

# Membrane Technologies for Tritium Recovering in the Fusion Fuel Cycle

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**Abstract.** Palladium and palladium-silver permeators have been obtained by coating porous ceramic tubes with a thin metal layer. Three coating techniques have been studied and characterized: sputtering, chemical electroless deposition and cold-rolling. The Pd-Ag membranes obtained by cold-rolling and annealing of thin metal foils have shown complete hydrogen selectivity and chemical and physical stability meeting the requirements of the fuel cycle applications. These rolled membranes have been tested at 300-400 °C with a hydrogen transmembrane pressure in the range of 100-280 kPa and hydrogen flow rates up to  $2.5 \cdot 10^{-6} \text{ m}^3/\text{s}$ . By filling the Pd-Ag membranes with a catalyst selective for the water gas shift reaction, membrane reactors have been obtained for recovering hydrogen isotopes in elemental form from tritiated water. Particularly, a closed-loop process based on a Pd-Ag membrane reactor has been studied for the tritium recovery system of an ITER scale fusion reactor.

## 1. Introduction

Palladium and palladium alloys membranes show very high performances in terms of hydrogen permeability because of the high solubility and diffusivity of the hydrogen isotopes in their lattice [1]. Particularly, adding silver to palladium both a reduced embrittlement of the metal and higher hydrogen permeability values than pure palladium are assured. Thus, this Pd-Ag alloy is used to prepare permeator tubes for hydrogen purification and separation.

The use of the membrane technologies has been proposed for applications in the fusion reactor fuel cycle in order both to reduce the number of process units and operate in continuous mode [2-4]. Therefore, several applications have been studied to apply the membrane technologies for process operations in the fusion fuel cycle in alternative to the traditional processes based on molecular sieves or cryogenics traps.

Particularly the membrane reactor technology, by coupling a selective membrane with a catalytic bed reactor, has been considered as a candidate technology to recover tritiated molecular hydrogen from tritiated water by the water gas shift reaction [5]:



The effect of the membrane is very clear since the reaction is moved towards the products (equilibrium shifting) because of the continuous hydrogen separation.

In order to reduce the tritium inventory and to maximize the hydrogen permeation fluxes, the thickness of the Pd-Ag has been reduced. Thin palladium and palladium-silver permeators have been obtained by coating porous ceramic tubes with a thin metal layer. Three coating techniques have been studied and characterized: sputtering, chemical electroless deposition and cold-rolling.

Furthermore, potential applications of the Pd-Ag membranes and membrane reactors to the fuel cycle have been studied.

## 2. Pd-Ag Membranes

Pd-ceramic permeator tubes have been obtained by coating ceramic porous tubes with a thin Pd-Ag layer. Three coating techniques have been studied and characterized [6, 7, 8]:

- sputtering of Pd-Ag thin layer (1-5  $\mu\text{m}$ ) on ceramic modified porous tubes,

- chemical electroless deposition of thin Pd-Ag film (2.5-20  $\mu\text{m}$ ) on ceramic modified porous tubes,
- cold-rolling of Pd and Pd-Ag foils to produce membrane tubes of thickness 60-70  $\mu\text{m}$  coated over ceramic porous supports.

Commercial alumina porous tubes of diameter 7/10 mm and a pore size of 12  $\mu\text{m}$  have been used as ceramic supports to be coated by the metal layer. Before sputtering and electroless deposition, the alumina tubes have been modified: the pore size of the ceramic tube has been reduced by the deposition of a ceramic top layer of 0.5  $\mu\text{m}$  pore size in order to obtain the closure of all the ceramic pores.

The electroless membranes have shown the presence of defects (pin-holes) in the Pd-Ag layer, then the lack of hydrogen selectivity and a poor physical-chemical stability have been observed. Also in the sputtered membrane the pores of the metallic film have not been completely closed and a not significant separation factor  $\text{H}_2/\text{inert gas}$  slightly better than in the ceramic support has been found.

Conversely, the rolled membranes have shown both a complete hydrogen selectivity and a good chemical and physical stability (mandatory requirements for the applications in the fusion fuel cycle). Particularly, these results have been obtained by using a new diffusion bonding technique to weld the thin rolled foils. This welding technique avoids the formation of thermal stressed zones in the permeator tubes assuring a good durability under the thermal and hydrogenation cycling.

## 2.1 Membranes Testing

The Pd-ceramic composite membranes have been characterized by measuring the permeated flux (of hydrogen or inert gas) under a controlled transmembrane differential pressure.

The electroless membranes have shown a not complete hydrogen selectivity and a poor stability. Particularly, with higher thickness of the metallic layer (15-20  $\mu\text{m}$ ), good values of selectivity were attained (separation factor of 50) but a rapid rupture of the membrane was observed after thermal cycling and hydrogen loading. Conversely, for the electroless membrane of reduced thickness (2.5-5  $\mu\text{m}$ ) low selectivity values were measured (similar to the ceramic support) and a good adhesion and stability of the metallic layer were observed in two weeks of operation. Also in the thickest sputtered membrane produced, 5  $\mu\text{m}$ , the pores of the metallic film were not completely closed and a separation factor  $\text{H}_2/\text{inert gas}$  slightly higher than in the ceramic support was found.

Two rolled membranes were prepared and tested [8]:

- a Pd tube thickness 56  $\mu\text{m}$  and length 140 mm,
- a Pd-Ag tube thickness 68  $\mu\text{m}$  and length 150 mm.

Both Pd and Pd-Ag rolled membranes have shown complete hydrogen selectivity and chemical and physical stability during several weeks of testing. The tests were carried out in the temperature range of 300-400  $^{\circ}\text{C}$ : a hydrogen transmembrane pressure in the range of 100-280 kPa and hydrogen flow rates up to  $2.5 \cdot 10^{-6} \text{ m}^3/\text{s}$  have been measured. The hydrogen permeability values measured for Pd and Pd-Ag rolled membranes are reported vs. the temperature in fig. 1.

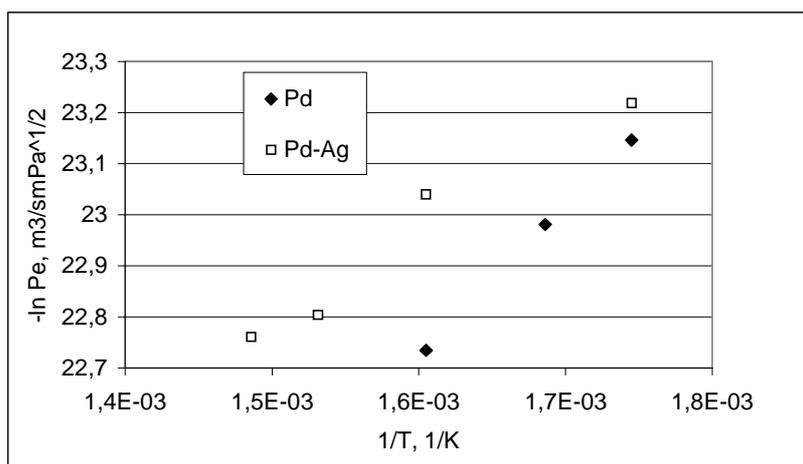


FIG. 1. Measured hydrogen permeability values through Pd and Pd-Ag rolled membranes.

### 3. Pd-Ag Membrane Reactors

Prototype membrane reactors have been realized by filling the membrane tubes with a catalyst for the water gas shift reaction. In these reactors, the hydrogen is recovered by inert gas purging or vacuum pumping in the shell so that the reaction conversion is moved towards the products. In agreement with a modeling study based on literature and kinetic data, in a CMR the conversion of the reaction can be close to 100 % since the equilibrium is displaced towards the products by the hydrogen extraction. Furthermore, the advantage to have in one device both the reaction and the hydrogen isotopes separation reduces the process unit number and then the tritium inventory.

As potential fuel cycle applications of the Pd-Ag membrane reactors, a closed loop process, based on batch mode of operation, has been studied [9]. In this process, tritium is recovered from tritiated water, see a schematic flow sheet in fig. 2.

The tritiated water is pumped into a stream of hot CO and routed to a membrane reactor where the reaction (1) of tritiated water with CO to produce hydrogen isotopes and CO<sub>2</sub> is promoted. The pure hydrogen isotopes, recovered on the permeate side of the membrane reactor, are sent directly to the Hydrogen Isotopic Separation System (HISS).

The CO needed for the conversion is drawn from a storage vessel holding the amount required for processing the whole batch of water plus a reasonable excess. The gas stream at the reactor outlet containing CO<sub>2</sub> product from the reaction is recycled to the storage vessel. Therefore the stream recycled to the membrane reactor becomes progressively enriched in CO<sub>2</sub>. The process lasts until all water is reacted and all the hydrogen isotopes have been recovered by permeation.

Then, in order to reconvert the CO<sub>2</sub> into CO and to avoid the generation of CO<sub>2</sub> wastes and CO consumption, the mixture of CO<sub>2</sub> with the residual amount of CO remaining in the storage vessel is added of hydrogen and sent to the membrane reactor. By effect of the introduction of hydrogen the water gas shift reaction (1) is reversed and the CO<sub>2</sub> is reconverted into CO:



This reaction is forced towards the complete conversion of CO<sub>2</sub> into CO by separating the formed water in a condenser. During this step it could be convenient to rise the temperature: as matter of fact, from thermodynamic considerations the conversion reaction is promoted by increasing the temperature. However, to avoid thermal cycling of the equipment, it is preferred to operate at constant temperature and to enhance the rate of conversion by

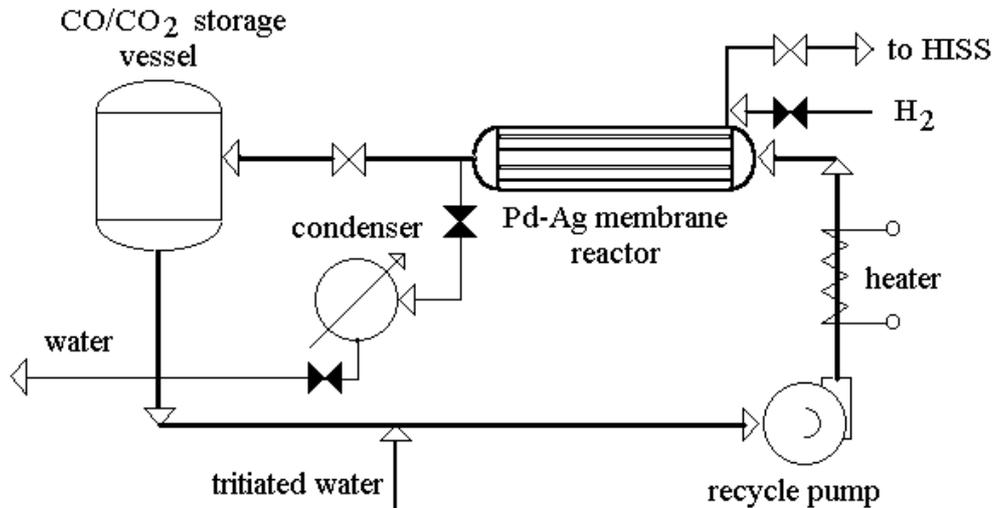


FIG. 2. Tritiated water conversion process flow sheet.

increasing the rate of gas circulation through the membrane reactor so that all the CO<sub>2</sub> is converted into CO. The dried gas stream is sent to the storage vessel and then back to the membrane reactor.

The main features of the proposed process are:

- the reaction conversion is increased and the process components are reduced by using a membrane reactor instead of a fixed bed reactor plus a hydrogen separator with advantages in terms of tritium inventory and availability,
- the CO<sub>2</sub> wastes generation and the CO consumption are avoided with respect to a traditional process in which the CO<sub>2</sub> produced in the membrane reactor is not regenerated.

An analysis of the performances of the membrane reactors has been carried out by a computer code developed for studying both the water gas shift reaction and the CO conversion.

The simulation code has allowed us to verify that for the water gas shift reaction the conversion is not really modified by using a rolled membrane (Pd-Ag thickness 50 μm) instead of an electroless one (Pd-Ag thickness 10 μm) [10]. As a matter of fact, the capability of the membrane and the CMR to separate and recover hydrogen can be evaluated by the reaction conversion:

$$\frac{H_2O_{fed} - H_2O_{out}}{H_2O_{fed}} \quad (3)$$

Figures 3 and 4 show the partial pressure profiles of water and hydrogen inside a membrane reactor operating at 200 kPa and 350 °C with a stoichiometric feed of CO and water. The Pd-Ag membranes have length 300 mm, diameter of 10 mm, and metal thickness 10 μm and 50 μm, for the electroless and the rolled membrane respectively. The water partial pressure calculated by the computer code at the reactor outlet is 7.13 and 7.89 kPa and the conversion is 96.2 % and 95.9 %, for the electroless and the rolled membrane respectively (the equilibrium conversion value under these operating conditions is about 82%). The difference in terms of the reactor performances is negligible; as matter of fact, the larger hydrogen mass transfer resistance of the rolled membrane (larger metal thickness) is compensated by the presence of the ceramic porous tube with a dense top layer in the electroless membrane.

Experimental tests have been also carried out confirming the achievement of high conversion values in the hydrogen recovery from water via the gas shift [10].

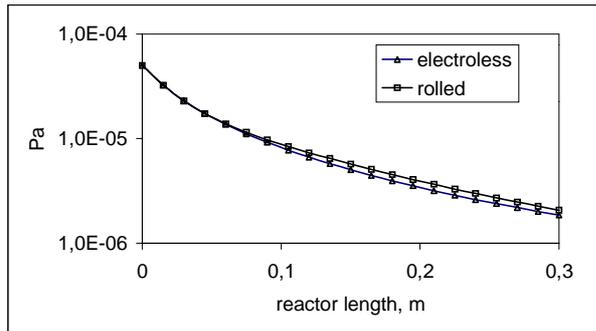


FIG. 3, Water partial pressure profile.

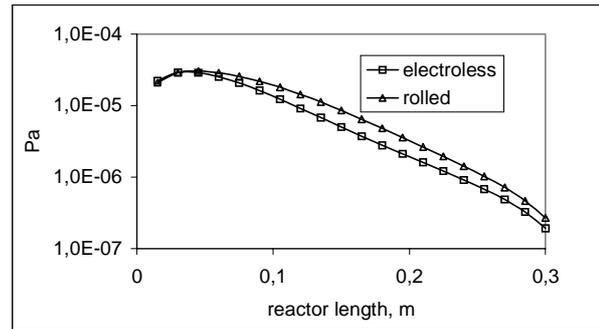


FIG. 4, Hydrogen partial pressure profile.

## Conclusions

A work of producing and characterizing thin Pd-ceramic composite membrane obtained by sputtering, electroless deposition, and cold-rolling has been carried out.

The rolled membranes have shown a metallic layer without defects adequate to ensure hydrogen selectivity but enough thin to give slightly higher mass transfer resistance with respect to the electroless and sputtered membranes. Thus, the rolled membranes have met the requirements of applications in the fusion fuel cycle, particularly, in terms of complete hydrogen selectivity and chemical and physical stability in long term tests.

Based on these Pd-ceramic membranes, membrane reactors for the water gas shift reaction and CO conversion have been realized. Particularly, a closed-loop process has been studied for tritium recovering from tritiated water for an ITER scale fusion reactor.

The main features of this process with respect to the alternative processes consist in the reduction of the components with advantages in terms of tritium inventory and availability of the plant. Furthermore, the closed-loop process avoids the CO<sub>2</sub> wastes generation and the CO consumption.

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