

PALLADIUM-COPPER ALLOY MEMBRANE PERFORMANCE UNDER CONTINUOUS H₂S EXPOSURE

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Abstract

Palladium-copper alloys continue to be of interest for hydrogen membrane applications because of their high catalytic activity for hydrogen dissociation, high hydrogen permeability, robustness, and degradation resistance in the presence of sulfur-containing compounds. This sulfur tolerance makes these alloys attractive for membrane applications where sulfur compounds are likely to be present, such as hydrogen production via coal or biomass gasification. In this study, the permeances of a series of palladium-copper alloys were determined using a continuously flowing 1000 ppm hydrogen sulfide in hydrogen gas stream. Palladium-copper alloys containing 80, 60 and 53 wt-% palladium as well as pure palladium were evaluated over the temperature range of 350 to 900°C. The membrane samples used in this continuous flow study consisted of 1000 µm thick metal foils that were supported on Hastelloy[®] porous substrates. Permeances determined under high-pressure, high-temperature continuous flow conditions were compared to those measured under pure hydrogen conditions and to previous results from low-pressure transient permeance measurements under 1000 ppm hydrogen sulfide in hydrogen. Permeance results were also correlated with the alloy crystal structure. The hydrogen sulfide test results indicate that the crystalline phase of a specific alloy (bcc vs. fcc) strongly influences both permeance and sulfur poisoning resistance, agreeing well with our previous transient permeance measurements. The alloys exhibited sulfur poisoning resistance at temperatures corresponding to their fcc crystalline phase, but there was a significant decrease in permeance when exposed to hydrogen sulfide under bcc phase stability conditions.

1. Introduction

The U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) is engaged in an aggressive program of testing metal alloys for their suitability as hydrogen separation materials. This testing program

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came about from the belief that fossil fuel resources, particularly coal, must provide the transition to a hydrogen economy by providing a near- to mid-term source of hydrogen [1]. Unlike fossil fuels, hydrogen is an energy carrier, rather than a source. Until sustainable and environmentally friendly energy sources can be more fully developed, fossil fuels represent the most practical source of hydrogen. The use of domestic fossil resources, such as coal, can enhance energy security by mitigating the national dependence on energy obtained from politically unstable regions of the world. In addition, advanced energy plants such as those promoted by the U.S. DOE's *FutureGen* initiative can use fossil fuels much more cleanly than current technology [2]. Coupled with carbon dioxide sequestration to mitigate environmental concerns associated with global climate change, such plants could represent an essentially emission free energy supply. In addition to their role in the production of hydrogen from coal and natural gas based systems, hydrogen separation membranes could also find application in alternative hydrogen delivery systems. Such delivery systems would include pipelines that carry hydrogen mixed with other fossil-derived gases, such as natural gas, requiring the hydrogen to be separated at the point of use.

Next generation fuel and power plants are likely to be based on gasification technology. In this scheme, coal, petroleum coke, biomass, waste, or other carbon-containing materials would be fed to a gasifier, along with air or oxygen, and steam. The gasifier would convert this feed material into what is called synthesis gas, or syngas – a mixture of hydrogen and carbon monoxide, small amounts of carbon dioxide, light hydrocarbons, and associated impurities. The syngas would be passed through a particulate removal and gas cleanup stage where much of the sulfur would be removed. From this point, the syngas could be burned directly for power, made into chemicals, or shifted to essentially all hydrogen and carbon dioxide. The advantage of shifting to hydrogen is that it simplifies the product stream. A hydrogen – carbon dioxide separation step would yield product hydrogen, available as an energy carrier or for advanced electric power production via fuel cell technology, and a concentrated carbon dioxide stream available for sequestration. In order to realize the vision of extraction of hydrogen from fossil fuels, more efficient gas separation methods are needed that are better integrated with this gasification infrastructure. Membrane separation would be ideal, if materials can be found to survive and function in the fossil fuel gasification environment.

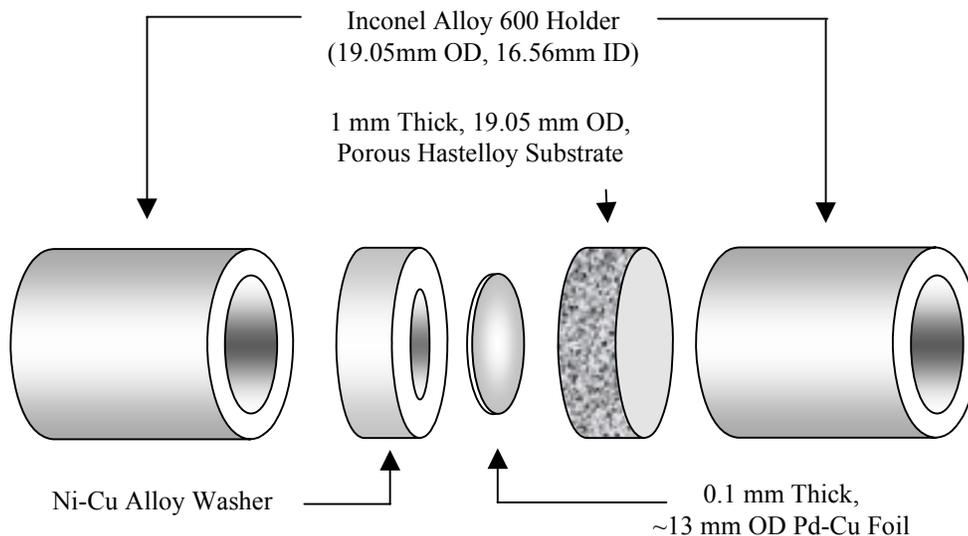
The best possible solution to the separation issue would be a *membrane reactor*. An appropriately designed reactor could combine the shift and separation steps into one, realizing a significant leap forward in efficiency and lowered cost of hydrogen produced. In this scheme, syngas and water are fed to the inlet of the membrane reactor and separated streams of hydrogen and carbon dioxide (with associated impurities) are removed from the product side. However, because of its multiple functions, a membrane reactor must be able to tolerate more divergent conditions than a membrane that only has to separate

hydrogen and carbon dioxide that has already been pre-cleaned to a given specification. A number of potential membrane materials have shown good hydrogen permeation at high pressures and temperatures. However, *resistance to impurities* found in fossil fuel gasification streams is an important prerequisite for the deployment of membrane reactors that has not been widely investigated. Hydrogen sulfide is arguably the most significant impurity in a fossil fuel gasification stream due to its ability to poison catalysts and corrode metal surfaces [3-6]. Palladium-copper alloys were chosen as the subject of the current study due to reports that they continue to possess good hydrogen permeation characteristics in the presence of sulfur-containing gases [7-9].

2. Experimental Section

Palladium foils, 99.9%, Alfa Aesar, and palladium-copper alloy foils, 99.9%, ACI Alloys, were obtained in approximately 100 μm and 1000 μm thicknesses for this study. The compositions of the palladium-copper alloy foils were 80, 60, and 53 wt-% palladium. The crystalline phase structure and alloy composition of the foils were verified by x-ray diffraction and inductively coupled plasma atomic emission spectroscopy analysis, respectively. Test membranes were fabricated using two methods. The 100 μm foils were brazed to nickel-copper alloy supports before being welded into the testing fixture. The 1000 μm foils were welded directly into the fixtures. Details of the procedures have been reported previously [10]. A schematic of the mounting assembly for a 100 μm thick palladium-copper alloy membrane is shown in Figure 1.

Figure 1. Schematic of the palladium-copper alloy membrane assembly.

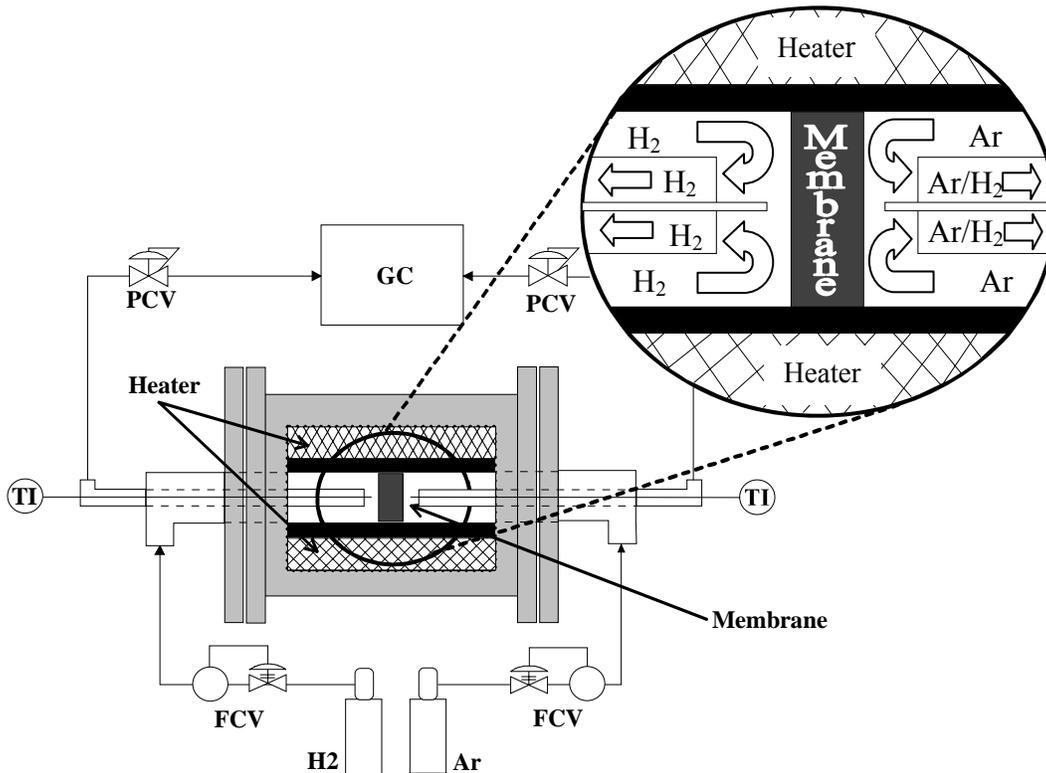


Membrane material samples were tested in the DOE/NETL Hydrogen Technology Research Facility, a unique resource designed for the testing of hydrogen separation materials and other processes involving the use of hydrogen at elevated temperatures and/or pressures. The facility contains two types of

permeability testing units – HMT units for in-depth studies at steady-state continuous flow conditions and MSS units for more rapid transient batch screening. Three steady-state hydrogen membrane testing (HMT) units were constructed from 1999 through 2002. The units are capable of testing at temperatures to 900°C and pressures to 1000 psi. The three HMT units are each adapted for different types of experiments. One HMT unit is reserved for “clean” testing, while another is dedicated to sulfur-laden gas feed stocks, and a third is used primarily for membrane reactor experiments. In addition to the HMT units, two transient membrane screening system (MSS) units were constructed in 2003. These are made using a simpler, batch design. Although they do not provide the same wealth of information as do the HMT units, they still have testing capabilities of temperatures to 900°C, pressures to 75 psi, and can employ both clean and sulfur-laden gas feed stocks.

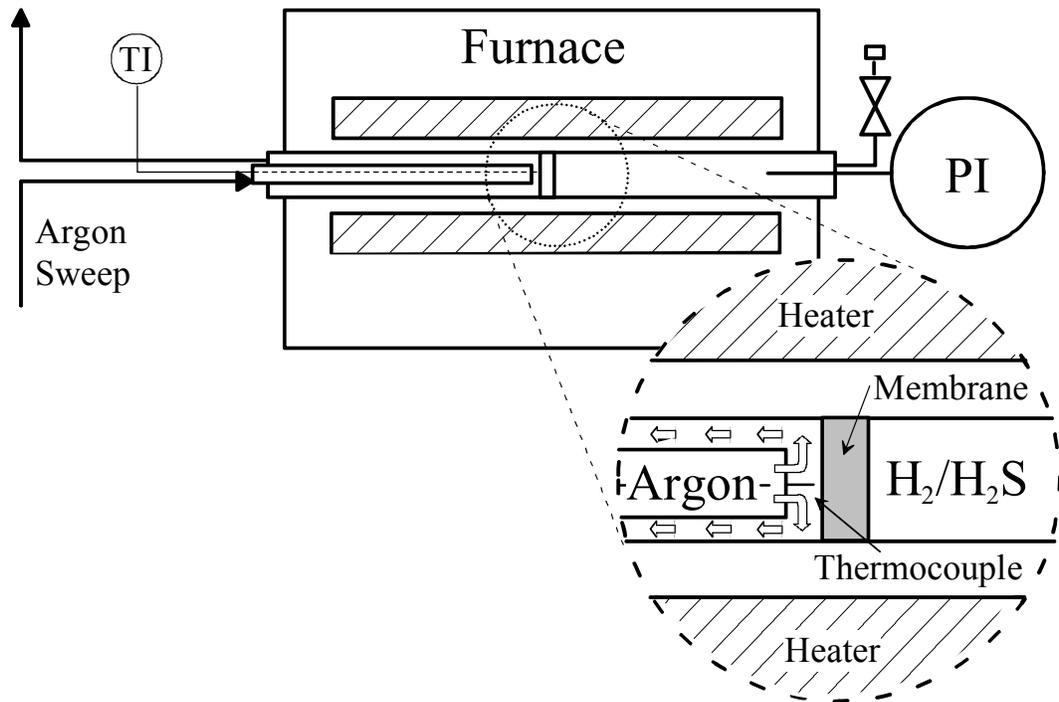
A schematic of the HMT apparatus is shown in Figure 2, which illustrates the gas flow pathways. A 90% hydrogen -10% helium mixture was fed to the unit on the retentate side and ultra-high purity argon sweep gas was supplied to the permeate side. Flow rates were controlled such that the concentration of hydrogen in the permeate did not exceed 4 mol-%. Although the HMT unit has the capability of operating at total pressure differentials in excess of 100 psi, the sweep gas pressure was adjusted to maintain a small total pressure gradient of 20 psi, though the hydrogen partial pressure gradient remained as high as 380 psi. Details of this unit have been reported elsewhere [11].

Figure 2. Schematic of NETL’s Hydrogen Membrane Testing (HMT) unit.



A schematic of the MSS unit used in this study is illustrated in Figure 3. In this configuration, the feed side of the membrane was charged with the test gas of interest, either pure hydrogen or a 1000 ppm hydrogen sulfide, balance hydrogen mixture. A concentration of 1000 ppm hydrogen sulfide was used to be certain sufficient hydrogen sulfide was present in the static system to saturate all metal surfaces. The assembly was placed within a Lindberg tube furnace and the temperature was monitored with a dual element, type-K thermocouple. Concentric tubes placed on the permeate side of the membrane allowed a constant argon flow to sweep diffusing hydrogen away from the surface of the membrane. The assembly was then heated to the desired temperature and the retentate transient pressure data was used to calculate the rate of hydrogen transport through the membrane. Details of this unit have been reported elsewhere [12].

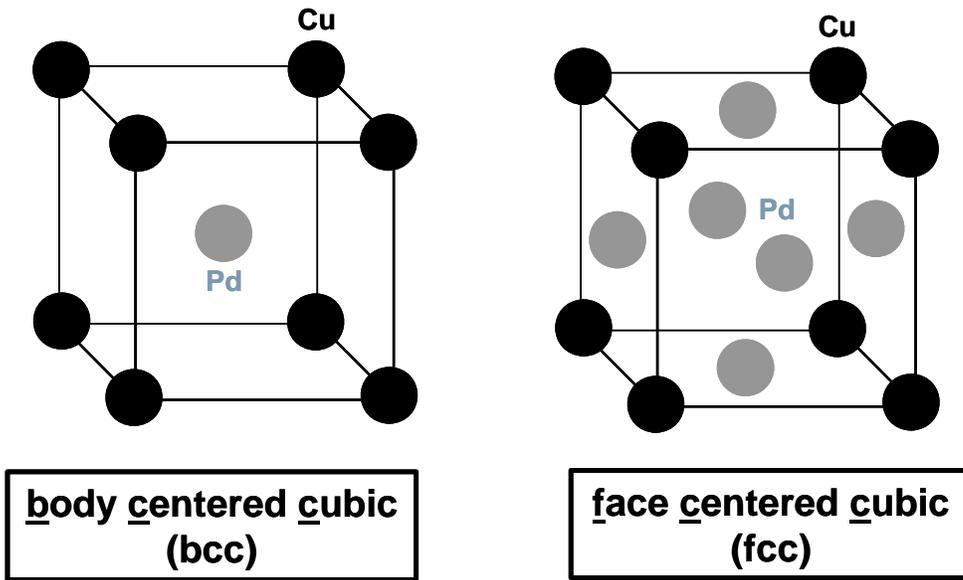
Figure 3. Schematic of transient membrane testing (MSS) apparatus.



3. Results and Discussion

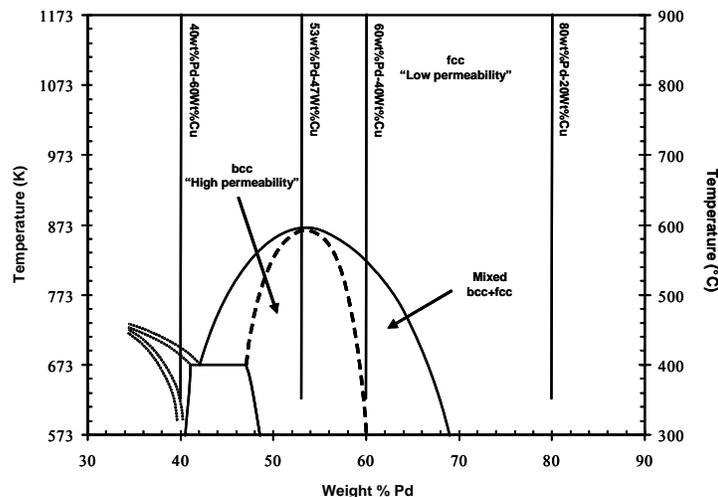
In order to understand the results of this study, one must first understand the phase behavior and crystal structure of palladium-copper alloys. Depending on conditions, this material can possess either a body centered cubic (bcc) structure or exist in a face centered cubic (fcc) disordered solid solution. Examples of both structures are shown in Figure 4.

Figure 4. Examples of bcc and fcc structure for palladium-copper alloys.



A phase diagram for palladium-copper is shown in Figure 5 [13]. It can be seen that above ca. 600°C, only the fcc structure exists. However, below 600°C, both structures can exist, depending on the alloy composition. Above about 70 wt-% palladium, only the fcc structure exists. However, the bcc structure dominates in a range from approximately 48 to 60 wt-% palladium. A zone consisting of mixed bcc and fcc phases exists between the two regions. Three compositions were chosen for testing. A 53 wt-% palladium alloy was chosen because it intersects the heart of the bcc region. A 60 wt-% palladium alloy was chosen because it borders the bcc and mixed phase region and has been reported to possess exceptionally high hydrogen permeability. An 80 wt-% palladium alloy was chosen because it lies completely in the fcc region.

Figure 5. Palladium-copper phase diagram based on data summarized by Subramanian and Laughlin [13]. Vertical lines represent alloy compositions and temperature ranges (steady-state testing) examined in this study.



Steady state (HMT) test results for the 80 wt-% palladium and 60 wt-% palladium alloy membranes are presented in Figure 6 a and b, respectively, as a function of inverse absolute temperature. Analogous results taken on the transient (MSS) unit for the 80 wt-% palladium, 60 wt-% palladium, and the 53 wt-% palladium alloy membranes are presented in Figure 7 a, b, and c, respectively [12]. A comparison of transient test results to steady state results for 80, 60 and 53 wt-%, 100 μm thick, palladium membranes using clean hydrogen was used to verify the validity of the transient test approach. Although the permeance values measured in this study via the transient analysis method (Figure 7) were slightly lower than those measured using the steady state method (Figure 6), the trends were identical. This observation validated any qualitative conclusions drawn from the transient test data. All palladium-copper alloys were completely selective for hydrogen. The hydrogen flux through each membrane was proportional to the difference of the square root of the hydrogen partial pressures on the retentate and permeate sides of the membrane.

Hydrogen permeability results in the absence of hydrogen sulfide have been reported by us previously at the NHA Annual Hydrogen Conference and in the literature [10, 14]. In review, the measured permeability was a function of both palladium content and crystal structure. The 60 wt-% palladium alloy exhibited the highest permeability values of any of the tested mixed alloys at temperatures below $\sim 500^\circ\text{C}$, in the bcc structure, but this value dropped approximately an order of magnitude at higher temperatures when the structure converted to fcc. The 80% wt-% palladium alloy, fcc over the entire temperature range examined, exhibited permeability values of roughly 30% of pure palladium, as shown in Figure 6. The 80 wt-% palladium alloy exhibited higher permeability values than the 53 wt-% palladium alloy at all temperatures, while it exceeded the permeability of the 60 wt-% palladium alloy at temperatures greater than 565°C .

In the presence of 1000 ppm hydrogen sulfide, shown in Figure 6a and 7a, the 80 wt-% palladium alloy membrane exhibited essentially no change in hydrogen permeance over the entire temperature range as compared to the results observed in the absence of hydrogen sulfide. The 80 wt-% palladium alloy corresponds to an fcc crystalline phase over the temperature range of the study, as seen in Figure 5.

The permeance of the 60 wt-% palladium alloy membrane exhibited significant changes over the temperature ranges and gas compositions of this study as illustrated in Figures 6b and 7b. The permeance values increased with temperatures between 350 and 450°C , decreased from 450 to ca. 600°C , and increased again from ca. 600 to 900°C . At the temperatures corresponding to the fcc crystalline phase (above $\sim 550^\circ\text{C}$) the 60 wt-% palladium alloy membrane exhibited only a 10% decrease in hydrogen permeance when hydrogen sulfide was added to the retentate. However, at temperatures less than 550°C (the bcc crystalline phase), the 60 wt-% palladium alloy exhibited decreases in permeance values of approximately one to two orders of magnitude.

Figure 6. Steady state (HMT) data showing hydrogen permeance as a function of inverse absolute temperature. Pure palladium data for reference represented by solid line. Solid symbols show permeance in the absence of hydrogen sulfide. Open symbols show permeance in the presence of 1000 ppm hydrogen sulfide. (a) 80 wt-% palladium, (b) 60 wt-% palladium.

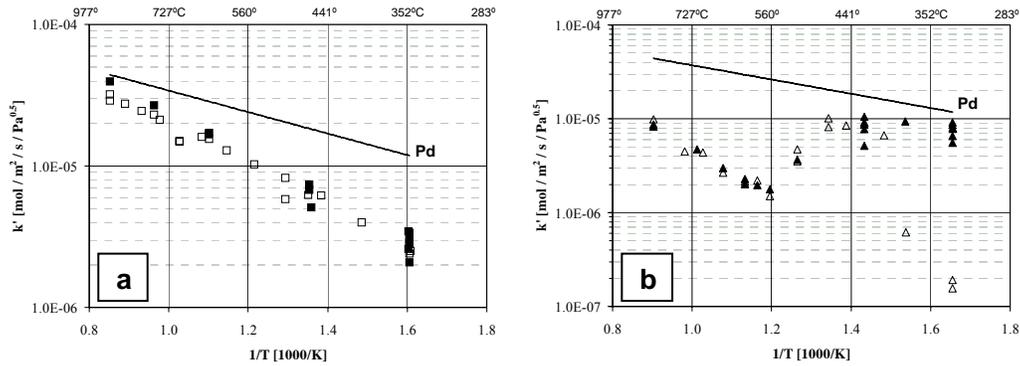
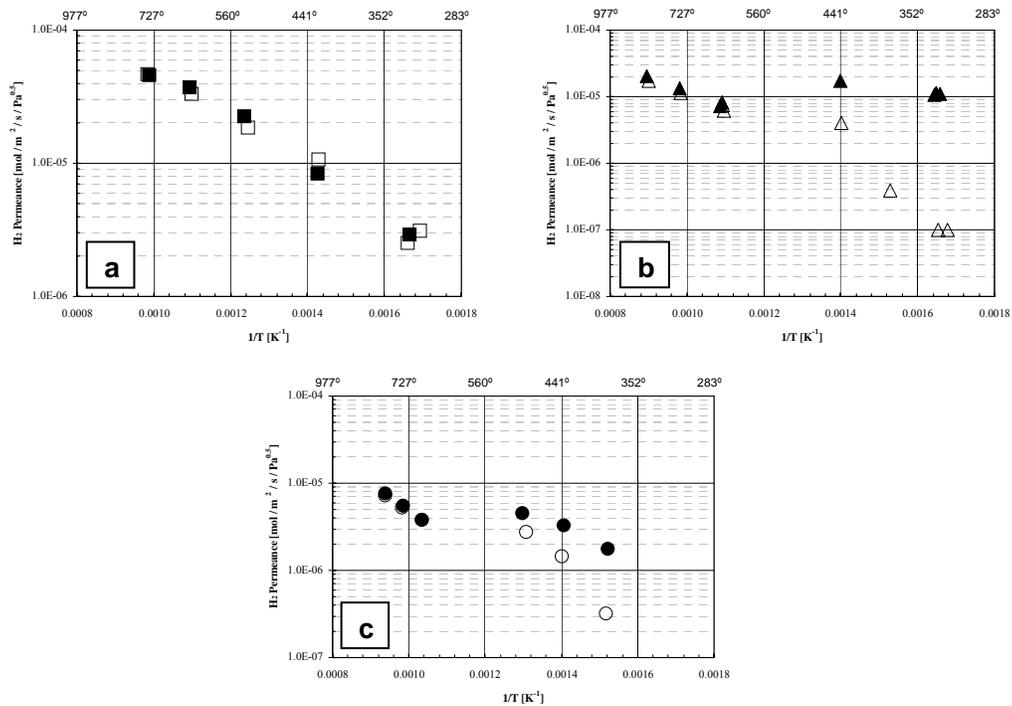


Figure 7. Transient (MSS) data showing hydrogen permeance as a function of inverse absolute temperature. Solid symbols show permeance in the absence of hydrogen sulfide. Open symbols show permeance in the presence of 1000 ppm hydrogen sulfide. (a) 80 wt-% palladium, (b) 60 wt-% palladium, (c) 53 wt-% palladium.



Hydrogen sulfide exposure results for the 53 wt-% palladium alloy are only reported for the transient testing method (Figure 7c), although hydrogen permeance in the absence of hydrogen sulfide agreed with steady state results (not shown). The sample exhibited similar trends as the 60 wt-% palladium alloy, as shown in Figures 6b and 7b. Permeance values corresponding to neat hydrogen increased with temperature below ca. 450°C and above ca. 640°C for the bcc and fcc phases, respectively, and decreased at temperatures between 450 and 640°C in the mixed phase region. The 53 wt-% palladium alloy also showed similar trends with respect to the hydrogen sulfide containing mixture. The 53 wt-% palladium alloy had the greatest resistance to hydrogen sulfide at temperatures above 640°C, which corresponds to the fcc phase of the alloy. Relative to the neat hydrogen values, permeance in the presence of hydrogen sulfide showed decreases of less than 10% over temperatures associated with the fcc phase of the alloy, while the permeance decreased as much as one order of magnitude over the bcc crystalline phase.

4. Conclusions and Future Work

In summary, hydrogen permeation behavior in the presence of 1000 ppm hydrogen sulfide correlated with crystalline structure of the palladium-copper alloy in both transient MSS and steady state HMT tests. Alloy compositions corresponding to the bcc-crystalline phase exhibited decreases in hydrogen permeance of approximately an order of magnitude, while those compositions corresponding to the fcc-crystalline phase exhibited decreases in hydrogen permeance of less than 20%. The 60 wt-% palladium-copper alloy exhibited the highest permeability values at temperatures below ca. 500°C, but showed little sulfur tolerance due to the bcc phase. The 80 wt-% palladium-copper alloy exhibited the highest permeability values at temperatures above ca. 500°C, and was sulfur tolerant throughout the entire temperature range due to the fcc phase.

The results presented in this study lead to a number of important questions that are the subject of ongoing investigations at DOE/NETL. In particular, an ongoing investigation of membrane surface alterations and modification as a function of hydrogen sulfide exposure will hopefully elucidate the nature of the sulfur resistance observed for the fcc structure. Computational chemistry techniques, already used with success in predicting permeability behavior in the absence of sulfur [15], are being used to gain improved understanding of sulfur poisoning [16-17]. In addition to hydrogen sulfide, hydrogen permeance will be evaluated in the presence of major WGS gas components such as water, carbon monoxide, carbon dioxide, and other gas impurities. Finally, other alloys will be considered in the search for the optimal hydrogen separation material in fossil fuel gasification environments.

Acknowledgement and Disclaimer

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Biography

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