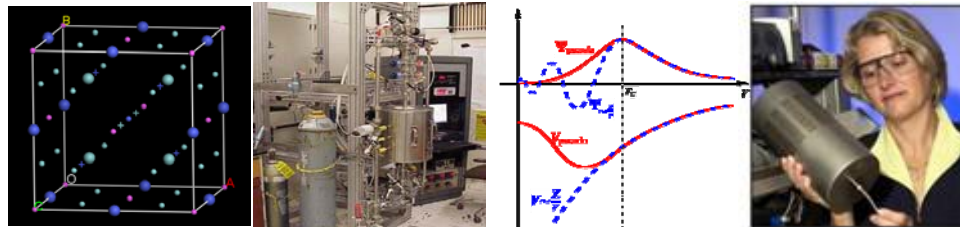


Composite Bulk Amorphous Hydrogen Purification Membranes

T. Adams, K. Brinkman, S. Garrison, & P. Korinko
Savannah River National Laboratory

May 19, 2009



Overview

Timeline

- **Start: 05/1/07**
- **End: 9/30/10**
- **Percent complete: 60%**

Budget

- **Funding received in FY08**
 - **\$200K**
- **Funding for FY09**
 - **\$0K**

Barriers Addressed

- **Reformer Capital Cost**
- **Operation and Maintenance**
- **Control and Safety**
- **Hydrogen Selectivity**

Partners

- **Howmet Research**
- **LiquidMetal Technologies**
- **MetGlas Inc.**

Relevance – 2010 DOE Technical Targets

Target	Units	2010
Flux	scfh/ft ²	200
Membrane Material and All Module Costs	\$/ft ² of membrane	1,000
Durability	years	3
Δ P Operating Capability	psi	400
Hydrogen Recovery	% of total gas	80
Hydrogen Purity	% of total (dry) gas	99.95

Hydrogen Delivery Targets for Dense Metallic Membranes

Relevance - Objectives

- Examine Novel Pd Free Membranes for Hydrogen Separation
 - Metallic Glass-multicomponent system comprised of species with varying atomic size, fast cooling rates to lock in amorphous structure
- Metallic glass materials offer the potential for excellent membrane function at a fraction of the cost of Pd based alloys (*cost estimates based on obtaining final micron level thicknesses of membrane material*)
 - 1 kg Pd= \$100,000
 - 1kg MetGlas=\$400
- Potential Challenge—Crystallization during operation at elevated temperature
- Quantify Hydrogen Permeation Properties of Commercially Available Metallic Glass Membranes
- Evaluate and Understand *Crystallization and Hydrogen Flux Behavior* in Metallic Glass Membranes
- **Integrate Permeation, Crystallization Behavior and Modeling Effort on Materials Chemistry to Guide Synthesis and Characterization of Novel MetGlass Materials for Hydrogen Separation**

Technology Summary and Approach - Flux Measurement

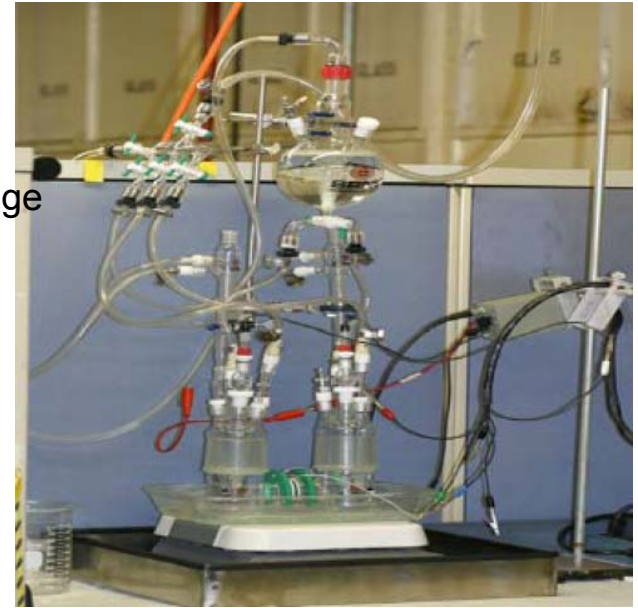
Gas Permeation Rig



- Advantage: High temperatures
In-situ experiments
- Disadvantage: hard to seal

Nernst Equation
Relation b/w pressure and voltage

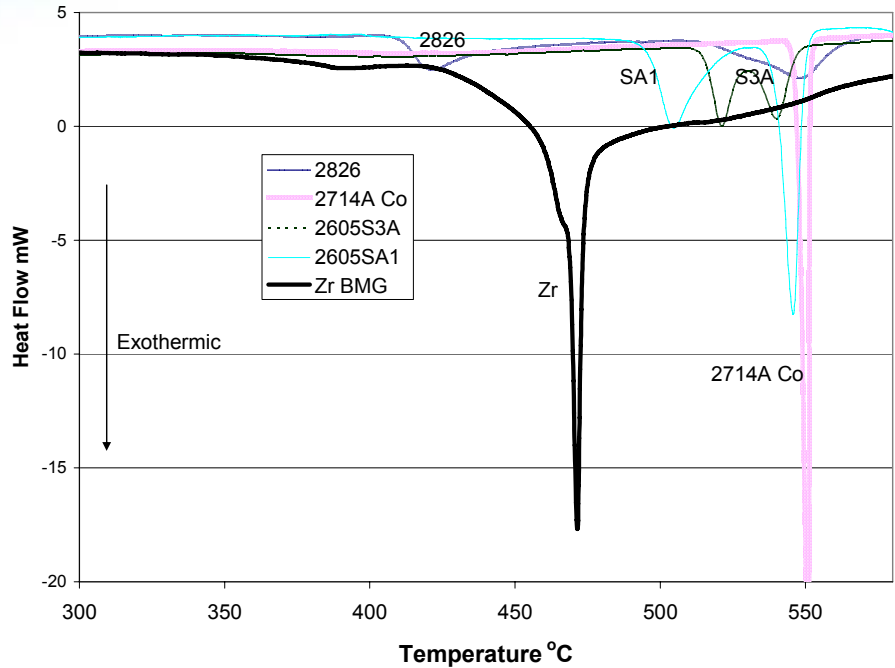
Electrochemical Permeation Cell



ASTM G148 Test Protocol

- Advantage: Facile sample loading
- Disadvantage: Limited to low temperatures

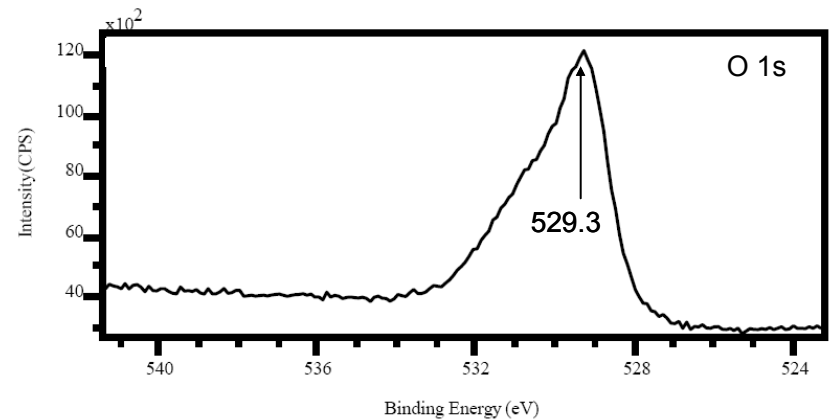
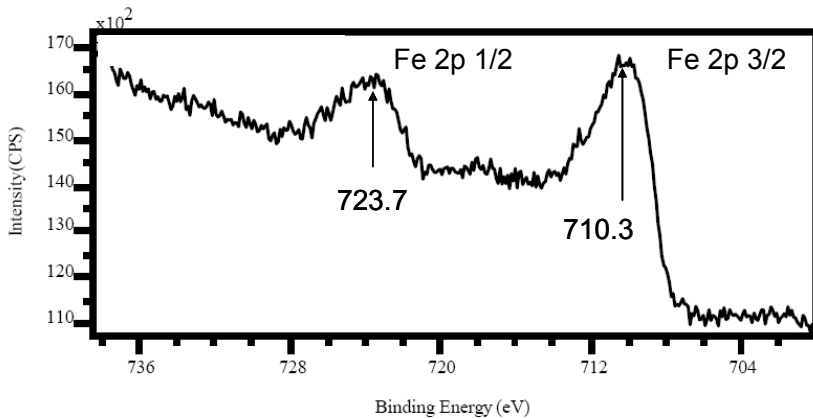
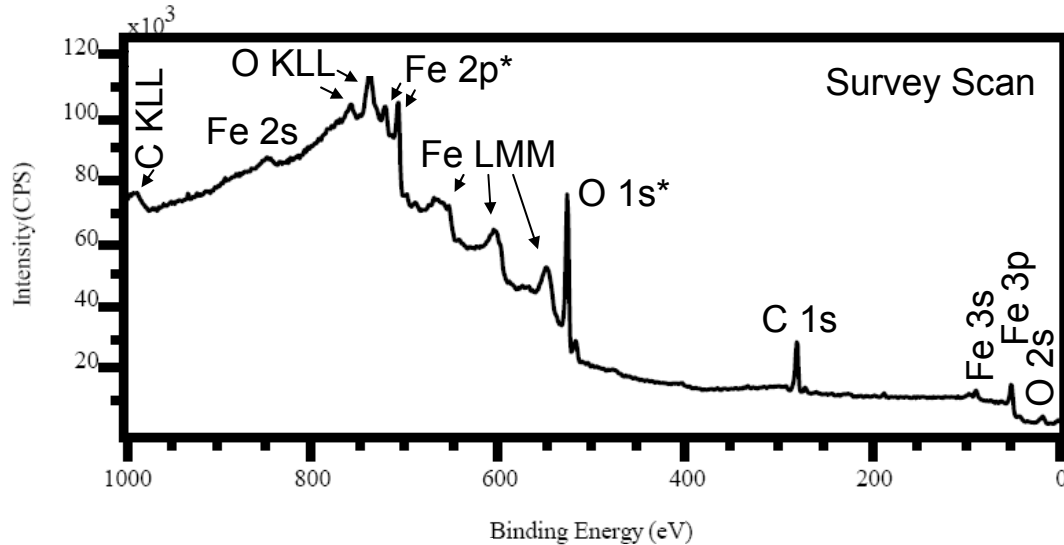
Structural Evolution: Crystalline State



Alloy	T ₁ cryst °C	Fe	B	Cr	Mo	Co	Ni	Si
2605S3A	521	85-95%	1-5%	1-5%	0%	0%	0%	1-5%
2714A	551	7-13%	1-5%	0%	0%	75-90%	1-5%	7-13%
2826	421	40-50	1-5%	0%	5-10%	0.3%	40-50%	0%
2605SA1	504	85-95%	1-5%	0%	0%	0.2%	0.2%	5-10%
Zr Alloy	471	<i>Proprietary</i>						

Differential Scanning Calorimetry MetGlass Samples 10°C/min ramp rate in Argon

XPS Surface Study: As-Received 2826 Alloy



X-ray Photoelectron Spectra (XPS) for surface of metallic glass. Elements identified are oxygen (O), carbon (C), and iron (Fe). Spectra were taken of the as received shiny side of the metallic glass using Mg $K\alpha$ ($h\nu = 1253.6$ eV) x-rays and corrected for charging using the C 1s adventitious carbon as 284.6 eV. Pass energy is 160 eV.

XPS Surface Study cont.: As Received 2826 Alloy

Material	Fe 2p 3/2	Fe 2p 1/2	O 1s	Ref.*
Fe	707	720	N/A	SSS, 4 (1997) 175.
Fe ₂ O ₃ /FeO	710.1	724	529.6	SSS, 4 (1998) 345.
gamma Fe ₂ O ₃	710.2	724.1	529.7	SSS, 4 (1998) 351.
Metallic Glass oxide	710.3	723.7	529.3	this work
alpha FeOOH	710.7	724.7	529.7	SSS, 4 (1998) 357.
Fe ₃ O ₄	711	723.8	530.3	SSS, 4 (1998) 266.

Material	O/Fe ratio
Fe	0
FeO	1
Fe ₃ O ₄	1.3
Metallic Glass oxide	1.4
Fe ₂ O ₃	1.5
FeOOH	2

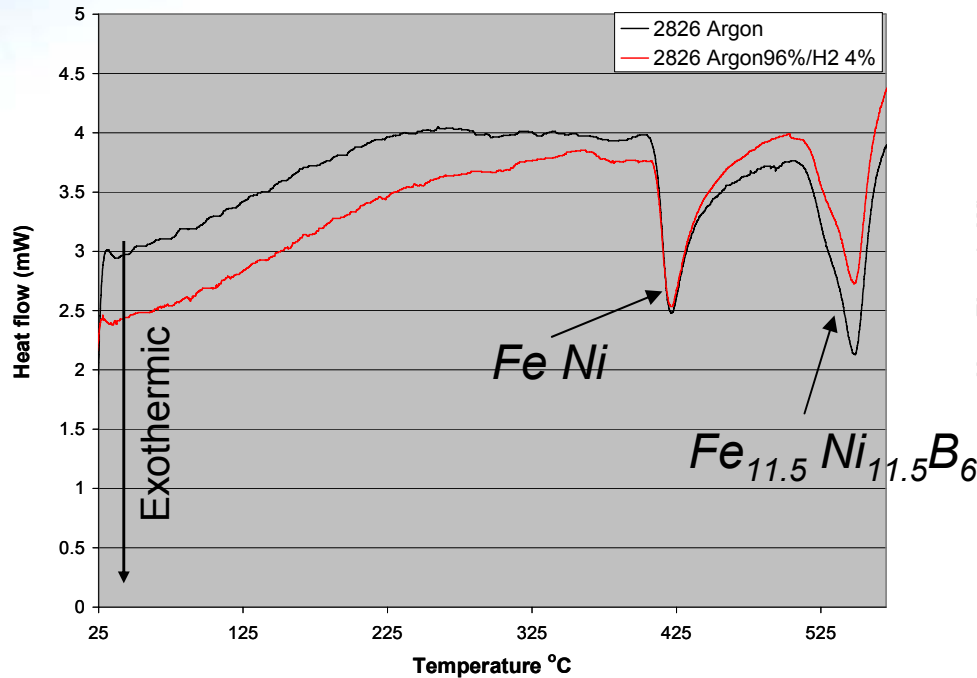
•Comparison of metallic glass surface oxide to candidate materials. Best matches are a thin film of Fe₂O₃ on FeO (Fe₂O₃/FeO)- which is simply Fe₂O₃, and gamma-Fe₂O₃- a form of Fe₂O₃.

•Comparison of O/Fe ratio of metallic glass surface oxide (with adsorbed water subtracted from the oxygen peak) to candidate materials. Fe₂O₃ and Fe₃O₄ are the closest matches.

At least 10 nm thick iron oxide Fe₂O₃ present on the surface metallic glass 2826

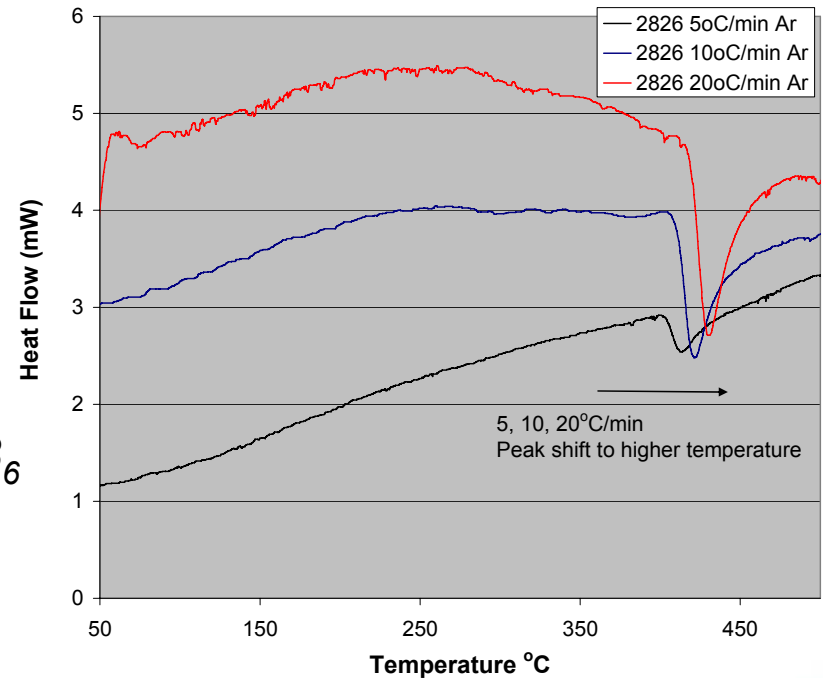
Crystallization: Kinetics and Gas Ambient Effects 2826 Alloy

2826 Ar vs. 4% H_2 /Ar



No Difference in crystallization temperature b/w Argon and 4% H_2 in Argon

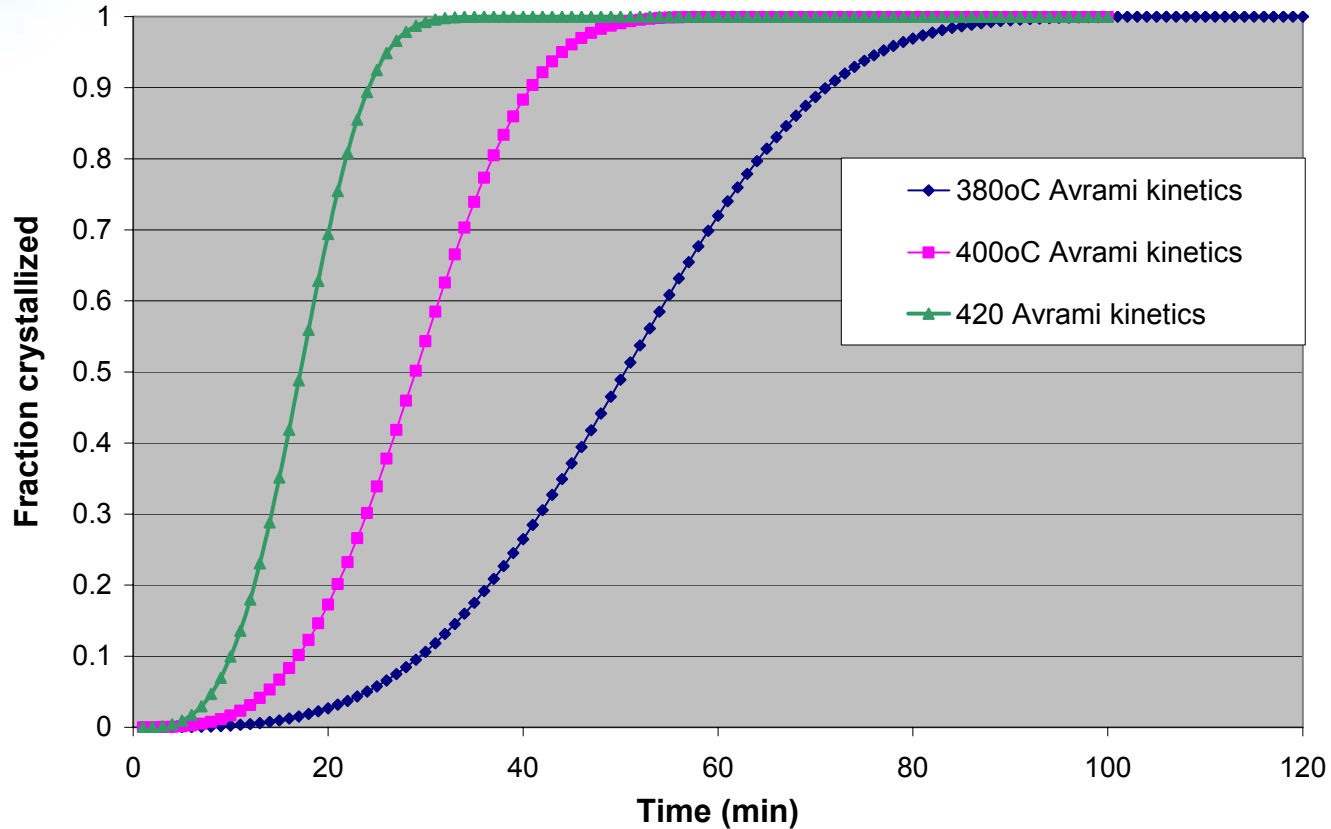
2826 Heating Rate in Argon



Kinetics from shift in peak crystallization temperature with different heating rates

Ozawa: ASTM E698-05

Time and Temperature Crystallization Map 2826 Alloy



Avrami kinetics:

$$x(t) = 1 - \exp(-kt^n)$$

Where:

x(t) fraction crystallization

k rate constant at temperature T

t is time

n experimentally determined exponent

n taken=3.5 from *Greer Acta Metallurgica* (1982)

High Temperature XRD- Summary of Phases vs. Gas Ambient

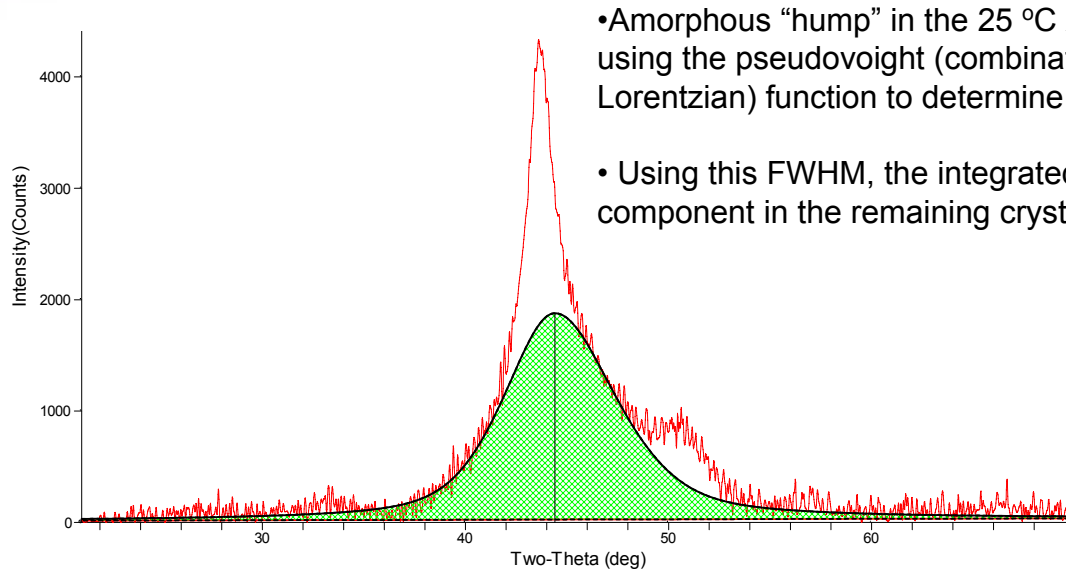
2826 Alloy				
Compound	Formula	5°/min in He (°C)	5°/min in 4% H₂ in He (°C)	5°/min in Air (°C)
Tetrataenite	FeNi	400-710	350-710	350-650
Boron Iron Nickel	Fe _{11.5} Ni _{11.5} B ₆	500-710	500-710	450-550
Boron Iron Molybdenum	Mo ₂ FeB ₂	?-710	?-710	
Iron Oxide Borate	Fe ₂ O(BO ₃)			450-710
Iron Borate	Fe(BO ₃)			500-710? ^a
Molybdenum Iron Oxide	Mo ₃ Fe ₃ O			500-710
Hematite	Fe ₂ O ₃			650-710
Nickel	Ni			?-710
Kamiokitei	Fe ₂ Mo ₃ O ₈			?-710 ^b
Sassolite ^c	B(OH) ₃	Residue only	Residue only	
Isostructural variation of Pinakiolite ^c	(Mg,Mn) ₂ Mn(BO ₃) ₂	Residue only		

a) FeBO₃ could be present at 710 °C in air. Its presence would be masked by the large hematite peaks.

b) Fe₂Mo₃O₈ was found only in the HTXRD residues at concentrations, which are too low to detect on the high temperature stage. It is assumed that it develops above 500 °C.

c) Formed during the cool down cycle as air infiltrated the camera. The gas cylinders had been valved off to conserve gas.

XRD Amorphous/Crystalline Content Estimation



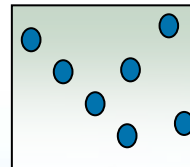
- Amorphous “hump” in the 25 °C XRD scans were profile fitted using the pseudo-voigt (combination Gaussian and Lorentzian) function to determine (FWHM)

- Using this FWHM, the integrated area for the amorphous component in the remaining crystalline scans was determined.

% crystallinity was estimated = $100 * (\text{total peak area} - \text{amorphous area}) / \text{total peak area}$

Atmosphere	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C	710 °C
He		25	36	67	79	78	79	82
4% H ₂ in He	16	30	47	77	79	81	80	80
Air	28	43	75	80	100	100	100	100

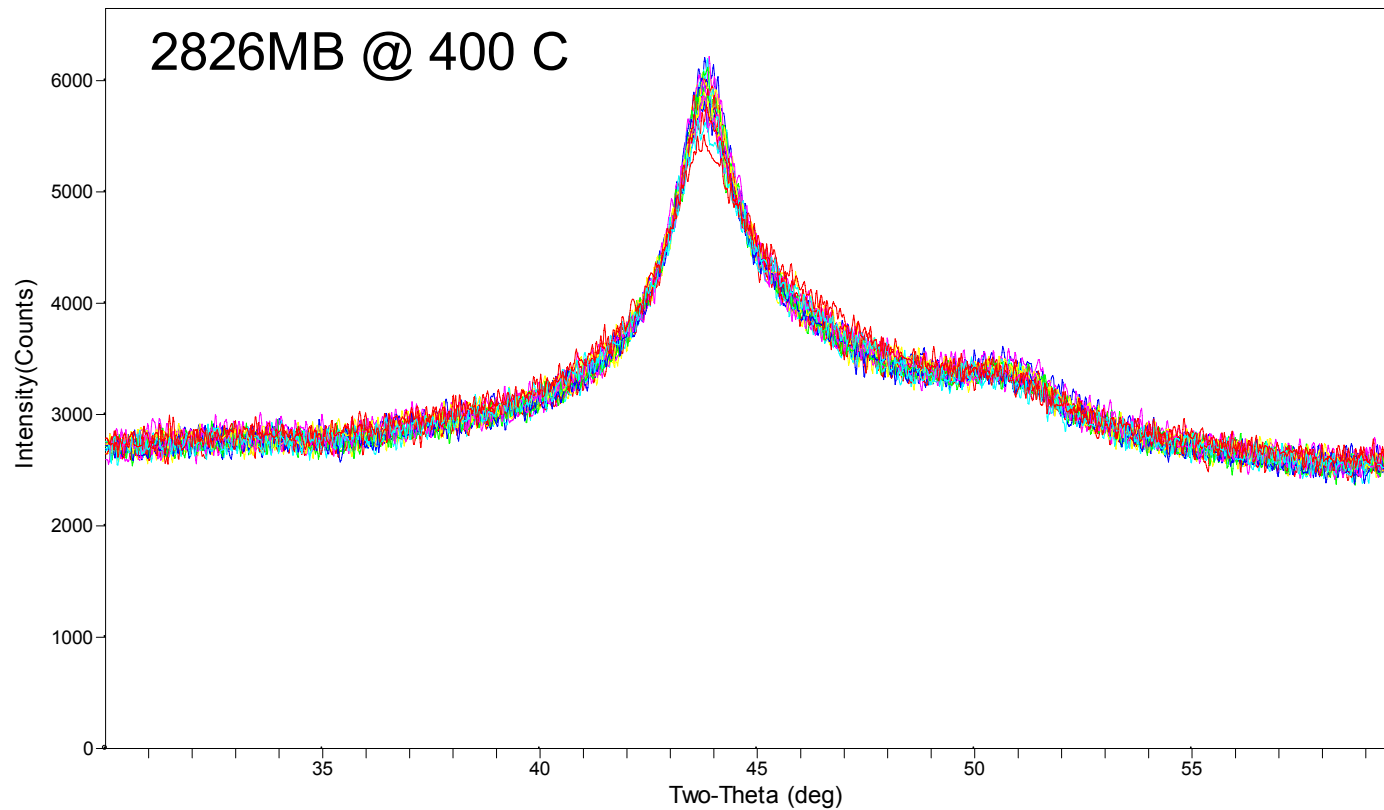
Amorphous →



Nanoscale Crystalline Precipitates

Ramanujan, Mat. Sci & Eng. A 2004

Isothermal XRD- 2826 Alloy

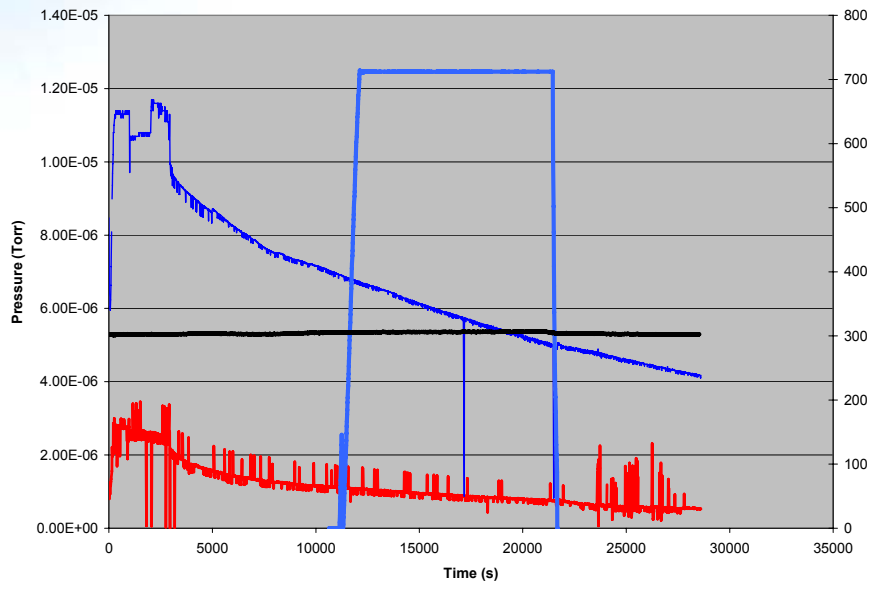


30% Crystalline fraction after 3 hours at 400°C

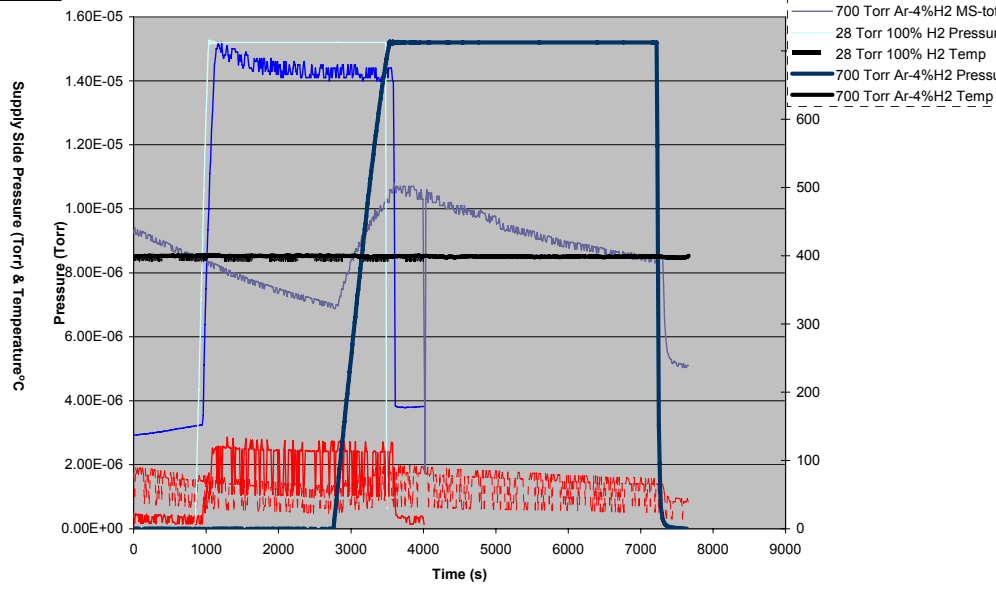
Dynamic Permeation: Ar/H₂ Mixtures 2826 Alloy

Dynamic permeation method: pressure proportional to flux

MetGlass 2826 300C 700T Ar 4% H2



Comparison of Ar-H₂ and Pure H₂ at the same partial pressure and 400°C

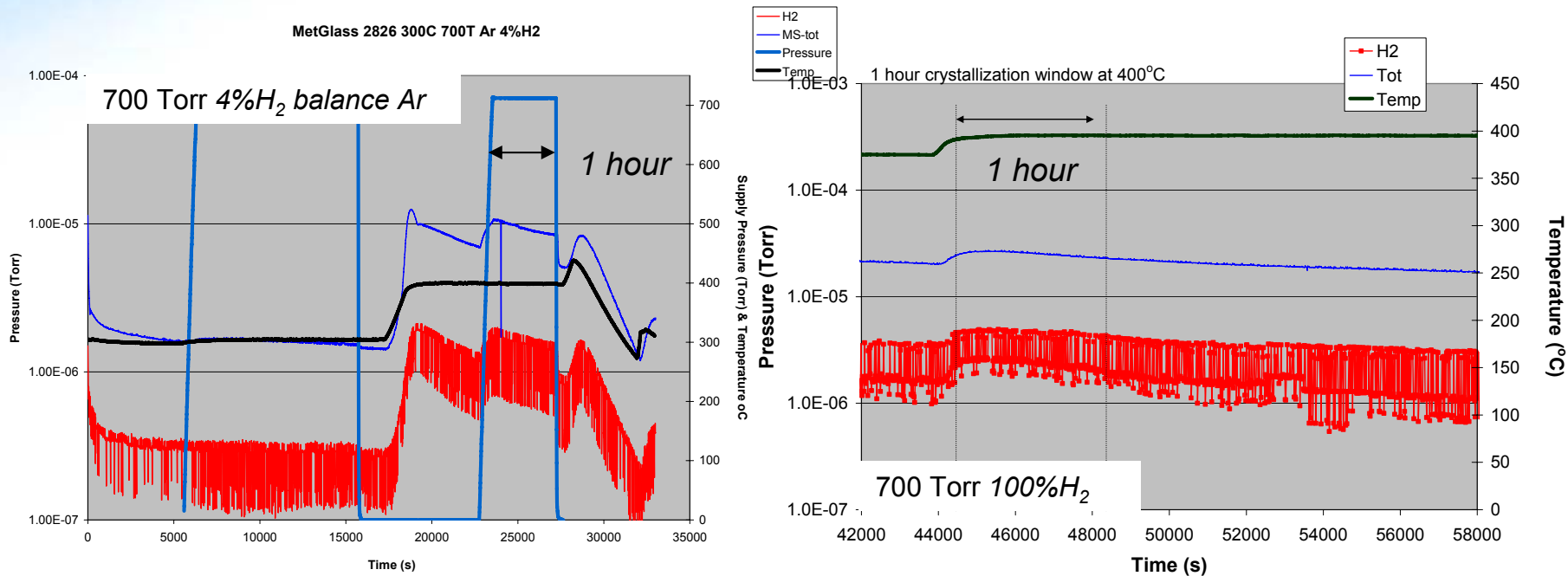


300°C amorphous region & 4% H₂/Ar
Below Detectable H₂ permeation

- Same Partial Pressure H₂:
- i) 700 Torr of 4% H₂ in balance Ar
 - ii) 28 Torr of 100% H₂

Slight Difference probably due to kinetics and Argon dilution surface active sites

Dynamic Permeation: Ar/H₂ Mixtures- 2826 Alloy



From kinetics @ 400°C

- Crystallization proceeds from 0 to 30% in 40 minutes
- XRD shows no change at 400°C from 1 hour to 3 hours (still 30% crystalline)
- H₂ Permeation @ 400°C with 700 Torr 4%H₂/Ar & 100%H₂ show similar behavior
- Decrease during one hour followed by stabilization of flux up to 3 hours: *Low sensitivity* → *Offgassing or crystallization induced permeation differences?*

Electrochemical Permeation

Calculate Flux and Permeation Rate

$$J_{SS} = \frac{J}{A} \cdot F$$

Where J_{SS} (mol/m² s) = steady state H₂ flux
 A (m²)= membrane area
 F =Faraday constant 9.6X10⁴ C/mol

$$P = J_{SS} * L$$

Where J_{SS} (mol/m² s) = steady state H₂ flux
 P (mol/m s)= permeation rate
 L (m)= membrane thickness

Calculate Diffusivity

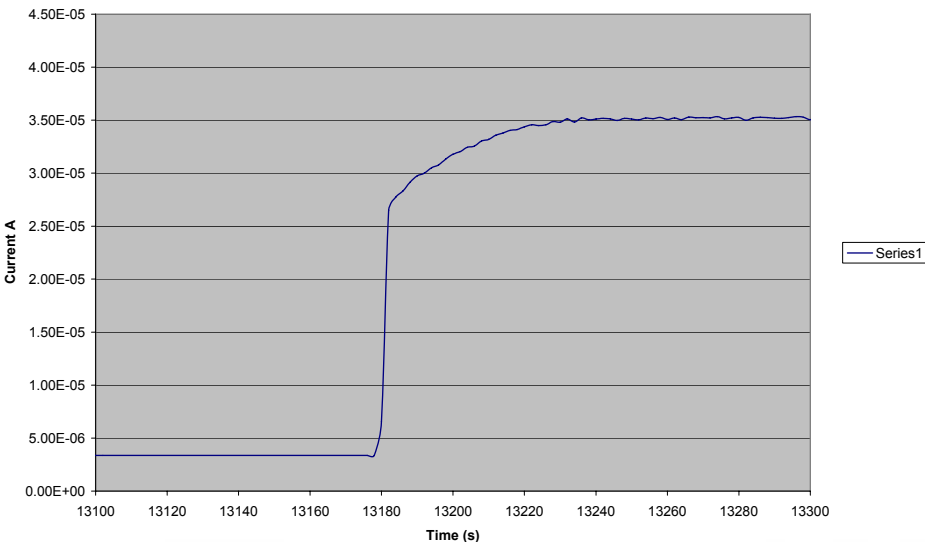
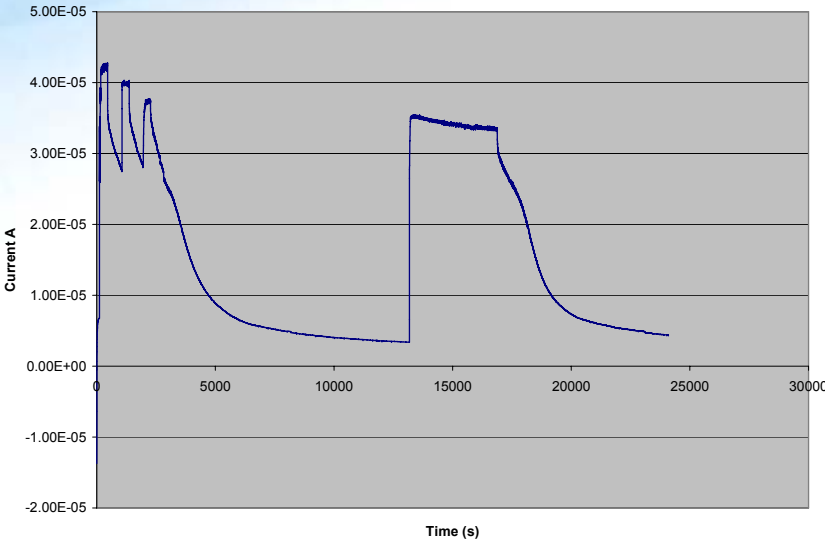
Fick's second law:

$$\frac{J(t)}{J_{SS}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-n^2 \pi^2 \frac{D^* t}{L^2}\right)$$

Where J_{SS} (mol/m² s) = steady state H₂ flux
 $J(t)$ (mol/m² s)=H₂ flux at time t
 L (m)= membrane thickness
 D (m²/s)=Diffusivity
 t (s)=time

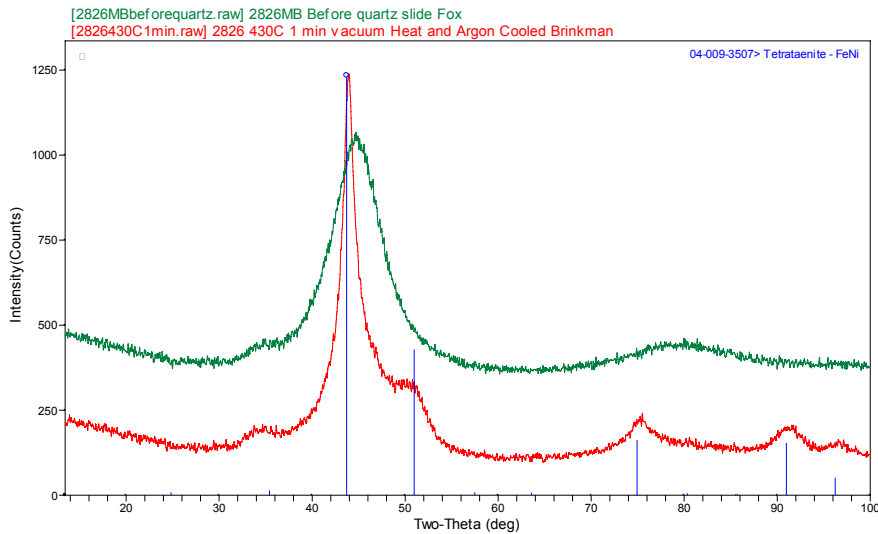
Solve→

Plot $J(t)/J_{SS}-1$ versus t for $n=1, 2, 3$
 Levenberg-Marquardt algorithm to fit best value for D

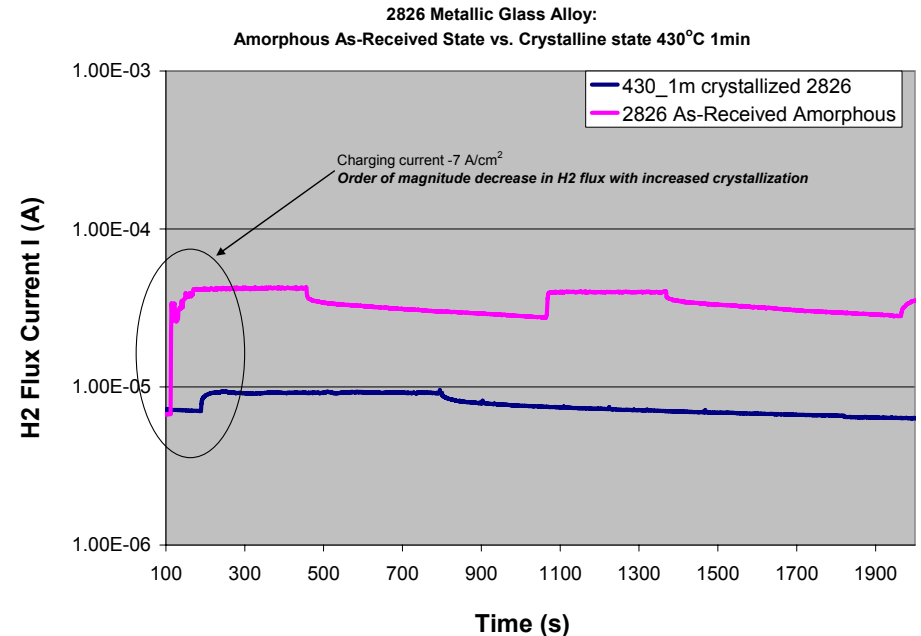


Electrochemical Permeation: Crystallization Effects 2826 Alloy

$\text{Fe}_{0.5}\text{Ni}_{0.5}$ FCC alloy ordered tetragonal superlattice
 $a=2.53 \text{ \AA}$, $c=3.58 \text{ \AA}$



- As-received amorphous vs. partially crystallized at 430°C 1min
- ~40% Crystalline fraction estimated from XRD



- Nearly an order of magnitude reduction in permeability of crystalline specimen

Permeability for Fe-Based Commercial Metallic Glass Alloys

Alloy	Permeability (mols H ₂ / m-s-Pa ^{1/2})			Comp. (wt%)
	Electrochem <i>Mol H₂/m s Pa^{1/2}</i> <i>Charging -1 mA/cm²</i> <i>~ 200mV SCE</i> <i>applied</i>	electrochem <i>Mol H₂/m s</i>	Gas Rig 400°C/700T	
Pd	1X10⁻¹⁰	3.5X10⁻⁹	1 X 10⁻⁸ J. Phair, Ind. Eng. Chem. Res. 45 (2006)	
2605S3A	6X10⁻¹²	2X10⁻¹⁰	2.5x10⁻⁹	Fe=85-95 Cr=1-5 Si=1-5 B=1-5
2826MB	a)1X10 ⁻¹² b)8X10 ⁻¹⁴	a)3x10 ⁻¹¹ b)2.6X10 ⁻¹²	5.3x10⁻⁹	Fe=40-50 Ni=40-50 Mo=5-10 B=1-5 Co=0.3 (max)

a= amorphous
b= crystalline
430°C 1min

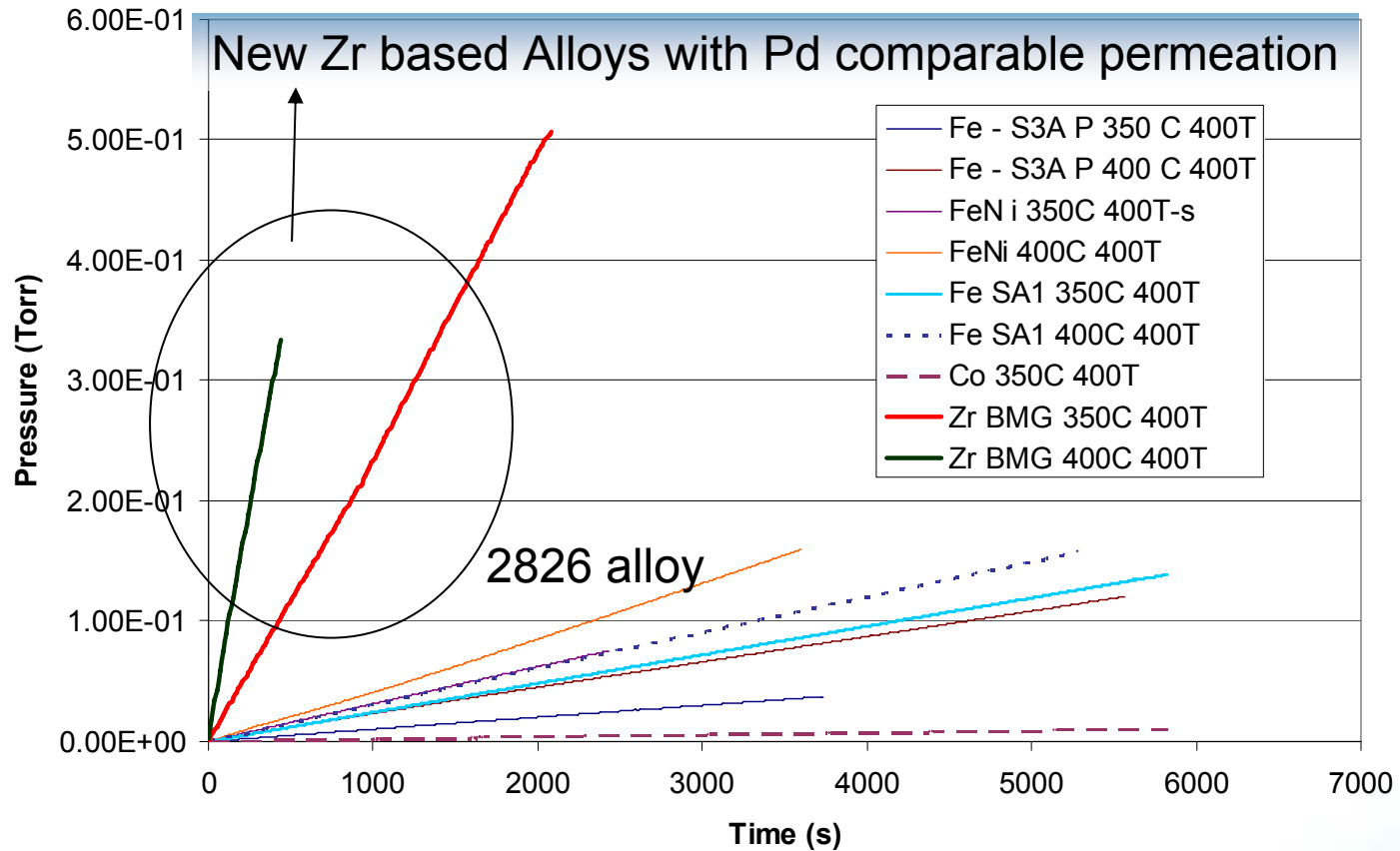
Literature Comparison 2826 Alloy

D. Santos J Non-Crystalline Solids 232 (1998)

Fe₄₀Ni₃₈Mo₄B₁₈, Permeability= 6X10⁻¹¹ mol H/m s

Hydrogen Permeation Comparison

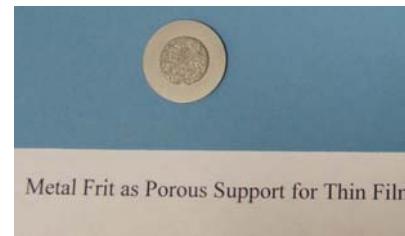
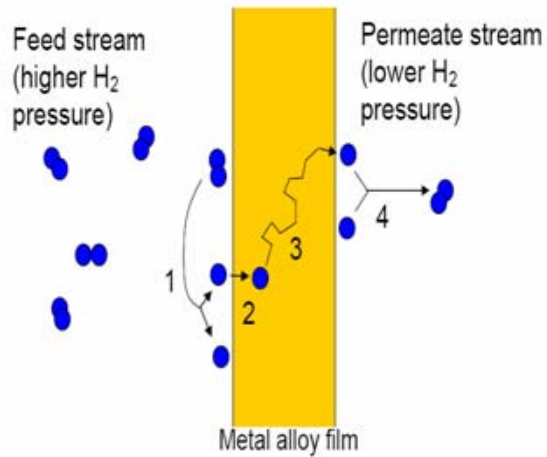
Metallic Glass Permeation Test Results by Base Alloy



Slope of saturation curve, dP/dt proportional to hydrogen flux ($\text{mol/m}^2 \text{ s}$)

Enhanced Hydrogen Permeation: Thin Films

Strategy: Thin Film Sputter Deposition on Porous Metal Frit Mechanical Support



$$JH_2 = \phi \exp\left(\frac{Ea}{RT}\right) \frac{(P^{n_{up}} - P^{n_{down}})}{L}$$

Flux JH_2 function of ϕ varying exponentially with temperature, P^n upstream and downstream H₂ pressure and membrane thickness L [1]

Film/Frit Sealed in VCR fitting

Enhanced Hydrogen Permeation: Materials Chemistry Modeling Effort

Methodology – Bulk System Description

- **Focus on Zirconium-based Bulk Metallic Glasses (BMGs)**

High Hydrogen Permeation: *role of Zr as strong hydride former in solubility, diffusivity and permeation properties?*

- **Commercially available Zr-Al-Co BMGs**

- LiquidMetals Technologies
- Allows for comparison and validation between experiment and computations

- **Initially modeled by hypothetical crystalline structures**

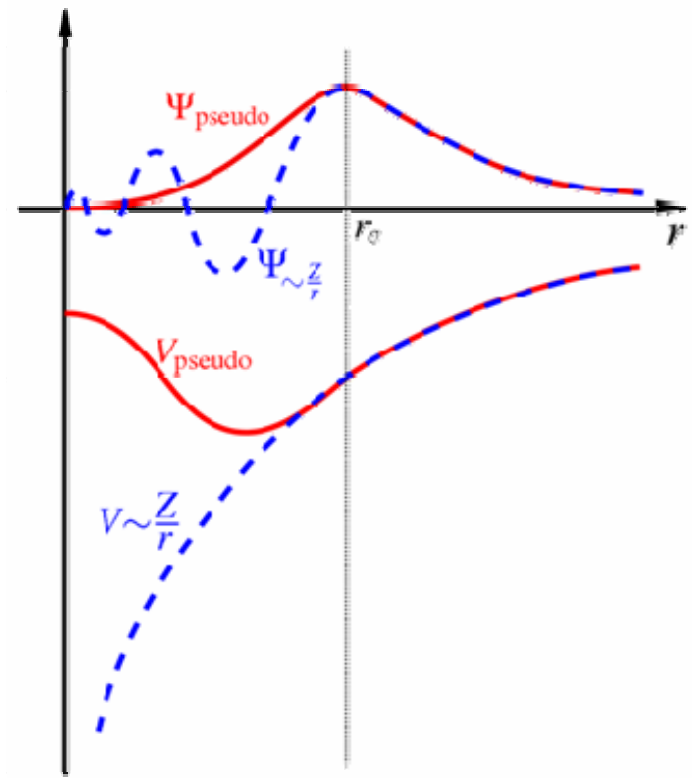
- Efficiently-packed, solute-centered clusters¹
 - Zr-Solvent
 - Al-Structure directing solute
 - Co-Secondary solute
- Optimized via Density Functional Theory (DFT)

¹ Miracle, D.B., *Acta Materialia*, **54** (2006) 4317-4336.

Methodology - DFT

•CASTEP®

- **Planewave DFT code**
- **Ultrasoft Pseudopotentials**
 - Represents the core electrons
 - Reduced computational cost
- **Spin-restricted Calculations**
 - Ignore spin/magnetic moments on Co



Methodology – Types of Calculations

- **Optimizations of ordered/crystalline structures**
 - Estimate atomic positions
 - Estimate “lattice” parameters
 - Provides comparison with experimental density
- **Molecular Dynamics (MD)**
 - **Without H₂ – Anneal atomic positions away from crystalline structure**
 - Compare with local order in EXAFS or radial distribution functions
 - **With H₂ – Hydrogen trajectories**
 - Suggest possible diffusion mechanisms
 - Estimate diffusion coefficients
 - Investigate propensity for trapping or hydride formation
- **Single-point energies and frequencies**
 - Estimate activation or “hopping” barriers
 - Estimate solubility

Initial Hypothetical Crystalline Structures: $Zr_{60}Co_{13.3}Al_{26.7}$ Alloy

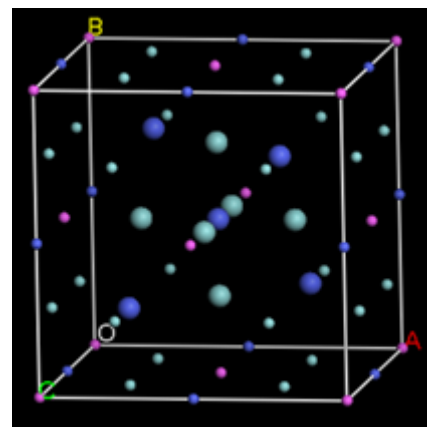
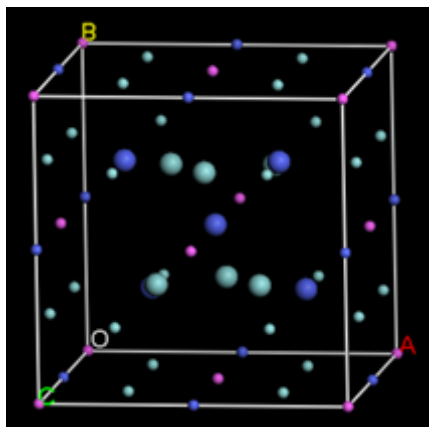
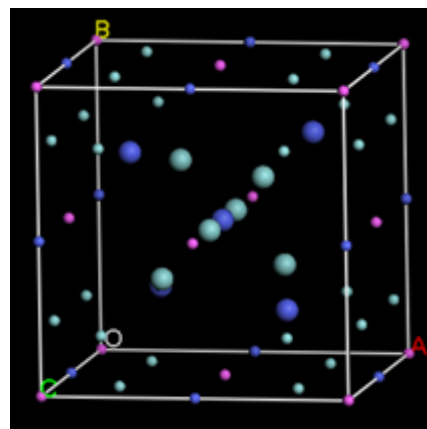
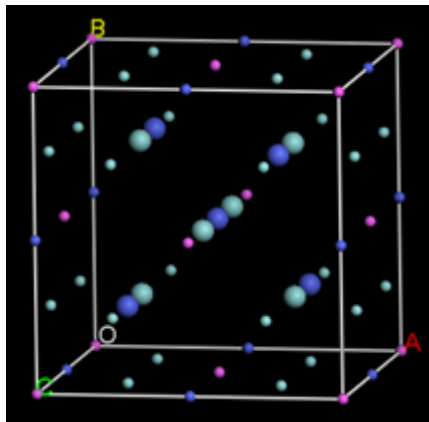
With Al FCC lattice: Different Options for Zr and Co atomic positions

30 atom "box"



Zr 18

Al 4

Co 8



Legend

Zr  

Al 

Co  

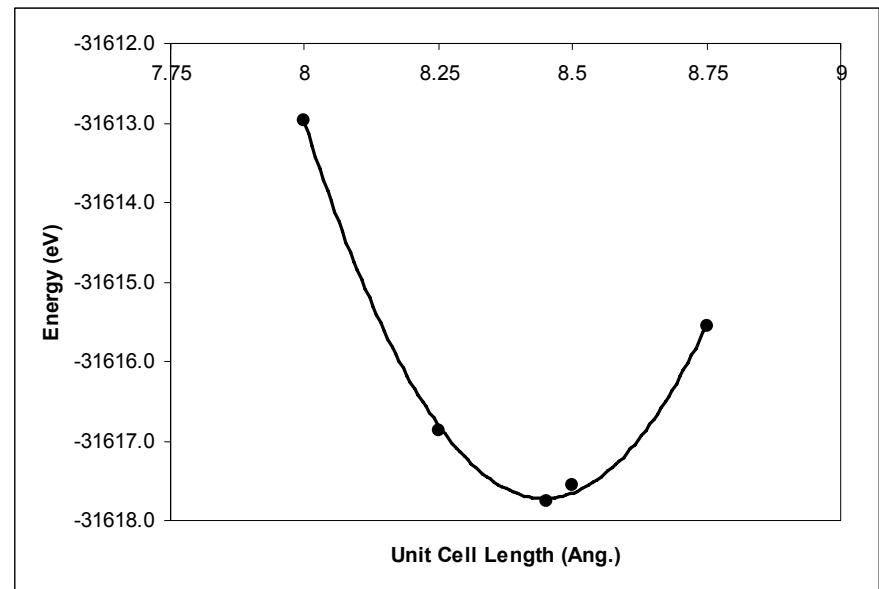
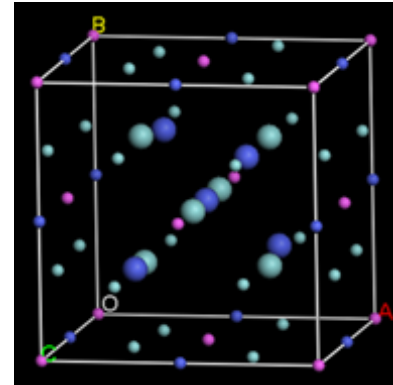
surface core

Strategy: Minimize Free Energy of Hypothetical Crystal Cell

Initial Results: $Zr_{60}Co_{13.3}Al_{26.7}$ Alloy

• One example

- Gamma point calculation
- LDA functional
- 300 eV cutoff energy
- Ultrasoft pseudopotential
- Atom positions allowed to change
- Optimized unit cell length
- Constrained to FCC-structure
 - $a=b=c$
 - $\alpha=\beta=\gamma=90^\circ$
- Calculated density
 - 6.11 g/cm^3
- Experimental Alloy Density
 - 6.39 g/cm^3



Summary

- Used calorimetry (DSC) to determine crystallization temperatures and operating window for a variety of Metglass alloys; identified crystallization kinetic parameters for Fe based system alloy 2826
- Intentionally crystallized 2826 sample by vacuum heating/argon quenching and examined hydrogen flux via electrochemical permeation techniques as compared to fully amorphous sample.
- Examined In-Situ crystallization behavior in gas permeation rig at temperatures near 400°C
- Quantified reduction in hydrogen flux with increased degree of crystalline fraction.
- Initiated experimental work on thin film fabrication on porous metal frit for enhanced hydrogen permeation
- Completed initial modeling strategy for bulk metallic glass structure determination and outlined path forward for molecular dynamic simulations of hydrogen behavior BMG

Proposed Future Work

- Continue thin film deposition and thickness dependence studies
- Continue crystallization parameter testing
- Continue permeation testing with deuterium, examine isotopic effects
- Modeling Effort

Anneal lowest energy crystalline, ordered structure

- Molecular Dynamics (MD) simulations without H₂
 - Compare calculated local structure with EXAFS or radial distribution functions
- Single-point energy calculations
 - Binding energies in tetrahedral and octahedral sites
 - Transition state energies – Energy barrier to “hopping”
 - Calculate/estimate solubility
- MD simulations with H₂
 - Suggest diffusion paths
 - Calculate/estimate diffusion coefficients
 - Investigate propensity of trapping and/or hydride formation