

II.C.6 Membrane Separation—Bulk Amorphous Hydrogen Purification/ Separation Membranes

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Accomplishments

- Evaluated hydrogen flux properties for five commercially available metallic glass materials.
- Evaluated crystallization parameters via calorimetry and X-ray crystallographic phase analysis as a function of temperature and gas environment.
- Kinetic crystallization parameters based on Avrami equation were obtained for the 2826 alloy and compared with literature.
- Baseline permeation properties of the amorphous alloys were characterized by gas phase permeation.
- The impact of crystallization on the permeation was studied in situ by measuring gas phase hydrogen permeation during crystallization.



Objectives

- Demonstrate the feasibility of using metallic glass materials in bulk form for novel advanced hydrogen purification membranes.
- Develop optimized bulk amorphous alloy compositions for hydrogen separation membranes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Cost
- (C) Operation and Maintenance (O&M)
- (F) Control and Safety
- (N) Hydrogen Selectivity

Technical Targets

DOE 2010 Separation Membrane Targets:

- Flux rate: 200 scfh/ft²
- Cost: <\$100/ft²
- Durability: 100,000 hours
- Operating Temperature: 300-600°C
- Parasitic Power: 2.8 kWh/1,000 scfh

Introduction

Separation and purification membranes must have high hydrogen solubility, high diffusivity and catalytic activity on the surface of the membrane. Hydrogen separation as described in this work can be accomplished by the use of bulk amorphous materials (namely, bulk metallic glasses) permeable to hydrogen. The focal point of the SRNL effort will be on the development and optimization of a bulk amorphous material for the dense metallic-based membrane substrate.

The current generation of gas separation membranes is based on palladium/palladium (Pd/Pd) alloys used either independently or in conjunction with porous ceramic supports. Pd/Pd alloys have been known to possess the ability to dissolve considerable amounts of hydrogen and to demonstrate increasing permeability with increasing pressure differential and temperature. However, the major drawbacks to their industrial use are the high cost for Pd, the relatively low flux, and that during cycling above and below a critical temperature an irreversible change takes place in the palladium lattice structure which can result in significant damage to the membrane. SRNL has previously worked with thin section (melt-spun ribbons) of metallic glass materials for membrane applications, however, with the relatively new ability to cast fully amorphous metallic glasses in bulk sections a new opportunity has opened for bulk metallic glasses (BMG) as hydrogen membranes. The ability to readily cast BMG alloys will allow for easier fabrication of membranes – machine thin membranes

from larger BMG casting – and will also ease mass production challenges in comparison to thin section (melt spun) metallic glass ribbons. These BMG alloys have been shown to possess high permeation rates.

Approach

Testing in Fiscal Year 2009 has centered on the determining the crystallization behavior and subsequent impact on hydrogen permeability of commercially available amorphous/metallic glass materials. The permeation of hydrogen through metallic membranes is a multi-function process involving adsorption, dissociation, diffusion, and recombination and desorption. Two of the inherent materials properties that play a critical role in these processes are the solubility and diffusion of hydrogen in the material. Though the long range structure is “disordered” in amorphous materials, the diffusivity has been thought to occur through interstitial mechanisms similar to crystalline materials. The solubility however, should be enhanced in amorphous materials due to the greater density of defects and distribution of sorption sites which can be occupied by hydrogen over a wide range of potential energies. For materials which are partially crystalline one of the critical factors determining the diffusion, solubility and ultimately the permeation properties is the role the secondary crystalline phase play in the composite structure. It has also been shown that the nature of the crystalline phase depends on the gas environment of crystallization or hydrogen content of the material. In order to systematically study the impact of partial crystallization in these materials a variety of compositions were purchased from commercial sources to obtain five Fe, Ni, Co and Zr based metallic glasses. These samples were subjected to differential scanning calorimetry (DSC) as a function of temperature under different gas compositions in order to quantify phase transition temperature and energies. X-ray diffraction (XRD) analysis was also performed as a function of temperature and gas composition. Finally, hydrogen permeation properties were measured in situ where crystallization took place during gas phase hydrogen permeation at elevated temperatures.

Results

Metallic glass samples with a nominal thickness of 25 microns in 2 inch wide ribbons were purchased from commercial sources (MetGlas Inc., Conway, SC) with the compositions given in Table 1. A 651 model TA Instruments DSC was used to evaluate crystallization temperatures at scan rates of 10°C/min from 25°C up to 590°C in 4% hydrogen and 96% argon gas flowing at 30 sccm. The instrument was temperature calibrated using an indium metal standard and the nominal metallic glass sample mass was ~8 mg. Permeation test samples were sealed by crimping between two VCR® fittings with a Ag-plated Cu gasket which were then connected to a standard 2.12” CF flanges and helium leak tested to confirm lower than 1×10^{-7} std cc/second at 1 atmosphere pressure. Measurement of the steady-state permeation flux was conducted under sub-atmospheric pressures (400 to 700 Torr), values typically used at the Savannah River Site for hydrogen isotope purification. The measured permeability was 5.3×10^{-9} mol H_2 $m^{-1} s^{-1} Pa^{-1/2}$ for the 2826 alloy at 400°C and 700 torr pressure differential compared to Pd flux of 2×10^{-8} mol H_2 $m^{-1} s^{-1} Pa^{-1/2}$.

In order to examine issues related to membrane crystallization, calorimetric techniques were used to determine the temperature of crystallization and the energy released of the five commercial available Metglas alloys indicated in Table 1 and Figure 1 using a ramp rate of 10°C/min under a flowing argon atmosphere. The 2826 alloy was chosen for further kinetic studies due to availability of literature data on kinetic crystallization parameters for comparison. Kinetic rate parameters were obtained from DSC experiments and Avrami kinetic expressions were used to compare experimental crystallization kinetics with literature. XRD were collected on a theta-theta PANalytical X'Pert Pro X-ray diffractometer using an Anton Paar HTK 1200 high temperature attachment. A summary of the crystalline phase formation in varying temperatures and gas environments is displayed in Table 2.

TABLE 1. Alloy Composition Investigated, Purchased from Metglas Company Inc. and Howmet Research Corporation [6]

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	Proprietary						

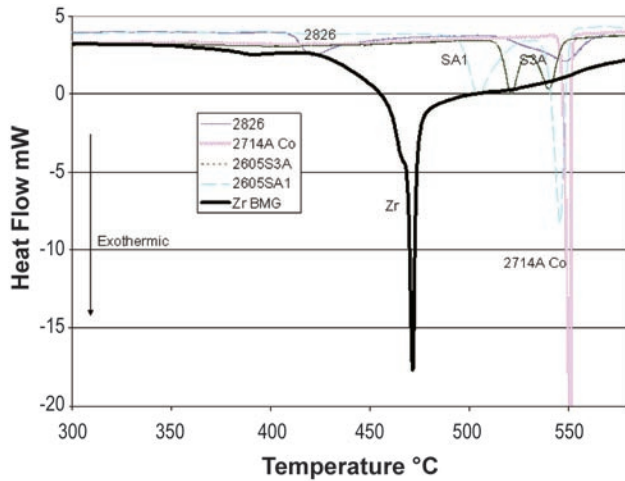


FIGURE 1. DSC performed on metglass alloys at 10°C/min under flowing Argon atmosphere 30 sccm from 25°C to 590°C.

TABLE 2. Summary of Identified Phases in 2826 Alloy

Compound	Formula	5°/min in He (°C)	5°/min in 4% H ₂ 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 Pinakioite ^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 high temperature XRD 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.

For the 2826 alloy, DSC indicates a crystallization temperature of ~420°C which is identified by XRD as a FeNi face centered cubic phase. Kinetic estimates of crystallization suggested that at 400°C the 2826 alloy would completely crystallize in less than 1 hour at temperature limiting the operating window of this

material in gas separation applications. However, the energy release determined by DSC for the crystallization event at 420°C is significantly less than other alloys and XRD of the material near 400°C after 1 hour showed evidence of a large fraction of remaining amorphous phase. Isothermal XRD measurements presented in Figure 2 were carried out at 400°C over a 3-hour duration demonstrated that limited crystallization (30% volume crystalline phase fraction) occurs over this extended period. These crystallization studies were compared with dynamic permeation measurements. In the dynamic measurement displayed in Figure 3, the permeation flux is directly proportional to the measured hydrogen partial pressure. Changes in the slope of this curve, dP/dt indicates apparent changes in the hydrogen flux. The hydrogen permeation at 400°C is seen to decrease slightly over the first hour, and then reaches steady-state values over the following 2 hours concurrent with crystallization measurements.

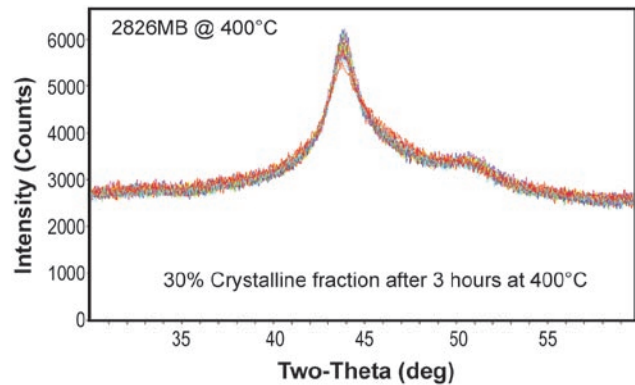


FIGURE 2. Isothermal XRD measurements for 2826 alloy at 400°C over 3 hours indicating 30% volume fraction crystallinity and remaining amorphous structure.

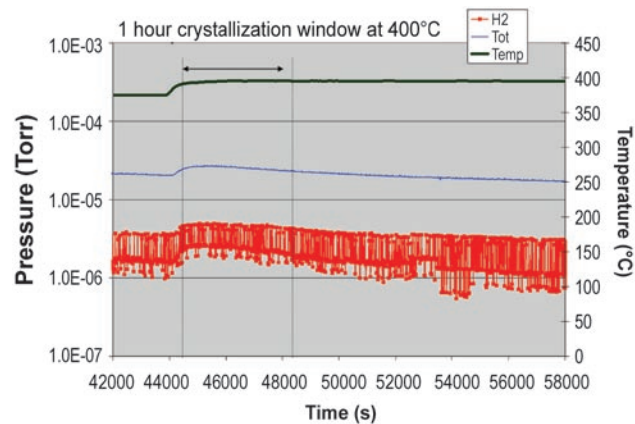


FIGURE 3. Dynamic permeation measurement, pressure versus time for 2826 alloy at 400°C.

Conclusions and Future Directions

Conclusions

- Commercially available metallic glass membrane materials have been demonstrated to possess permabilities/fluxes on par with Pd-based membrane materials.
- Metallic glass membranes have been demonstrated to provide efficient and effective separation of hydrogen from a mixed gas feed stream.
- DSC and XRD at elevated temperatures show a partial transformation of 2826 amorphous alloy to cubic FeNi crystalline phase (30% by volume) at temperatures near 400°C.
- Dynamic permeation measurements showed this crystallization behavior reduces the flux during the first hour when crystallization occurs and then stabilizes (due to stable amorphous/crystalline phase fraction co-existing) over longer time periods up to 3 hours.

Future Work

- Thin film metallic glass membrane fabrication on porous substrates by sputter deposition.
- First principles modeling in order to investigate compositional effects in metallic glass systems.
- Contaminant effects on hydrogen separation (CO, H₂S etc.).

FY 2009 Publications/Presentations

1. Kyle S. Brinkman, Elise B. Fox, Paul Korinko, Thad Adams, and Arthur Jurgensen: *The Impact of Partial Crystalline on the Permeation Properties Bulk Amorphous Glass Hydrogen Separation Membranes*, in Solid-State Ionics–2008, edited by E. Traversa, T. Armstrong, K. Eguchi, M.R. Palacin (Mater. Res. Soc. Symp. Proc. Volume 1126, Warrendale, PA, 2009), 1126-S09-13.
2. P. Korinko, K.S. Brinkman, T.M. Adams, G.B. Rawls, *Development of a Non-Noble Metal Hydrogen Purification System* TMS Annual Meeting conference proceedings, symposium Materials in Clean Power Systems IV: in Clean Coal-, Hydrogen Based-Technologies proceedings of TMS Annual Meeting, San Francisco, CA Feb 15–19 2009.

3. K. Brinkman, E. Fox, P. Korinko, T. Adams, *The Impact of Partial Crystallization on the Permeation Properties of Bulk Amorphous Glass Hydrogen Separation Membranes*, Materials Research Society (MRS), Fall Meeting, Boston, MA Dec 1–5, 2008.
4. P. Korinko, K.S. Brinkman, T.M. Adams, G.B. Rawls, *Development of a Non-Noble Metal Hydrogen Purification System* TMS Annual Meeting conference proceedings, symposium Materials in Clean Power Systems IV: Clean Coal-, Hydrogen Based-Technologies, TMS Annual Meeting, San Francisco, CA Feb 15–19 2009.
5. K. Brinkman, E. Fox, P. Korinko, A. Jurgensen, T. Adams, *The Effects of Partial Crystallinity On The Hydrogen Permeation Properties of Bulk Amorphous Metallic Systems* in TMS San Francisco “bulk metallic glasses symposium” February 15–21, 2009.
6. K. Brinkman, E. Fox, P. Korinko, T. Adams, *Hydrogen Permeation Properties of Metallic Glass Materials*, National Hydrogen Association (NHA) Annual Meeting, Columbia, SC March 30th–April 2nd, 2009.
7. Stephen L. Garrison, Kyle S. Brinkman, Paul S. Korinko, and Thad M. Adams, *Molecular Modeling of Bulk Metallic Glass Membranes for H₂ Separation/Purification*, at North American Membrane Society (NAMS), Charleston, SC June 2009.