# Development of a Porous Support for Thin Palladium Membranes

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# Partners & collaborators

- Iver E. Anderson, *Ames Laboratory*
  - development of Pd/iron-aluminide composite membranes
- Ames Laboratory Material Preparation Center
  - alloy development, casting, and disc fabrication
- Robert E. Buxbaum, *REB Research & Consulting*
  - industrial partner
- Michael V. Ciocco, Bret H. Howard, Bryan D. Morreale, and Richard P. Killmeyer *National Energy Technology Laboratory*
  - membrane testing and analysis

AMES LABORATORY
United States Department of Energy

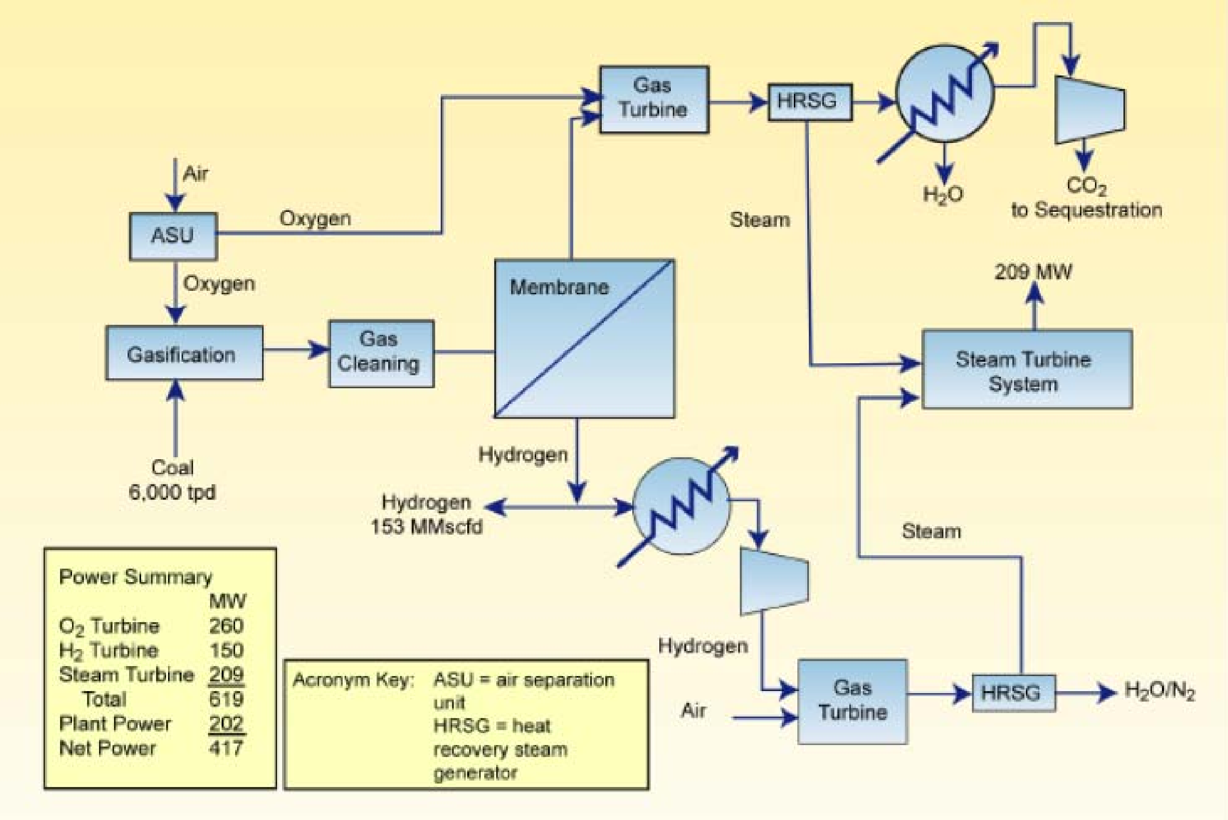
REB Research & Consulting

NETL

# Outline

- Background
  - hydrogen separating membranes for FutureGen and distributed hydrogen generation
- Iron aluminide porous membrane support
  - metallic interdiffusion barrier
  - fabrication, optimization, and characterization
- Fabrication, testing, and analysis of Pd-coated Group 5 membranes
  - assessment of Nb alloys
  - V-10at%Pd
  - hydrogen permeation testing

# FutureGen: Coal derived hydrogen/electricity/chemicals



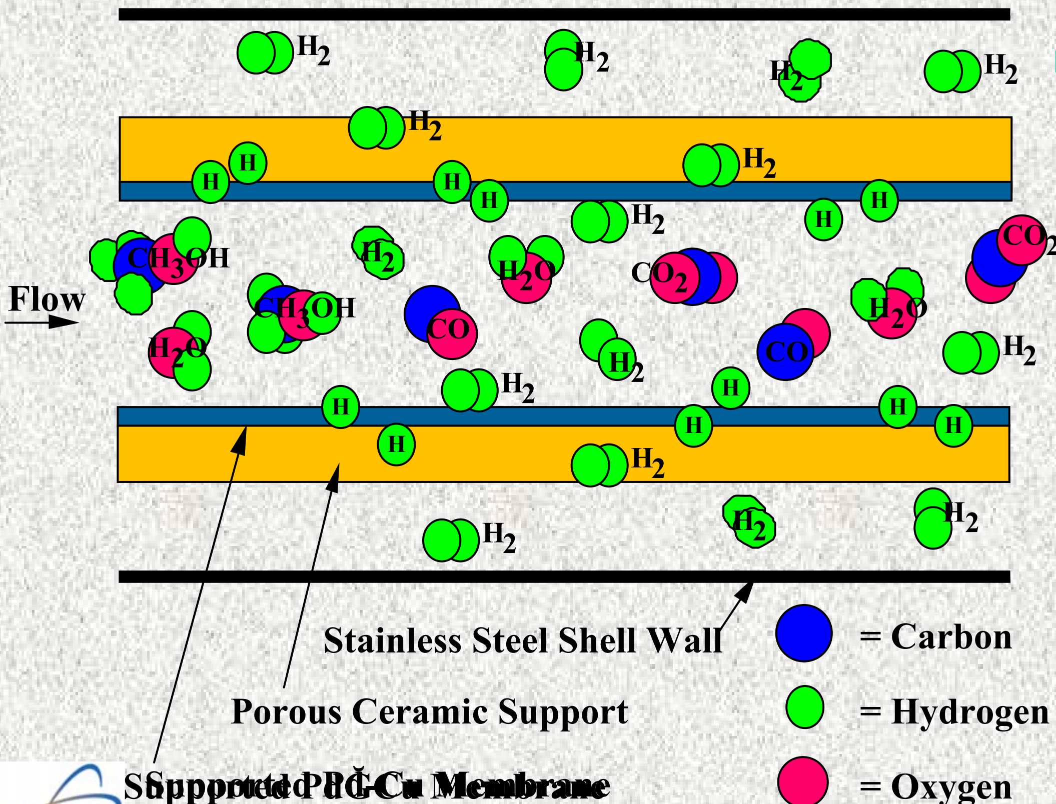

Source: Gray, D. and Tomlinson, G. Mitretek Systems. Hydrogen from Coal, Mitretek Technical Paper MTR 2002-31. July 2002.

**www.fossil.energy.gov**

# Fuel reforming for hydrogen

Challenge: *apply membranes to small-scale distributed [hydrogen] production in a one-step shift reactor that is feedstock flexible*

– Arlene Anderson, Tech. Devel. Manager, DoE $H_2$, Fuel Cells & Infrastructure Tech.

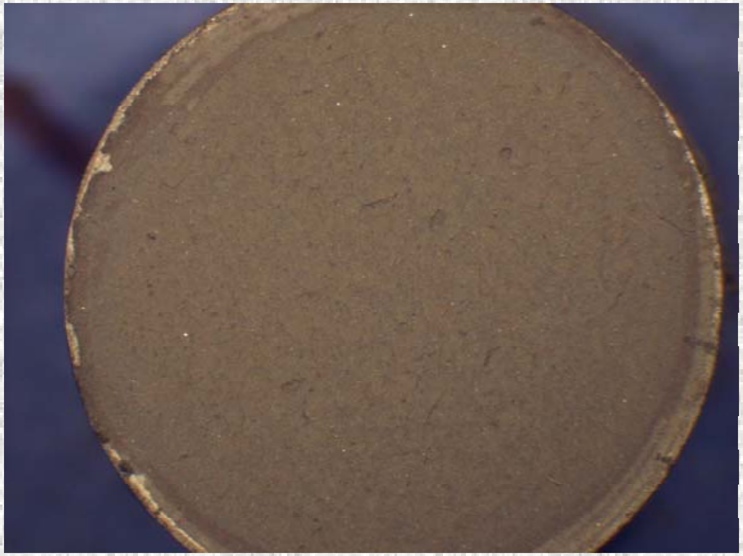



- Membrane reactor
  - fuel flexible (liquid, gaseous, coal, biomass)
  - $C_nH_m + nH_2O \leftrightarrow nCO + [(m+2n)/2]H_2$
  - $CO + H_2O \leftrightarrow CO_2 + H_2$
  - produces pure $H_2$ plus a high-pressure, $CO_2$ rich stream in a single unit operation facilitates carbon sequestration

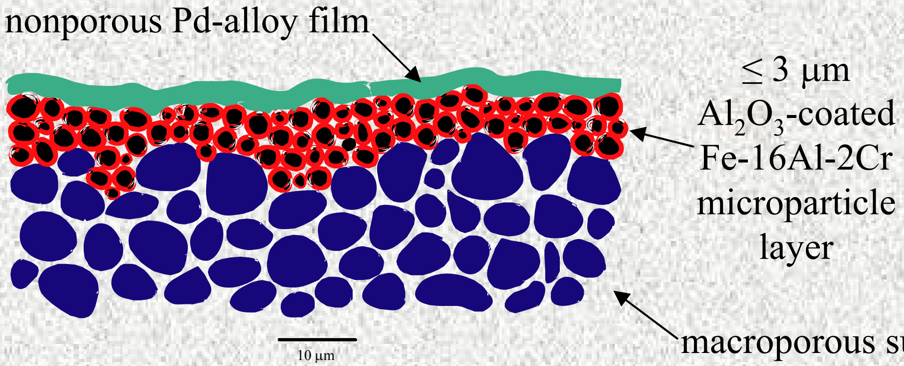
# Innovative goals

- Develop robust, high flux hydrogen separation membranes
  - reduce equipment size and costs required for $H_2$ production
  - smaller footprint
  - for reforming various fuels using membrane reactors
  - function in coal gas environment ($H_2S$ resistant)
- Fabricate a thermally stable porous support
  - ultra-thin (< 5 μm), pinhole-free Pd alloy composite membranes
  - inhibit metallic interdiffusion between the substrate and Pd-alloy membrane at temperatures > 400°C for extended lifetime
- Increase the durability and reduce the cost of Group 5 metal membranes for hydrogen separation and purification
  - necessary for industrial scale deployment
  - hydrogen permeability and resilience comparable to Pd-Ag/Pd-Cu

# *Asymmetric* porous membrane support



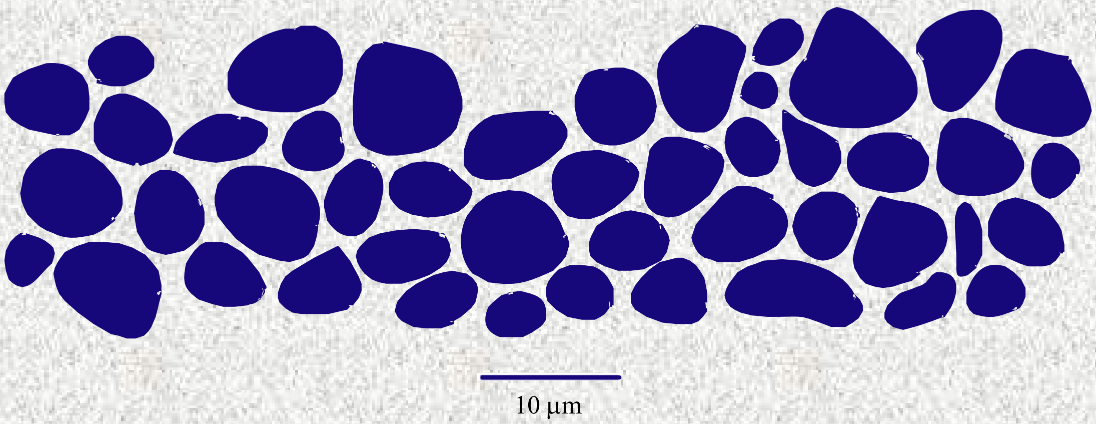
- Slurry of uniform iron aluminide microparticles is applied to a porous substrate and sintered
  - $\leq$ 3 µm Fe-16Al-2Cr microparticles
- A thin oxide layer forms on all exposed post-sintered surfaces
  - aluminum diffuses to the surface
- Forms a barrier to metallic interdiffusion
  - $Al_2O_3$ interlayer between a thin Pd alloy film and the particles in the porous support




*High pressure gas atomized powder preparation method:* I.E. Anderson, R.L. Terpstra & B. Gleeson. *Mater. Sci. & Eng. A*, **326**(1) 101 (2002).

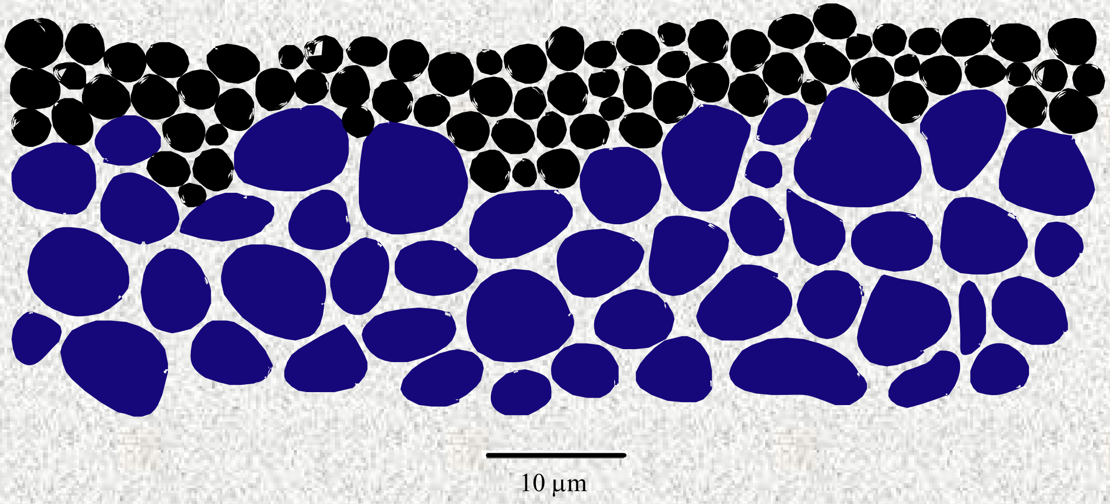
# Membrane fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off



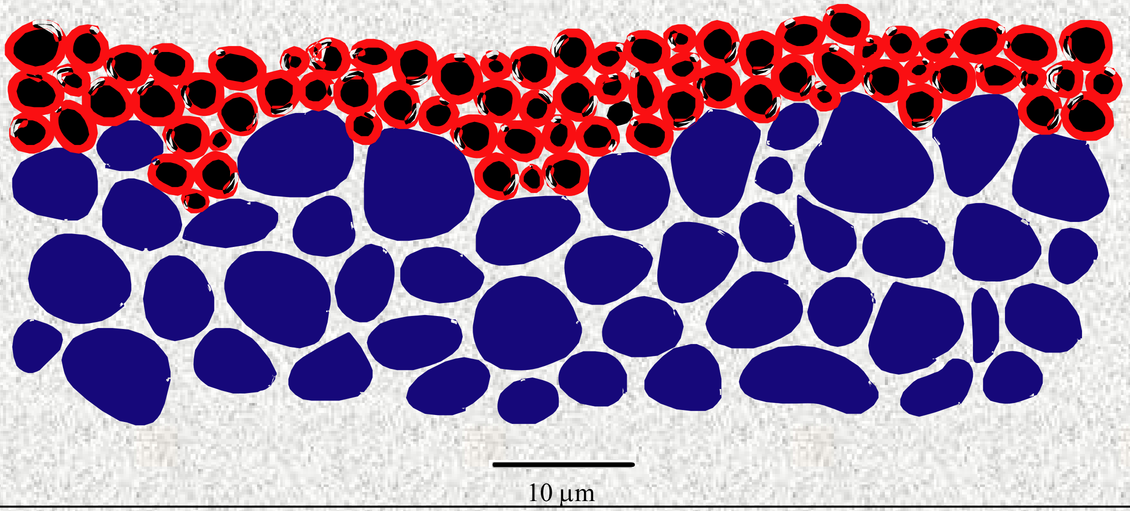
# Membrane fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off
- Fe-16Al-2Cr microparticle slurry applied, dried, sintered



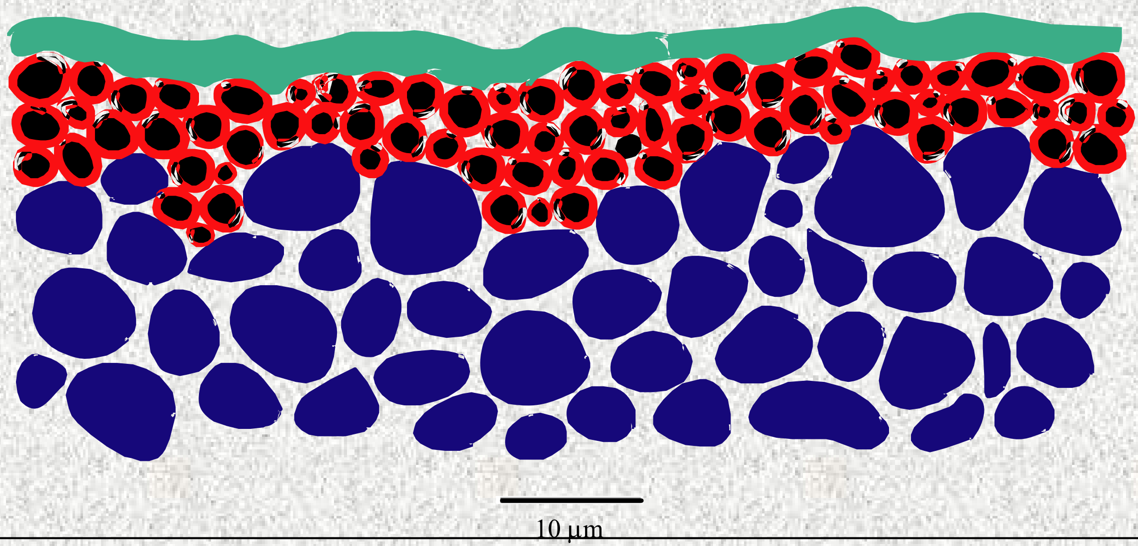
# Membrane fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off
- Iron-aluminide microparticle slurry applied, dried, sintered
- Post treat to form thin alumina layer



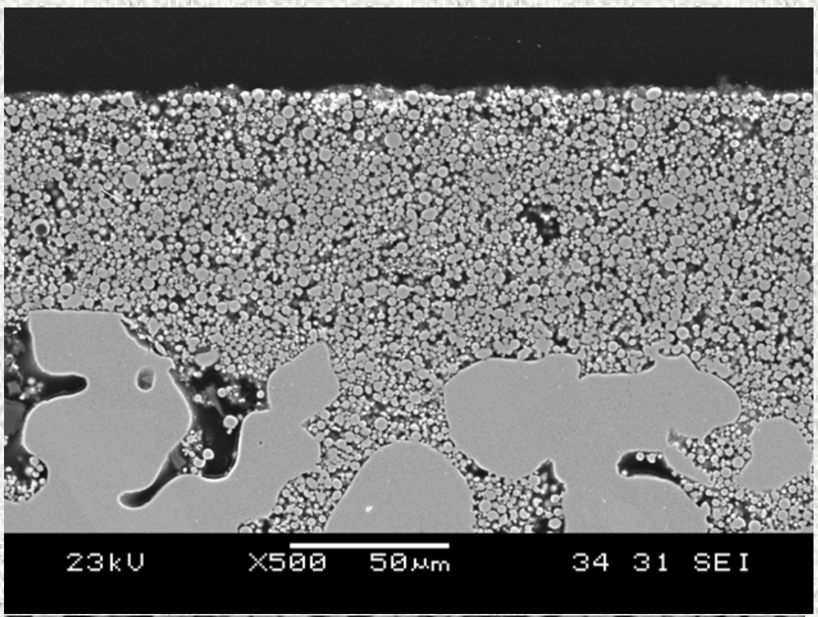
# Membrane fabrication

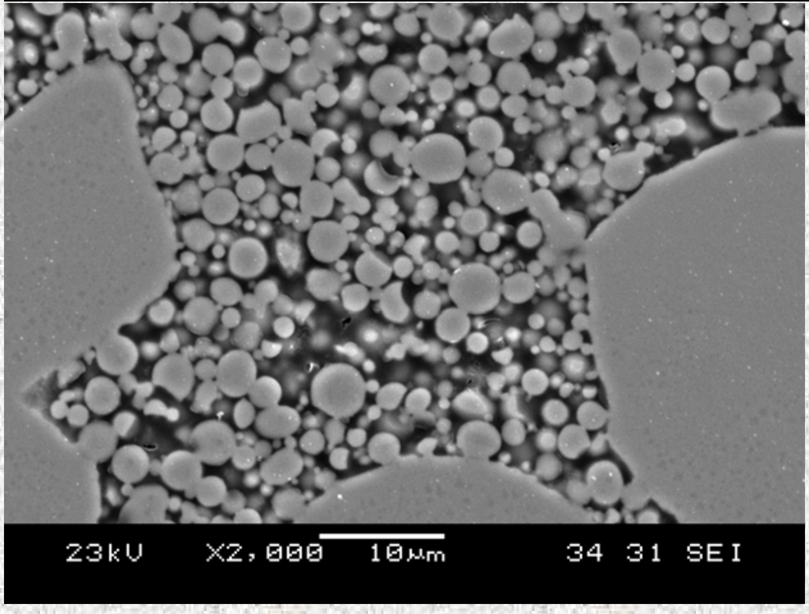
- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 µm particle cut-off
- Iron-aluminide microparticle slurry applied, dried, sintered
- Post treat to form thin alumina layer
- Deposit thin hydrogen selective layer
  - PVD, CVD, electroless plating



# SEM of Sintered Membrane

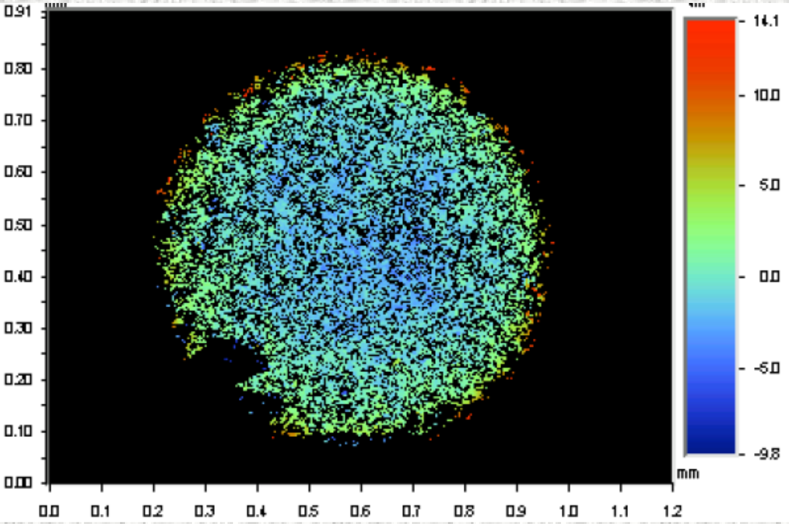
- Fe-16Al-2Cr (wt.%) powder
- < 3 µm particles
- Sintered at 975°C for 1 h
  - I.E. Anderson et al.



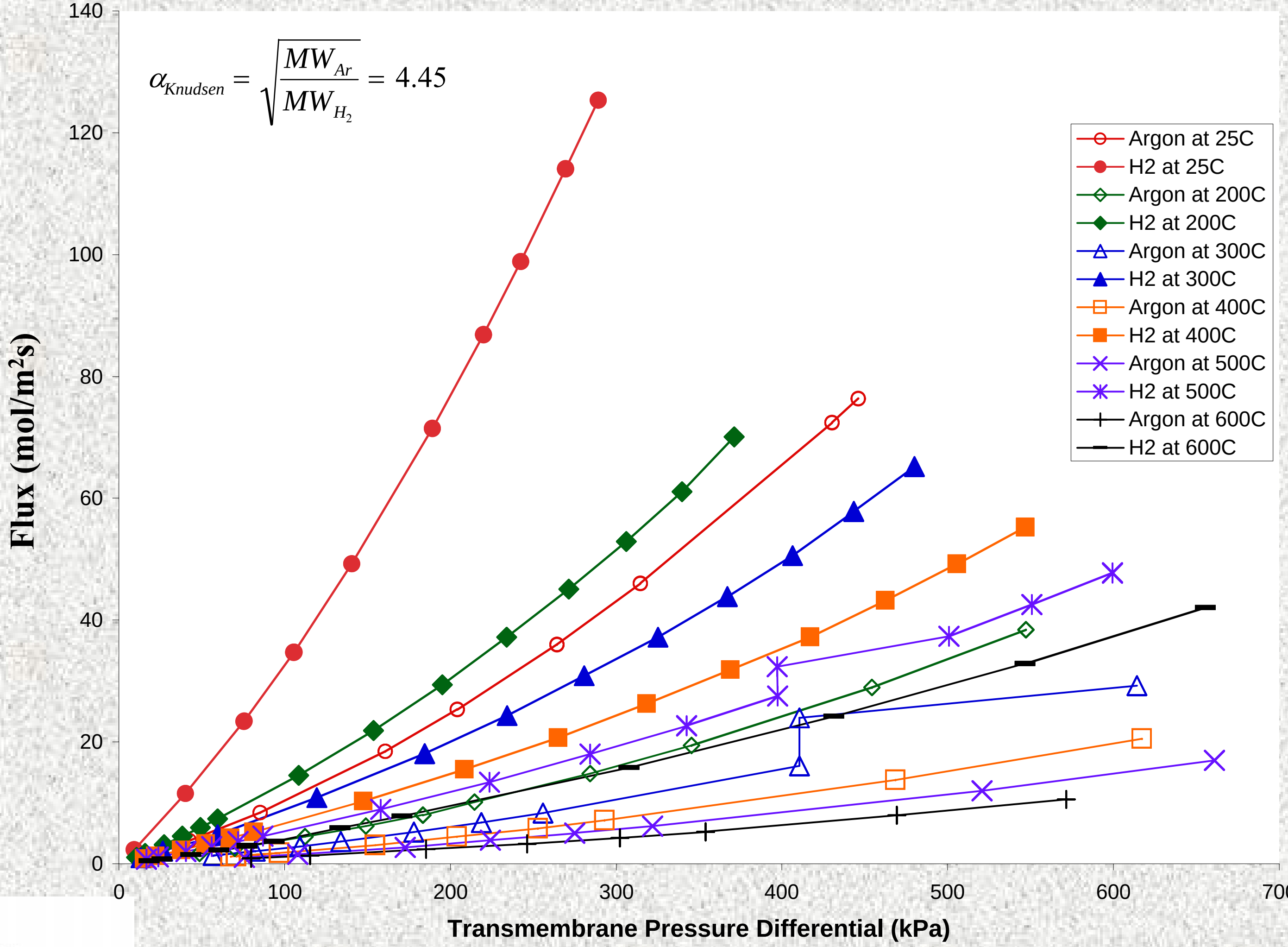



# Membrane characterization

- Top view of porous Fe-16Al-2Cr membrane
- Optical profilometry
  - WYKO NT2000 Profiler
  - Vertical scanning interferometry
  - $R_a = 1.51\ \mu m$
- Surface roughness is a key parameter for depositing a thin, defect-free Pd film

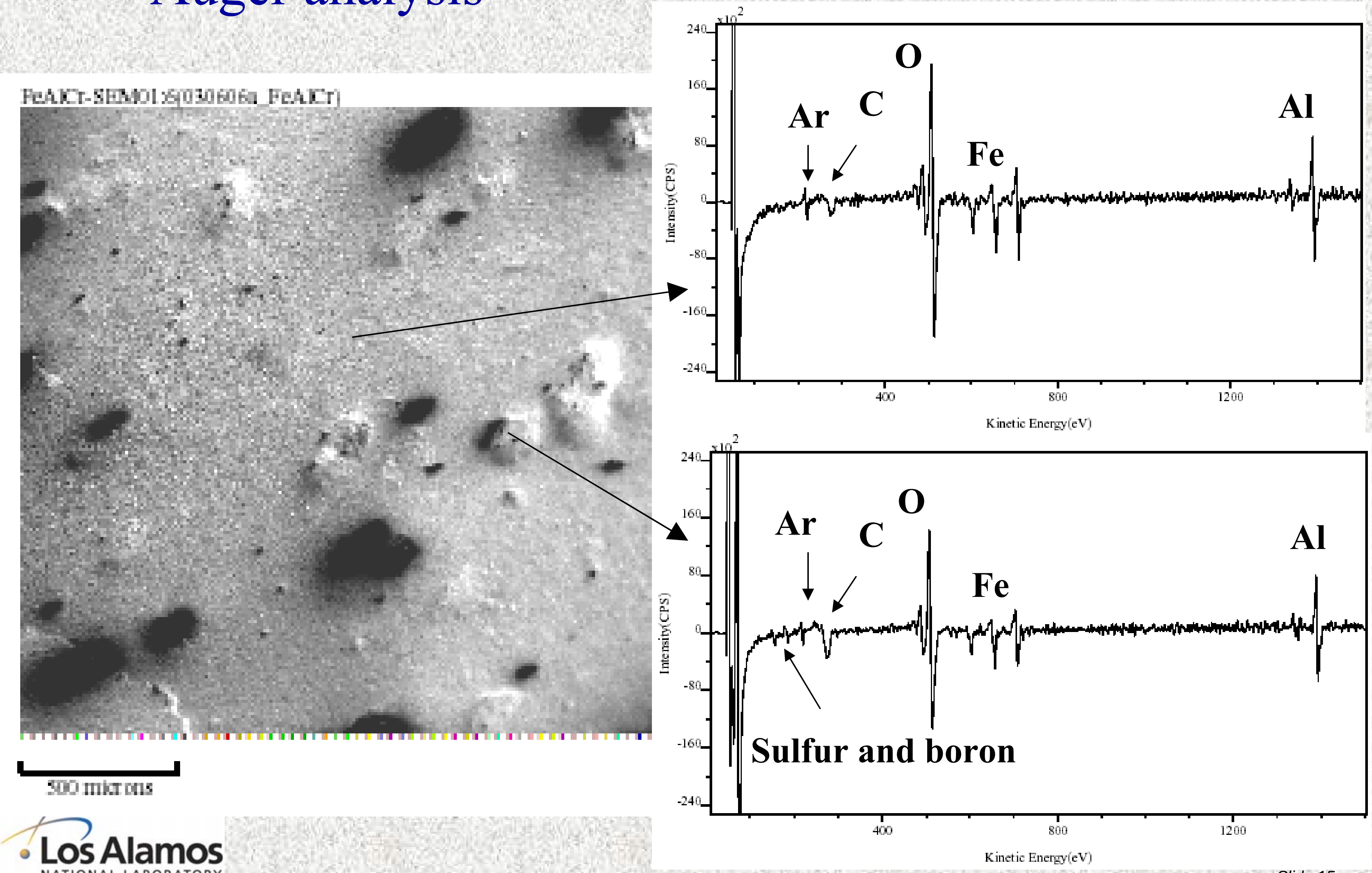


# $H_2$ and Ar Flowrates through Fe-16Al-2Cr (< 3-μm Particle) Membrane at 350°C and ΔP = 0-35 psia




Los Alamos NATIONAL LABORATORY EST. 1943

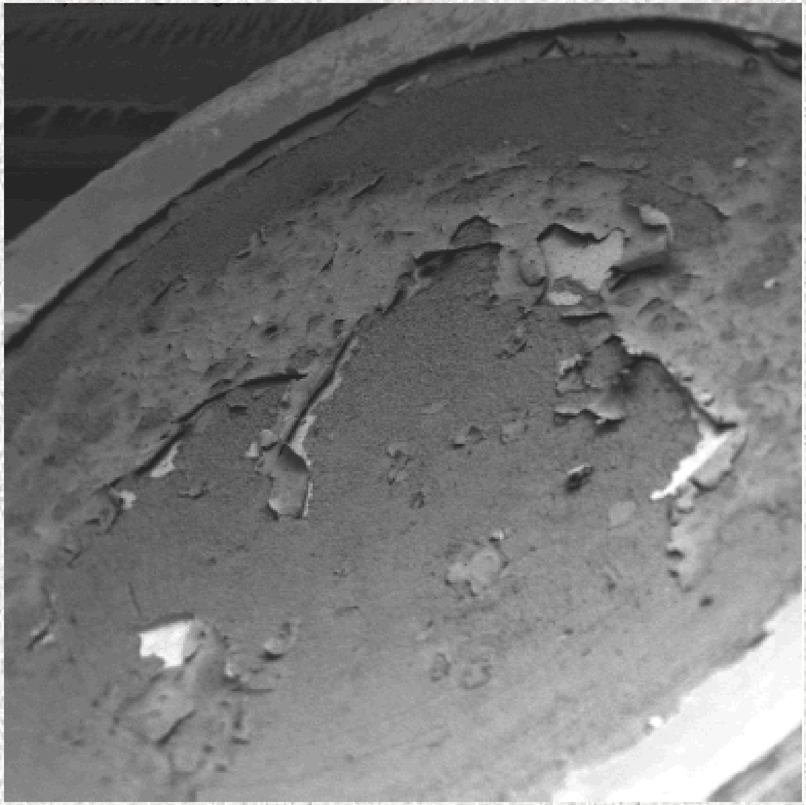
# Auger analysis



# *Results of XPS analysis of Fe-16Al-2Cr surface, heat-treated at 800°C for 24 h in UHP Ar*

| Element | Atomic % |
|---|---|
| carbon | 25 |
| nitrogen | 6 |
| oxygen | 29 |
| aluminum | 36 |
| chrome | 1 |
| iron | 3 |

# *Results of XPS analysis of Pd/Fe-16Al-2Cr surface, heat-treated at 500°C for 100 h under vacuum*



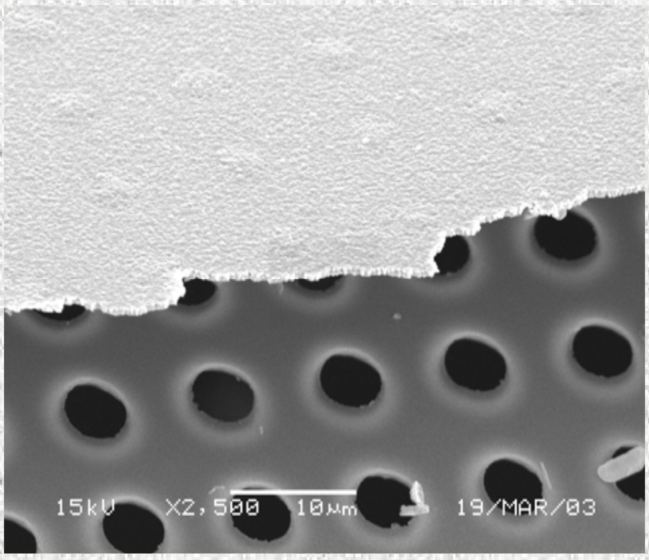
Bare region

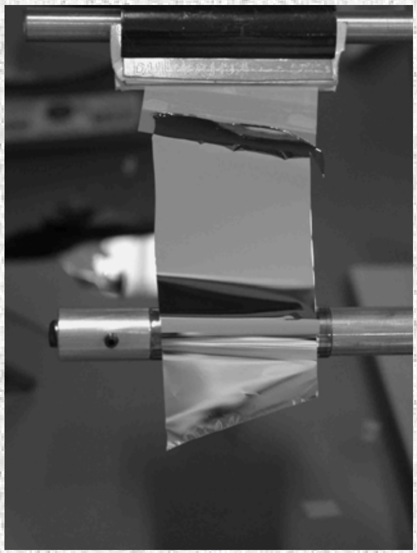
| Element | Atomic % |
|---|---|
| oxygen | 51 |
| carbon | 21 |
| sodium | 1 |
| iron | 26 |
| palladium | 1 |

Palladium

| Element | Atomic % |
|---|---|
| oxygen | 56 |
| carbon | 23 |
| sodium | 0.5 |
| iron | 6 |
| palladium | 14 |

# Typical composite membrane configurations



- Pd-Ag film supported by a micromachined membrane
  - H.D. Tong et al. *Thin Solid Films* **479** (2005) 89.
- Bundle of 0.8 m long (14-mm diameter) Pd-Ag coated tubes
  - P.P.A.C. Pex et al. *Proc. Int. Conf. Inorg. Membr.* (2004).
- Thin Pd-Ag foil prepared by PVD, supported on porous SS
  - H. Klette et al. *Membrane Technology* **5** (2005) 7.

# Summary & conclusions

- A porous membrane support was prepared from < 3-µm Fe-16Al-2Cr particles
  - optical profilometry showed a fairly smooth surface
  - heat treatment produced an alumina surface
  - Membrane has high porosity, minimal flux resistance

# Present work

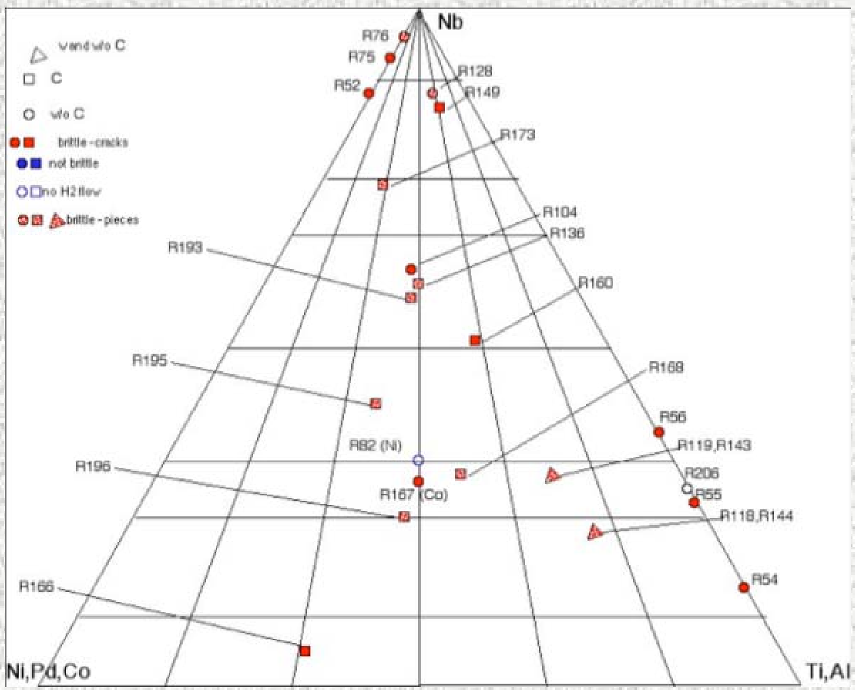
- deposit a defect-free, gas-tight palladium film onto the porous iron aluminide membrane
  - optimize the formation of an alumina layer
  - determine layer effectiveness at preventing metallic interdiffusion

# Membrane testing

- Coated foil cut into 1.9 cm diameter discs
- disc sealed into testing module between two VCR gaskets
  - upstream side purged with argon during heating
  - downstream side evacuated continuously


0.37-mm thick V-6Ni-5Co (at%) membrane (coated with 100 nm Pd per side) after testing at 450°C for 170 h.

# Investigation of Nb alloys

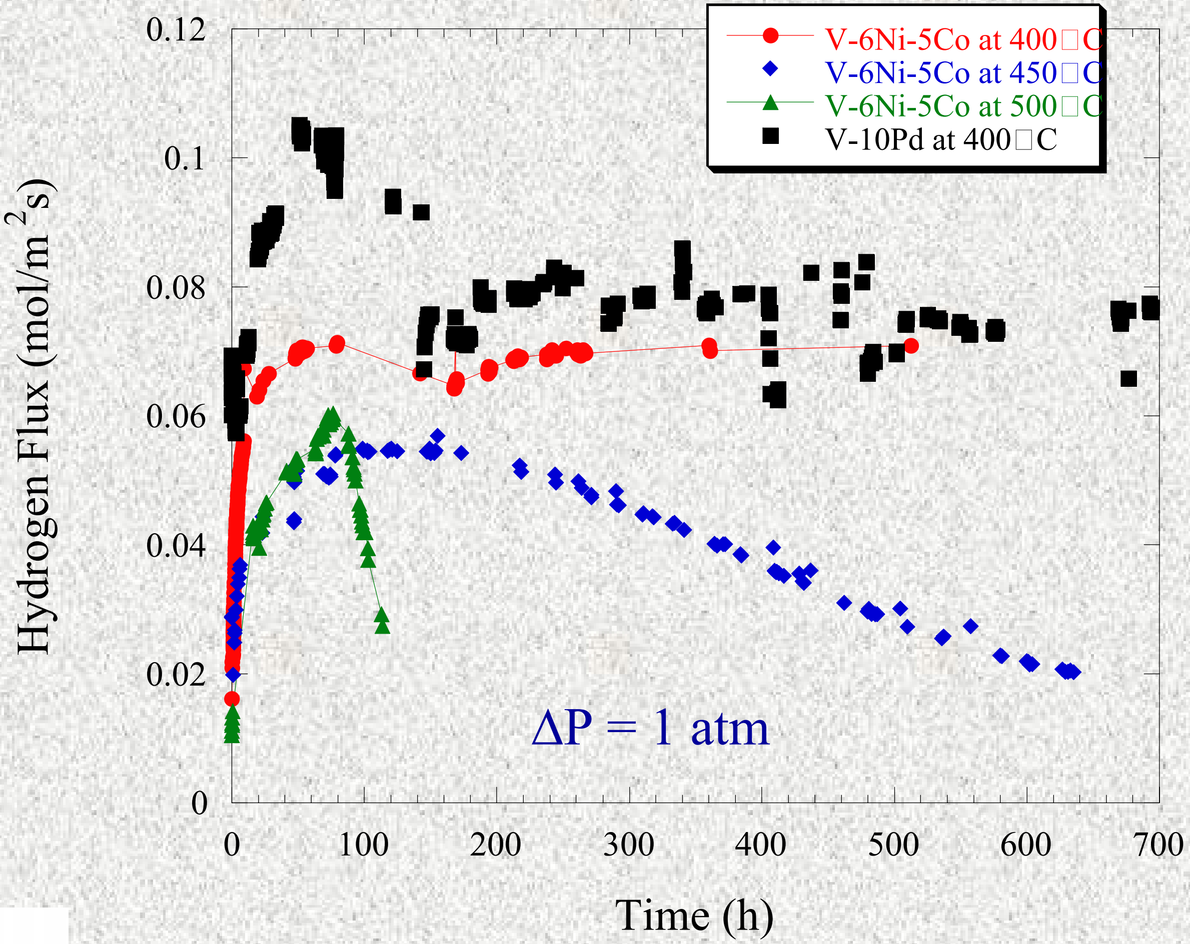



- Nb alloyed with Al, Cu, Mo, Ni, Pd, Ru, Ti, Zr
- Almost all alloys were either:
  - brittle as-cast
  - embrittled when exposed to hydrogen
- Exceptions: :
  - $H_2$ permeable Nb-50Cu
  - Nb-29Ni-24Ti (equimolar)
  - Nb-1Zr

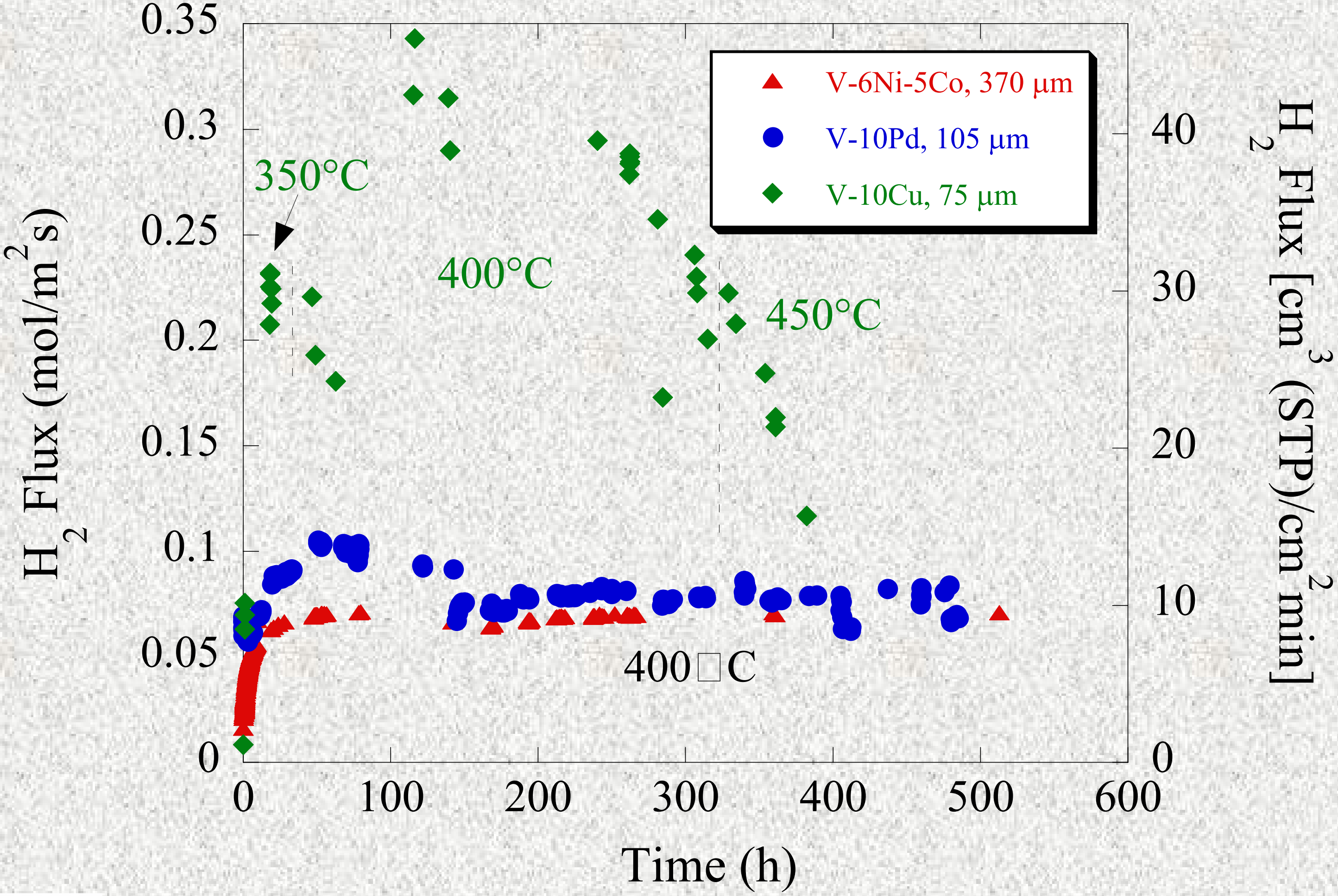
# Evaluation of some niobium alloys

- **Brittle As-Cast**
  - Nb-14Ru
  - Nb-25.6Mo
  - Nb-15Cu
  - Nb10Pd-5Cu
  - Nb-10Ru-10Rh
  - Nb-8Pd
  - Nb-5Pd
  - Nb-15Pd
  - Nb-8Ru
  - Nb-7.7Ru-7.7Pd
  - Nb-5.9Ru-5.9Pd
  - Nb-71Ru-11Ni-12Ti
  - Nb-6Ru-6Pd-0.3C
  - Nb-5Ru-5Pd-9Ti-0.3C
  - Nb-6Pd-12Ni-12Ti
  - Nb-5Pd-5Ti
  - Nb-5Pd-5Ti-0.3C
  - Nb-6Pd-12Ni-12Ti-0.3C
  - Nb-6Pd-11Ni-20Ti-0.2C
  - Nb-6Pd-10Ni-20Ti-0.2C
  - Nb-4Pd-4Ti-9Co-0.3C
  - Nb-4Pd-12Ti-8Ni-8Co-0.2C
  - Nb-5Pd-25Ni-16Ti-0.2C
  - Nb-40Ti-9Al-17Ni
  - Nb-32Ti-4Al-17Ni-0.3C
  - Nb-37Ti-9Al-17Ni-0.3C
  - Nb-25Ti-3Al-25Ni-0.2C
  - Nb-21Ti-3Al-38Ni-0.2C
  - Nb-5Ru-5Pd-9Ni-8Ti-0.3C
  - Nb-32Co-26Ti
  - Nb-26Co-21Ti-17V
- **Embrittled in hydrogen**
  - Nb-9Mo
  - Nb-44Ti-10.7Al
  - Nb-38.3Ti-5.2Al
- **Not brittle**
  - Nb-50Cu
  - Nb-29Ni-24Ti (equimolar)
  - Nb-1Zr

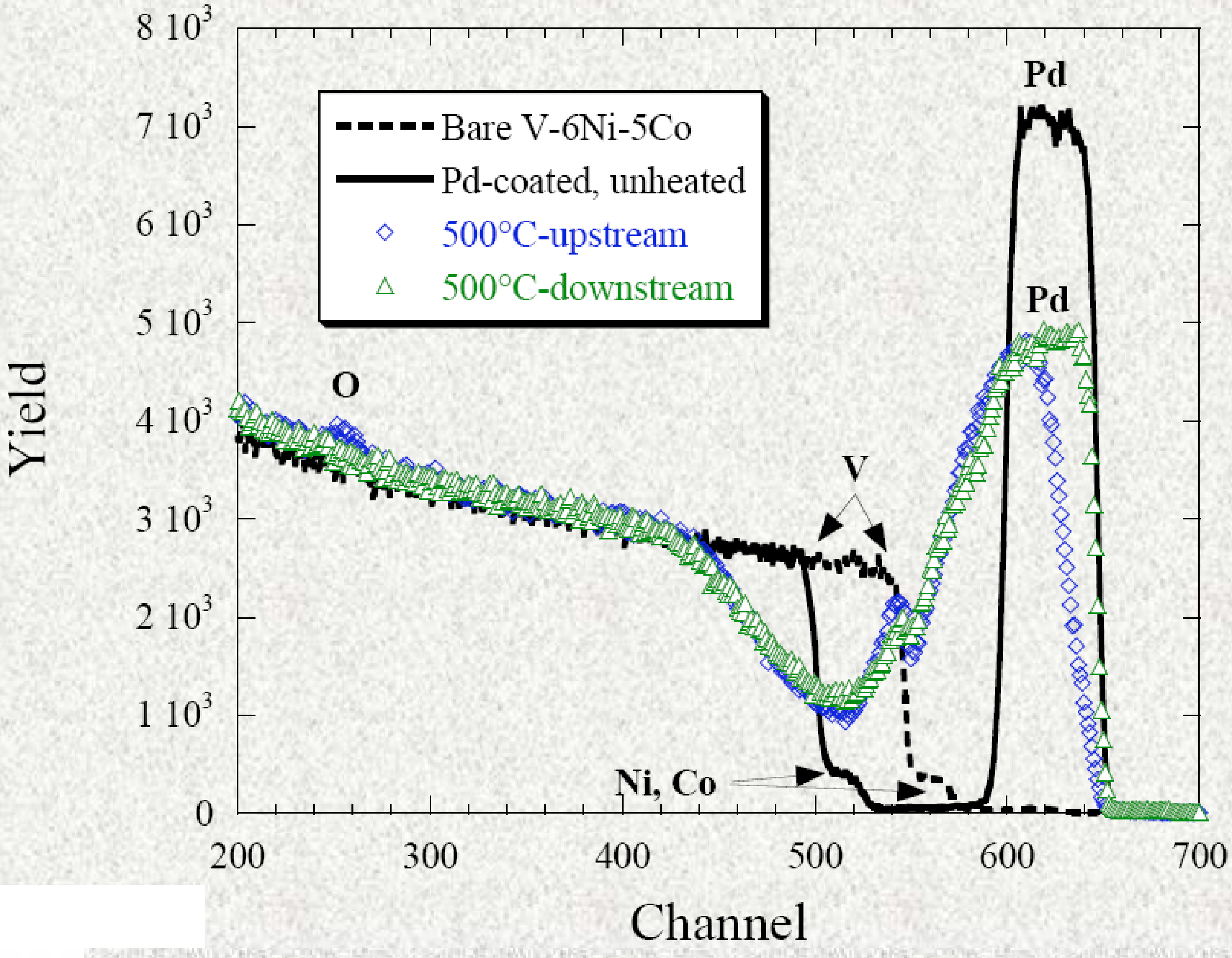
# $H_2$ Flux at 400, 450, or 500ºC Through 0.37-mm-thick V–6Ni-5Co and 0.1-mm-thick V-10Pd (at.%) Foils



# $H_2$ flux through V-10Cu, V-10Pd and V-6Ni-5Co membranes (100 nm Pd per side) at 350-450ºC and ΔP = 101 kPa



# RBS spectra of V-6Ni-5Co membranes



# Durability studies: Hydrogen embrittlement

| Membrane Composition (wt.%) | Failure Temperature (°C) | Failure Pressure ΔP (psia) |
|---|---|---|
| V-15Cu | 350 | 44 |
| V-5Ti | 322 | 15 |
| V-18Pd | 150 | 16 |
| Pd-23Ag | < r.t. | NA |

# DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Targets for Dense Metallic Membranes

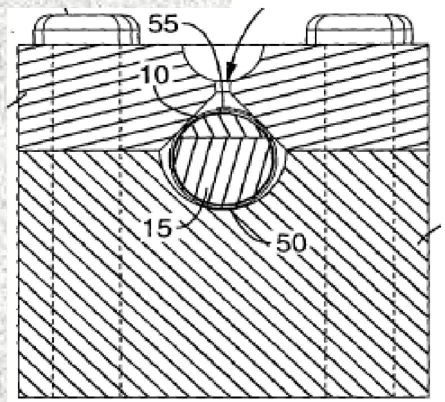
| Performance Criteria | 2010 Target | This work |
|---|---|---|
| Flux @ 400ºC, 20 psi ΔP $H_2$ partial pressure & >15 psia permeate side pressure | 250 scfh/$ft^2$ | 58 scfh/$ft^2$ (ΔP = 44 psi, vacuum on permeate)* |
| Module cost (including membrane material) | \$1000/$ft^2$ | < \$2/$ft^2$ (membrane only) |
| Durability | 26,280 h | > 1400 h |
| Operating Capability | 400 psi | > 100 psi |
| Hydrogen Recovery | > 80% | > 80% |
| Hydrogen Quality | 99.99% | > 99.99% |

*0.1-mm-thick V-10Pd membrane coated with 100 nm of Pd per side

Source: Multi-Year Research, Development and Demonstration Plan (2007)
http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf

# Joining Pd/V-alloy/Pd membranes

- *e*-beam welded along the seam into the shape of a tube
  - patented fixture/process
  - 75-µm thick foil
  - brazed to standard SS VCR fittings
- Very thin Pd coating
  - 1000 Å on both sides



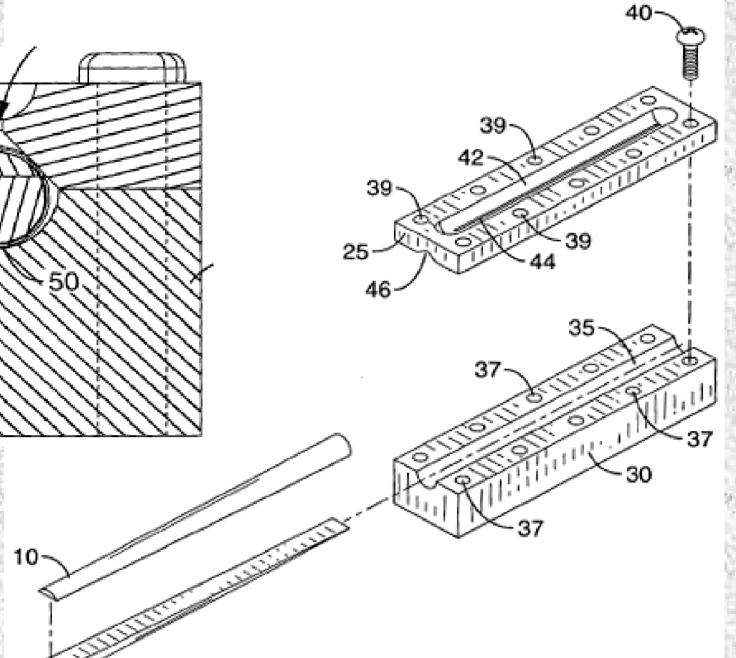



FIG. 9

# Summary & conclusions

- numerous niobium and some vanadium-based alloys were tested for hydrogen permeability and durability
  - most Nb alloys embrittled
  - $H_2$ flux through V-6Ni-5Co and V-10Pd membranes was stable at higher temperatures than V-Cu
  - hydrogen flux constant at 400°C for > 1400 h (V-10Pd)
  - V-10Pd survived thermal cycling to 200°C in hydrogen but cracked at 150°C: embrittlement still needs to be reduced

# Present work

- investigate other Group V alloys with palladium alloy surface coatings
  - test hydrogen flux stability and impurity resistance of membrane materials/coatings
  - durability tests: thermal cycling in hydrogen
- joining methods and module development

# Acknowledgments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- Ames Laboratory Material Preparation Center
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- John Moya, Stan Bennett, Stephen Cole, Jerry Schobert, & Richard Basinger – experimental setup
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