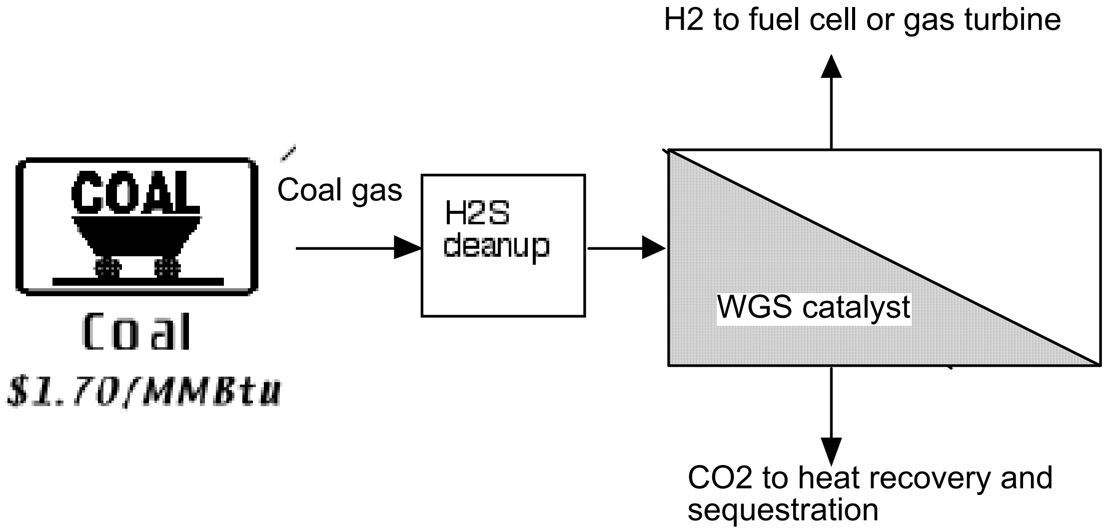
Pd alloy coat; 0.5μ thick



Pd alloy coat; 0.5μ thick

With some alloys, the coat is not neede(

Basic Coal to H2 process



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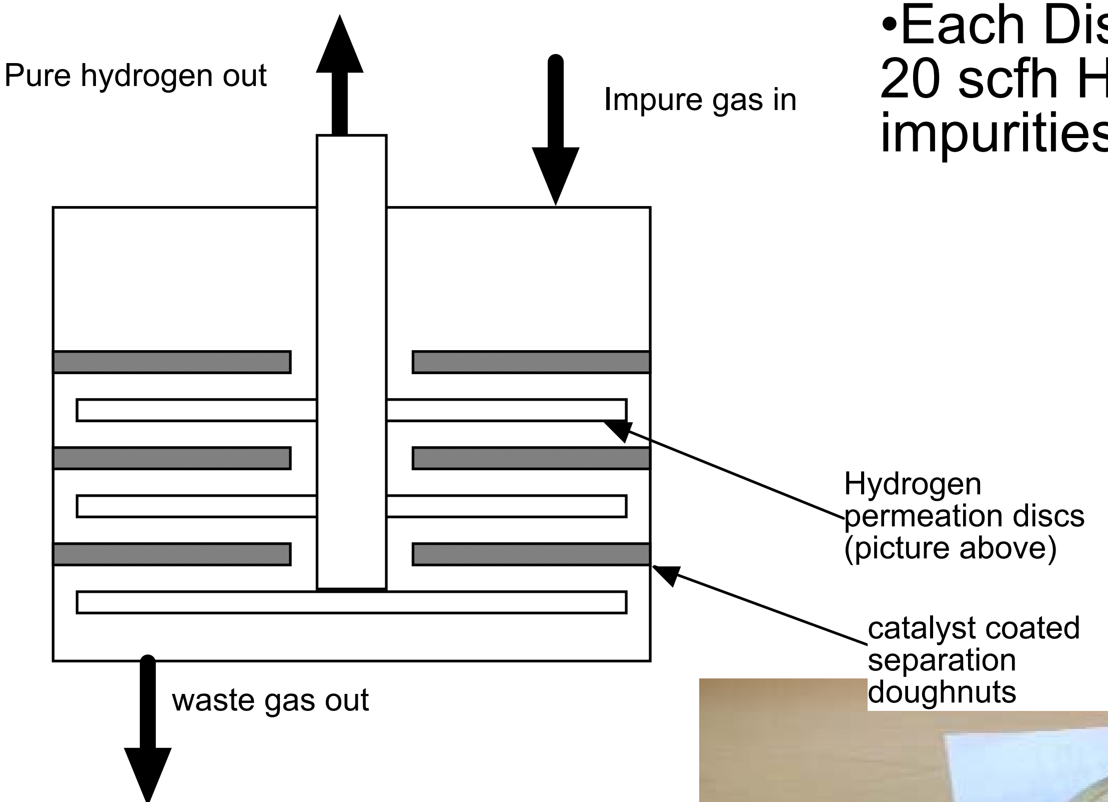
are needed to see this picture.

All our products to date use tube membranes: lots of surface/volume

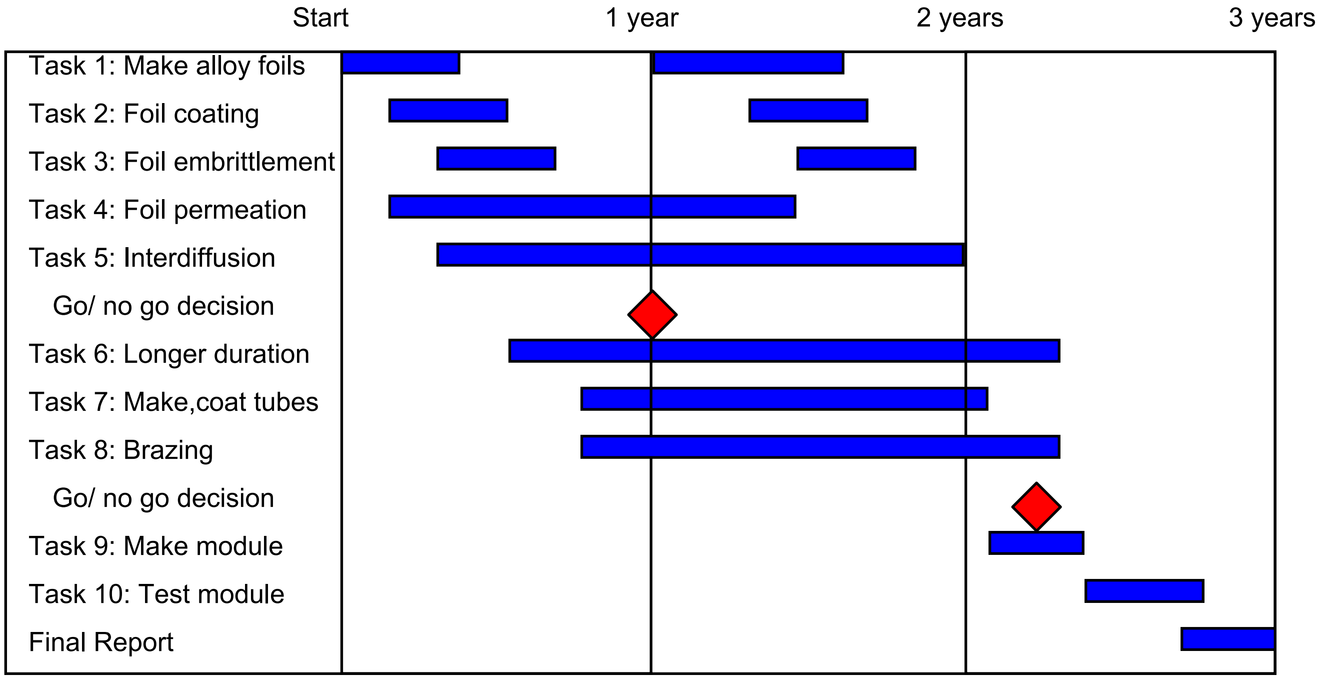
Result 1:
B2 alloys require a new design



- Each Disk expected to deliver 20 scfh H_2 at 250 psi ΔP w/coal impurities

Schedule

Figure 7: Gantt Chart of Project Schedule by Task



Accomplishments: Pick B2 alloys

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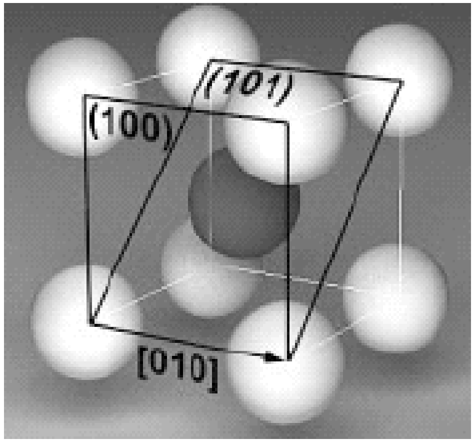

At left, note that several metals: V, Nb, and Ta have 100 times higher permeabilities than Pd at 350-400°C They cost only 1/100 as much as Pd. Unfortunately they embrittle in H_2.

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)

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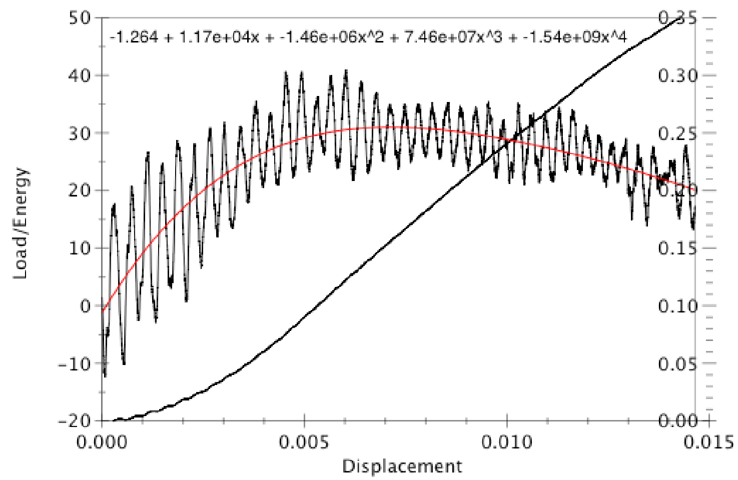
TIFF (LZW) decompressor
are needed to see this picture.

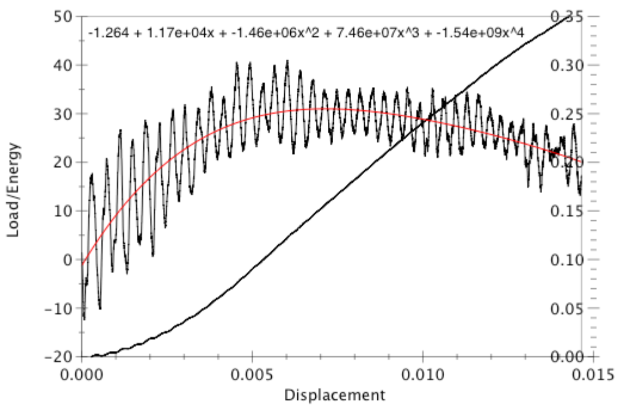


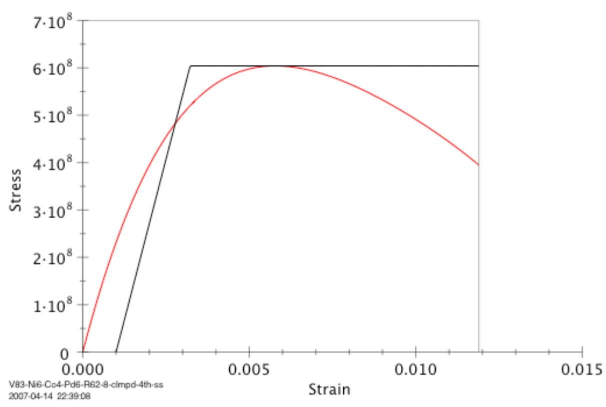
Two newly discovered, ductile B2 alloys
Al 3105 shown for comparison.
Alloys are ductile to over 20% strain

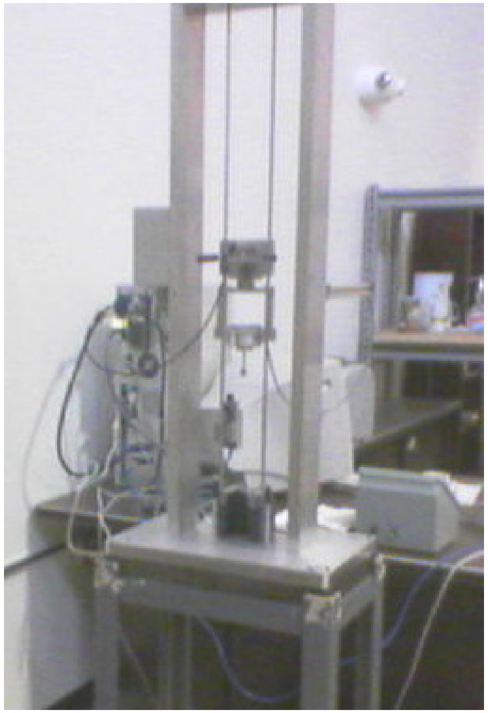
Charpy Mechanical Tests

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

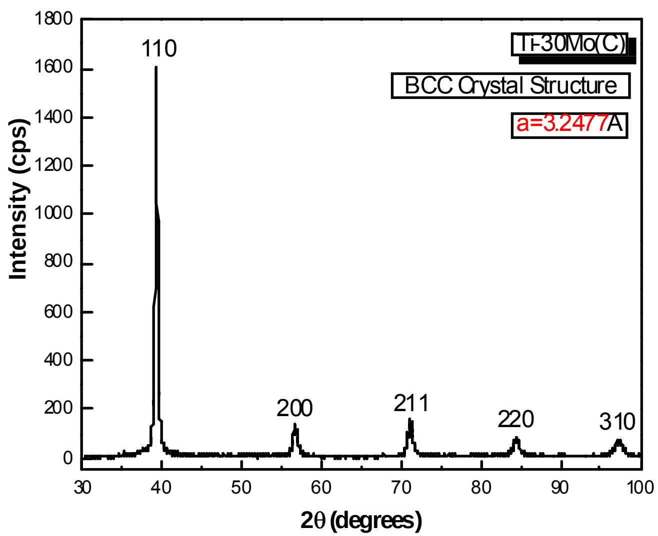
•Determine stress-strain curve before and after hydriding



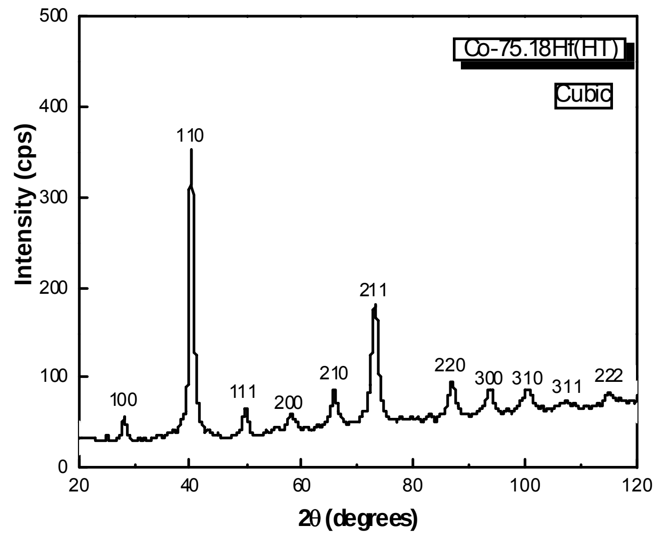




X-ray pictures

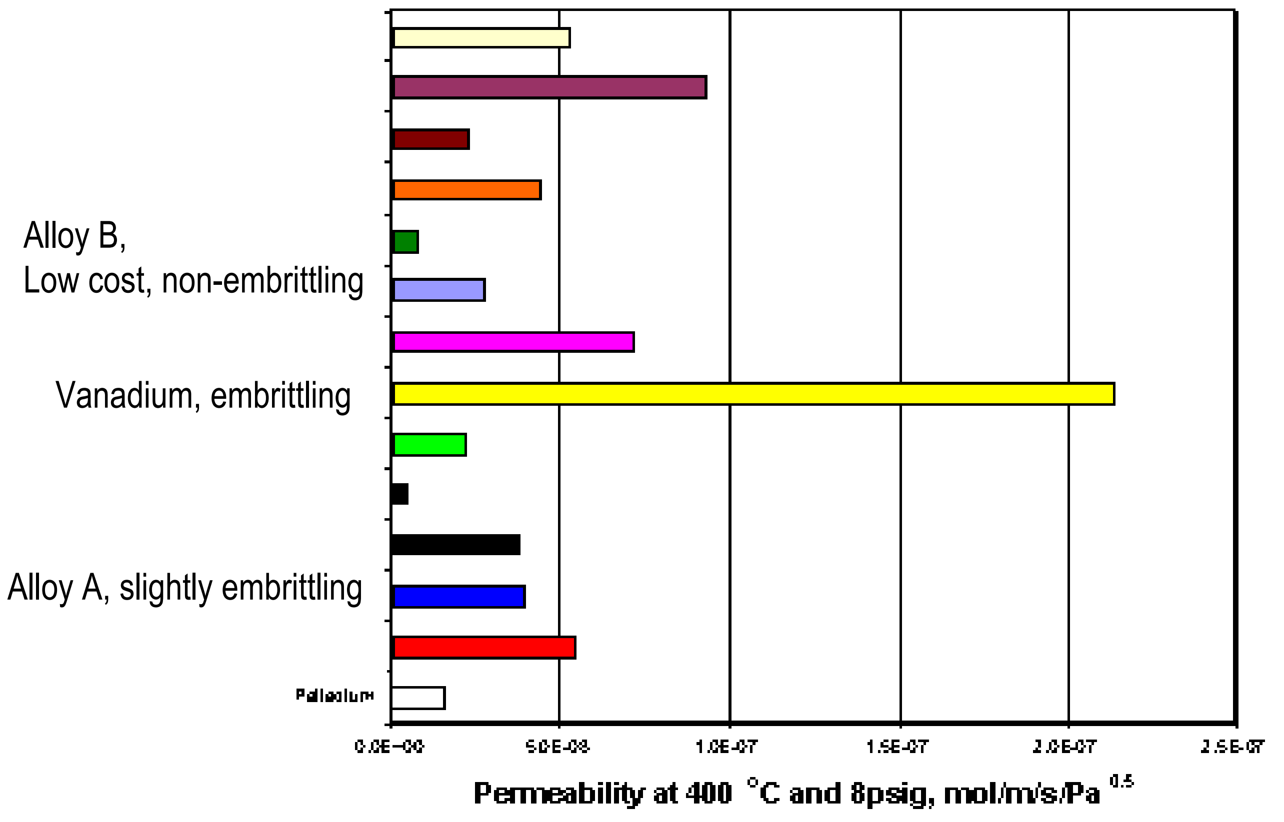


Random BCC structure



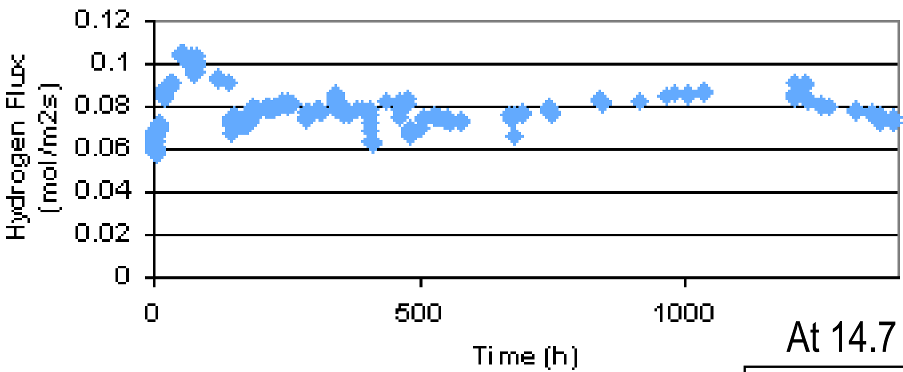
B2 cubic structure

Result of Hydrogen Permeability Measurements



Lifetime Tests: Flux versus time for alloy “A”

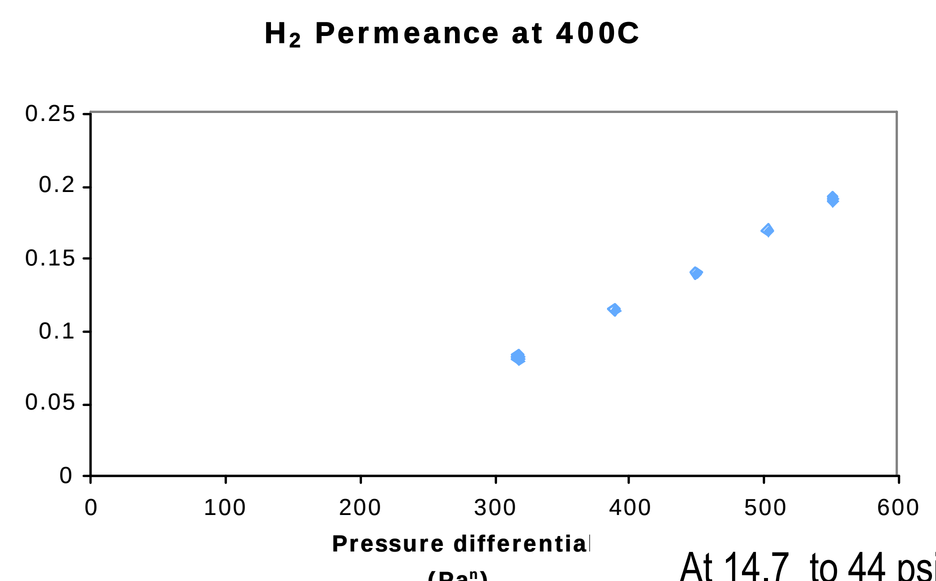
Accelerated aging test
400°C, 46 days 0.1µ coat
> 0.2 mol/m2s (51 scfh/ft2) at ²P= 44 psi.
Equivalent of 250scfh at 200 psi; 15 years at 1.1µ coat



At 14.7 psi

- 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.

- Price of this membrane about $95/ft^2 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.



At 14.7 to 44 psi

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Brazing experiments:

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.

Technical Accomplishments:

- 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 √
  - 100% selectivity like Pd √
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi √
  - 15+ life projected √
  - low embrittlement √
  - Welding + manufacturing (1/2 done)
- Found several new B2 alloys with useful properties.

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)

Future Work (2008)

- Make larger non-porous membranes (Great Western, REB)
- Fabricate and test purifier w/coal gas (REB/WRI, NETL)
- Make membrane reactor w/new membranes (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, $\$16$MMBtu,

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

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

www.rebresearch.com buxbaum@rebresearch.com

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Thank you for your support!

Additional Slides

Questions?

Contact: Robert E Buxbaum

REB Research & Consulting

www.rebresearch.com buxbaum@rebresearch.com

Thank you for your support!

NETL permeation setup

(Not a template slide – for information purposes only)

- *What did the previous membrane grant (SBIR) accomplish?*
- *We studied B1 (random BCC) alloys and found three that were better than PdAg*
  - *1 had 5 times the flux, but was only good for low P, nuclear applications*
  - *1 had 1.5x the flux/$ main membrane we use today*
  - *1 had same flux/$ and was H_2S tolerant.*
  - *None quite as good as we think we can achieve*

Critical Assumptions and Issues

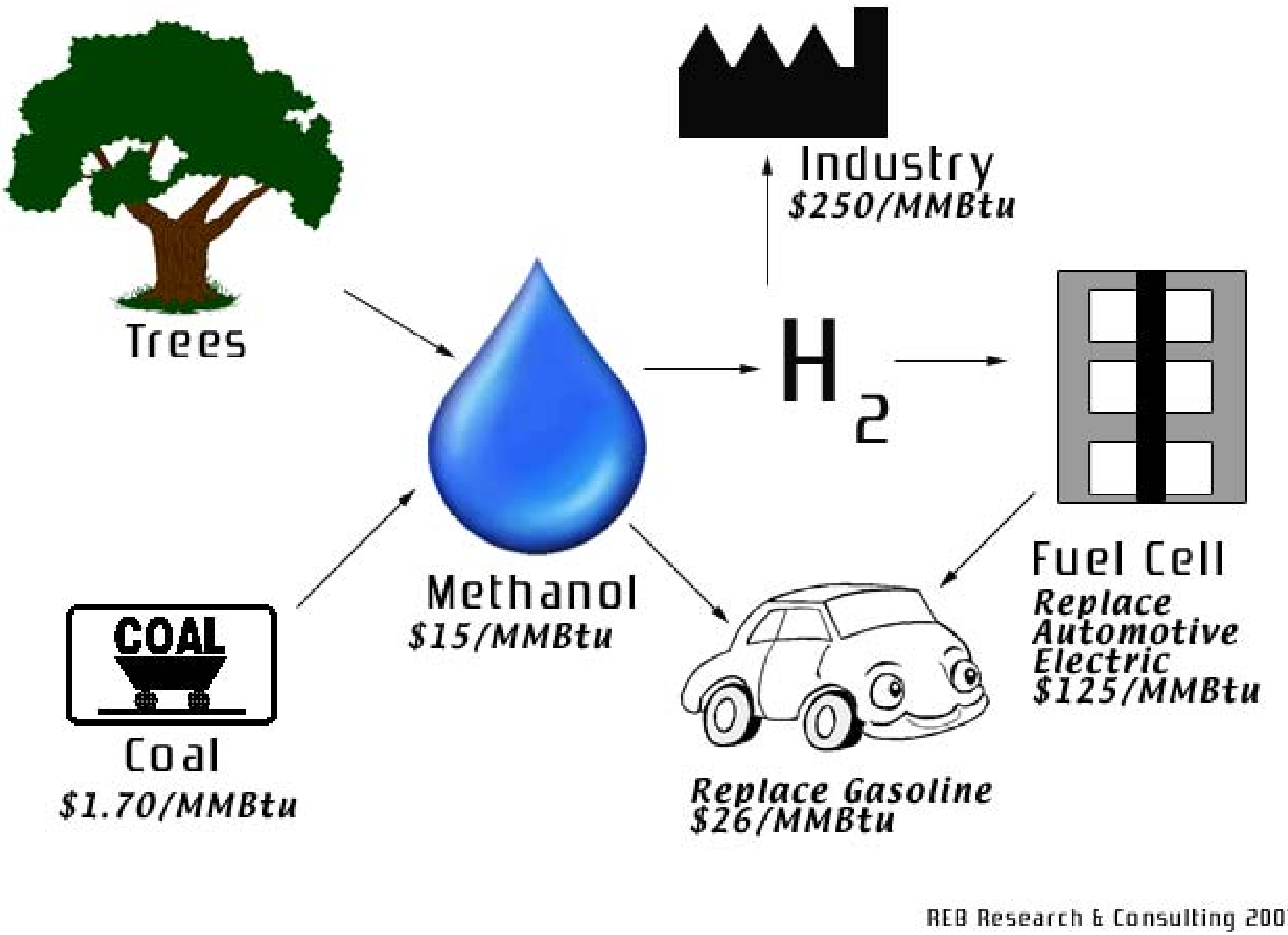
- **B2 alloys should last longer since the structure of the alloy should reduce metallic interdiffusion.**
- **B2 alloys should share the same high interstitial diffusion coefficient of BCC metals since the structure is the same for an interstitial**
- **B2 alloys can be more robust than Pd, since some are super-elastic, like nitinol.**
- **We’ll have low embittlement and high flux when we find an alloy that absorbs about .1 H/M at STP**

Publications and Presentations

- S. N. Paglieri, Y. Wang, T. J. Venhaus, H. Oona, R. C. Snow, B. P. Nolen, R. E. Buxbaum, K. S. Rothenberger, B. H. Howard, and R. P. Killmeyer. Characterization of V-6Ni-5Co Membranes for Hydrogen Separation. *Proceedings of the 9th Int. Conf. on Inorganic Membranes*, Lillehammer, Norway, June 25-29, 2006.

- S. N. Paglieri, I. E. Anderson, R. L. Terpstra, T. J. Venhaus, Y. Wang, R. E. Buxbaum, K. S. Rothenberger, B. H. Howard. Metal Membranes for Hydrogen Separation. *Proc. 20th Annual Conf. Fossil Energy Mater.* Knoxville, Tennessee, USA Jun. 12-14, pp. 236-243, 2006. (http://www.ornl.gov/sci/fossil/)
- R.E.Buxbaum, patent applied for

REB's View of Hydrogen and the Energy Picture



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Comparison of Metals, Intermetallics and Ceramics

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