II.C.1 Membrane Separation–Bulk Amorphous Hydrogen Purification/ Separation Membranes

Thad Adams
Savannah River National Laboratory (SRNL)
773-41A/151
Aiken, SC 29808
Phone: (803) 725-5510; Fax: (803) 725-4553
E-mail: thad.adams@srnl.doe.gov

DOE Technology Development Manager:
Sara Dillich
Phone: (202) 586-7925; Fax: (202) 586-2373
E-mail: sara.dillich@ee.doe.gov

Project Start Date: May 1, 2007
Project End Date: October 1, 2012

Objectives

- Demonstrate the feasibility of using metallic glass materials in bulks 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/ft^2
- Cost: <\$100/ft^2
- Durability: 100,000 hours
- Operating Temperature: 300-600°C
- Parasitic Power: 2.8 kWh/1,000 scfh

Accomplishments

- Evaluated hydrogen flux properties for five commercially available metallic glass materials.
- Conducted manufacturability studies to investigate sealing technologies for fabrication of metallic glass membrane assemblies.
- Initiated hydrogen separation efficiency testing for monolithic metallic glass membrane materials.
- Performed preliminary raw materials based cost comparison for metallic glass membrane materials.

✧ ✧ ✧ ✧ ✧

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 (BMGs) 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. BMG alloys are traditionally processed from multi-component systems comprised of metallic species of varying atomic size. It is this vast difference in atomic sizes that results in slow diffusion/redistribution kinetics and allows for deep undercoolings to the point of freezing in the "liquid" structure to produce amorphous metallic alloys at relatively slow cooling rates (10-100 K/s). These BMG alloys have been shown to possess high permeation rates. For example the permeation rate for a Zr-Al-Co-Ni-Cu BMG alloy–1.13 x 10^{-8} mol/m s $Pa^{1/2}$–is comparable to the permeation rate measured for pure Pd metal. Furthermore, these BMG alloys have also been shown to possess high elastic toughness and excellent resistance to hydrogen degradation. Both of these properties–high permeation and high elastic toughness–potentially makes these materials attractive for gas separation membranes.

Approach

Testing in Fiscal Year 2008 has centered on the evaluation of hydrogen permeability of commercially available amorphous/metallic glass materials. Two aspects that are critical to the successful demonstration of the use of amorphous/metallic glass materials for hydrogen separation membranes are flux of hydrogen through the membrane and manufacturability of the membrane stack. As such, permeation testing using the SRNL low-pressure gaseous test rig and employing mechanical sealing techniques for the metallic glass membrane materials has continued. These tests are conducted by introducing hydrogen to the feed sides of the planar membrane at an elevated pressure and monitoring the pressure increase on the permeate side of the membranes which has previously been evacuated (on the order of 10^{-6} torr). Testing has been conducted at both 350°C and 400°C with feed pressures of 400 torr and 700 torr. Single permeation breakthrough curves have been run for each sample followed by multiple saturation curve experiments. The multiple saturation curve experiments allows for a more accurate determination of the slope of the permeate pressure rise versus time data which is subsequently used for a determination of the flux and permeability values associated with the membrane materials being tested. Additionally, from a manufacturability focus effort has been conducted in FY 2008 with respect to development of appropriate sealing technologies for metallic glass membrane assemblies. SRNL has employed the following techniques to attempt to achieve a high integrity seal between the metallic glass foils and the stainless steel flange bodies: 1) electron beam welding, 2) brazing–Au-Sn, Au-In, and Au-Ge, and 3) mechanical sealing.

Results

Membrane flux testing in FY 2008 has focused on the evaluation of four Fe/Co-based and one Zr-based commercially available metallic glass alloys. Single permeation breakthrough curves have been run for each sample since there is little lag time. These tests were followed by multiple saturation curve experiments. The multiple saturation curve experiments allows for a more accurate determination of the slope of the permeant pressure rise versus time data which is subsequently used for a determination of the flux and permeability values associated with the membrane materials being tested. Figure 1 displays the flux data for three of the four Fe/Co-based metallic glass alloys tested under this project. From this data plot we see good reproducibility between the multiple saturation curve experimental runs and the expected increase in flux with increasing temperature. From this flux data, the average permeabilities at the specific test conditions have been determined for each of the commercially available Fe-based metallic glass materials as shown in Table 1. An examination of this average permeability data indicates that the most promising of the Fe-based metallic glass alloys is the 2826MB alloy. This alloy has a measured permeability very close to Pd/Pd-alloys (5 x 10^{-9} vs. 1 x 10^{-8} mol $H_2/s/m^2/Pa^{1/2}$). A potential drawback to this alloy, however, is that it possesses the lowest crystallization temperature of the four alloys tested which could ultimately limit the upper operating temperature of a membrane reactor system.

Furthermore, a critical technical target for dense metallic membranes as outlined in the April 2007 Hydrogen Production Multi-Year Program Plan is the ability for dense metallic membranes to effectively and efficiently produce high purity output hydrogen streams. With this in mind, SRNL initiated some preliminary separations testing of the metallic glass membrane materials. This testing was conducted using the SRNL gaseous permeation test rig interfaced with a gas chromatograph mass spectrometer unit to measure partial gas pressures. Testing was conducted at using a mixed H_2-He feed gas at 400°C and 700 torr. Preliminary separations data for the Metglass Inc., Co-

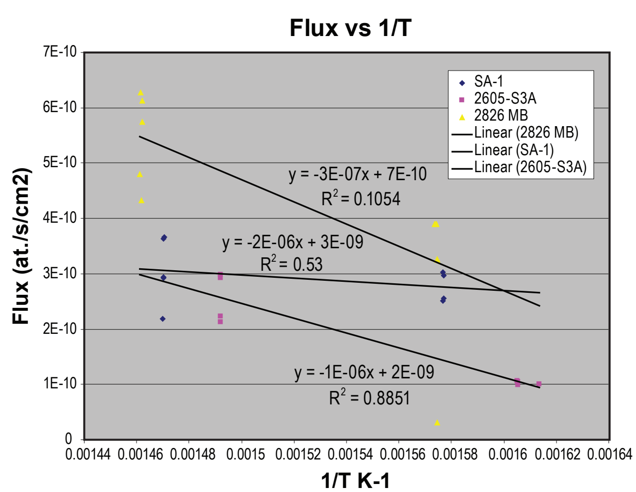

FIGURE 1. Saturation Curve Flux Data for Fe-based Metallic Glass Alloys

TABLE 1. Average Permeability for Fe-Based Commercial Metallic Glass Alloys

Alloy Name	Permeability 350°C/400T (mols/m·s· $Pa^{1/2}$)	Permeability 350°C/700T (mols/m·s· $Pa^{1/2}$)	Permeability 400°C/400T (mols/m·s· $Pa^{1/2}$)	Permeability 400°C/700T (mols/m·s· $Pa^{1/2}$)	Reported Crystallization Temperature (°C)	Composition (wt%)
2605SA1	5.95 e^{-10}	8.83e^{-10}	8.97e^{-10}	1.33e^{-9}	510	Fe=85-95 Si=5-10 B=1-5 Co=0.2 (max) Ni=0.2 (max)
2605S3A	1.16e^{-9}	1.09e^{-9}	2.40e^{-9}	2.51e^{-9}	535	Fe=85-95 Cr=1-5 Si=1-5 B=1-5
2826MB	3.66e^{-9}	3.36e^{-9}	5.44e^{-9}	5.25e^{-9}	410	Fe=40-50 Ni=40-50 Mo=5-10 B=1-5 Co=0.3 (max)
2714A	6.5e^{-10}	1.30e^{-10}	—	—	550	Co=75-90 Fe=7-13 Si=7-13 Ni=1-5 B=1-5

Fe-Si-Ni-B metallic glass alloy 2714A alloy are displayed in Figure 2. From this data is clear that the 2714A metallic glass alloy can successful separate the H_2-He to provide a pure H_2 output form the test membrane system.

In addition to the permeation/flux testing conducted on the Fe-Co-based metallic materials, further preliminary testing has also been conducted on the Zr-based metallic glass alloy. Preliminary flux testing of the Zr-Cu-Ni-Al-Y metallic glass alloy has shown fluxes significantly higher that the Fe/Co-based materials. Testing in FY 2008 will continue to focus on evaluation of the Zr-based metallic glass alloy and will also initiate testing to investigate the manufacture of defect free porous substrate supported Zr-based metallic glass membrane assemblies.

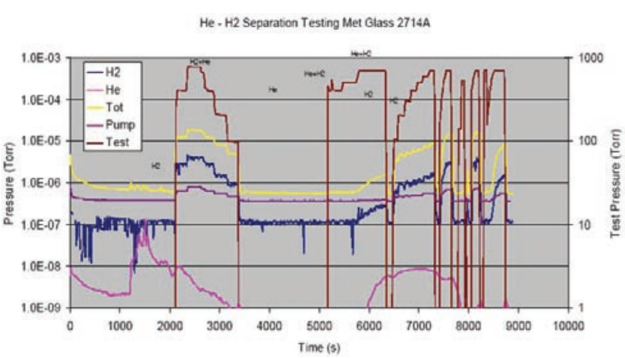

FIGURE 2. Preliminary H_2-He Separations Data for 2714A Metallic Glass Alloys

The ability to seal the membrane to the system flanges to a minimum level of 1 x 10^{-7} cc/sec leak rate is critical to ensure that acceptable separation efficiency will be achieved when the membrane unit is employed for purification of impure gaseous hydrogen feed streams. SRNL has employed the following techniques to attempt to achieve a high integrity seal between the metallic glass foils and the stainless steel flange bodies: 1) electron beam welding, 2) brazing–Au-Sn, Au-In, and Au-Ge, and 3) mechanical sealing. Results from these experiments have shown that electron beam welding of the Zr-based metallic glasses is inadequate. Cracking of the membrane foil occurs both during welding and post-welding most likely due to issues with differential thermal expansion and residual stress in the Zr-metglass material. Brazing of the Zr-based metallic glass materials was conducted using two techniques–induction brazing and vacuum furnace brazing. Induction brazing was plagued by issues related to surface cleanliness and sample wetting and was unable to achieve any successful or partially successful braze seals. Vacuum furnace brazing, however, was able to achieve a partially successful seal braze. The vacuum brazing techniques required the use of Ti-sponge getter bed and slow ramp rates for heat-up and cool-down but this technique was able to achieve a wetted surface and successful seal. However, issues with the vacuum brazed sample did result in cracking of the membrane during installation of the sample in the test rig. This failure was attributed to embrittlement of the metallic glass material as a result of the brazing treatment. Lastly, mechanical sealing using a commercial available VCR-to-conflat flange designed membrane holder was successful. Thus, in order to evaluate the flux properties of these metallic glass materials mechanical sealing using this device was employed for testing in FY 2008.

Lastly, in addition to demonstration of the technical viability of the metallic glass materials in the areas of hydrogen flux, separation efficiency, and manufacturability a fourth critical challenge is in the area of module cost. The current 2010 DOE technical target for total module cost–raw materials and fabrication costs totaled–is set at $1,000/ft^2 of membrane. In order to begin to develop a module cost estimate, SRNL has initiated a basic raw materials cost analysis that involves a measure of hydrogen flux per membrane raw materials cost. Table 2 displays a listing of this flux/$ analysis for the Metaglass Inc., Fe/Ni-based metallic alloys as compared to a conventional Pd-based alloy membrane. Evaluation of the preliminary cost analysis results indicates that due to the significantly greater raw materials cost for the Pd-alloy material and greater flux per dollar value is achievable using the metallic glass alloys in spite of the fact that the inherent flux properties of the metallic glass are approximately an order of magnitude lower for the metallic glass alloys compared to the Pd-alloy materials. Thus, assuming that the fabrication costs for a module are comparable and although more surface area of metallic glass membrane may be required to achieve a comparable flux the large delta in raw material costs can overcome the flux delta and can allow for a lower cost membrane module using the metallic glass materials. There is, however, a "balance-of-plant" cost that may not be adequately characterized by this simple model.

TABLE 2. Average Permeability for Fe-Based Commercial Metallic Glass Alloys

Alloy Name	Composition (wt%)	Flux Cost (mols H_2/ft^2 s)/$raw material
2605SA1	Fe=85-95 Si=5-10 B=1-5 Co=0.2 (max) Ni=0.2 (max)	1.38 x 10^{-6}
2605S3A	Fe=85-95 Cr=1-5 Si=1-5 B=1-5	2.48 x 10^{-6}
2826MB	Fe=40-50 Ni=40-50 Mo=5-10 B=1-5 Co=0.3 (max)	3.96 x 10^{-6}
2714A	Co=75-90 Fe=7-13 Si=7-13 Ni=1-5 B=1-5	3.07 x 10^{-7}
Pd-Alloy	Pd-Ag	6.55 x 10^{-9}

Conclusions and Future Directions

Conclusions

- Commercially available metallic glass membrane materials have been demonstrated to possess permeabilities/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.
- Sealing of metallic glass materials in membrane assemblies requires further investigation in order to provide high integrity seals without causing crystallization of these amorphous materials.
- Preliminary cost analysis indicates that on a hydrogen flux/$ cost of raw membrane materials that metallic glass alloys possess the potential to offer a significant cost reduction for hydrogen purification.

Future Work

- Evaluation of the Zr-based metallic glass flux properties with temperature and pressure.
- Initiation of defect free Zr-based thin film metallic glass membrane fabrication techniques.
- Separation efficiency testing for both monolithic and defect-free thin film membranes.
- Preliminary membrane module design concepts.

FY 2008 Publications/Presentations

1. *Alternative Materials to Pd Membranes for Hydrogen Purification,* Materials Innovations in an Emerging Hydrogen Economy Conference, Cocoa Beach, FL, February 2008.

2. *Joining Technology for Metglass Sealing*, NNSA Welding/Joining IMOG, Sandia National Laboratory, Albuquerque, NM, March 2008.

3. Paper and Presentation presented and submitted, *Alternative Materials to Pd Membranes for Hydrogen Purification,* International Symposium on Materials Issues in a Hydrogen Economy, Virginia Commonwealth University, November 12-15, 2007.

4. *SRNL Membrane Research*, Presentation, PURWIG Meeting, Baltimore, MD, November 7, 2007.

5. *Alternative Materials to Pd Membranes for Hydrogen Purification,* Presentation, Tritium Focus Group Meeting, PNNL, May, 2008.