Amorphous Alloy Membranes for High Temperature Hydrogen Separations:

Kent Coulter, Ph.D.
June 8, 2010

Project ID: PD010

This presentation does not contain any proprietary, confidential, or otherwise restricted information

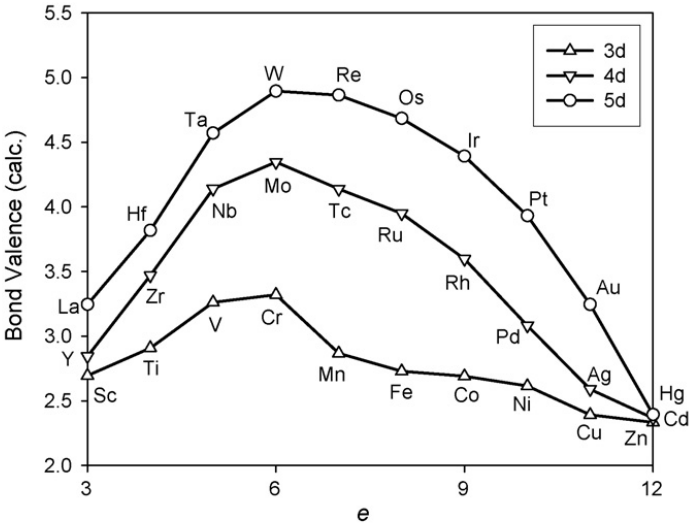
Background

Composition and Operation of Hydrogen-Selective Amorphous Alloy Membranes
Journal of Membrane Science 285 (2006) 30–55
M.D. Dolan, N.C. Dave, A.Y. Ilyushechkin, L.D. Morpeth, K.G. McLennan
CSIRO Division of Energy Technology, Kenmore, Qld 4069, Australia

Composition	*Tg (◦C)*	*Permeability*	*Pd* coating?
Zr60Ni8Al15Cu15Co2	–	≈Pd	Y
Zr36Ni64	550	<Pd	N
Zr36Ni64	550	≈Pd	Y
(Zr36Ni64)1−*α(Ti39Ni61)α*	*550–535*	*<Pd*	*Y*
(Zr36Ni64)1−*α(Hf39Ni61)α*	*550–610*	*<Pd*	*Y*
Pd80Si20	340	>Cryst. Pd80Si20	N
Zr60Al15Co2.5Ni7.5Cu15	~380	≈Pd	Y
(Ni0.6Nb0.4)100−*xZrx*	–	*>Pd*	*Y*

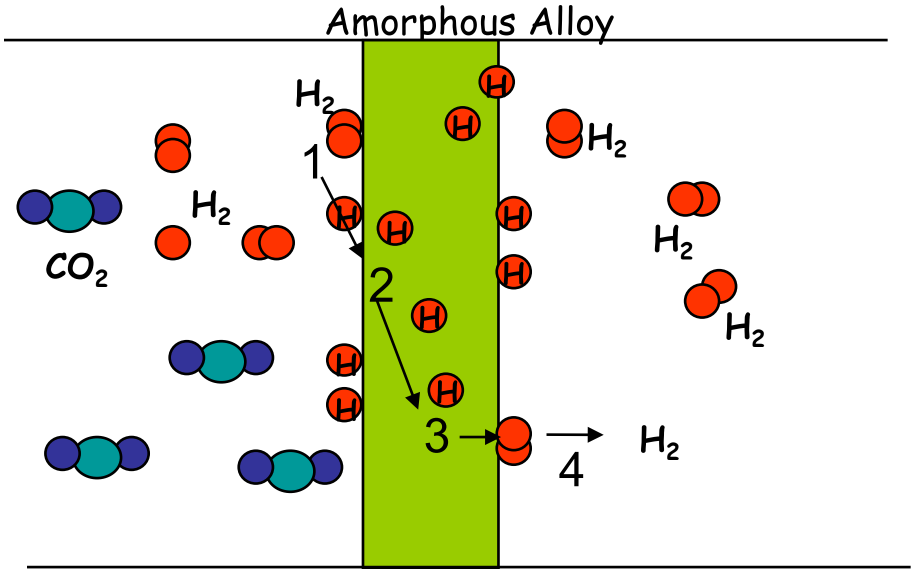
The often-quoted three empirical rules for BMG formation were first presented by Inoue:

- *(i) More than three constituent elements*
- *(ii) Atomic size ratios greater than 12%*
- *(iii) Negative heats of mixing*



Objectives

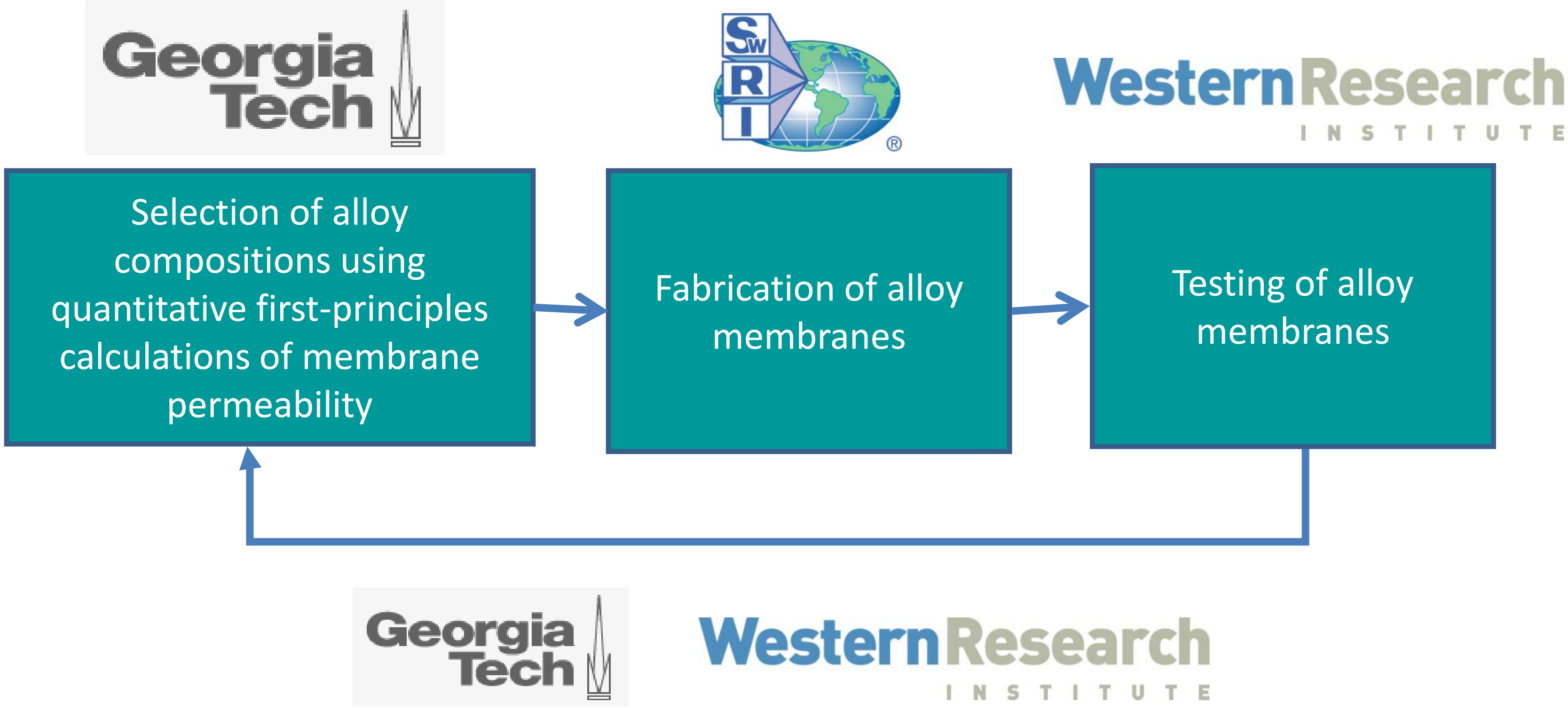
Hydrogen and Clean Fuels Program Goal: Develop advanced and novel energy technologies which will facilitate the use of our nation's abundant coal resources to produce, deliver, store, and utilize affordable hydrogen in an environmentally clean manner.



What alloys can be used to maximize H_2 flux and/or maximize stability and/or minimize cost??

Amorphous Alloy Membranes

Scope of Work: The proposed program will model, fabricate, and test thin film amorphous alloy membranes which separate hydrogen from a coal-based system with performance meeting the DOE 2015 targets of flux, selectivity, cost and chemical and mechanical robustness, without the use of PGMs (platinum group metals).



Selection of alloy compositions using quantitative first-principles calculations of membrane permeability

Fabrication of alloy membranes

Testing of alloy membranes

Key Contributors

Kent Coulter, Ph.D., Manager, Surface Engineering Section, Southwest Research Institute®

- Presently conducting research on flexible thin film batteries, solid state hydrogen storage materials, carbon nanotubes and nano-bio applications.
- Previously Director of Science and Technology for the Flex Products Division of JDS Uniphase and was with Flex for ten years in a variety of R&D and Product Launch positions.
- Group has 25 Scientists & Engineers & ~$3.5MM/year in applied R&D.

David Sholl, Ph.D., The Michael E. Tennenbaum Family Chair & GRA Eminent Scholar for Energy Sustainability, School of Chemical & Biomolecular Engineering , Georgia Institute of Technology

- Research focuses on materials whose macroscopic dynamic and thermo-dynamic properties are strongly influenced by their atomic-scale structure.
- Has performed DOE-supported research projects on topics including H_2 permeation through metal alloys, H_2 storage in complex metal hydrides, and the surface chemistry of chiral chemicals on metal catalysts.

Thomas Barton, Ph.D., Principal Engineer, Energy Production and Generation, Western Research Institute

- Currently contributing to NETL projects concerning coal and biomass gasification and combustion.
- Research has focused on the application and testing of materials in the extreme environments found during gasification and combustion.
- Dr. Barton worked at Eltron Research Inc. in Boulder, Colorado between October 1997 and December 2003 as the Manager for Natural Gas Systems.
- Has recently initiated a research project called Thermal Cycle Absorption to produce a high pressure hydrogen stream using a cyclic process and ceramic absorbents.

Georgia Tech

Western Research INSTITUTE

Overview

Timeline

- Project Start: September 30, 2009
- Project End: September 29, 2012
- Percent Complete: 10%

Budget

- Total Project Funding
  - DOE Share: $799,786
  - Contractor Share: $199,950
- Year 1
  - DOE Share: $249,965
  - Contractor Share: $63,970

Barriers

A. High Cost

G. Hydrogen Embrittlement of Metals

H. Thermal Cycling

I. Poisoning of Catalytic Surfaces

J. Loss of Membrane Structural Integrity and Performance

L. Defects During Fabrication

M. Low Selectivity

N. Technologies do not Operate at Optimal Process Temperatures

Q. Impurities in Hydrogen

Scope of Work

1) Materials Modelling and Composition Selection:
2) Fabrication of Alloy Membranes:
3) Membrane Testing and Evaluation:

Budget

DOE Share				
Team Member	**Year 1**	**Year 2**	**Year 3**	**Total**
Georgia Institute Of Technology	$ 133,334.00	$ 133,333.00	$ 133,333.00	$ 400,000.00
Southwest Research Institute	$ 66,666.00	$ 66,667.00	$ 66,402.02	$ 199,735.02
Western Research Institute	$ 49,964.98	$ 80,053.00	$ 70,033.00	$ 200,050.98
Total	**$ 249,964.98**	**$ 280,053.00**	**$ 269,768.02**	**$ 799,786.00**
Cost Share				
Team Member	**Year 1**	**Year 2**	**Year 3**	**Total**
Georgia Institute Of Technology	$ 42,469.00	$ 32,080.00	$ 33,038.00	$ 107,587.00
Southwest Research Institute	$ 16,667.00	$ 16,667.00	$ 9,029.00	$ 42,363.00
Western Research Institute	$ 14,025.00	$ 19,964.00	$ 16,011.00	$ 50,000.00
Total	**$ 73,161.00**	**$ 68,711.00**	**$ 58,078.00**	**$ 199,950.00**
Total				
Team Member	**Year 1**	**Year 2**	**Year 3**	**Total**
Georgia Institute Of Technology	$ 175,803.00	$ 165,413.00	$ 166,371.00	$ 507,587.00
Southwest Research Institute	$ 83,333.00	$ 83,334.00	$ 75,431.02	$ 242,098.02
Western Research Institute	$ 63,989.98	$ 100,017.00	$ 86,044.00	$ 250,050.98
Total	**$ 323,125.98**	**$ 348,764.00**	**$ 327,846.02**	**$ 999,736.00**

Milestones

Phase I (Year 1)
The first year will consist of demonstrating an amorphous alloy with the following milestones identified for this initial phase (Note: the milestones are numbered according to the corresponding tasks):

Milestone 2.2: Fabricate at least six membrane samples with compositions consistent with those used by Georgia Tech for H_2 flux modeling.

Milestone 2.3: Test and establish thermal stability of amorphous alloys.

Phase II (Year 2)
The focus of the effort will be to evaluate the performance and fabrication options to produce membranes that are an improvement over those published in the literature. The following milestones have been identified for this second phase:

Milestone 3.2: SwRI will fabricate a minimum of 20 doped amorphous alloy membrane specimens based on Georgia Tech hydrogen transport predictions for the most promising ternary element additions.

Milestone 3.3: Testing at WRI of a second set (≤ 12) of alloys from the optimization trials by pure gas (H_2 and N_2) permeation experiments.

Phase III (Year 3)
The final year will focus on optimization of identified compositions and fabrication techniques through an iterative progress approach of modeling, making and testing the amorphous alloys. The following milestones have been identified in this final phase:

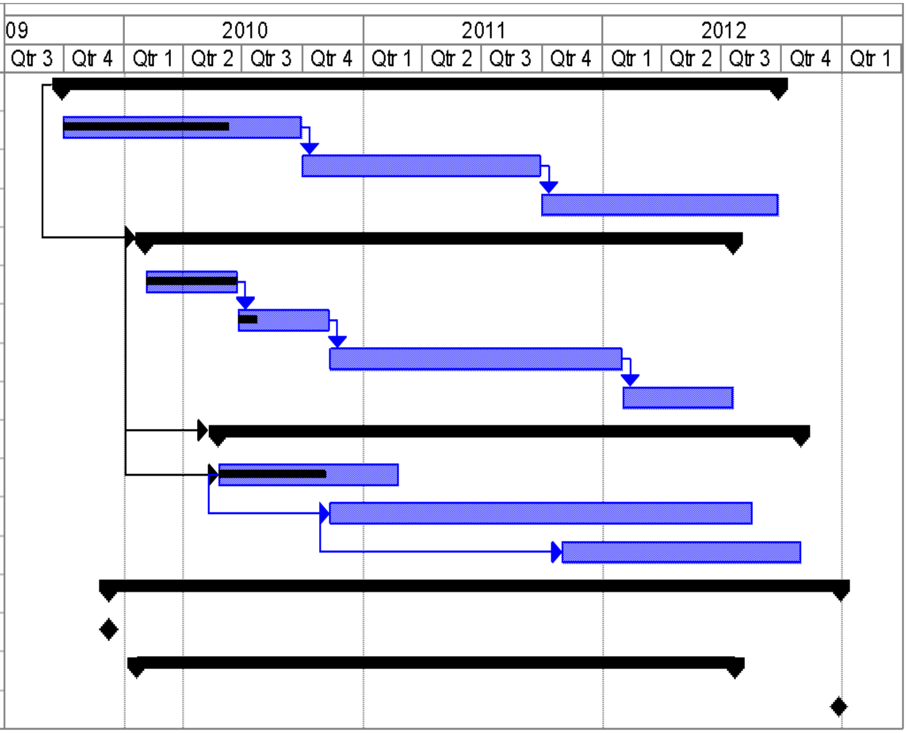
Milestone 4.2: SwRI will produce a minimum of four optimized membranes for testing at WRI.

Milestone 4.4: Complete two gasifier tests (or a smaller number of longer duration tests) at WRI on optimized membrane materials with multiple additions of H_2S, COS, HCl, and metallic impurities.

Task 1: Project Management and Planning (PMP)

- Quarterly management progress report shall use the scope, schedule, and cost included in the PMP as the baseline, and either verification that the PMP is still valid or suggested PMP revisions deemed desirable for optimum achievement of program objectives.
- SwRI will submit reports in accordance with Attachment 4 -- Federal Assistance Reporting Checklist.

ID	Task Name
1	**GT Modeling**
2	Model ZrNi alloy and one amorphous ZrNiNb
3	Model four ternary amorphous Zr-based alloys
4	Model H2 permeance as a function of the dopant concentration
5	**SwRI PVD Fabrication**
6	Fabricate Zr36Ni64
7	Optimize Zr36Ni64 Process Conditions
8	Fabricate Dopant identified additives
9	Fabricate optimized ternary amorphous alloys
10	**WRI Testing**
11	Thermal Stability Tests of Amorphous Alloys
12	Test Protocol of Hydrogen Separation Membranes
13	Gasifier Test of Hydrogen Separation Membranes
14	**Program Management**
15	Kickoff Meeting
16	**Quarterly reports**
28	Final Report



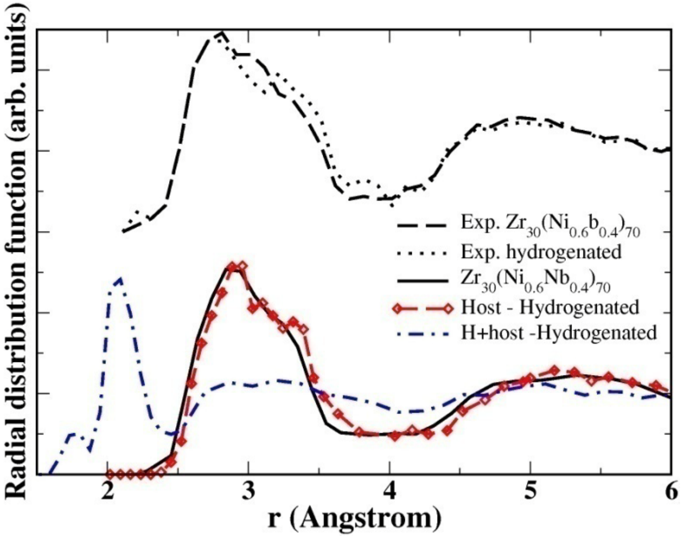
Task 2: Modeling/Material Prediction

- The steps in accomplishing this task for any of the selected materials are:
  - (i) use *ab initio* Molecular Dynamics to develop an atomic structure for the amorphous metal with the desired composition,
  - (ii) use efficient heuristic methods to generate approximate locations for the energy minima and diffusive transition states of interstitial H in the material,
  - (iii) use DFT to refine the energy and geometry of all interstitial energy minima and transition states,
  - (iv) use DFT to characterize the effect of H-H interactions for nearby interstitial H atoms,
  - (v) use Grand Canonical Monte Carlo to rigorously predict the solubility of interstitial H as a function of the external H_2 pressure and temperature, and
  - (vi) use Kinetic Monte Carlo simulations based on local hopping rates defined by Transition State Theory to predict the diffusivity of interstitial H.

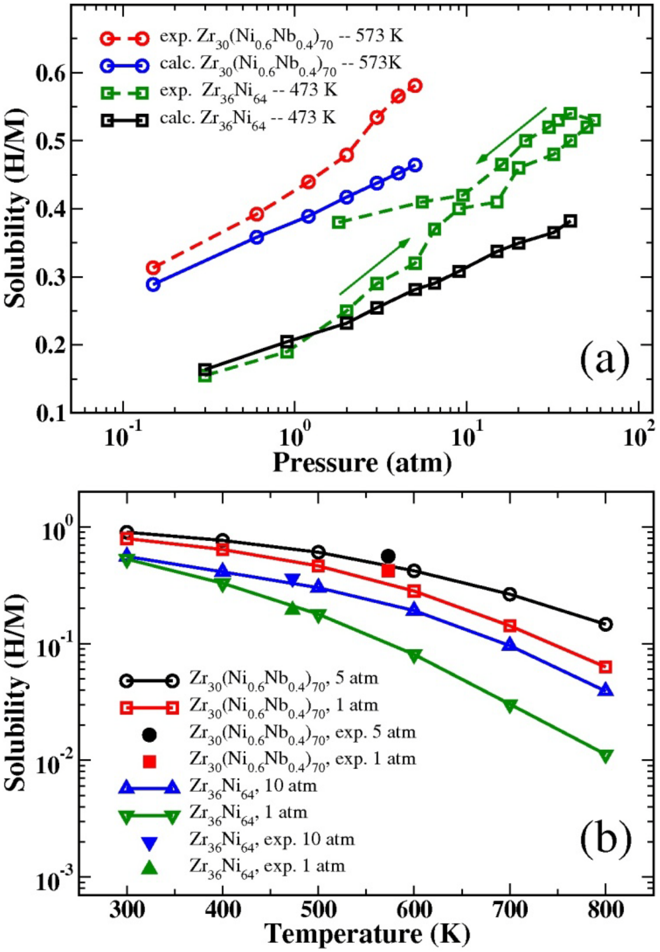
- In Year 1 of the project, Georgia Tech will focus on making predictions for Zr-Ni and Zr-Ni-Nb alloys for which experimental data is already available and are known to exhibit H_2 fluxes comparable to Pd membranes. This will provide an important opportunity to validate our modeling methods and to provide data for our initial experimental activities, which will also examine these materials.

- In Years 2 and 3, Georgia Tech will extend our modeling to novel alloy compositions with the aim of identifying new high flux materials while retaining acceptable materials properties during fabrication and operation.

Modeling Approach is Sufficient to Generate Realistic Samples of These Amorphous Materials



Comparison of calculated and experimental radial distribution functions for *a*-$Zr_{30}(Ni_{0.6}Nb_{0.4})_{70}$ before and after hydrogenation. The curves in the lower (upper) part of the figure are calculated (from experiment). The curve labeled “Host – Hydrogenated” shows the results for the hydrogenated material when H atoms are not included in calculating the radial distribution function.

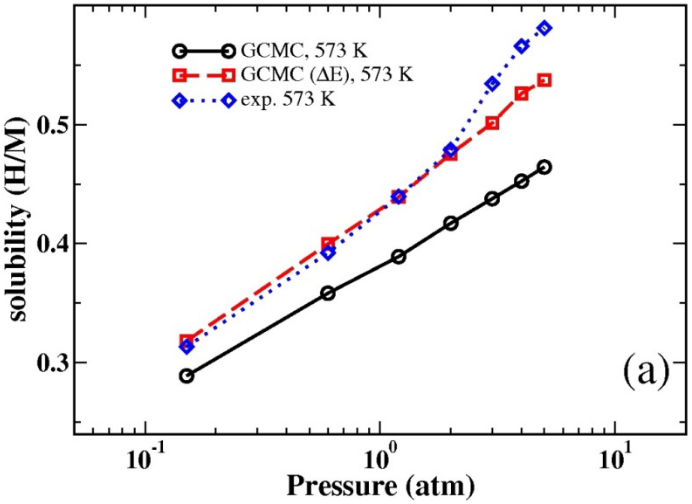


Comparison of calculated and experimental H solubility in *a*-$Zr_{36}Ni_{64}$ and *a*-$Zr_{30}(Ni_{0.6}Nb_{0.4})_{70}$.

Modeling Methods Based on First-Principles Calculations Give Quantitative Predictions for H_2 Permeance Through Amorphous Films *Using No Experimental Data*

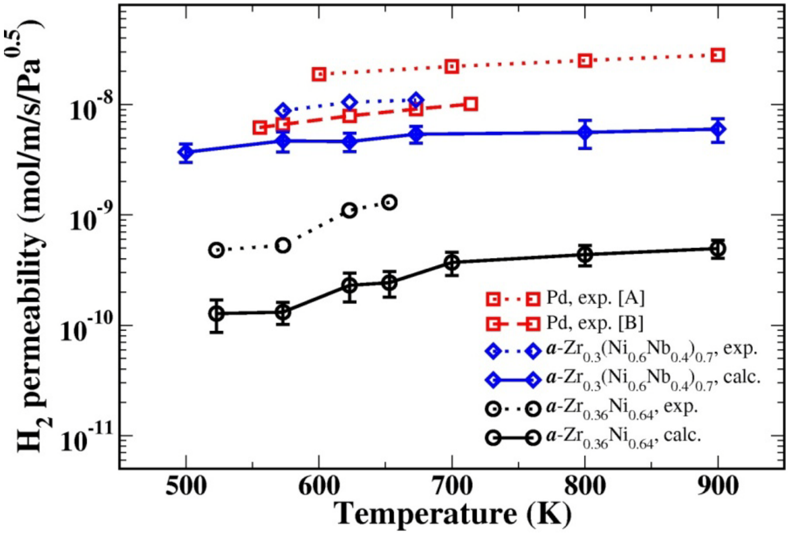
Hao and Sholl, *Energy Env. Sci.*, **1** (2008) 175
Hao, Widom and Sholl, *J. Phys. Condens. Matt*. 21 (2009) 115402

Comparison of predicted H solubility (red) with experiment (blue) in Zr-Ni-Nb



Structural and solubility data for $Zr_{30}(Ni_{0.6}Nb_{0.4})_{70}$ from Yamaura et al., Acta Mater. 53 (2005) 3703

Comparison of predicted H permeability (solid curves) with experiment (dotted) in Zr-Ni-Nb (blue) Zr-Ni (black). Red shows crystalline Pd



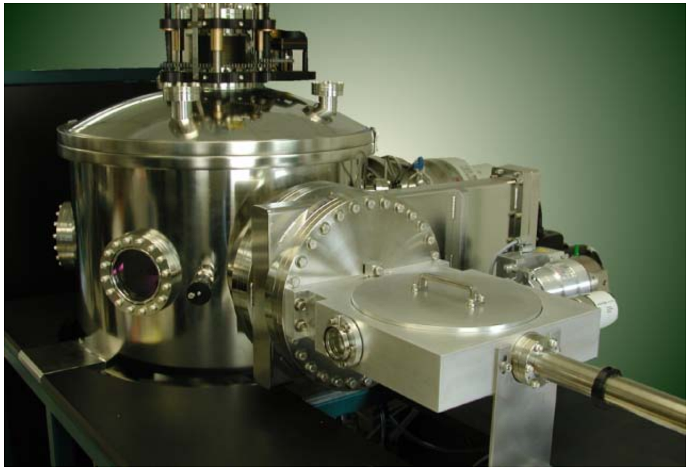
Membrane data for $Zr_{36}Ni_{64}$ [$Zr_{0.3}(Ni_{0.6}Nb_{0.4})_{0.7}$] from Hara et al., J. Membrane Sci. 211 (2003) 149 [Yamaura et al., Acta Mater. 53 (2005) 3703]

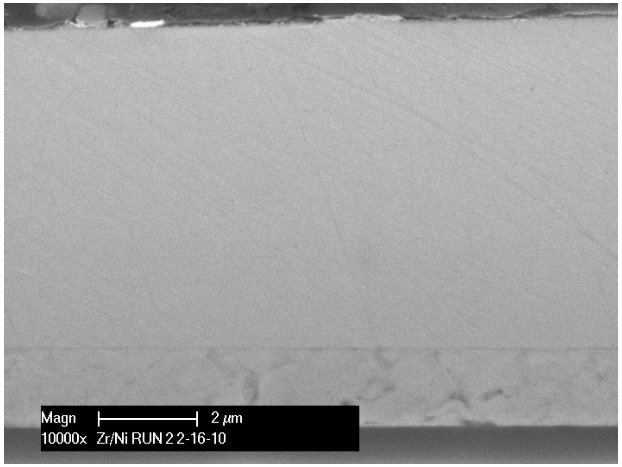
Paper describing validation of methods with experimental data submitted to J. Membrane Sci.

Task 3: Membrane Deposition, Composition and Microstructure Optimization

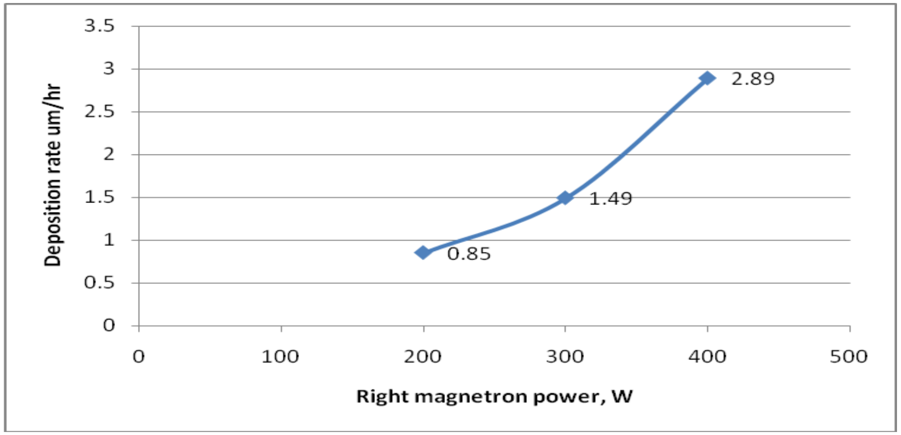
- Based upon SwRI's experience in processing of Pd alloys established under previous DOE support, magnetron sputtering is well suited for the reproducible fabrication of impurity-tolerant membranes.
- Key advantages of this method include the ability to deposit alloy films of virtually any composition over large areas by simply constructing a target of the appropriate size and composition.
- The critical glass forming range of Zr based thin films of amorphous metal alloys have been studied as a function of composition, substrate temperature and condensation temperature as well as the kinetic energy of the condensing particles.
- Background academic studies will be utilized as the baseline for depositing supported amorphous alloys as H_2 separation membranes.
- In addition to co-sputtering, SwRI will procure the building-block materials needed to construct sputtering targets of the desired stoichiometry. Initial membrane tests will be performed with membranes fabricated with no PGMs.
- If membranes from new compositions are found to have performance limited by low activity for H_2 dissociation, very thin coatings (<100nm) of Pd-Pt will be deposited on subsequent membranes to enhance surface dissociation of H_2.
- This approach would introduce a very small PGM content into our membranes. Pd-Pt will be used rather than simply Pd because of the reported robustness of this bimetallic catalyst in the S-containing environments.

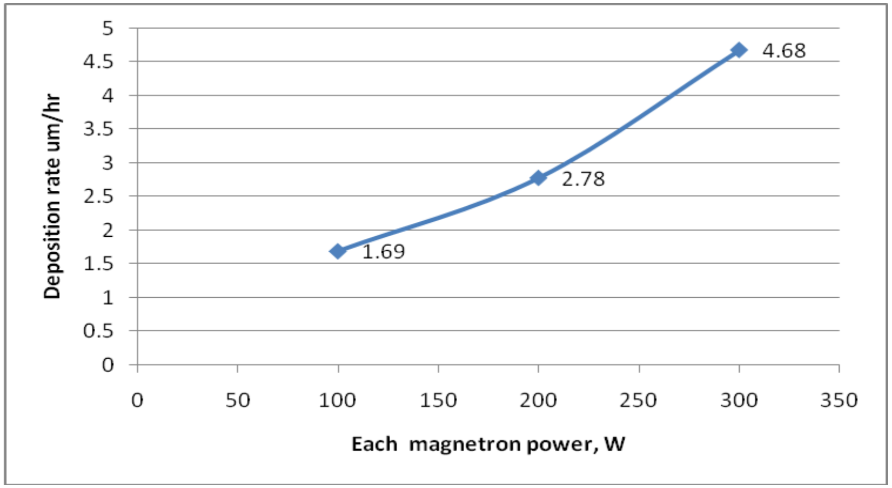
Membrane Fabrication

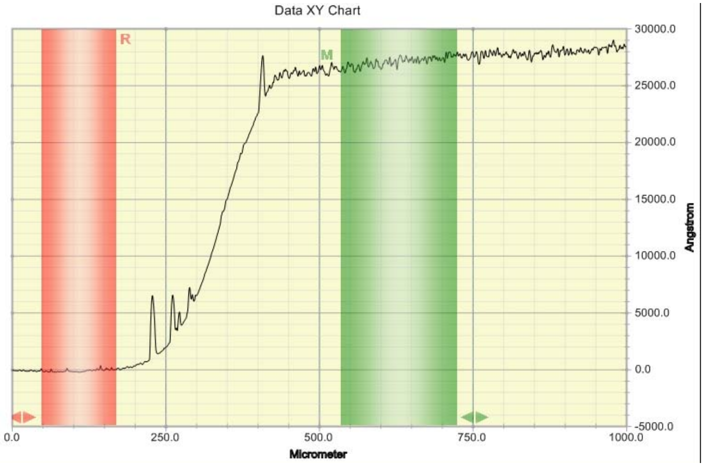




Co-deposition of Nickel from Two Magnetrons







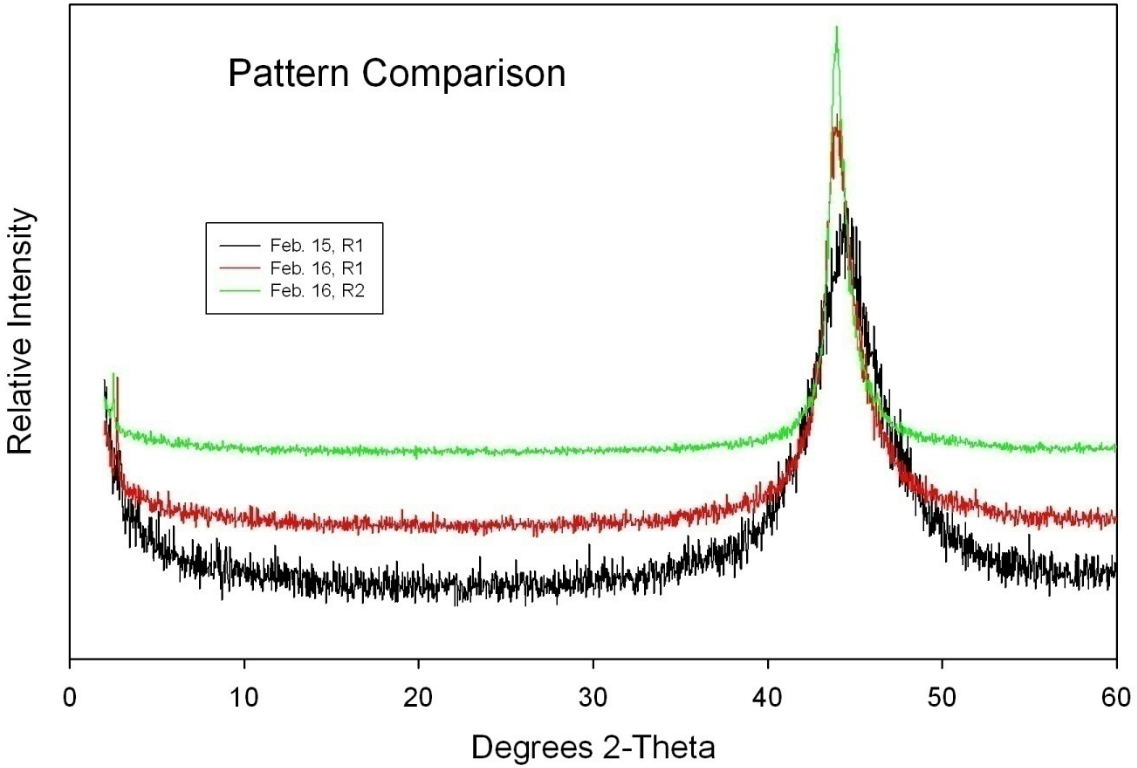
EDS Compositional Analysis of Deposited NiZr Films

Feb. 15, 2010 -- Run #1						AVE	Std.Dev.
	Element Wt. %'s						
C	1.47	1.49	1.62	1.48	1.25	1.46	0.13
Ni	84.98	84.88	84.72	84.83	85.07	84.90	0.14
Zr	13.56	13.64	13.66	13.69	13.68	13.65	0.05
	Element Atomic %'s						
C	7.1	7.2	7.8	7.18	6.09	7.07	0.62
Ni	84.25	84.11	83.53	84.09	85.1	84.22	0.57
Zr	8.65	8.7	8.67	8.74	8.81	8.71	0.06

Feb. 16, 2010 -- Run #1							
	Element Wt. %'s					AVE	Std.Dev.
C	1.23	5.18	1.22	1	1.40	2.01	1.78
Ni	86.51	86.67	86.42	86.9	86.22	86.54	0.26
Zr	12.26	12.27	12.35	12.1	12.37	12.27	0.11
	Element Atomic %'s						
C	6.01	5.18	5.97	4.89	6.79	5.77	0.75
Ni	86.13	86.9	86.11	87.28	85.33	86.35	0.76
Zr	7.86	7.92	7.92	7.82	7.88	7.88	0.04

Feb. 16, 2010 -- Run #2							
	Element Wt. %'s					AVE	Std.Dev.
C	1.22	1.2	1.35	1.23	1.45	1.29	0.11
Ni	87.79	87.96	87.62	87.76	87.5	87.73	0.17
Zr	11	10.84	11.02	11.01	11.05	10.98	0.08
	Element Atomic %'s						
C	5.9	5.83	6.53	5.97	6.96	6.24	0.49
Ni	87.08	87.25	86.46	87.01	86.04	86.77	0.50
Zr	7.02	6.92	7	7.03	7	6.99	0.04

Diffraction Pattern of NiZr-Deposited Films

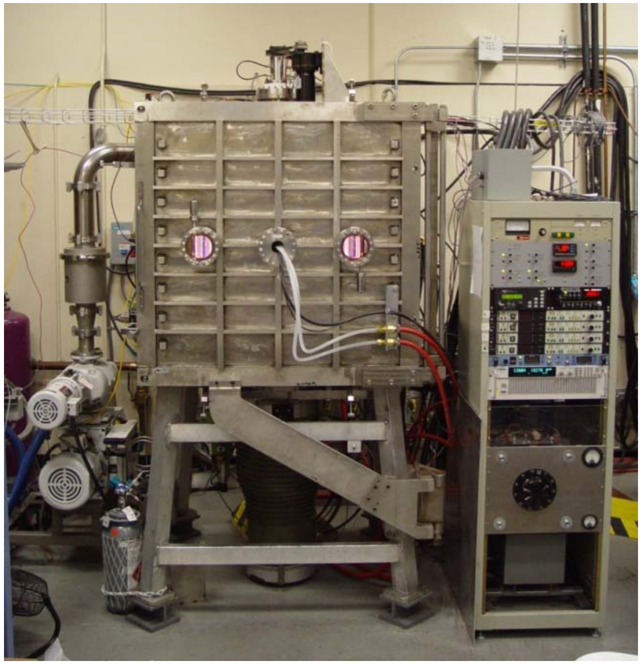


	PEAK 1				PEAK 2				
Sample	**2-θ**	**d**	**FWHM**	**Imax**	**2-θ**	**d**	**FWHM**	**Imax**	**Area**
Feb. 15, Run 1	Not Observed				44.82	2.035	5.1	104	109K
Feb. 16, Run 1	2.723	32.42	0.22	105	44.10	2.056	2.1	236	123K
Feb. 16, Run 2	2.472	35.71	0.10	155	44.00	2.056	1.1	490	121K

Economics

Cost Contributors using PVD

— Equipment Depreciation
— Fully Burdened Labor Costs
— Cost of Utilities and Maintenance
— Throughput per Minute
— Operational Time
— Raw Material Cost



- $\$35/\text{ft}^2$ of Pd Alloy
- Total Final Cost - $\$45.50/\text{ft}^2$
- **Material is 77% of the Cost**

Kitco Metals (December 7, 2009)
Pd - $5,952/lb
Ni - $6,82/lb

Task 4: Testing

Subtask 4.1: Thermal Stability Tests of Amorphous Alloys: Thermal tests will be conducted on a number of alloys to determine the stability of the amorphous character of the alloys with time and temperature. Coupons will be prepared at 1" square of glass and of stainless steel. Films of the amorphous alloys will be deposited on the coupons at 10 microns thick. X-ray diffraction will be conducted on the coupons to confirm the amorphous character of the alloys. The coupons will be put into a furnace between 250 and 800ºC under argon and maintained at temperature for up to 100 hours. After thermal treatment, the coupons will be re-examined by XRD for amorphous character. X-ray photoelectron spectroscopy will be used on a small number of coupons to investigate any surface segregation of doping elements following thermal tests. The choice of glass and stainless steel coupons will be used to determine if substrate crystallinity influences the stability of the alloys.

Subtask 4.2: Test Protocol of Hydrogen Separation Membranes: NETL has established a protocol for testing of hydrogen separating membranes which includes criteria for gas composition, sweep gas, feed pressure and temperature. Supported amorphous alloy membranes will be prepared of a number of alloy compositions with a nominal size of 1" diameter cylinder with an active length of 6". The hydrogen flux of these membranes will be measured in equipment previously used for testing vanadium disc membranes. Helium leak tests at 200 psig will be conducted first to determine the presence of any membrane defects. Baseline tests will be conducted using pure hydrogen at 100 psig and argon sweep near atmospheric pressure. A gas chromatograph will be used to measure hydrogen product concentrations. Each membrane will then be tested in the protocol test mixture #1 and flux values recorded over 8 hours. The alloys showing best performance will be then tested under protocol test mixtures 2a, 2b, and 2c. The best performing alloy will be tested under a chosen test mixture for 100 hours.

***Subtask 4.3: Gasifier Test of Hydrogen Separation Membranes*:** WRI operates a 7" diameter fluidized bed coal gasifier. The gasifier uses 35 lb/hr Powder River Basin coal and operates under a steam oxygen regime. A slip stream is filtered and compressed to supply 2 scfm at 200 psig of the following composition: H_2 - 30%, CO- 18%, CO_2 - 25%, CH_4 - 2%, Steam - 25%, H_2S - 125 ppm. Supported amorphous alloy membranes will be tested in the gasifier slipstream after passing helium leak tests at 200 psig. The membranes will be tested with 8 hour cycles for up to 48 hours each. Flux measurements will be made to record performance versus time. Membranes will be examined after exposure for evidence of contamination.

Testing Protocol

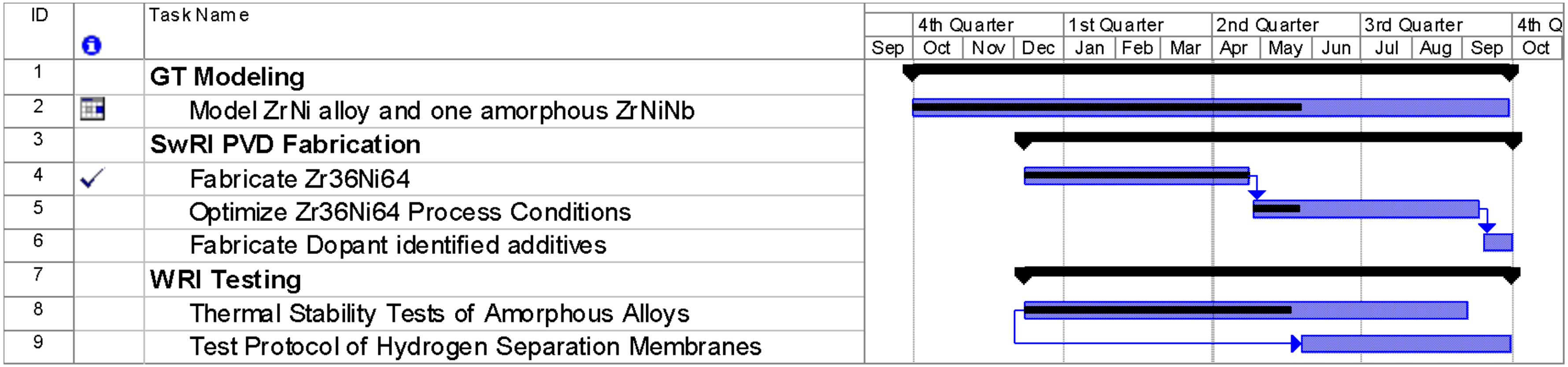
	Test Phase			
	Test 1	Test 2a	Test 2b	Test 2c
Feed Gas Composition (Before correction for addition of He)				
H_2 (%)	50.0	50.0	33.0	4.8
CO (%)	1.0	1.0	1.3	2.0
CO_2 (%)	30.0	30.0	40.0	57.0
H_2O (%)	19.0	19.0	25.0	36.2
H_2S (%)	0.000	0.002	0.003	0.004
Sweep Gas Composition				
Ar (%)	100	100	100	100
Total Feed Pressure (psia)	200	200	200	200
H_2 Feed Pressure (psia)	100	100	66	9.6
Total Sweep Pressure (psia)	<30	<30	<30	<30
$(P_{H2S}/P_{H2})_{Feed}$	0.00E+00	4.00E-05	9.09E-05	8.33E-04
Temperature (^{o}C)	300-600	300-600	300-600	300-600

WRI’s Coal Gasifier

Year 1 Summary

Phase I (Year 1)
The first year will consist of demonstrating an amorphous alloy with the following milestones identified for this initial phase (Note: the milestones are numbered according to the corresponding tasks):

> ***Milestone 2.2***: Fabricate at least six membrane samples with compositions consistent with those used by Georgia Tech for H_2 flux modeling.
>
> ***Milestone 2.3***: Test and establish thermal stability of amorphous alloys.



ID	ℹ	Task Name
1		**GT Modeling**
2	▦	Model ZrNi alloy and one amorphous ZrNiNb
3		**SwRI PVD Fabrication**
4	✓	Fabricate Zr36Ni64
5		Optimize Zr36Ni64 Process Conditions
6		Fabricate Dopant identified additives
7		**WRI Testing**
8		Thermal Stability Tests of Amorphous Alloys
9		Test Protocol of Hydrogen Separation Membranes

Contact Information

Georgia Tech
Dr. David Sholl
Michael Tennenbaum Family Chair and GRA Eminent Scholar in Energy Sustainability
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology
Atlanta, GA, 30332-0100
david.sholl@chbe.gatech.edu
P: 404-894-2822

SwRI
Kent Coulter, Ph.D.
Manager, Surface Engineering & Materials Chemistry
Southwest Research Institute
6220 Culebra Rd
San Antonio Texas, 78238
kent.coulter@swri.org
P:210-522-3196

Vladimir Gorokhovsky, Ph.D.
Staff Scientist
Southwest Research Institute
6220 Culebra Rd
San Antonio Texas, 78238
vladimir.gorokhovsky@swri.org
P:210-522-6801

Western Research Institute
Dr. Thomas F Barton
Principal Engineer, Energy Production and Generation
Western Research Institute
365 N. 9th Street
Laramie, WY 82072
TBarton@uwyo.edu
P:307-721-2472

NETL
Steven R. Markovich
Project Manager, Fuels Division
National Energy Technology Laboratory
Mailstop P03B
3610 Collins Ferry Rd.
Morgantown, WV 26507-0880
Steven.Markovich@netl.doe.gov
P:304-285-4735