

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

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 $\alpha \rightarrow \beta$ 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
THE CANADIAN J. OF CHEMICAL ENG. VOLUME 69, OCTOBER 1991

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

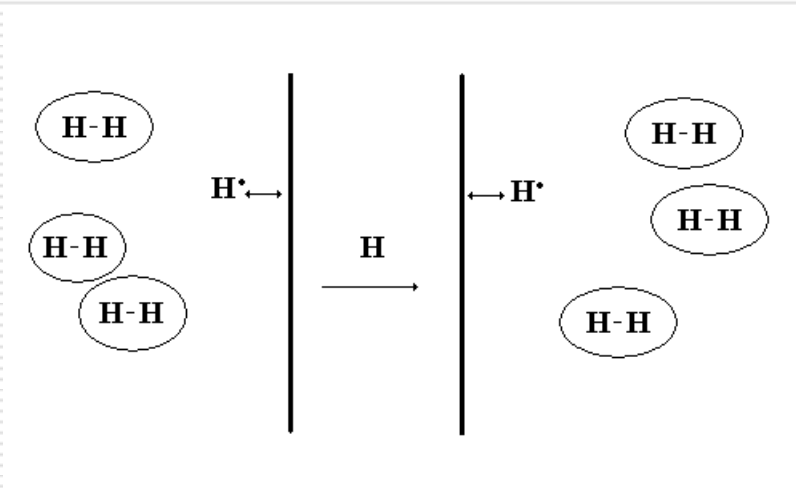
Main characteristics: high hydrogen permeance and complete selectivity

“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 consisting of several steps:

- hydrogen interaction with the metal surface (adsorption in atomic form)
- diffusion through the metal lattice
- atomic hydrogen desorption from metal and H₂ formation



Diffusion in the metal lattice

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

Hydrogen concentration

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

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

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 Arrhenius' 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:

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

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 expands much more than ceramic
- the ceramic support compresses the thin metal layer via shear stresses at the interface metal/ceramic

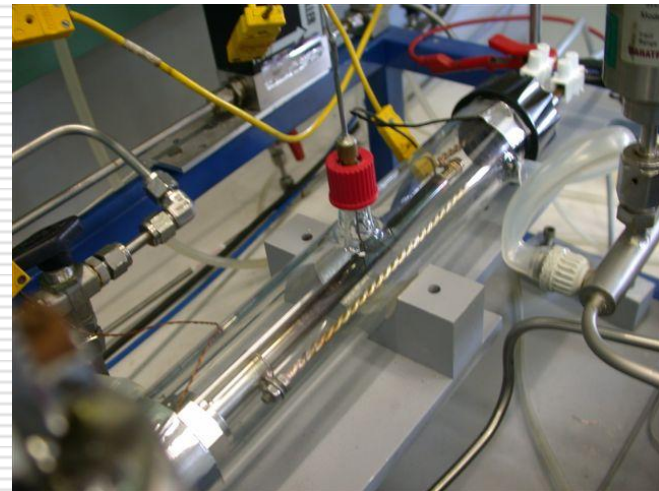
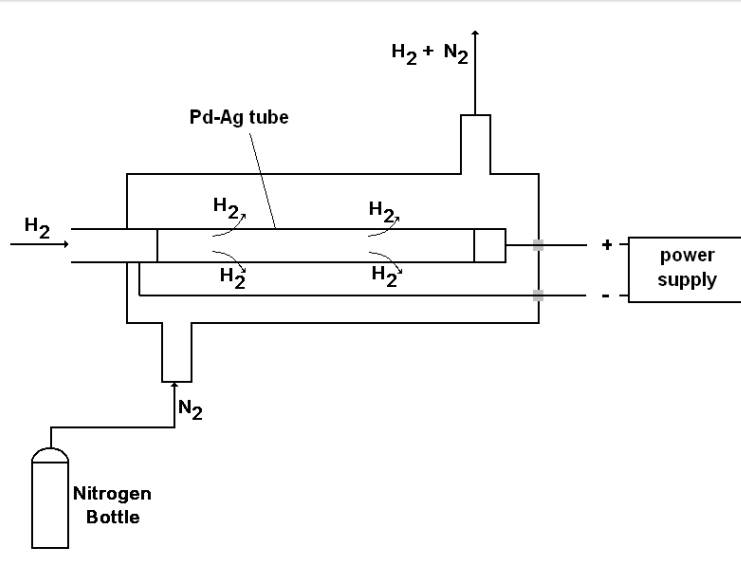
Introduction: Pd-Ag membranes

**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

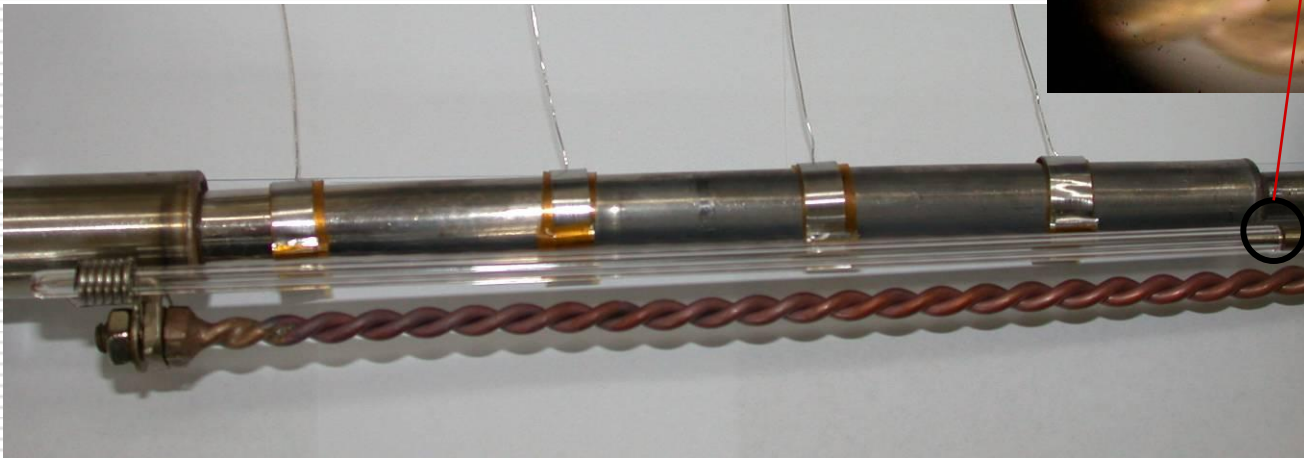
A Pd-Ag permeator tube (0,200 mm wall thickness) has been tested at ENEA labs:

- $T = 50\text{-}400\text{ }^{\circ}\text{C}$
- 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 Transactions A, Volume 29A, 1023 (1998)

Experimental results: hydrogen permeability

Temperature K	Pressure kPa	P_{e_0} $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$	E_a 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.)



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

Membrane module design: use of metal bellows

**Use of pre-tensioned
metal bellows gives an
initial traction stress**

**During operation
(under hydrogenation)
the membrane tube
elongates**

**-> the traction stress
reduces**

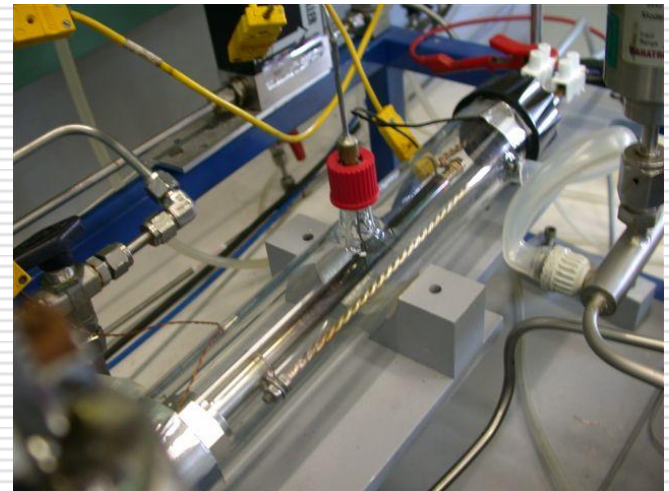
**-> at least (when
elongated of 7.5 mm) it
is not stressed ($F=0$)**

**-> the tube is never
compressed**

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**



“Dispositivo 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 resistivity of Pd-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**