Pd-based metallic membranes for hydrogen separation and production

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ABSTRACT

Low cost composite metallic membranes for the hydrogen separation and production have been prepared by using thin Pd-Ag foils reinforced by metallic (stainless steel and nickel) structures. Especially, "supported membranes" have been obtained by a diffusion welding procedure in which Pd-Ag thin foils have been joined with perforated metals (nickel) and expanded metals (stainless steel): in these membranes the thin palladium foil assures both the high hydrogen permeability and the perm-selectivity while the metallic support provides the mechanical strength.

A second studied method of producing "laminated membranes" consists of coating non-noble metal sheets with very thin palladium layers by diffusion welding and cold-rolling. Palladium thin coatings over these metals reduce the activation energy of the hydrogen adsorption process and make them permeable to the hydrogen. In this case, the dense non-noble metal has been used as a support structure of the thin Pd-Ag layers coated over its surfaces: a proper thickness of the metal assures the mechanical strength, the absence of defects (cracks, micro-holes) and the complete hydrogen selectivity of the membrane.

INTRODUCTION

Palladium and palladium alloy membranes have been proposed for producing hydrogen separators. In fact, Pd-based membranes have the capability to separate hydrogen from gas mixtures; basically, the Pd-Ag alloy (Ag 25 wt.%) shows high hydrogen permeation fluxes and a reduced embrittlement under hydrogenation and thermal cycling [1, 2] and the recently proposed applications for these membranes consist of housing them in stainless steel modules in order to produce membrane reactors [3-6]. Nevertheless, a practical limit in the use of these palladium membranes is given by the cost of the precious metal and several techniques have been studied in order to reduce the use of the palladium in these membranes. Generally, composite Pd-ceramic membranes have been produced by covering glass or ceramic porous supports (discs, tubes, etc.) with thin palladium layers: this allowed significant cost reduction as well as high performances in terms of permeation fluxes [7-9]. However, the hydrogen perm-selectivity, required in the processes for the production of highly pure hydrogen, can only be attained at the price of losing the chemical and physical stability [10].

SUPPORTED METAL MEMBRANES

Stainless steel grids and nickel perforated foils have been used as supports for thin Pd-Ag foils [11]. Specifically, the steel or nickel supports gives to the membrane the mechanical strength needed to withstand high operating differential pressures, while the reduced thickness of the Pd-Ag foils provides low mass transfer resistance and reduced costs. Furthermore, the use of a diffusion welding procedure assures the production of reliable and durable joints between the palladium foils and the support.

♦ Stainless steel support
The procedure studied consists of the following two steps:
- the coating of a nickel thin layer (1-2 μm) and/or of an extra silver layer over the stainless steel support through electroless plating, electrochemical deposition, chemical vapor plating or sputtering,

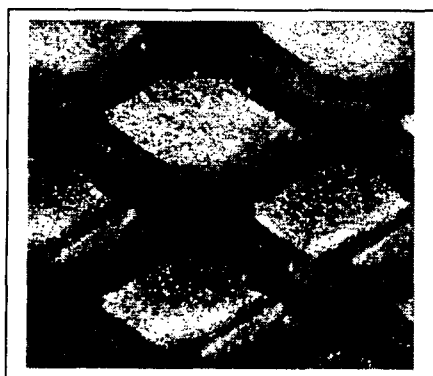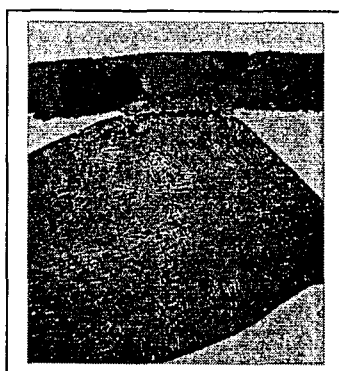- the joining of the steel support to the Pd-Ag thin foil by diffusion welding.
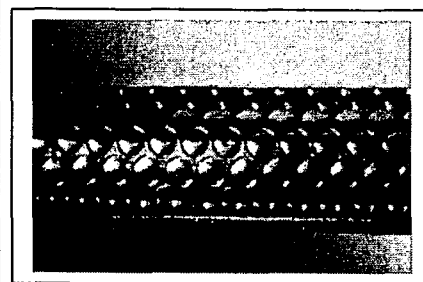

| Fig. 1 | Fig. 2 | Fig. 3 |

The details of the sample joints obtained can be observed in fig. 1 and fig. 2. In particular, fig. 1 shows the snapshot of a Pd-Ag foil, 50 μm thick, welded to a stainless steel grid coated by electrochemical deposition with a Ni layer of 1-2 μm. Fig. 2 shows a metallograph picture of the cross section of this sample. This detail illustrates the presence of an intermediate layer between the Pd-Ag foil (higher in the picture) and the nickel grid (downward): this layer could be caused by the formation of an inter-diffused Ag-based compound that assures the adhesion of the Pd-Ag foils over the metal support.

♦ Nickel support

In spite of higher cost than stainless steel, nickel presents a higher chemical inertia than stainless steel throughout several applications concerning the hydrogen separation and production. Furthermore, nickel supported membranes have been produced by joining directly Pd-Ag foils over the metallic support without any deposit of a nickel thin layer. According to this procedure, a composite membrane sheet has been prepared by joining a nickel perforated sheet (thickness 210 μm, holes diameter 2.5 mm) with a Pd-Ag foil (thickness 42 μm), by using the procedure described above for stainless steel supports. A 75 mm long membrane tube (see fig. 3), with an internal diameter of 11 mm, and Pd-Ag effective permeation surface of $9.27 \cdot 10^{-4}$ m^2 was prepared through a procedure previously studied [12].

With pressure values for the hydrogen feed in the range of 141-234 kPa, the measured hydrogen permeability through the Pd-Ag effective surface area has been $1.60 \cdot 10^{-9}$ and $1.8 \cdot 10^{-9}$ mol m^{-1} s^{-1} Pa$^{-0.5}$, at 350 and 375 °C, respectively. These values of permeability are in agreement with the literature data for Pd-Ag alloy [13].

LAMINATED METAL MEMBRANES

Several metals (including Nb, Ta and V) have been predicted to have higher hydrogen permeability values than palladium and palladium alloys, while other low cost metals (Ni and Fe) present significant permeability values [14]. Unfortunately, all of these metals have a stronger surface resistance to hydrogen transport than Pd: these poor surface properties are associated with high reaction to gas under many operating conditions. Thin palladium coatings over these metals reduce the activation energy of the hydrogen adsorption process and increase the hydrogen permeation flux. In this case, the dense non-noble metal is the support structure for the thin Pd-Ag layers coated over its surfaces: proper thickness of the non-noble metal assures the mechanical strength, the absence of defects (i.e. cracks and micro-holes) and the complete hydrogen selectivity of the membrane. The Pd-Ag foils have been attached to non-noble metal sheets with the diffusion welding procedure and by using the same apparatus described above for the supported membranes. After this step, the laminated metal obtained needs to be cold-rolled in order to reduce the total thickness of the

composite membrane down to an optimum value for supporting the required characteristics of permeability, chemical and physical stability, and also reduced costs (i.e. thin Pd-Ag layer).
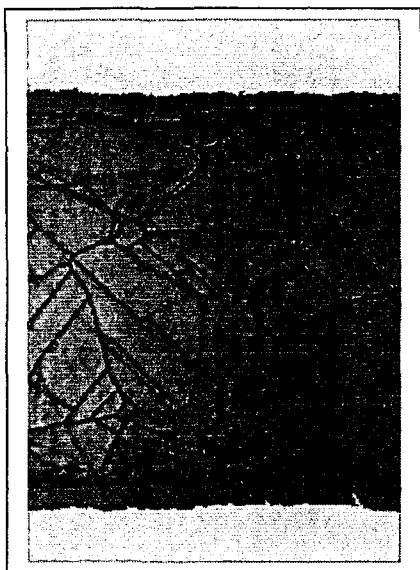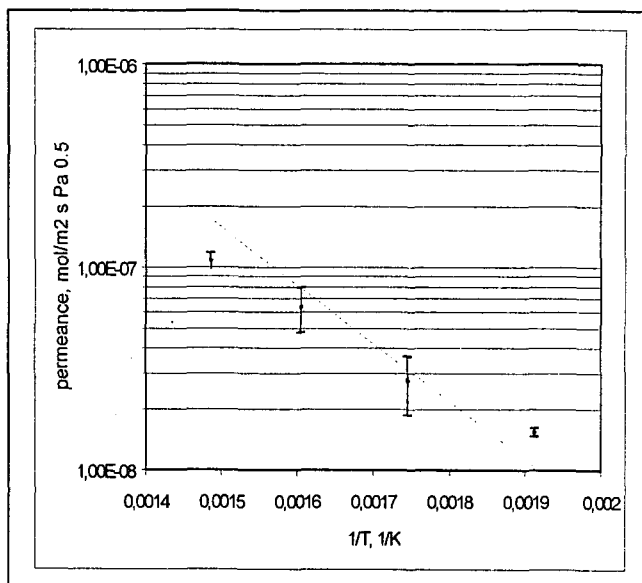

Fig. 4

Fig. 5

♦ Ni-based laminated membrane

A laminated nickel membrane has been prepared by covering a nickel sheet (Ni ≥ 99.0 wt. %), 500 μm thick, with two 28 μm thick Pd-Ag foils by by means of diffusion welding. The total thickness of the composite membrane has been reduced down to 141 μm through cold-rolling. Fig. 4 illustrates a metallograph picture of the cross section of the laminated membrane sheet before rolling. Also in this case, a permeator tube has been built according to the above reported method. The tube has an external diameter of 10.2 mm, a length of 97 mm and a permeation surface area of 3.05 ·10^{-3} m^2. Permeance values measured in the temperature range 250-400 °C are reported in fig. 5 where a comparison with the theoretical permeance (dash line) calculated from the literature permeability data of the Pd-Ag and Ni is also shown.

DISCUSSIONS AND CONCLUSIONS

Supported membranes have shown high hydrogen permeation fluxes and cost reduction, based on the employment of the precious metal, by a factor 5-10 with respect to the commercial Pd-Ag permeator tubes (thickness 100-150 μm). As an example, at 375 °C, with hydrogen pressure of 234 kPa, a supported (Pd-Ag/Ni) permeator tube membrane has the capability of separating 1.9 m^3 (STP) h^{-1} per square meter of the same membrane area.

As a next step, a further reduction of the Pd-Ag thickness (down to 20 μm) seems to be practicable and higher hydrogen permeation fluxes as well as reduced costs can be easily predicted. As a main result at this point, both the complete hydrogen selectivity and the chemical and physical stability of these membranes have been demonstrated during the tests. In fact, these membranes are able to separate high pure hydrogen and none formation of defects (cracks, holes) with loss of selectivity has been observed.

Laminated membranes have shown a poorer performance than supported membranes. Particularly, metals (such as Nb) with hydrogen permeability higher than palladium have indicated a quick worsening (swelling due to the high hydrogen solubility) and the rupture of the membrane. In any case, the effectiveness of the Pd-Ag coating in reducing the surface resistance and increasing the hydrogen adsorption and permeation was demonstrated. Future studies about proper metals and metal alloys alternative to the palladium could lead to a significant cost reduction. Among the

metals with permeability lower than palladium, the nickel one has shown an ideal behaviour exhibiting permeability values according to the literature.

Recent proposed applications for these membranes consist of housing them in stainless steel modules in order to produce membrane reactors, where a fixed bed reactor and a membrane are coupled in one device. As a main advantage, beside the size and cost reduction, we can obtain reaction conversions higher than in traditional system (reactor plus membrane separator). Examples of such a kind of application are found in the nuclear processes, i.e. separation of hydrogen and its isotopes (via water gas shift) in the fuel cycle of the nuclear fusion reactor [15-17]. Among the other energy applications, the production of pure hydrogen for PEM fuel cells by reforming of hydrocarbons seems to be promising [18, 19].

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