II.G.5 High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

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Objectives

- Investigate new alloys of lower-cost transition elements to achieve basic improvements in metallic membrane technology to separate out hydrogen at the appropriate purity.
- Find a base metal replacement for palladium ($470/ounce) which is: stable at 350-400ºC, 100% selective like Pd, costs $100/ft^2 vs. $3,000/ft^2, has at least a 15-year life with no embrittlement and produces 50 scfh/ft^2 ultra-high purity H_2 at $\Delta P =$ 200 psi.
- Screen 50 more alloys in addition to the 82 that were prepared and tested in the past.
- Test brazing and welding to create the first tubes.
- Fabricate and test a membrane reactor.

Introduction

Palladium silver membranes have been used for decades to provide hydrogen purification, but palladium silver is expensive and soft. This project will investigate new alloys of lower-cost transition elements to achieve basic improvements in metallic membrane technology to extract hydrogen at the appropriate purity. It has been shown that, when coated with palladium, tubes and foils of Group 5B metals and alloys are substantially superior to palladium-silver in terms of hydrogen flux, uncontrolled failure and, most importantly, expense. These alloys will be experimentally evaluated as candidate membrane materials.

Approach

About 100 alloy and intermetallic compositions are to be fabricated and tested for toughness, embrittlement, permeation, and ease of manufacture. The embrittlement will be tested by determining a stress-strain curve before and after hydriding. Permeability will be tested by comparing alloy B (low cost non-embrittling), vanadium (embrittling) and alloy A (slightly embrittling) at 400ºC and 8 psig, mol/m/s/Pa. The most innovative of these are B2 intermetallics, though higher-melting-temperature refractory alloys will also be studied. Originally, two types of coatings will be tried: palladium and B2 phase palladium copper. Both materials dissociate and permeate hydrogen readily, and the B2 phase alloy is sulfur tolerant as well. It is expected that B2 phase alloy will exhibit less inter-diffusion. The first alloy samples will be produced as foil coupons, and later (once the alloy selections are narrowed) as tubes. The first small runs of membrane samples will be coated by vapor deposition in vacuum. Subsequent membranes and all tubes will be coated by electroless deposition or cladding, since these methods are amenable to commercial use.

Accomplishments

- Fabricated and tested several alloy and intermetallic compositions for toughness, embrittlement, permeation, and ease of manufacture and identified several that could serve as Pd replacements.
- Prepared foil coupons of alloy samples of palladium and B2 phase palladium copper based on tests that showed both materials dissociate and permeate

hydrogen readily with added sulfur tolerance from the B2 phase alloy.

- Prepared 60 intermetallic discs and coated each disc with a thin Pd layer.
- Measured the mechanical properties of these discs before and after hydriding.
- Conducted an accelerated aging test and demonstrated a suitable flux (around 0.08 mol/m^{2}sec) for over 1,000 hours.
- Tested the manufacturability and embrittlement of the first 50 alloys using a Charpy hammer.

FIGURE 1. Successful Braze of Membrane Alloy to Stainless Steel

- Tested several alloys for their ability to be brazed with stainless steel – two successful brazes are shown in Figure 1.
- Showed that brazing in a hydrogen atmosphere was much better than brazing in vacuum for these alloys.

Future Directions

- Prepare larger non-porous membranes.
- Conduct higher pressure tests and sulfur tests with tweaked alloys.
- Test membranes and hydrogen purifier with coal gas.
- Continue life tests with new tweaked alloy.
- Construct disc-membrane reactor with new alloy membranes.
- Verify and confirm that membrane reactor behavior matches DOE's flux, cost, and durability goals.