Electrical resistivity and linear expansion of a hydrogenated Pd/Ag permeator tube

A. Santucci, F. Borgognoni, S. Tosti

ENEA, Dip. FPN, C.R. ENEA Frascati, Via E. Fermi 45, Frascati, Roma I-00044, Italy

silvano.tosti@enea.it

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Overview

- **Introduction: Pd-Ag membranes**
- **Electrical resistivity and elongation measurements**
  - **Testing apparatus**
  - **Experimental results**
- **Membrane module design**
- **Conclusions**

Introduction: Pd-Ag membranes

- **A membrane is a permeable phase, often in the form of a thin film, made of a variety of materials ranging from inorganic solids to different types of polymers.**
- **The main role of the membrane film is to control the exchange of materials between the two adjacent fluid phases. A membrane is able to act as a selective barrier, which separates different species either sieving or by controlling their relative rate of transport through itself.**
- **Transport processes across the membrane are the result of a driving force, which is generally associated with a gradient of concentration, pressure, temperature, electric potential, etc.**
- **All dense metals are selectively permeable to hydrogen: especially, the Pd-Ag alloy (25% wt. of Ag) is used for preparing commercial membranes.**

Introduction: Pd-Ag membranes

By alloying Pd with Ag, the hydrogen embrittlement is reduced: in fact, there is a significant decrease in the critical temperature and pressure for the α -> β transition and a significant increase in hydrogen solubility at a specific pressure.

J. SHU et al., Catalytic Palladium-based Membrane Reactors: A Review
THE CANADIAN J. OF CHEMICAL ENG. VOLUME 69, OCTOBER 1991

Introduction: Pd-Ag membranes

The addition of Ag increase the hydrogen permeability and the mechanical strength

J. SHU et al., Catalytic Palladium-based Membrane Reactors: A Review
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ASM Handbook, Formely Tenth Edition,

Metals Handbook, Volume 2

Introduction: Pd-Ag membranes

Pd-Ag thin wall (0.050 mm) tubes produced via cold-rolling and diffusion welding

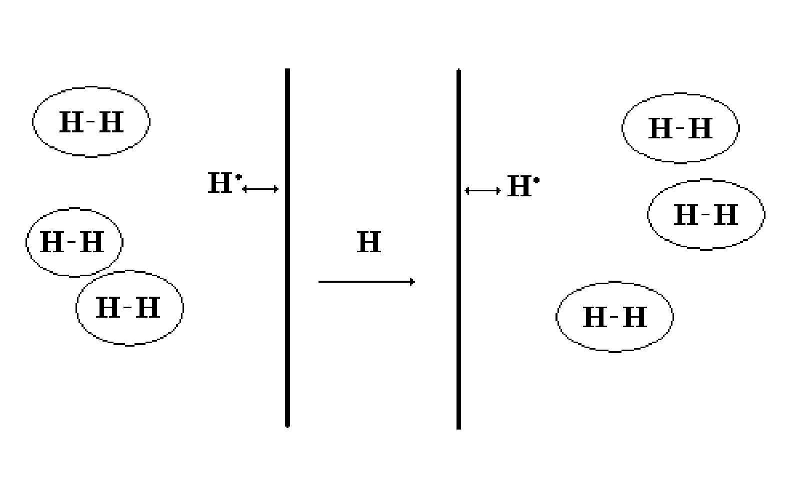
Main characteristics: high hydrogen permeance and complete selectivity

"Method of bonding thin foils made of metal alloys selectively permeable to hydrogen, particularly providing membrane devices, and apparatus for carrying out the same" European Patent EP 1184125, 2001

Introduction: Pd-Ag membranes

The hydrogen mass transfer through a metal (Permeation) is an overall process consiting of several steps:

- hydrogen interaction with the metal surface (adsorption in atomic form)
- diffusion through the metal lattice
- atomic hydrogen desorption from metal and H_2 formation



Diffusion in the metal lattice

Fick's law: $J = -D \frac{c_1 - c_2}{\delta}$

Hydrogen concentration

Sieverts' law: $c = S\,p^{0,5}$

By combining: $J = Pe \frac{p_1^{0,5} - p_2^{0,5}}{\delta}$

The permeability coefficient is obtained by multiplying the diffusion and the solubility coefficients:

$$Pe = D\,S$$

Introduction: Pd-Ag membranes

The diffusion, solubility and permeability coefficients vs. T follow an Arrehnius'law:

$D = D_0 \exp(-E_D/RT)$

$S = S_0 \exp(-E_S/RT)$

$Pe = Pe_0 \exp(-E_P/RT)$

The complete expression describing
the hydrogen permeation
is the Richardson's law:

$$J = Pe_0 \exp\left(-\frac{\boldsymbol{E_P}}{\boldsymbol{RT}}\right)\frac{p_1^{0,5} - p_2^{0,5}}{\delta}$$

Introduction: Pd-Ag membranes

- The hydrogen uploading into Pd-Ag alloy involves important technological issues:
  - composite membrane preparation
  - membrane module design
  - membrane module heating systems

- Measurements of Pd-Ag tubes linear expansion and electrical resistivity under thermal and hydrogenation cycling is required

Introduction: Pd-Ag membranes

- **Pd-ceramic membranes:**
  - **under hydrogenation Pd-Ag layer expandes much more than ceramic**
  - **the ceramic support compresses the thin metal layer via shear stresses at the interface metal/ceramic**

Introduction: Pd-Ag membranes

Thermal and hydrogenation cycling of Pd-Ag permeators produces significant deformation of the tubes

(200-400 °C, 100-200 kPa, over 1 year of testing)

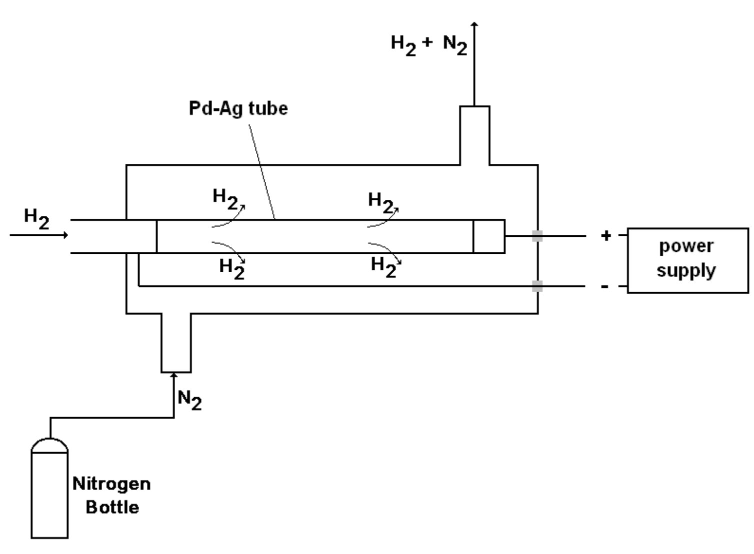
Testing apparatus

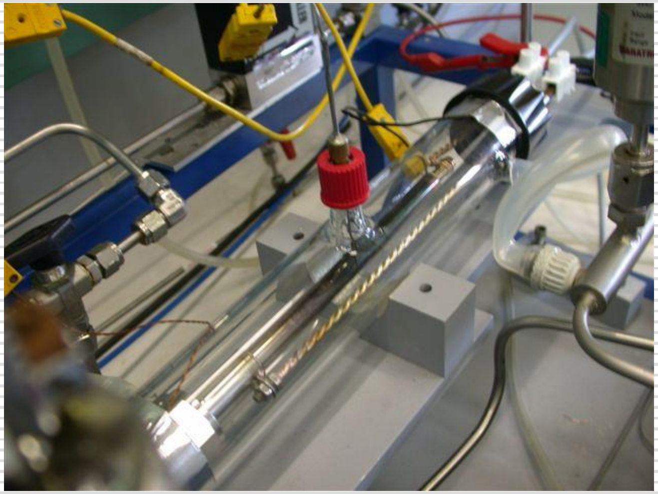
A Pd-Ag permeator tube (0,200 mm wall thickness) has been tested at ENEA labs:

- T= 50-400 °C

- Hydrogen pressure lumen side = 100-400 kPa

- Nitrogen sweeping in shell side (500 sccm)

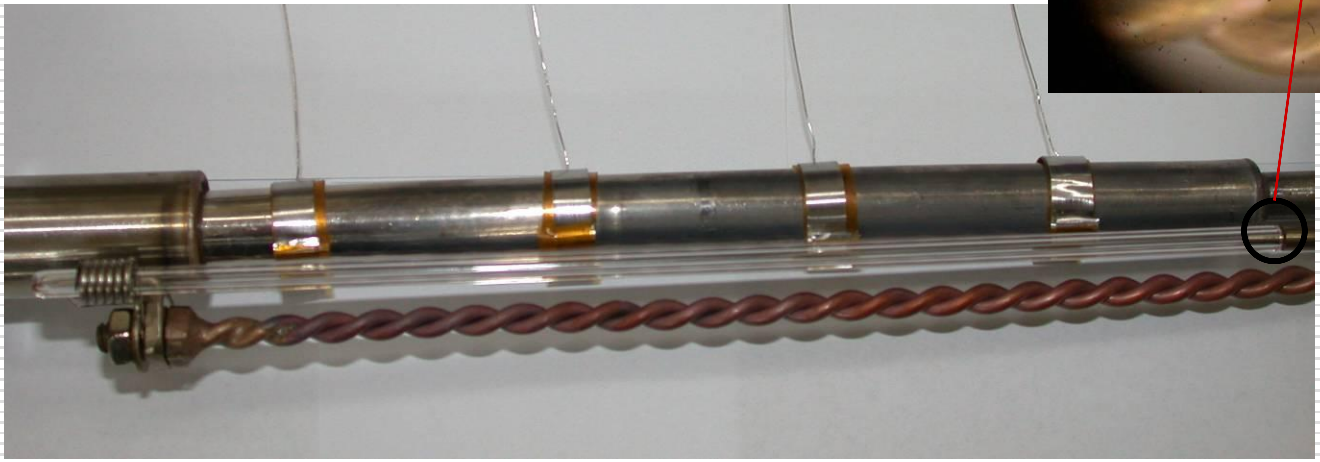


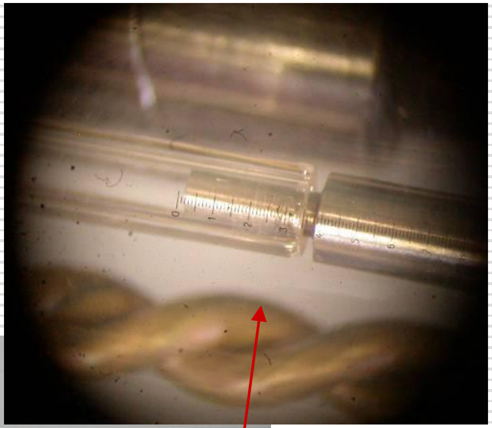


Testing apparatus

- Direct ohmic heating (DC)

- Measurements of elongation by optical microscope and voltage by multimeter





Experimental results: hydrogen solubility

The hydrogen solubility has been assessed by applying the Sieverts' law:

$$s = K_s p^{0.5}$$

$$K_s{}^{*} = 0.182\exp\left(\frac{19598}{RT}\right)\ (\text{mol m}^{-3}\ \text{Pa}^{-0.5})$$

* Serra et al., "Hydrogen and Deuterium in Pd-25 Pct Ag Alloy: Permeation, Diffusion, Solubilization, and Surface Reaction", Metallurgical and Materials Transitions A, Volume 29A, 1023 (1998)

Experimental results: hydrogen permeability

Temperature K	**Pressure kPa**	**Pe_0 mol m^{-1} s^{-1} $Pa^{-0.5}$**	**Ea kJ mol^{-1}**
373-423	100-400	3.38E-05	19.7
474-673	100-400	3.43E-07	3.4

Membrane module design

- **the shell (gas tight fixed to the membrane) compresses the Pd-Ag tube when it is hydrogenated**

- **the mechanical design has to permit the free expansion/contraction of the permeator tube without producing compressive mechanical stresses:**
  - **Finger-like configuration**
  - **Use of metal bellows**

Membrane module design: finger-like configuration

- **In the finger-like (tube-in-tube) configuration the membrane tube is free in its elongation/contraction (hydrogenation/dehydrogenation) -> any mechanical stress is avoided**

Membrane module design: finger-like configuration

Multi-tube Pd-Ag membrane module for producing ultra-pure hydrogen

via ethanol steam reforming

European Patent EP 1829821 - "Membrane process for hydrogen production from reforming of organic products, such as hydrocarbons or alcohols"

Membrane module design: use of metal bellows

PERMCAT is a Pd-Ag membrane reactor proposed for processing plasma exhaust gases (tritiated water, methane, etc.)

$$2H_2 + CQ_4 \Leftrightarrow CH_4 + 2Q_2$$

$$H_2 + Q_2O \Leftrightarrow H_20 + Q_2$$

The Pd-Ag tube thickness 50 µm, length 500 mm and diameter 6 mm

Dispositivo per la rimozione di trizio da correnti gassose, Italian Patent n. RM2005U000165, 2005

Membrane module design: use of metal bellows

Use of <u>pre-tensioned</u> metal bellows gives an initial <u>traction</u> stress

During operation (under hydrogenation) the membrane tube elongates

-> the traction stress reduces

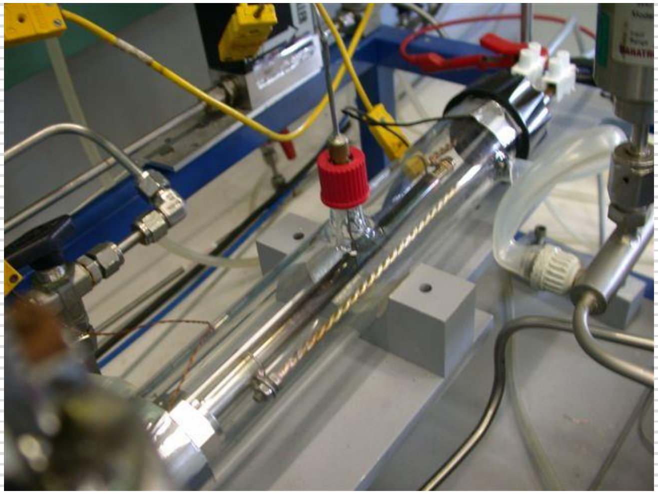
-> at least (when elongated of 7.5 mm) it is not stressed (F=0)

-> <u>the tube is never compressed</u>

Membrane module design: ohmic heating

- **No significant resistivity variation with hydrogenation (and T): the Pd-Ag tubes can easily be heated by Joule effect**

- **A new heating system has been developed by ENEA – Main characteristics:**
  - **Reduced power consuming (about 50 % of indirect heating)**
  - **rapid temperature ramping**



"Dispsoitivo a membrana di permeazione per la purificazione di idrogeno" Italian Patent n. RM2009U000143, 2009

Summary/Conclusions

- **Pd-25% wt. Ag alloy is considered for manufacturing hydrogen separators**
- **The linear expansion and resisitivity of Pg-Ag membranes have been measured under operating conditions typical of hydrogen separation processes**
- **Membrane module design (finger-like tube assembly, ohmic heating) has been based on the results of the experimental tests**

THANK YOU

FOR YOUR ATTENTION