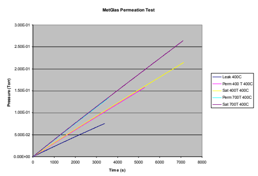
SRNL Membrane Research



SRNL™

SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

Thad Adams, Paul Korinko, Marie Kane
Savannah River National Laboratory
Aiken, SC

PURIWG
Nov. 7, 2007

Membrane Separation Technology and Economic Needs

- Low cost separation technology
- Lower cost capital investment than Pd
- Efficient removal of impurities
  - CO, CO_2, N_2 CH_4, H_2O, S, and ash & tar
  - Purity dependant on end use
    - 99-99.99%
  - Multiple stages optional
    - Adds cost

SRNL™

Cost Factors—Distributed Steam-Methane Reformer Natural Gas at 1500 kg H_2/day

Cost Factor	2005	2010 Target for $1.50/Kg H_2	% Change from 2005
Capital Costs ($MM)	$3.2	$1.4	-56%
Non-Feedstock O&M Costs ($/kg)	$0.80	$0.48	-40%
Energy Efficiency (%)	65%	75%	+16%

SRNL

Report of the DOE Workshop on Hydrogen Separations and Purifications, Sept. 2004

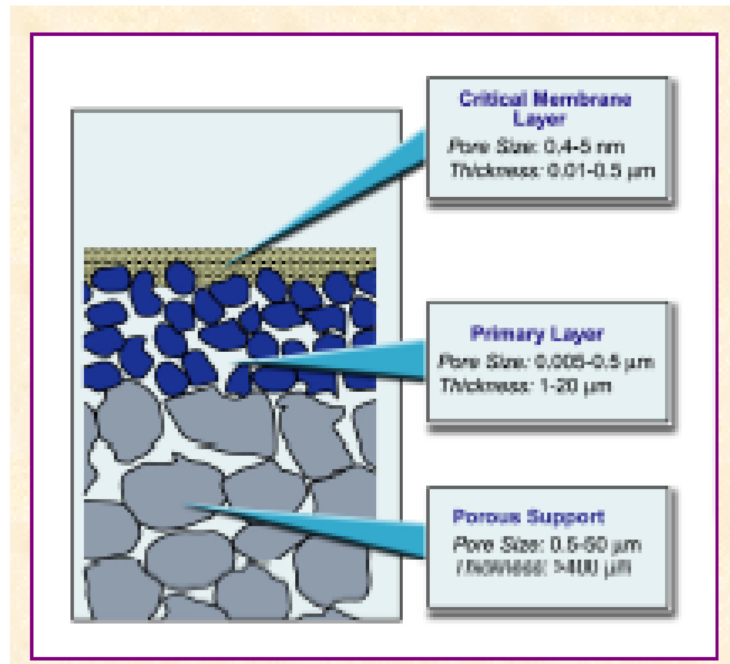
Membrane Technologies Required

- High flux
- Low pressure drop
- High contaminant tolerance
  - S, CO, solids, etc.
- Low cost
- Moderate operating temperature
  - 250 – 600^{o}C
- Types of membrane separation
  - Molecular
  - Atomic
  - Ionic
- Manufacturability
  - Joining
  - Design
  - Heating

SRNL™

Molecular Membranes

- Porous media
  - Physical size separation
    - $\Phi_{H2} = 2.89$ Å
  - Small pore ceramics, metals, etc. $\Phi_{Holes} = 10$ Å
    - Zeolites, SiC, SiO_2, Al_2O_3, metals
  - Mean free path dependant
  - Flux α P_{H2}
  - 99% purity achievable



Oak Ridge National Laboratory

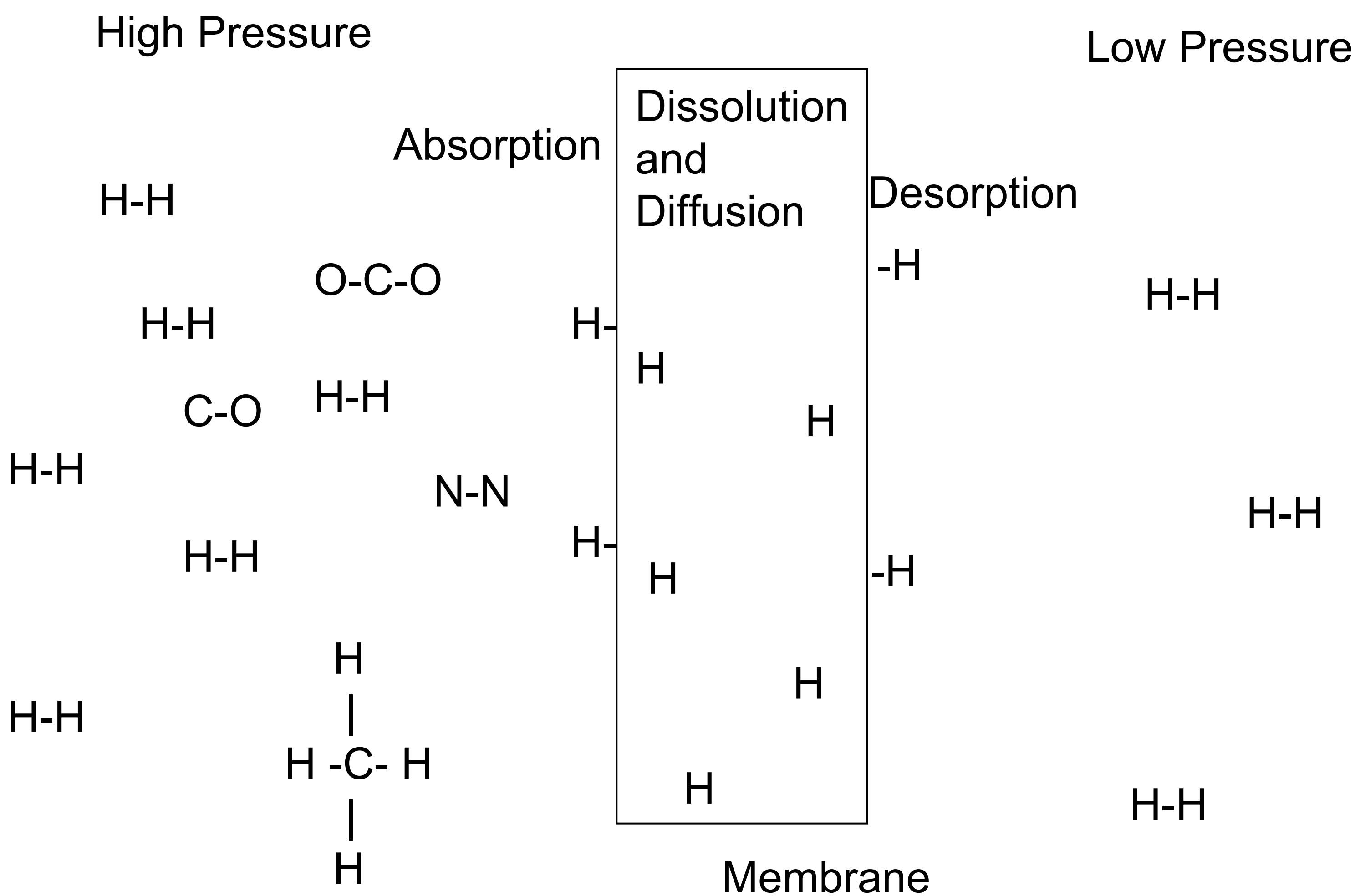
Atomic Membranes

- Dense metallic membrane
  - Thin metal sheets / tubes
    - Active surfaces
      - Dissociates H_2
      - H diffuses
      - H recombines to H_{2+}
    - May need supports
      - Porous metals
  - May be poisoned
    - CO, S, etc

- Dense metallic membrane (cont)
  - Not thermally stable
    - High temp phase change
    - Low temp hydriding
    - No long range order possible
  - Flux $\alpha \sqrt{P_{H2}}$
  - High purity possible > 99.99%

SRNL

Metallic Membrane Hydrogen Purification



Proton Transport

- Protons and electrons transported separately
  - Single or dual phase materials
  - Mixed conductor materials
    - Ceramic oxides
    - High temp (>800^{o}C)
    - Flux currently lower than target
  - Cermet
    - Ceramic and metal composite
    - Higher electron flow and proton flow
    - May use separate membranes
    - Flux α fn(e^- & p^+ conductivities)
    - Flux α ℓn (P_{H2}, T)

SRNL™

H_2 Membrane Targets

Table 2. Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification					
Performance Criteria[a]	Units	Calendar Year			
		2003 Status[b]	2005 Target	2010 Target	2015 Target
Flux[c]	$scfh/ft^2$	60	100	200	300
Membrane Material and All Module Costs[d]	$\$/ft^2$ of membrane	$2,000	$1,500	$1,000	<$500
Durability	Years[e]	<1[f]	1	3	>5
ΔP Operating Capability[g]	psi	100	200	400	400-1,000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity[h]	% of total (dry) gas	>99.9	>99.9	>99.95	99.99%

SRNL

Report of the DOE Workshop on Hydrogen Separations and Purifications, Sept. 2004

H_2 Membrane Targets

Table 3. Technical Targets: Microporous Membranes for Hydrogen Separation and Purification					
Performance Criteria[a]	Units	2003 Status	2005 Target	2010[b] Target	2015[b] Target
Flux[c]	$scfh/ft^2$	100	100	200	300
Membrane Material and All Module Costs[d]	$\$/ft^2$ of membrane	\$450-\$600	\$400	\$200	<\$100
Durability	Years[e]	<1[f]	1	3	>5
ΔP Operating Capability[g]	psi	100	200	400	400-1000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity[h]	% of total (dry) gas	>90%	95%	99.5%	99.99%

SRNL

Report of the DOE Workshop on Hydrogen Separations and Purifications, Sept. 2004

SRNL Plan

- Investigate non-precious metal membrane materials
  - High H_2 solubility (S)
  - High H_2 diffusivity (D)
    - High Permeability ($\Phi = D*S$)
- Bulk amorphous metals
  - Bulk metallic glasses (BMG)
    - Commercially available
      - Low cost
  - Dense metallic membranes

SRNL

SRNL Plan Needs Addressed

- Durabiility
- Impurity
- Membrane defects
- H_2 selectivity
- Operating temperature
- Flux
- Testing and analysis
- Cost

SRNL

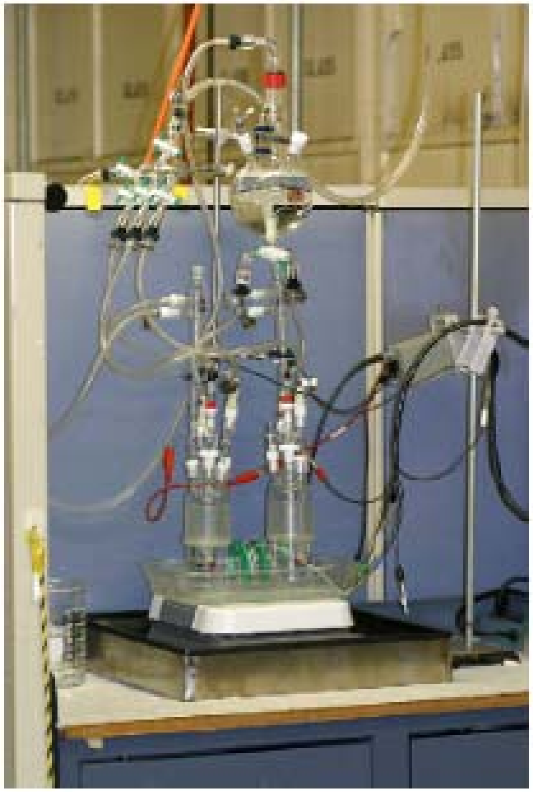
Membrane Design Targets

- Flux rate 250 scfh/ft^2 (76.2 m^3 / h / m^2)
- Module cost \$1000 / ft^2 (\$10840 / m^2)
- Durability 26,280 hours (3 years)
- Operating pressure 400 psi (27 atm)
- Recovery > 80% H_2
- H_2 quality 99.99%

SRNL™

FY06 Accomplishments

- Electrochemical cell H_2 testing
  - Test method ASTM G148
  - Materials tested
    - Four Metglass samples
  - Results
    - Breakthrough not detected after 8 hours
  - Technique verified using Pd
    - Breakthrough < 10 s at RT
  - Screening method only



SRNL

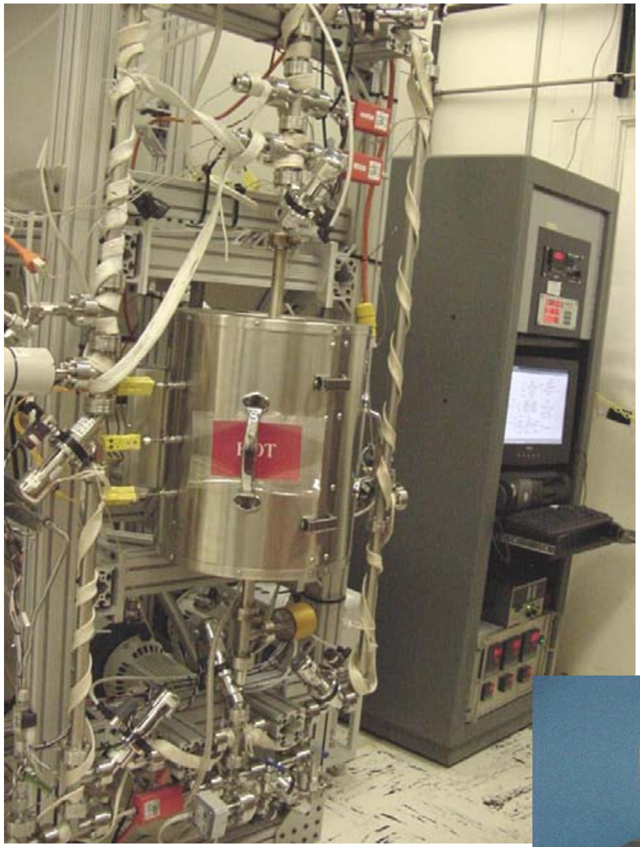
Experimental Equipment Gas Permeation

- Modular design
- Vacuum system
  - Dry scroll pumps
    - Edwards
  - Turbo-Molecular pump
  - 10^{-6} Torr capability
  - All metal seals
  - 10 solenoid controlled valves
  - Pressure control valve
  - Manual metering valve
  - Up to 1 atm pressure
- Instrumentation
  - 3 capacitance manometers
    - Multiple ranges
      - 4 decades each range
  - 5 Pirani gauges
    - 75 Torr - .75 mTorr
  - 2 ion gauges
    - Lower and upper chamber
  - 2 Mass Spectrometers
    - 2 - 48 AMU
    - 10 mTorr Max. operating P
- Tube Furnace
  - Custom three zone
    - Independent heating control
  - 1000^{o}C maximum
  - Screw drive mounting

SRNL

FY06 Accomplishments

- H_2 gaseous testing
  - Low pressure (P<760 Torr)
  - Temperature 300-400^{o}C
  - Mechanically sealed disks
- Permeation fluxes within two decades of Pd alloys



SRNL

Other SRNL Programs

- Tested V-Ni-Ti alloys as dense metallic membranes
  - Complex microstructure
  - Comparable H_2 permeability to Pd
  - Poor durability during cycle 250^{o}C to RT
    - Forms Hydride

SRNL™

Why Ni-Ti-Group 5A Alloys?

Pd/Pd-Alloy Membranes

•Pd and Pd-Alloys posses good solubility and diffusion characteristics
•Permeation through Pd is on the order of 10^{-9} - 10^{-8} mol H_2/m s $Pa^{1/2}$
•Embrittlement of Pd limits longevity, Pd-alloys (Cu,Ag) Reduce Susceptibility to Poisoning and Embrittlement
•Pd/Pd-Alloys High Cost

Alternatives to Pd/Pd Alloys Membranes

•Pd-Coated Porous Ceramics
- *•Pin-holes/Holidays Create Short Circuit Pathways*

•LANL Investigating V and V-alloys
•Japanese Investigating V-Al and V-Ni
- *•V has high solubility and diffusivity but suffers severely from embrittlement*
- *•Attempts at Alloying V have not made significant decrease in embrittlement susceptibility*

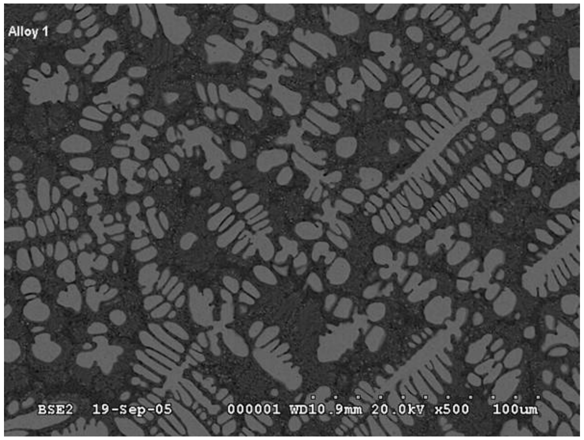
•Group 5A-Ti-Ni Alloys
- ***•Ni-Ti alloys have been researched for decades due to their shape memory properties***
- ***•NI-Ti Alloys are susceptible to H_2 Embrittlement and Do Not Posses High Permeability***
- ***•Additions of Group 5A Metals (Nb, V, and Ta)***
- ***•Nb Additions have produced high permeation and good resistance to embrittlement***
- ***•Duplex Structure—$Ni_4Ti_{13}Nb_{83}$ and Eutectic***

•Further Work to Optimize Volume Fraction of $Ni_4Ti_{13}Nb_{83}$ (high diffusivity phase)
•Explore Other Group 5A Additions—i.e., V to promote $Ni_x Ti_y V_{(1-x+y)}$ Phase

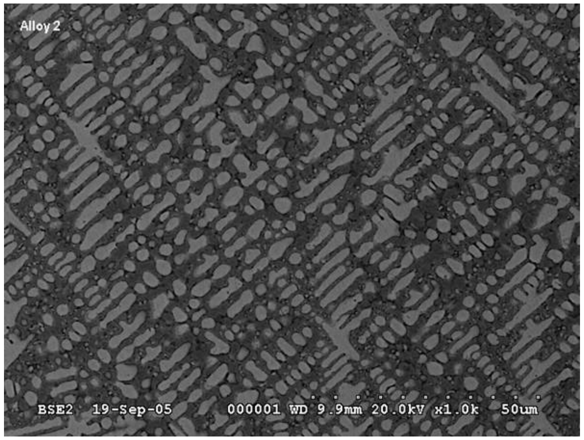
SRNL

Results

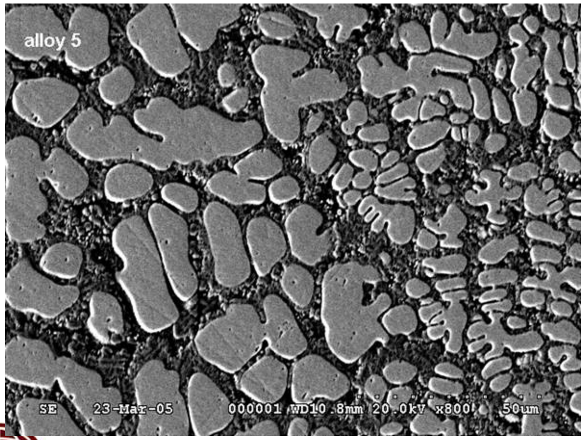
Scanning Electron Microscopy



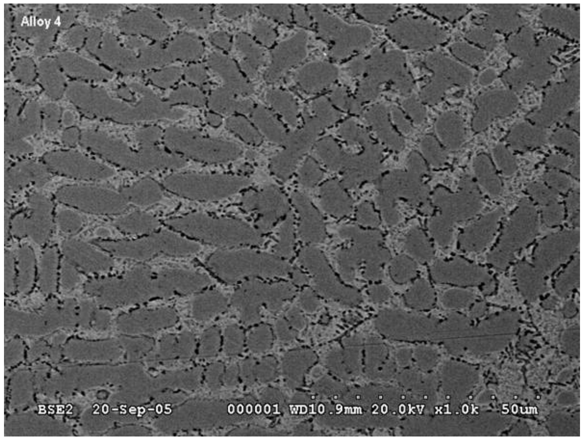
Nb51-Ti28-Ni21



Nb48-Ti28-Ni24



Nb54-Ti28-Ni18



V51-Ti28-Ni21

SRNL

Electrolytic Permeation Results

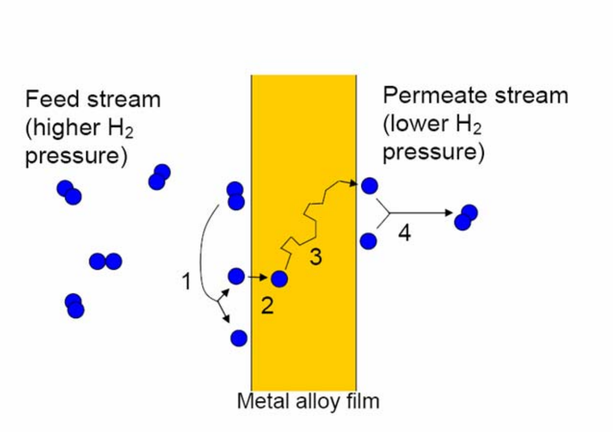
Material	Permeation Rate (mol H_2/m s)
Palladium	$3.26\text{-}4.25 \times 10^{-10}$
Nb48 Alloy	$6.58 \times 10^{-11} - 1.65 \times 10^{-10}$
Nb51 Alloy	$2.96 \times 10^{-10} - 6.0 \times 10^{-9}$
Nb54 Alloy	3.25×10^{-10}
V51 Alloy	$1.0 - 3.7 \times 10^{-9}$

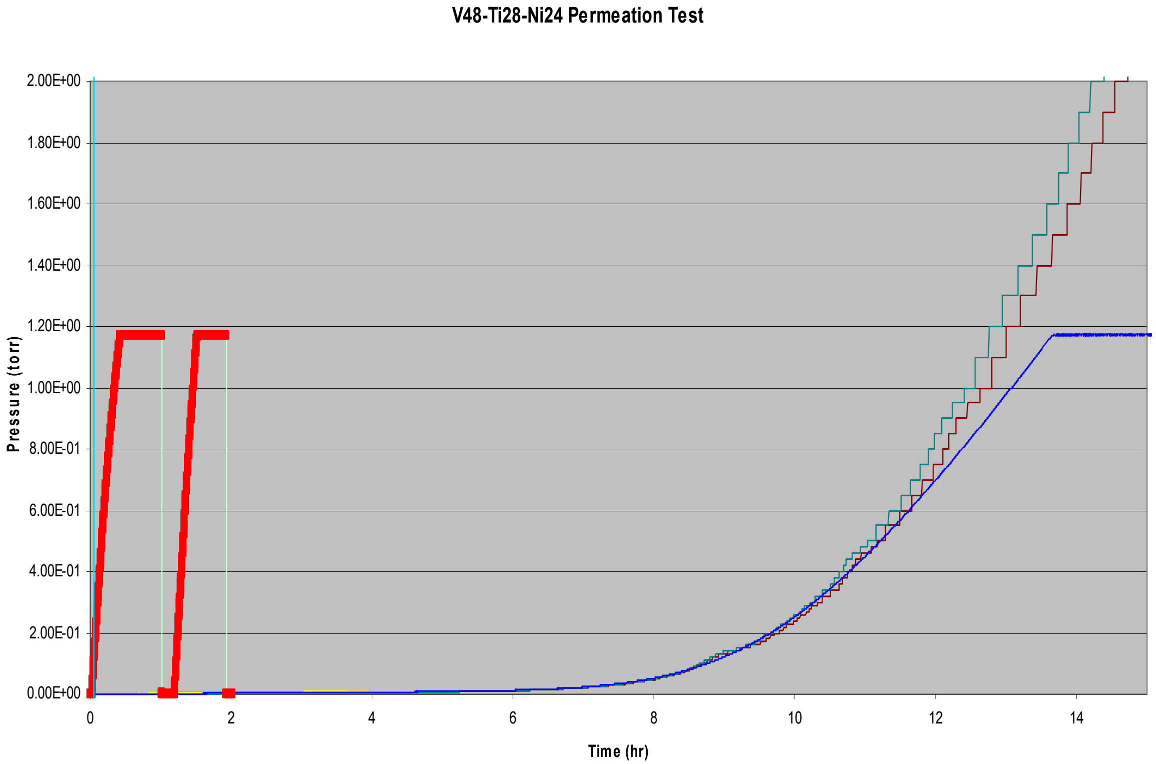
SRNL™

Results—V48-Ti28-Ni24 Alloy

Test Conditions

- Temperature: 400°C
- H2 Pressure: 700T
- Thickness: 0.089cm (0.035in)
- SA:≅ 5 cm^2



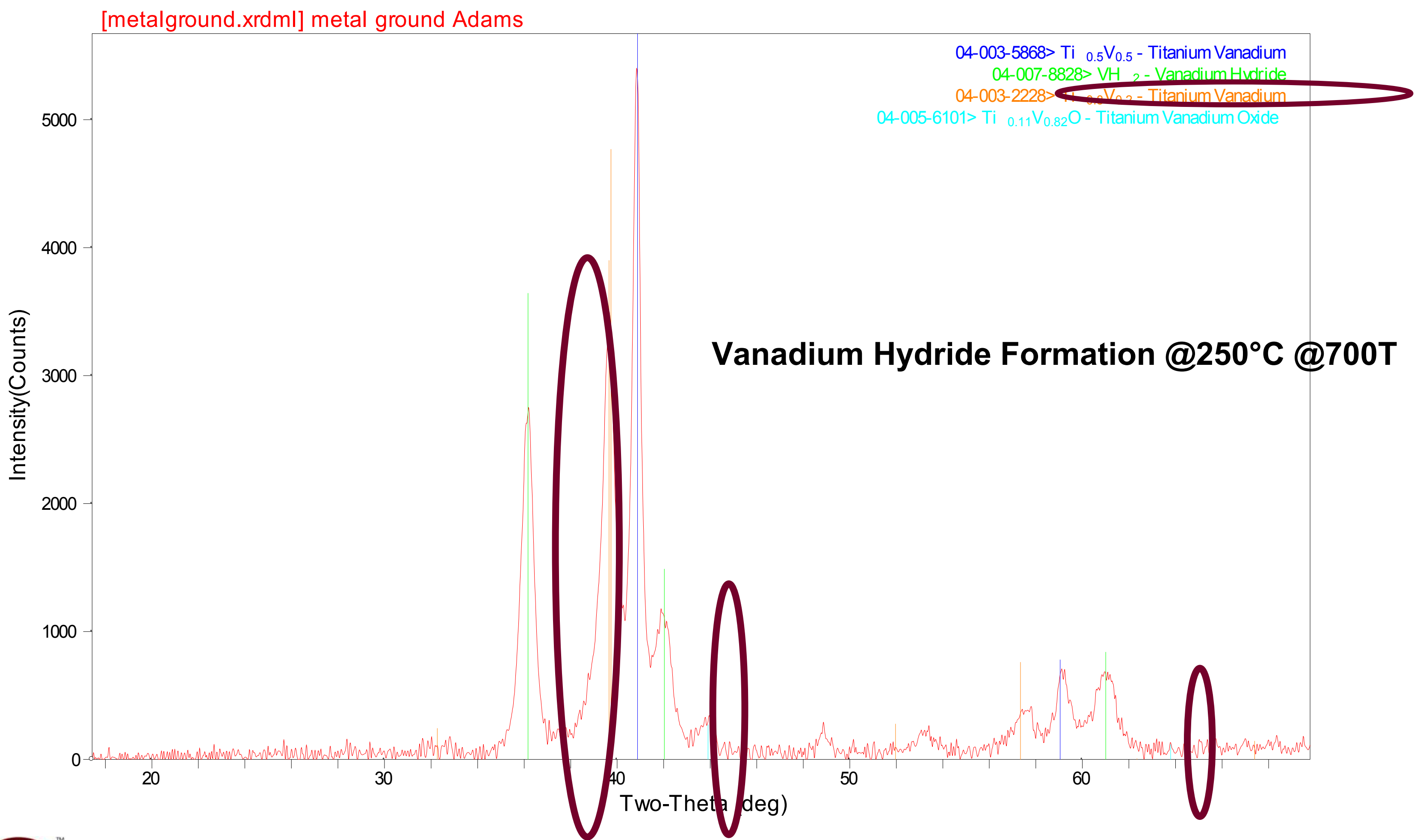


Determine Permeability at Steady-State

- Slope of Saturation Data= Torr/hr—convert to mols H_2/min
- Flux (J)= K/l ($P_{feed}^{1/2}$)
- Flux (J)= (Sat Slope (mols H_2/min)/Area Permeating (m^2)) = mols H_2/min m^2
- l=m and P_{feed}=Pascals and Solve for K=Permeability (mols H_2/m s Pa$^{1/2}$)
- For V48-Ti28-Ni24 Permeability = 1.0 x 10^{-9} mols H_2/m s Pa$^{1/2}$

SRNL

Results—V48-Ti28-Ni24 Alloy



SRNL

FY07 Tasks

- Test low cost BMG
  - Zr-Cu-Ni-Al-Y
  - Fe and Co based MetGlass
  - H_2 permeability
    - ASTM G148-97 Electrochemical Method
    - Gas permeation
- Develop sealing technology
  - Mechanical
  - Soldering
  - Welding

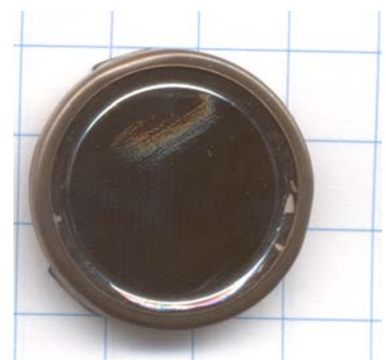
SRNL

FY07 Accomplishments MetGlass Samples

- **Mechanical Sealing**
  - Leak rates lower than 10^{-7} sccm He / s
  - VCR type fitting

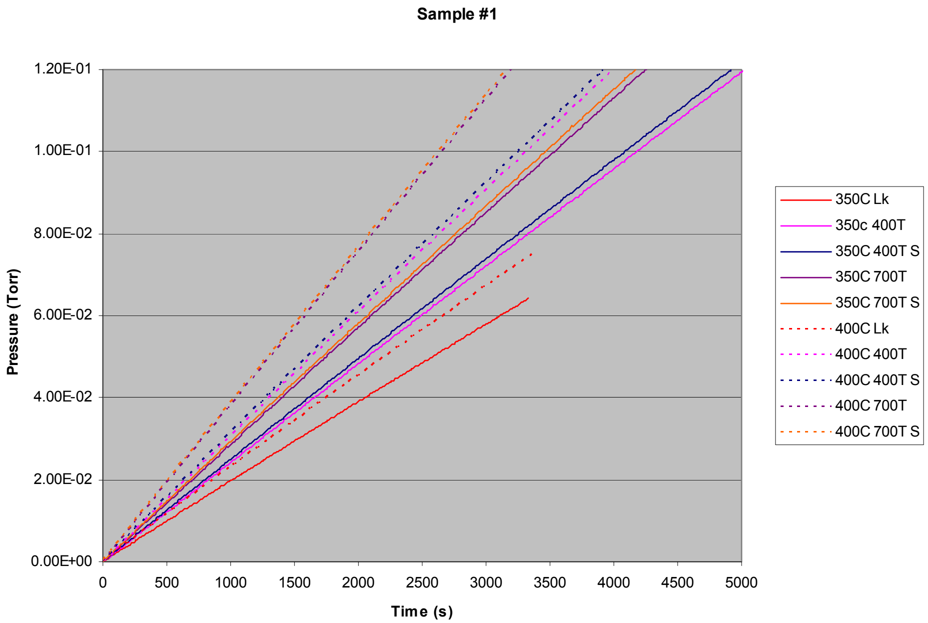
Alloy	Tests	Number successful	
1	6	3	
2	4	3	damaged 1 membrane
3	4	4	
4	4	1	1 damaged

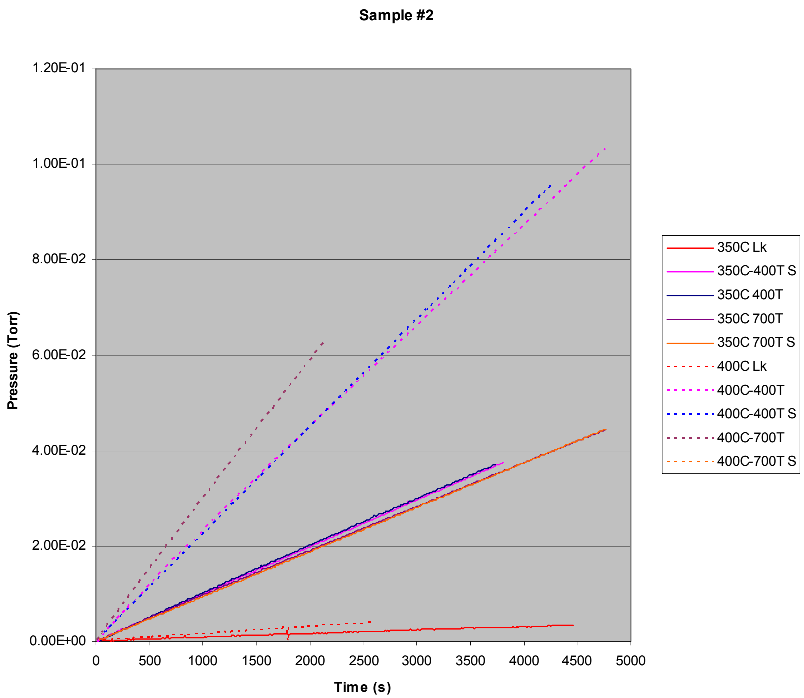
  - Small sample diameter
  - Sample thickness may experience cutting



SRNL™

BMG Raw Results





SRNL™

FY07 Accomplishments

- Brazing / Soldering
  - Methods
    - Induction in Ar
    - Vacuum furnace
  - Issues
    - Devitrification temperature below common braze alloys
    - Reactive alloys oxidize to inhibit wetting
    - Sample thickness may require backing plate

SRNL

MetGlass Membrane Cost

Alloy	1 kg price (As Cast)	mols/m²/s/$
2605S3A	$ 436	
2826MB3	$ 529	
2605SA1	$ 425	4.5×10^{-6}
2714A	$ 665	
Pd	$427,000	7.0×10^{-7}

- MetGlass requires 100 x surface area to achieve comparable throughput

SRNL

FY08 Plans

- Commercially available BMG testing
  - Test Met Glass materials
    - Moderate temperatures 300-400°C
    - Cycle temperature with H_2 pressure
      - Causes failure in Pd based materials
  - Desirable properties
    - High permeation reported
      - 1.13×10^{-8} mol/m/s/Pa$^{1/2}$
    - High elastic modulus
    - Good H_2 degradation resistance

SRNL™

FY08 Plans

- Pd coating on base materials
  - Inexpensive material
  - Surface activated
  - Contamination resistant
  - Acceptable mechanical properties
  - Not as susceptible to coating defects as Pd coated ceramics
    - Modifications in local flux not unmitigated flow of contaminants

SRNL

Summary

- SRNL is developing Pd free dense metallic membranes
- SRNL data indicate permeation rates and fluxes at similar orders of magnitude to Pd membranes
- Continued work is needed to bring materials, designs, and reactors to fruition