

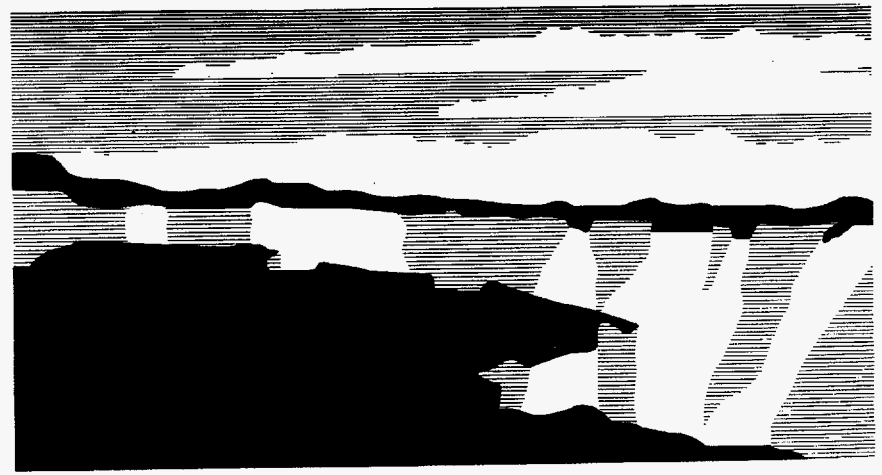
Title: ENGINEERING MATERIALS FOR HYDROGEN SEPARATION

Author(s): T.S. Moss MST-7
R.C. Dye MST-7

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
ph

Submitted to: Hydrogen and the Materials of a Sustainable Energy Future
Los Alamos, NM
October 29, 1996

MASTER



Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ENGINEERING MATERIALS FOR HYDROGEN SEPARATION

T.S. Moss and R.C. Dye
Los Alamos National Laboratory
Los Alamos, NM 87545

Key Words: Hydrogen separation, x-ray diffraction, mass spectroscopy.

Prerequisite Knowledge: Because hydrogen gas is used in this workshop, a working knowledge of *hydrogen safety is required*. Basic Materials Science is helpful but not necessary.

Objective: To understand the fundamentals of designing and engineering membranes for the purpose of hydrogen separation and to learn about the characterization and testing equipment that is used in experimental evaluation of these materials.

Introduction:

With the steady depletion of fossil fuel reserves, hydrogen based energy sources are becoming increasingly more attractive. This drive is creating a continued and building interest in developing economically viable methods for hydrogen production and separation from alternative hydrocarbon sources, such as natural gas and methanol. Although hydrogen selective membranes have been considered and applied in this area, their use has been minimal because of their high cost and limited lifetime due to embrittlement. The most popular metal used for hydrogen separation has been palladium and its alloys; these materials and their interaction with hydrogen have been well studied, with published work dating back over one hundred years.¹ While palladium is an attractive membrane material because of its ability to readily dissociate molecular hydrogen into atomic hydrogen, several inherent problems remain.

First, palladium undergoes an α - β phase transformation at temperatures below

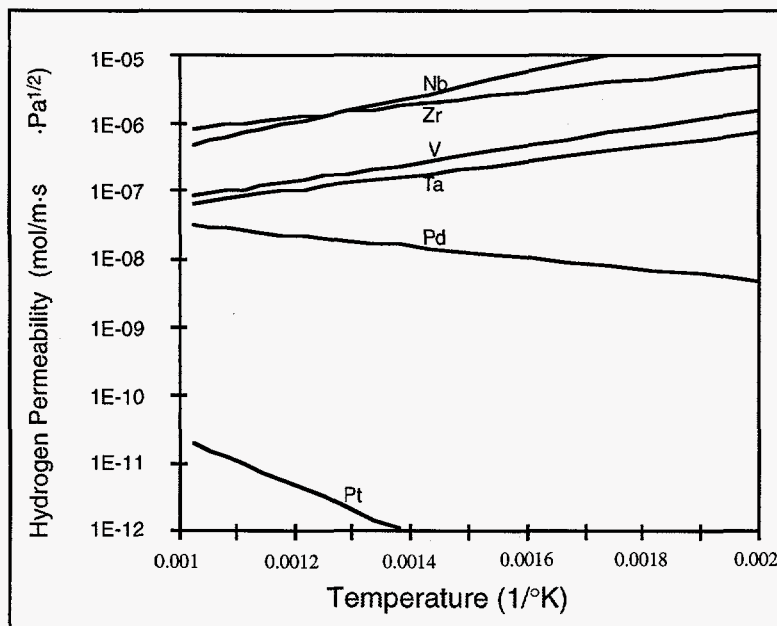


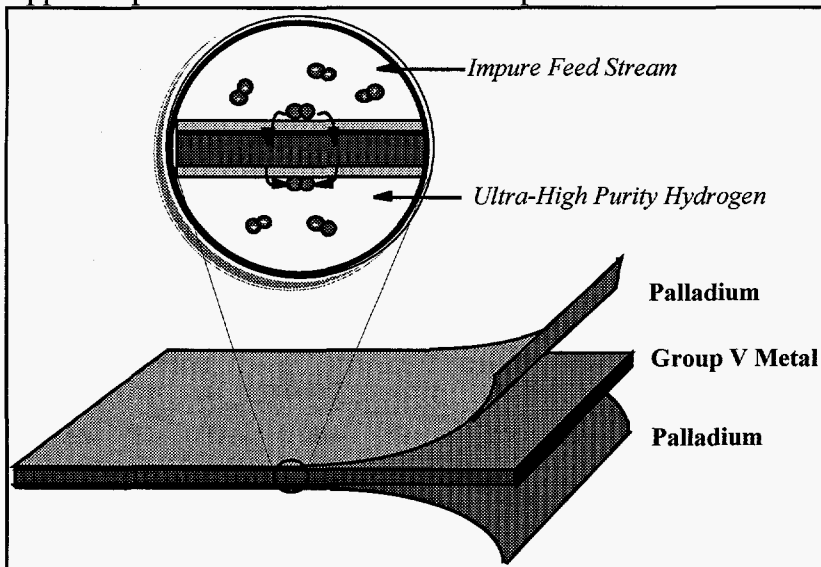
Figure 1. The bcc-refractory metals have a higher transport rate than palladium.

still dominated by the palladium cost. Furthermore, the bulk transport of hydrogen in face

300°C; the actual transformation temperature depends on the hydrogen concentration in the metal.² Expansion and contraction of the lattice from the phase transformation leads to embrittlement and fracture of the metal. Some control of this problem can be gained by alloying the palladium with silver. Inclusion of silver significantly reduces the critical temperature and pressure of the phase transformation.³ This reduces the embrittlement of the metal and extends the lifetime of the membrane. However, these alloys are still very expensive because the bulk of the material is

centered cubic (*fcc*) metals, such as palladium and palladium alloys, is inherently lower than in a number of refractory, body centered cubic (*bcc*) metals.^{4,5} As seen in Figure 1, zirconium, niobium, tantalum, and vanadium all have significantly higher bulk hydrogen permeabilities than does palladium.⁶ Unfortunately, the direct replacement of palladium for cheaper refractory metals as membranes is not possible because of the lack of catalytic ability and because of the self-passivating oxide layers formed on these metals which slow the flux of hydrogen through the metals.

To exploit the rapid bulk diffusion of hydrogen through the refractory metals, a composite structure can be fabricated where a thin palladium layer is placed on each side of the *bcc* metal. This allows the dissociation of the molecular hydrogen by the surface palladium layer, transport through the refractory metal bulk, and finally reassociation on the opposite palladium surface. This composite membrane is shown in Figure 2. Such a structure has several advantages.



First, greater overall hydrogen fluxes are possible because bulk diffusion is not limited by the *fcc* structure of the palladium. The membrane structure can then be thicker providing improved mechanical stability while still yielding acceptable gas fluxes. Second, because these refractory metals are significantly cheaper than palladium and only two thin layers (< 5,000Å) of palladium are required, these membranes are much more economical. While

Figure 2. The composite membrane has thin palladium layers on both sides of a Group V-B metal foil.

the Group V-B metals are still subject to hydrogen embrittlement, the temperature where this is a problem is well below room temperature.⁷⁻⁸ Finally, should the surface palladium layer develop a crack or multiple defects, the membrane would not catastrophically fail. Instead, only a minuscule portion of the membrane would be made inoperative.

The obvious advantages of this composite metal membrane have not escaped previous investigators. Indeed, about 30 years ago, Makrides filed a patent for plating foils of Group V-B metals with thin layers of palladium.⁹ In recent years, additional patents have been filed by other groups for similar structures.¹⁰⁻¹² While it is clear that viable composite membranes have been constructed, improvements of the material are still required to make these structures more efficient. A critical area for improvement is the removal of the surface oxide layer which forms as a self passivating layer when the pure metal is exposed to the atmosphere. Various chemical and mechanical techniques have been used to achieve a stripping of this layer but most allow some amount of regrowth of the oxide before coating with the palladium layers. Another area of concern is the quality of the palladium layers.

To address the need for enhanced hydrogen separation techniques using metal membranes, a different fabrication technique was utilized that would overcome these concerns. The objectives for the fabrication were: obtaining a highly clean surface on the refractory foil, forming a palladium coating without subsequent surface contamination, and providing a high degree of purity, crystallinity, and crystallographic orientation. To

achieve these objectives, the process of physical vapor deposition was used. Within a high vacuum chamber, both sides of a tantalum or vanadium foil were ion milled to remove the surface oxide and, without ever breaking the vacuum, both sides of the cleaned foil were coated with thin palladium layers. The palladium was deposited using either e-beam evaporation or sputtering. Foils produced by this technique have yielded exceptionally high hydrogen flow rates.¹³

Membrane Characterization:

After the membranes have been fabricated in the deposition system, they need to be characterized to determine the crystalline phases that are present and the crystallographic orientation of these phases. By determining a picture of the membrane composition before passing hydrogen through, the effects of the hydrogen transport can be better determined and the effect of the deposition parameters can be correlated to the observed permeability of the membrane. Among the available characterization techniques, the process of x-ray diffraction (XRD) has proved to be the most effective.

XRD is a non-invasive technique, i.e., the membrane does not have to be destroyed to undergo the testing and is typically not affected by the characterization process. The most common and versatile diffractometer geometry is the theta-2 theta. In this type of diffractometer, x-rays are generated from a metal target, typically made of copper; these x-rays are focused onto the sample which is fixed at an angle of theta degrees to the beam. A detector collects the reflected x-rays from the sample and is held at an angle of 2 theta to the sample. The sample and the detector are moved through a range of theta-2 theta angles, and data is constantly collected for analysis, typically using a computer interface. Peaks in the reflected x-ray signal, as recorded by the detector, correspond to the presence of particular crystalline phases. The diffraction peaks are related to the characteristic d-spacing of the material using Bragg's Law:

$$n\lambda = 2d \cdot \sin(\theta)$$

where n is any integer and is usually taken as 1, λ is the wavelength of the x-rays used in Å, d is the characteristic d-spacing of the crystalline phase in Å, and θ is the angular position of the peak. This data can later be used for a number of purposes, such as qualitative and quantitative phase analysis, particle size measurements, particle micro- and macro-strain estimation, and texture/preferred orientation determination. For a better and more complete explanation of the process of x-ray diffraction, a number of sources are available.¹⁴⁻¹⁵

For the purposes of characterizing the membrane, the most important features of the diffraction trace is the identification of all of the peaks and the relative intensities of the peaks. By identifying the peaks, it is possible to determine if the membrane contains any impurities, such as oxides or hydrides, left over from the deposition process or the exposure to hydrogen. This is done by matching the peak locations, usually determined by the computer software, to a set of published values, such as those found in the JCPDS powder diffraction files. After all of the peaks have been attributed to the known phases, i.e., palladium and vanadium/tantalum, any remaining peaks must be identified to the contributing phase. Also of importance are the relative peak intensities, supplied by the computer software. By comparing the intensities before and after the exposure to hydrogen, it is possible to learn about the effect of hydrogen transport on orientation of the grains, especially along particular crystallographic directions. Of interest are the close packed planes in the metals: the 111 planes for the bcc structure and the 110 planes for the fcc structure.

Membrane Testing:

The ability to properly and effectively test the performance of the membrane is important and requires a thought out testing apparatus. A schematic of the one developed

and used at Los Alamos National Laboratory is shown in Figure 3. This system allows for the testing of membrane efficiency, purity and flow rate as a function of several variables, such as temperature, feed and permeate pressures, feed composition, and total flow rate. The membrane test system consisted of a membrane holder unit in which the membrane was sealed between the

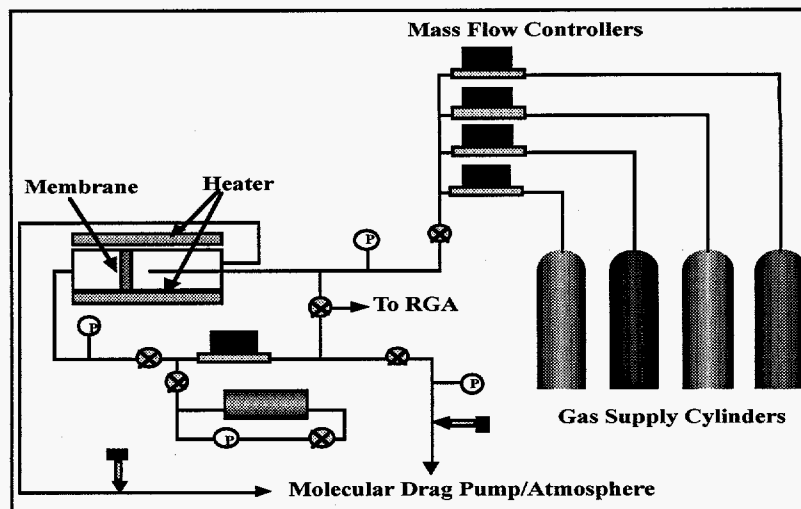


Figure 3. Permeation testing apparatus.

The feed and permeate streams. The feed flows were composed of up to four constituents could be used in the feed supply and were controlled using independent MKS mass flow controllers so that mixtures of various compositions could be used. The pressure on the feed side of the membrane was controlled by either pumping using a turbo pump (in the case of sub-atmospheric pressures) or by restricting the flow of the exhaust from the feed side using a needle valve (in the case of elevated pressures). The pressure of the feed was measured using a Baritron pressure transducer for pressures up to 1000 torr and using a dial gauge for higher pressures. The permeate side of the membrane allowed the gas flow to pass through an MKS mass flow meter to determine the flow rate of gas passing through the membrane. The pressure on the permeate side of the membrane was also controlled either by pumping for low pressures or by restricting the flow for high pressures. The composition of both the feed and permeate gas streams could be analyzed using a Residual Gas Analyzer (RGA).

The testing system contained an RGA which uses a quadrupole mass spectrometer to determine the particular species and isotopes and their relative amounts present in the gas stream. The quadrupole mass spectrometer consists of four cylindrical rods to which a combination of a.c. and d.c. potentials are applied. For a given applied a.c. frequency, only ions of a particular value of e/m can pass through to the collector. The spectrum of e/m ions is collected by varying the a.c. frequency through a programmed range or through selected values. The mass spectrometer is important in the testing of the membrane because it can determine the purity of the gases that are passing through the membrane. This information can then be used to determine if the membrane is not completely selective to hydrogen only or if it has developed a leak. Furthermore, the relative passage rate of various isotopes can be determined from the spectrum.

Conclusions:

In this paper, the method by which a novel metal membrane for the separation of ultra high purity hydrogen gas from an impure feed stream has been described. This composite metal membrane having exceptionally high hydrogen flows was fabricated using palladium coated Group V-B foils. The cleaning of the refractory metal using ion milling and subsequent deposition of the palladium layer in the same vacuum chamber provides a method of constructing a membrane having high purity, crystalline palladium bonded to a very clean metal foil surface. The characterization and testing apparatus has also been described, with particular attention paid to the processes of x-ray diffraction and mass spectrometry. These two techniques provide the most versatile and revealing insight to the

structure and performance of the membrane. By using several different techniques, an integrated solution has been engineered to a problem to produce a material that has superior performance to anything that has come before.

References:

1. Graham, *Phil. Trans. Roy. Soc. (London)*, **156**, 415 (1866).
2. Wicke, H. Brodowsky, Züchner, pg. 73 in *Hydrogen in Metals II*, Topics in Advanced Physics, Vol. 29, eds. G. Alefeld and J. Völkl, Springer-Verlag, New York (1978).
3. J Shu, B.P.A. Grandjean, A. Van Neste, and S. Kaliaguine, *Can. J. Chem. Eng.*, **69**, 1036 (1991).
4. G. Alefeld and J. Völkl, pg. 321 in *Hydrogen in Metals I*, eds. G. Alefeld and J. Völkl, Springer-Verlag, New York (1978).
5. R.E. Buxbaum and T.L. Marker, *J. Membrane Sci.*, **85**, 29 (1993).
6. S.A. Steward, *Review of Hydrogen Isotope Permeability through Materials*, Lawrence Livermore National Laboratory Report #UCRL-53441 (1983).
7. C.V. Owen and T.E. Scott, *Metallurgical Trans.*, **3**, 1715 (1972).
8. T. Schober and H. Wenzel, pg. 11 in *Hydrogen in Metals II*, Topics in Advanced Physics, Vol. 29, eds. G. Alefeld and J. Völkl, Springer-Verlag, New York (1978).
9. A.C. Makrides, M.A. Wright, and D.N. Jewett, Separation of Hydrogen by Permeation, US Patent 3,350,845, Nov. 7, 1967.
10. R.E. Buxbaum, Composite Metal Membrane for Hydrogen Extraction, US Patent 5,215,729, June 1, 1993.
11. D.J. Edlund, Hydrogen-Permeable Composite-Metal Membranes, US Patent 5,139,541, Aug. 18, 1992.
12. D.J. Edlund, Composite Hydrogen Separation Metal Membrane, US Patent 5,393,325, Feb. 28, 1995.
13. N.M. Peachey, R.C. Snow, R.C. Dye, and S. Birdsell, Composite Metal Membranes for Hydrogen Separation, US Patent applied for.
14. B.D. Cullity, Elements of X-Ray Diffraction, 2nd Ed., Addison-Wesley, Reading, MA (1978).
15. H.P. Klug and L.E. Alexander, X-Ray Diffraction Procedures, 2nd Ed., Wiley, New York (1974).