

The Influence of Copper Concentration on the Permeability of Pd-Cu Alloy Membranes

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Abstract

Hydrogen membranes have been identified as a promising technology for extracting pure hydrogen from processes such as coal gasification, hydrocarbon steam-reforming or any hydrogen producing process. Novel palladium-copper (Pd-Cu) alloys continue to be of interest due their highly catalytic surface, high performance, suppression of the hydride-phase transition, tolerance to sulfur compounds, and decreased costs. In this study, the influence of copper concentration on the performance of the Pd-Cu alloy was measured as a function of temperature (350 to 900°C) and pressure (0.1 to 4 MPa) both in the presence of neat hydrogen and a 1000 ppm H₂S-H₂ mixture.

Permeability results indicated that the crystalline phase of the Pd-Cu alloy has significant impact on permeability in the presence of neat hydrogen, with the body-centered-cubic (bcc) structure yielding higher performance results than the face-centered-cubic (fcc) structure. Furthermore, studies conducted in the presence of hydrogen-sulfide yielded “resistance” to poisoning at temperatures corresponding to the fcc crystal structure.

Introduction

Membranes have been identified as a promising technology for extracting pure hydrogen from large-scale but impure sources. Current research in the area of membrane separation is focused on such technologies as dense, hydrogen permeable metals, micro- and nano-porous materials (including highly structured porous materials like metal-organic-framework compounds, zeolites, and carbon nanotubes), polymeric materials and combinations of these. Each of the aforementioned membrane technologies have specific beneficial characteristics, for example, infinite selectivity for dense metals, very high flux potential for pore-based materials and low operating temperatures for polymeric materials.

Of specific interest to the U.S. Department of Energy’s National Energy Technology Laboratory (NETL) is the identification of membrane materials that can withstand the harsh environments associated with gasification effluent streams. Gasification technologies, particularly gasification of coal, are envisioned to provide the transition to a “hydrogen economy” by providing a near- to mid-term large-scale hydrogen source [Collot, 2003]. Fossil fuels such as coal are the most practical domestic

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source of hydrogen available until sustainable, environmentally friendly energy sources can be more fully developed. In addition, the utilization of such domestic resources can enhance energy security by reducing U.S. dependence on imported energy sources such as oil and natural gas.

However, to realize the benefits that membrane technologies offer for the separation of hydrogen from a gasification source, the membrane material must possess certain characteristics. Potential membrane materials must be capable of maintaining their performance and mechanical integrity at temperatures and pressures associated with gasification, possibly as severe as temperatures to 1273 K and pressures to 7 MPa. In addition, the membrane must have chemical resistance to major gasification stream components including CO, CO₂ and H₂O as well as the trace contaminants such as H₂S, NH₃, COS, Hg, HCl, and others. The environmental conditions and contaminant concentrations that a given membrane must withstand will depend on the specific gasification feedstock considered, efficiency of gas clean-up technologies, and placement of the separation unit within the process scheme. Hydrogen sulfide is often considered the most significant impurity in a coal-derived gasification stream because of its ability to poison catalysts and attack metals [Collot, 2003]. NETL continues to study palladium-copper alloys due to several desirable membrane characteristics - a highly catalytic surface, high permeance values, suppression of the hydride-phase transition, decreased Pd cost, and reported tolerance to sulfur compounds [Edlund, 1993; Edlund, 1996; McKinley, 1967].

In this paper, NETL's investigations into the influence of copper concentration on performance of the Pd-Cu alloy system, especially in the presence of H₂S, are reviewed and some current work on this system is presented.

Experimental

Materials

Metal foils having a minimum purity of 99.9% (metals basis) were used in this study. These foils were obtained from Alfa Aesar, ACI Alloys and/or were fabricated at NETL. Alloys fabricated in-house were made by melting the components together under vacuum and rolling the resultant ingot into a foil through cycles of cold rolling and annealing until the target thickness was obtained. All foils discussed here had thicknesses of either ~100 or ~1000 microns. Thick foils were used for ease of handling and to ensure sufficient lifetimes for adequate data collection. Actual measured thicknesses were used in permeability calculations. The alloy compositions, expressed as weight percents, used in this study were as follows: Pd_{100wt%}, Pd_{95wt%}Cu, Pd_{90wt%}Cu, Pd_{80wt%}Cu, Pd_{60wt%}Cu, Pd_{53wt%}Cu, Pd_{40wt%}Cu, and Cu_{100wt%}. The crystalline phase, alloy composition and surface morphology of the foil samples were verified by x-ray diffraction (XRD), inductively coupled plasma (ICP), and scanning electron microscopy (SEM).

Flux Testing

Flux testing of the membrane alloys was conducted in two of NETL's hydrogen membrane test units (HMTs). The HMTs have an operating envelope extending to 1173 K and 7 MPa and can operate with a variety of gases including pure hydrogen under these

conditions. The HMTs were designed for flexibility and can accommodate a range of sample geometries. The HMT units and membrane mounting procedure used in this study have been reported in detail previously [Howard, 2004]. Baseline permeance values of the alloys were determined using a flowing 10%-He balance H_2 mixture in order to develop a performance baseline where He was used for the detection of membrane leaks. Both 1000 and 100 μm foils were tested. Each test condition was maintained until permeance equilibrium was attained. 1000 μm foils were tested with a flowing 1000 ppm H_2S -10%-He balance H_2 mixture.

Upon completion of flux testing, the membrane assembly was removed from the HMT and the membrane was cut out of the assembly for characterization. Membrane samples were typically examined by stereomicroscope and then analyzed by XRD, SEM and, in some cases, by X-ray photoelectron spectroscopy (XPS) to determine phases present, changes in surface morphology and for certain cases, alloy segregation.

Alloy Coupon Testing

Coupon samples were used to study the effect of H_2S on the Pd-Cu alloys in more detail. The purpose is to determine experimentally the sulfide growth rate, sulfide phases formed, and surface morphologies and correlate these observations with membrane permeance results as well as the thermodynamics of the system. Exposure of coupons, typically 100 μm thick by about 1 cm square, was accomplished using a specially designed exposure chamber recently constructed at NETL. The relatively simple exposure chamber consisted of a quartz tube, tube furnace and a quartz covered thermocouple with appropriate gas supplies and flow and pressure controls, illustrated in Figure 1. The coupons were placed in the conditioning chamber where they were heated to a selected temperature in a He flow. Once at temperature, a 1000 ppm H_2S -10% He-balance H_2 gas mixture was flowed through the reactor for a specified time. Testing was conducted at atmospheric pressure, temperatures ranging from 623 to 1038 K and durations of 1 to 168 hours. The mass, composition, crystalline phase and surface morphology of the coupons was verified prior to exposure and re-examined following exposure to determine changes.

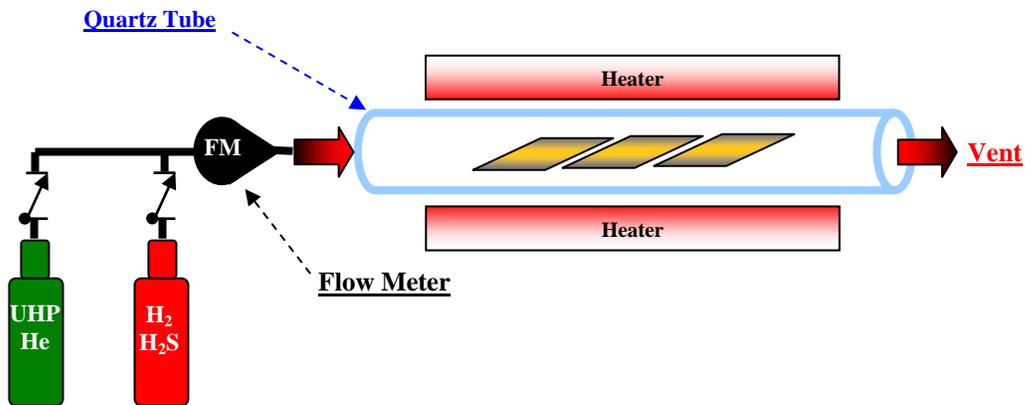


Figure 1. Schematic of the chamber used for sample conditioning at NETL.

Preliminary Results

The hydrogen permeability of several of the alloys of interest in this study has been reported previously [Howard, 2004]. In review, the measured permeability was a function of both palladium content and crystal structure. The Pd_{60wt%}Cu alloy exhibited the highest permeability values of any of the tested mixed alloys at temperatures below ~773 K (B2 structure), but this value dropped approximately an order of magnitude at higher temperatures when the structure converted to face-centered-cubic (fcc). The Pd_{80wt%}Cu alloy (fcc over the entire temperature range examined) exhibited higher permeability values than the Pd_{53Cu₄₇} at all temperatures, while only exceeding Pd_{60wt%}Cu at temperatures greater than 838 K.

Steady state flux testing in the presence of 10% He-balance H₂ as well as the aforementioned H₂S mixture is illustrated in Figure 2 for the Pd₈₀Cu₂₀ and the Pd₆₀Cu₄₀ alloy membranes as a function of absolute temperature. At temperatures associated with the fcc crystalline phase, both the Pd_{80wt%}Cu and the Pd₆₀Cu₄₀ showed minimal decreases in performance for the membrane samples studied. However, at temperatures corresponding to the B2 phase of the Pd_{60wt%}Cu alloy, varying results were obtained. At ~623 K an approximately 2-orders-of magnitude decrease in permeance was observed, however this phenomenon rapidly diminished as temperature increased to a value of ~698 K where almost no deviation in permeance was detected in the presence of H₂S.

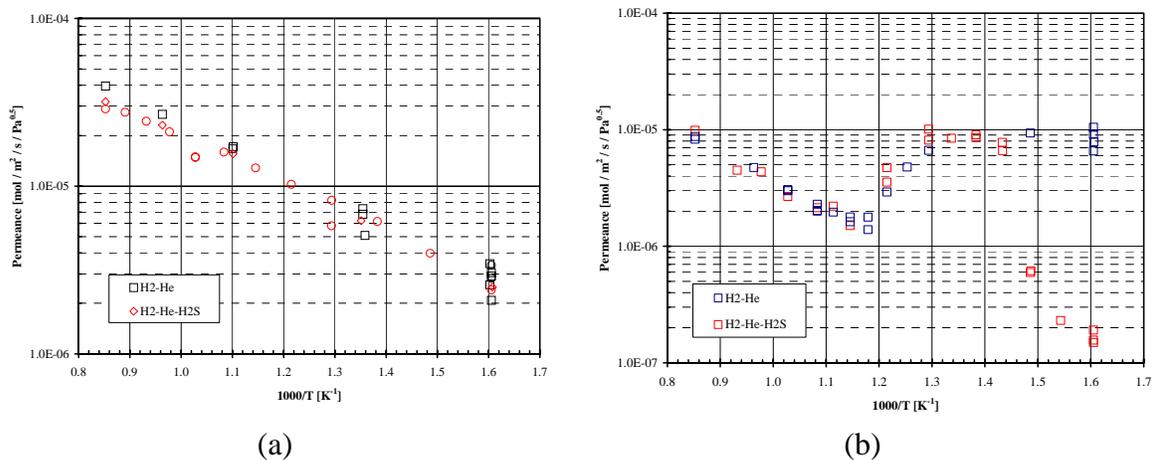


Figure 2. Permeance results for 1000 micron thick, (a) Pd_{80wt%}Cu and (b) Pd_{60wt%}Cu as a function of absolute temperature in the presence of either a 10%He-H₂ or 0.1%H₂S-10%He-H₂ mixture.

Preliminary coupon exposure studies have given insight into the materials issues associated with pure palladium as noted in the literature [Edlund]. Figure 3 illustrates SEM images of the surface morphology changes of pure palladium after exposure to 1000 ppm H₂S-10% He-balance H₂ for various exposure times. Increased exposure times of the Pd samples results an increase in surface roughness associated with the formation of a palladium sulfide surface layer. The palladium sulfide was identified as Pd₄S by XRD. Additionally, as exposure time of the palladium coupons increases so does the

thickness of the sulfide scale, up to a thickness of approximately 15 μm for an exposure duration of 168 hrs.

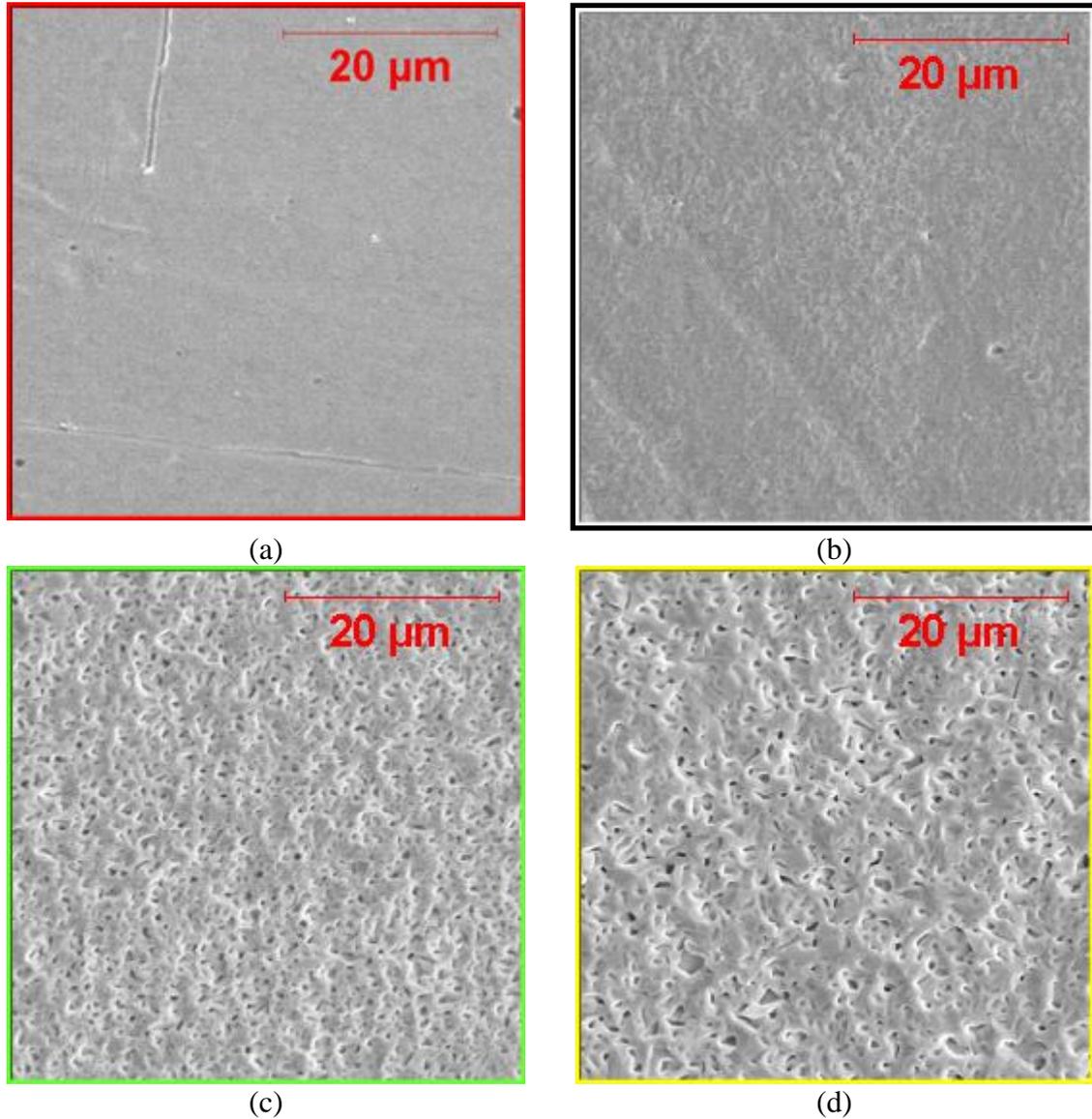


Figure 3. SEM images of Pd_{100wt%} after exposure to 0.1% H₂S-10% He-H₂ balance for (a) 0 hr, (b) 1 hr, (c) 24 hrs, (d) 168 hrs.

Currently, similar coupon conditioning studies are being conducted on various Pd-Cu alloys as well as additional flux testing to in an effort to correlate “surface” characteristics and performance.

Conclusions

- Steady-state flux testing in the presence of 1000 ppm H₂S for the 1000 micron thick, Pd_{80wt%}Cu alloy revealed minimal changes in performance over the conditions of this study.
- The Pd_{60wt%}Cu alloy exhibited decreases in performance at temperatures less than ~425°C in the presence of H₂S. At temperatures greater than 425°C, a minimal change in performance was observed in the presence of H₂S.
- Exposure of pure palladium coupons to a flowing stream containing 1000ppm H₂S-10%He-Bal H₂ at 350°C resulted in dramatic roughening of the surface. The roughening was attributed to the formation of a “porous-like” scale of Pd₄S.

References

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