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

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- G&S Titanium, Inc., Wooster, OH

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Objectives

- Investigate new alloys of lower-cost transition elements to achieve basic improvements in metallic membrane technology to extract hydrogen at the appropriate purity.
- Find a base metal replacement for palladium ($470/ounce) which is: stable at 350ºC, similar to Pd in that it has 100% selectivity, 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.
- Develop an additional 50 stronger alloys in addition to the 82 that were made this past year.
- Test brazing and welding to create the first tubes.
- Make and test 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, strength and, most importantly, expense. Unfortunately, many suffer from uncontrolled failure, either because of embrittlement or substrate-coat interdiffusion. We plan to evaluate some higher body centered cubic (BCC) alloys, and some ductile B2 phase, structured alloys as low-cost replacements for Pd-Ag.

Approach

About 100 alloy and intermetallic compositions will 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. 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 Pd-Cu 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. To save time and cost, 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 205 BCC and B2 intermetallic alloys for brittleness, ease of fabrication (rolling), hydrogen permeation, and hydrogen embrittlement. For the hydrogen permeation tests, we had the alloys coated with 100 nm of palladium by vapor deposition.
- Made large-area rolled foils on the less-embrittling, higher flux alloys. Did long-term testing on these alloys, and Auger testing of the coat interdiffusion to confirm that these alloys should give 15+ year lifetimes if coated with 2 microns of Pd

(2,000 nanometers of Pd, or 0.00008"). Tested the alloys for ability to withstand slow decrease in operating temperature to RT under 100 psig of H2 to see if any can withstand this. So far none withstood this last test, but we have a few new alloys that we think will based on preliminary tests.

- Successfully brazed the alloy to steel (Figure 1).

FIGURE 1. Successful Braze of Membrane Alloy to Stainless Steel

- Tested the manufacturability and embrittlement of the first 50 alloys using a Charpy hammer.
- Demonstrated a hydrogen flux of 51 scfh/ft^2, at 44 psi and 400ºC in an alloy predicted to give 15+ years of service life in terms of interdiffusion.

Future Directions

- Prepare tube samples of selected alloy samples and coat 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.
- Modify the alloys for high flux and no embrittlement.
- Continue creating welding tubes and continue braze testing in order to prepare the alloys for commercial testing.
- Fabricate and test the best two alloys as a purifier, membrane reactor.
- Confirm that the behavior of the alloys matches flux, cost and durability goals.
- Screening tests will be completed on approximately 50 tweaks of alloys developed under this project. These tests will determine the best candidate alloys for hydrogen membranes in harsh environments.