II.D.4 Amorphous Alloy Membranes for High Temperature Hydrogen Separation

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Objectives

The objective of this project is to 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 platinum group metals.

Technical Barriers

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

(K) Durability
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(R) Cost

Technical Targets

Year 1: The first year consisted of demonstrating an amorphous alloy with the following targets identified for this initial phase:

- Fabricated at least six membrane samples with compositions consistent with those used by Georgia Tech for H_2 flux modeling.
- Tested and established thermal stability of amorphous alloys.

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 targets have been identified for this second phase:

- 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.
- Testing at WRI of a second set ($\leq$12) of alloys from the optimization trials by pure gas (H_2 and N_2) permeation experiments.

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 targets have been identified in this final phase:

- SwRI® will produce a minimum of four optimized membranes for testing at WRI.
- Complete two gasifier tests (or a smaller number of longer duration tests) at WRI on optimized membrane materials with multiple additions of H_2S, carbon oxysulfide, HCl, and metallic impurities.

Table 1 lists current test information for a number of membranes and compares it with DOE target values.

Accomplishments

- Have demonstrated our modeling approach is sufficient to generate realistic samples of these amorphous materials.
- Have concluded that the quantitative discrepancy between theoretical predictions and the amorphous film experiments is relatively small and that our methods are capable of making useful predictions about these properties.

TABLE 1. Progress towards Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	SwRI® Membranes
Flux (scfh/ft^2)	200	300	
Operating Temperature (°C)	300-600	250-500	200-300
Sulfur Tolerance (ppmv)	2	20	
System Cost (\$/ft^2)	500	<250	
ΔP Operating Capability (psi)	400	800-1,000	
Carbon Monoxide Tolerance	Yes	Yes	
Hydrogen Purity (%)	99.5	99.99	
Stability/Durability (years)	3	>5	

- Have demonstrated the permeabilities by 32 atom cells are in good agreement with those by 108 atom cells as published in J.Mem.Sci. 350, 402 (2010).
- Have identified several new novel binary and ternary amorphous alloys with predicted permeabilites similar to Pd.
- The precise deposition of metal coatings by two magnetron sources and by co-deposition using two magnetron sources have been demonstrated for deposition of NiZr coatings.
- WRI has conducted all X-ray powder crystallography and elemental composition tests of the as deposited samples and has begun thermal annealing tests.
- Completed multiple project conference calls and joint calls with the other DOE-funded team at the University of Nevada, Reno working on amorphous alloy membranes.
- Presented slides at the U.S. Department of Energy 2010 Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting held on June 7–11, 2010 in Washington, D.C.

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Introduction

Thin film amorphous alloy membranes are a nascent but promising new technology for industrial-scale hydrogen gas separations from coal-derived syngas. This project uses a combination of theoretical modeling, advanced physical vapor deposition fabricating, and laboratory and gasifier testing to develop amorphous alloy membranes that have the potential to meet all DOE targets in the testing strategies outlined in the National Energy Technology Laboratory Membrane Test Protocol.

Approach

The approach of the project is to incorporate modeling, fabricating, and testing all operating concurrently to develop 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 precious group metals. This collaborative effort will involve work at SwRI®, Georgia Tech and WRI. The proposed project can be summarized in the three primary tasks that will run concurrently:

1. **Materials modeling and composition selection**: Building upon recent work at Georgia Tech using density functional theory (DFT) to identify promising ZrNi alloy compositions with improved hydrogen permeability, an expanding range of additive concentrations will be investigated. New calculations based on refined assumptions and boundary conditions will be used to direct the materials development effort in an iterative manner.
2. **Fabrication of high-performance amorphous alloy membranes**: SwRI® will lead the development of thin amorphous alloy membranes using advanced physical vapor deposition methods including magnetron sputtering. The unique feature of these techniques is the ability to rapidly produce membranes of almost any alloy composition with good uniformity and large areas (up to 100 in^2) onto stainless steel supports.
3. **Membrane testing and evaluation**: WRI will perform initial screening testing of experimental membranes under controlled atmospheres and confirm that the targeted structures and compositions have been produced. Initial performance data will be used to further refine DFT-based modeling and guide the vacuum deposition effort. Once one or more promising classes of alloys have been identified, WRI will evaluate these membranes under DOE specified test conditions for extended periods up to several hours. Compositional and structural analysis of exposed membranes by scanning electron microscopy (SEM), energy dispersive X-ray, and X-ray diffraction (XRD) will be employed in an effort to identify likely degradation pathways.

Results

Modeling

Georgia Tech has developed a general method based on first-principles calculations and statistical modeling to predict the permeability of pure H_2 through amorphous metal films [1,2]. This approach requires no experimental input or parameterization, so it is suitable for use in materials screening efforts. However, this method was based on DFT calculations with 108 atom supercells, which requires large amount of calculations and thus is time-consuming to perform screening from multiple candidates.

To accelerate the calculation, we use different size supercells to check the convergence of the calculated permeability convergence for $Zr_{55}Co_{25}Al_{20}$. We use 32, 64, 108-atom supercells to calculate solubilities, diffusivities and permeabilities. Figure 1 shows the calculated permeability. Although there is some variation between the calculations with the smaller supercells and the results when using a 108-atom supercell, these differences are small enough that we can use the smaller calculations as a screening tool.

We have therefore performed extensive calculations for amorphous alloys that have not been studied in previous experiments with the aim of novel materials discovery using 32-atom supercells. To this end, we examine amorphous $Ta_{40}Ni_{60}$, $Ta_{25}Ni_{60}Ti_{15}$, $Ti_{33}Co_{67}$, $Hf_{44}Cu_{56}$, $Hf_{25}Cu_{60}Ti_{15}$, $Zr_{45}Cu_{45}Al_{10}$, $Zr_{30}Cu_{60}Ti_{10}$, $Zr_{54}Cu_{46}$, and $Nd_{60}Fe_{30}Al_{10}$. Selection of these materials are based on the relative high crystallization temperatures reported experimentally for these materials (at least >720 K). To make permeability predictions, first principles methods were used to predict the solubility and net diffusivity of interstitial H in each amorphous material.

Membrane Deposition, Composition and Microstructure Optimization

The coating system setup used in this work is shown in Figure 2. Two direct current magnetrons using 4” diameter targets were installed at the bottom of the vacuum processing chamber for a co-sputtering deposition process of the amorphous alloy with argon as the processing gas.

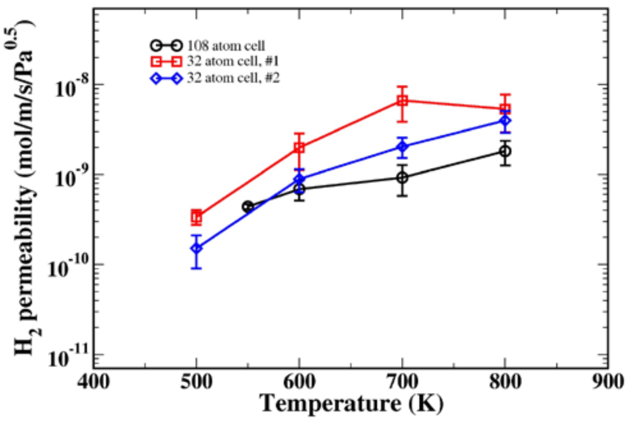

FIGURE 1. Permeability Comparison of Different Size of $Zr_{55}Co_{25}Al_{20}$. $P_{feed} = 3$ atm, $P_{permeat} = 0.01$ atm.

XRD analysis of the crystallinity of NiZr coatings and ribbons has demonstrated a strong correlation between their structure and thermal stability vs. their composition. Coatings with higher concentrations of Zr survived annealing for 1 hour at 250°C without re-crystallization. The re-crystallization started during 1 hr of annealing at 300°C in coatings with lower Zr content (Figure 3 plot #1), while coatings with Zr content >12 at% (#4 & 5) do not re-crystallize, showing XRD patterns after annealing similar to the melt-spun ribbon (#13) with optimal Zr content associated with amorphous NiZr alloy as shown in Figure 3 (Ni0.64Zr0.36 ribbon sample #12). On the other hand, the ribbon sample #13 having Ni0.3Zr0.7 composition was fully transformed into the polycrystalline state after 1 hr of annealing at 300°C. The optimal composition of

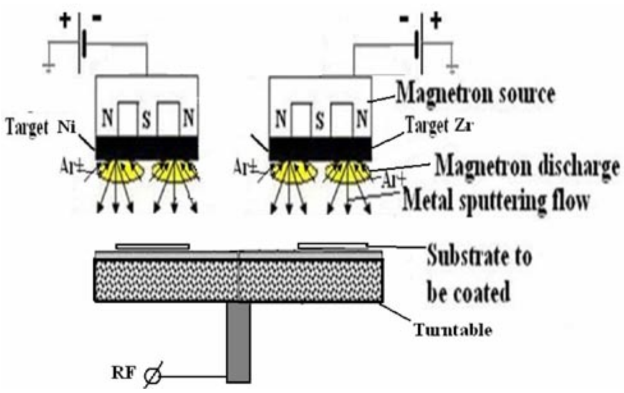

FIGURE 2. Magnetron Co-Sputtering Scheme

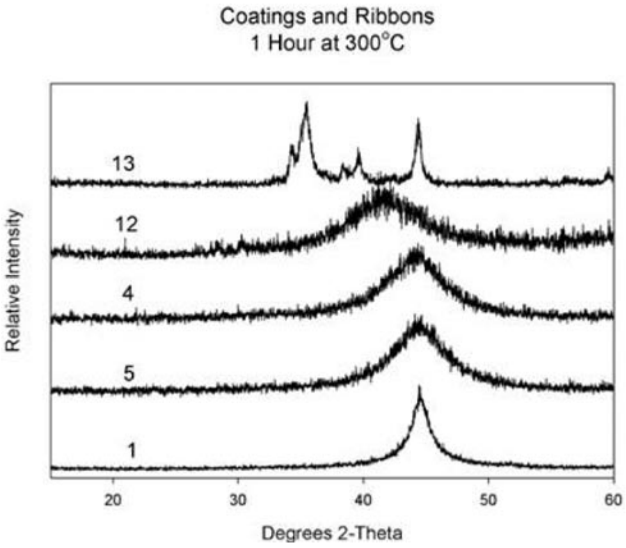

FIGURE 3. XRD Patterns of NixZr1-x Coatings and Bulk Metallic Glass Ribbons Subjected to 1 Hour Annealing at 300°C.

the NiZr amorphous alloys with Zr concentration near 30 at% is in agreement with published work presented in Refs. [3,4].

Conclusions and Future Directions

The project is on schedule and on budget with SwRI®, Georgia Tech, and WRI all operating independently and concurrently. Georgia Tech has demonstrated the modeling approach is sufficient to generate realistic samples of these amorphous materials. The precise deposition of metal coatings by one magnetron source and by co-deposition using two magnetron sources have been demonstrated for deposition of NiZr coatings. NixZr1-x coatings with x ranging from 0.71 to 0.93 were deposited by magnetron co-sputtering process. It was found that as-deposited films are more amorphous with an increase of Zr content starting from $x = 0.9$ and reaching a XRD-amorphous state at $x > 0.88$. Mechanical properties of these coatings are strongly correlated with their composition. Amorphous films with higher Zr content have retained their XRD measured amorphous state after 1 hr annealing in an argon/2% hydrogen atmosphere at 300°C. Further amorphization of some of the coatings, with lower Zr content, occur during thermal annealing below their re-crystallization temperature which may indicate the influence of a solid reaction amorphization mechanism on the coating structure evolution. The partial re-crystallization in films with the highest Zr content occurs after 24 hours of annealing. The Ni0.71Zr0.29 coating has demonstrated the best thermal chemical stability developing a mixture of a polycrystalline phase embedded within an amorphous matrix during annealing. The XRD spectrum of this film is nearly identical to the XRD spectrum of a melt-spun bulk metallic glass ribbon subjected to the same annealing treatment, indicating that thin film coatings deposited by co-sputtering and bulk metallic glass ribbons prepared by the melt-spinning technique have about the same thermal stability which is determined by their elemental composition and not by the method of fabrication.

Future work will consist of:

- Georgia Tech performing both solubility and diffusion calculations on ZrCu, ZrCuTi, HfCu, and HfCuTi systems.
- Future work will be conducted to better understand the mechanisms of formation of amorphous metal coatings and their thermal stability, which is critical for their applications in hydrogen separation membranes.
- 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.
- Testing at WRI of (≤12) of alloys from the optimization trials by pure gas (H_2 and N_2) permeation experiments.
- Complete two gasifier tests (or a smaller number of longer duration tests) at WRI on optimized membrane materials with multiple additions of H_2S, carbon oxysulfide, HCl, and metallic impurities.

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