

CATALYTIC MEMBRANE REACTOR FOR DEHYDROGENATION OF WATER VIA GAS-SHIFT

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ABSTRACT

Pd-ceramic composite membranes and catalytic membrane reactors (CMR) have been studied for hydrogen purification and recovery in the fusion reactor fuel cycle. The development of techniques for coating microporous ceramic tubes with Pd and Pd/Ag layers is described: composite membranes have been produced by electroless deposition (Pd/Ag film of 10-20 μm) and rolling of thin metal sheet (Pd and Pd/Ag membranes of 50-70 μm).

Experimental results on electroless membranes showed that the metallic film presented some defects and the membranes had not complete hydrogen selectivity. Then the catalytic membrane reactors with electroless membranes can be applied for some industrial processes that do not require a complete separation of the hydrogen (i. e. in the dehydrogenation of hydrocarbons). The rolled thin Pd and Pd/Ag membranes separated the hydrogen from the other gas with a complete selectivity and exhibited a slightly larger (about a factor 1.7) mass transfer resistance with respect to the electroless membranes. Experimental tests confirmed the good performances in terms of durability.

INTRODUCTION

The membrane technologies are considered an interesting process alternative for the fusion reactor fuel cycle such as fuel purification and waste processing [1, 2]. Pd based membranes and catalytic membrane reactors are used both to separate and recover hydrogen and its isotopes from gas mixtures. This technique is developed and proposed in the ITER (International Thermonuclear Experimental Reactor) design. In this process a CMR is proposed to recover hydrogen isotopes in elemental form from tritiated water by using a catalyst selective for the water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. In this way it is possible both to recycle the tritium to the reactor and to limit the generation of tritium contaminated wastes. The main advantages of the process consist in the possibility to reduce the number of process items and controls and the tritium inventory and then increasing both the reliability and safety of the fuel cycle plant.

The results obtained in the development of Pd-ceramic composite membranes are promising also for applications in hydrogenation/dehydrogenation processes, i. e. pure hydrogen production from hydrocarbon reforming for fuel cell.

ELECTROLESS MEMBRANES

Composite membranes, composed of a thin film of Pd/Ag alloy (10 μm thick) supported by a porous ceramic tube, have been produced [3, 4] with a modified electroless technique, see scheme in fig. 1.

The selected support is a commercial macro-porous tube of Al_2O_3 (average size about 12 μm) with the following dimensions: length 250 mm, outside diameter 10 mm, inside diameter 7 mm.

In order to guarantee the deposition of the PdAg film the dimension of the external pores are reduced by vacuum aspiration of an alumina powder (0.1-1 μm size) suspension with polyethylenglykol in water. When a permeability value $Pe = 0.5 \cdot 10^{-6} \text{ m}^3/\text{m}^2 \text{ s Pa}$ is reached, a thermal treatment is carried out. After two more cycles of aspirations, drying at 120°C and thermal treatments at 1200°C, a stable permeability value $Pe = 0.5 \cdot 10^{-6} \text{ m}^3/\text{m}^2 \text{ s Pa}$ is obtained.

Ceramic membranes produced in this way showed, at SEM analysis, external pore size of 0.5 μm . In order to activate the ceramic surface for the electroless plating deposition an activation bath having the following composition is used: PdCl_2 : 0.68 g/l, SnCl_2 : 4.75 g/l, HCl conc.: 100 ml/l.

After this critical step, a classical palladium and silver electroless depositions are carried out. When palladium and silver have been deposited in proper ratios (Pd 77%, Ag 23%) a heat treatment performed at 650°C for 5 days assures the achievement of the palladium-silver alloy. Then the composite membrane has been waterproofed at the edges by an end-sealing treatment based on a vitreous material coating.

An improvement of the deposition technique is still required as some microscopic defects (micro-holes) are found on metallic surfaces, although the deposited film is always well sticking to the support.

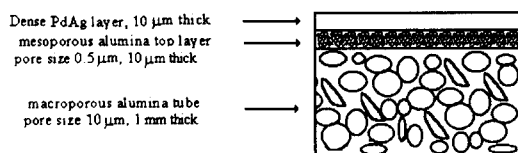


Fig. 1, scheme of an electroless membrane

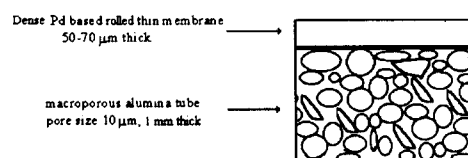


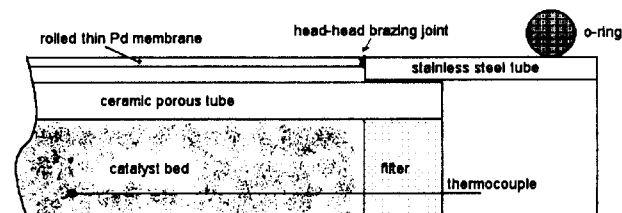
Fig. 2, scheme of a rolled membrane

ROLLED MEMBRANES

Thin Pd-based rolled membranes (50-70 μm), see scheme in fig. 2, have been developed in order to have a metallic layer enough thick to avoid defect of the metallic layer and ensure a complete selectivity without giving large mass transfer resistance with respect to the electroless thin film membranes.

Thin Pd and Pd/Ag sheets have been cold-rolled by a two-high laboratory mill [5]. Several steps of cold rolling and annealing of the palladium and palladium silver foils have been needed in order to relieve the mechanical stresses due to the work hardening upon rolling, particularly for the alloyed palladium. Measurements of Vicker hardness have been carried out during the rolling process in order to characterize the hardening status and to evaluate the workability of the specimens before going on the annealing step. The annealing of the metal palladium and alloy foils has been carried out by heat treatment in a furnace at 1200°C and at atmospheric pressure for 2-3 hours under Ar atmosphere to avoid the oxidation and tarnishing of the palladium surfaces.

After rolling the metallic foils have been closed by TIG arc welding for obtaining two permeating tubes of length 150 mm, internal diameter 10 mm and thickness 70 (for Pd) and 50 μm (for PdAg). At the ends of the metallic membranes two stainless steel tubes, 100 μm thick, have been jointed by brazing in order to



have, under operating conditions, a thermal gradient able to reduce the temperature in the o-ring zone of the reactor. Finally a porous ceramic tube, containing the catalyst bed in the CMR version, has been put inside the metallic membrane to avoid the contact between the palladium and the catalyst, as shown in scheme of fig. 3.

Fig. 3, scheme of a CMR with a rolled membrane

Pd-CERAMIC MEMBRANE AND CMR MODELLING

A mathematical model of a CMR for the water gas shift reaction and a computer code, WGSR, have been developed. The code WGRS has proved to be a useful tool both to understand the processes occurring in the CMR and to find the optimum operating conditions and has been used both to foresee the results of the experimental tests and to assess the potential fuel cycle applications of Pd/Ag thin film permeators and of CMR.

The model is based on the following main assumptions: isothermal and steady state conditions, constant longitudinal temperature, negligible pressure losses, perfect gas behavior, negligible radial temperature and concentration profiles (one dimensional model), negligible effect of competitive reactions, no isotope effects. The tubular catalytic membrane reactor is divided into finite volume elements where composition of the gas, the rate of reaction and the permeation of hydrogen through the walls can be considered constant (perfect

mixing). With minor modifications concerning the reaction kinetic expression, the WGSR code can be used for studying other hydrogenation/dehydrogenation reactions in a CMR.

The simulation code WGSR allowed us to verify that for the water gas shift reaction the conversion is not really modified by using a thin rolled Pd/Ag metallic membranes (50-70 μm) over a macroporous ceramic tube instead of an electroless thin film (10 μm) coated on an asymmetrical ceramic tube with a dense top layer for the considered working temperature (350 $^{\circ}\text{C}$).

The potential fuel cycle applications of Pd/Ag thin membrane permeators and of CMRs have been also studied. A closed-loop process for the conversion of tritiated water into elemental hydrogen has been proposed with reference to the design requirements of the ITER blanket tritium recovery system. The conversion of the tritiated water collected as impurity in the cryotrap is attained in a process characterized by a low processing rate. The main advantages are related to the absence of secondary wastes, low tritium inventories, moderate operating temperatures and pressures increasing both the reliability and safety of the nuclear plant.

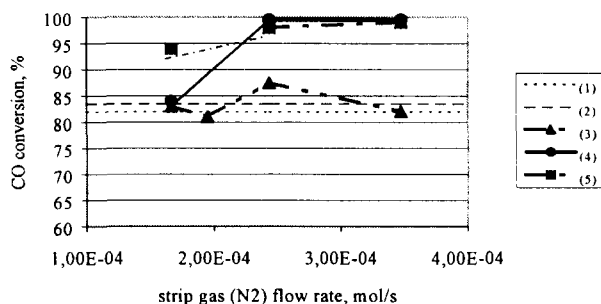
RESULTS

Experimental tests have been carried out to characterize both composite membranes and catalytic membrane reactors.

Measurements on pure Pd rolled membrane of 56 μm of thickness at 350 $^{\circ}\text{C}$ and 0.12 MPa exhibited a permeability value of $2.654 \cdot 10^{-10} \text{ m}^3/\text{m s Pa}^{0.5}$ with a complete hydrogen selectivity.

Tests for the water gas shift reaction on CMR with electroless membranes showed that the reaction conversion is always above the equilibrium and increases when the flow rate reduces (the residence time increases). The effect of the membrane is very clear since the reaction is shifted towards the products because of the continuous hydrogen separation. The comparison between the experimental results and the model calculations shows an excellent accordance.

Tests on prototype CMR with Pd rolled thin membrane (70 μm thick) have been carried out, too. Fig. 4 shows the results obtained at 331 $^{\circ}\text{C}$ (co-current and countercurrent mode) and 350 $^{\circ}\text{C}$ (countercurrent mode). The feed flow rate range is $3.05 \cdot 10^{-5} \text{ mol/s}$ and $7.13 \cdot 10^{-4} \text{ mol/s}$ with a stoichiometric composition. Nitrogen was sent in the strip side. The internal pressure is $1.1 \cdot 10^5 \text{ Pa}$. The results exhibit the reaction conversion arising up to 100% by increasing the strip flow rate. Due to the characteristics of the catalyst, the



reaction yield optimum is obtained at 330°C.

fig. 4, CMR with rolled thin membrane, CO conversion vs. the N₂ strip flow rate: (1) equilibrium value at 350° C, (2) equilibrium value at 331 °C, (3) co-current with feed flow rate $7.13 \cdot 10^{-4}$ mol/s at 350° C, (4) counter-current with feed flow rate $3.05 \cdot 10^{-5}$ mol/s at 331° C, (5) co-current with feed flow rate rate $3.05 \cdot 10^{-5}$ mol/s at 331° C.

CONCLUSIONS

The PdAg thin film membranes obtained by electroless showed a not complete hydrogen selectivity. Nevertheless, according to the theoretical previsions, the experimental tests confirmed that the equilibrium shift towards the dehydrogenation with a very high conversion. Thus, the CMR with electroless thin film membranes is already applicable for some industrial processes, i. e. in the dehydrogenation of hydrocarbons.

Rolled thin Pd and Pd/Ag membranes have been also produced and tested. These membranes separated the hydrogen from the other gas with a complete selectivity and exhibited a slightly larger mass transfer resistance with respect to thin film membranes. Experimental tests confirmed the theoretical previsions and the good performances in terms of durability.

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