JOURNAL OF MATERIALS SCIENCE **39** (2004) 3041 – 3046

Diffusion bonding of Pd-Ag rolled membranes

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Cold-rolled and annealed Pd-Ag 25% at. foils of thickness 50 μm have been joined by diffusion bonding in order to obtain permeator tubes used in laboratory applications for hydrogen separation and purification. The tubes produced present a sound and effective joint along the generatrix line: particularly, this procedure has shown better performance than arc welding, responsible for formation of thermally stressed zones and embrittlement of permeators.

Based on the high diffusion of the Ag atoms, the joining procedure of the tubes consists of a thermal treatment at 1100°C for 1 h under controlled atmosphere (Ar-H 5%), where the overlapped limbs of the metal foil have been compressed in a special device.

This joint obtained by diffusion bonding has shown absence of defects and good chemical and physical stability after thermal and hydrogenation cycling of the permeator tubes under their operating conditions. Characterization tests carried out in the temperature range 300–400°C on these membrane tubes have given hydrogen permeability values according to the literature.

1. Introduction

Hydrogen is a potential energy vector for a sustainable future: nevertheless, the major challenges for its widespread use concern the development of available and low cost technologies for his production and separation.

Palladium and its alloys are presently being used to produce devices for hydrogen separation and production [1]. Particularly, the palladium metal lattice presents high hydrogen solubility and diffusivity, and palladium-silver alloys show reduced embrittlement and values of hydrogen permeability higher than pure palladium. Commercial permeator tubes of thickness about 100 μm are being produced by using a palladium alloy with silver content 25% at. The Pd-Ag membranes are also proposed to produce membrane reactors. In these devices, a palladium membrane is coupled with a fixed bed catalytic reactor [2, 3]: hydrogen is selectively removed from the reaction system through the membrane, and the reaction is shifted to the product side, thus obtaining reaction yields higher than in a traditional reactor. At the present time, the cost of palladium is a key issue in the applicability of these technologies to industrial processes (e.g., hydrogenation or dehydrogenation reactions). In order to obtain membrane permeators thinner than the commercial ones, and completely selective to hydrogen, thin palladium and palladium silver foils of thickness up to 50 μm have been cold-rolled. Permeator tubes have been produced in our laboratory by joining the thin metal foils along the generatrix line: this joining is a critical point in the manufacturing process of the permeator tube. As a matter of fact, the operating conditions of the Pd alloy separator tubes consist of both thermal cycling (from ambient temperature to 400°C) and hydrogen loading cycling. Therefore, the welding technique used to join the tubes must avoid melting and, as a consequence, the micro structural degradation of the material which could weaken the hydrogenated metal and promote crack formation with loss of membrane selectivity.

In a previous work [4] a technique of joining Pd and Pd-Ag thin foils based on gas tungsten arc welding was developed to produce the permeator tubes. Nevertheless, this welding procedure produced heat-affected zones where, as a consequence of the thermal and hydrogenation cycling of the membranes, formation of cracks was observed after some weeks of operation of the permeators. Furthermore, the brazing could not be applied because of the introduction of metal elements in the Pd-Ag which may contaminate the alloy and reduce the hydrogen permeability.

Therefore, a diffusion bonding procedure based on the high mobility of the silver atoms has been developed [5]. By means of this technique, defect-free membranes have been produced: permeation tests have confirmed their complete hydrogen selectivity and a better chemical and physical stability than the membranes previously produced.

2. Experimental procedure

2.1. Tube manufacturing

Tapes of width about 40 mm and thickness 50 μm have been produced starting from thick Pd-Ag (silver content 25% at.) foils by means of a procedure of cold-rolling and annealing [4]. These tapes have been cold-rolled in

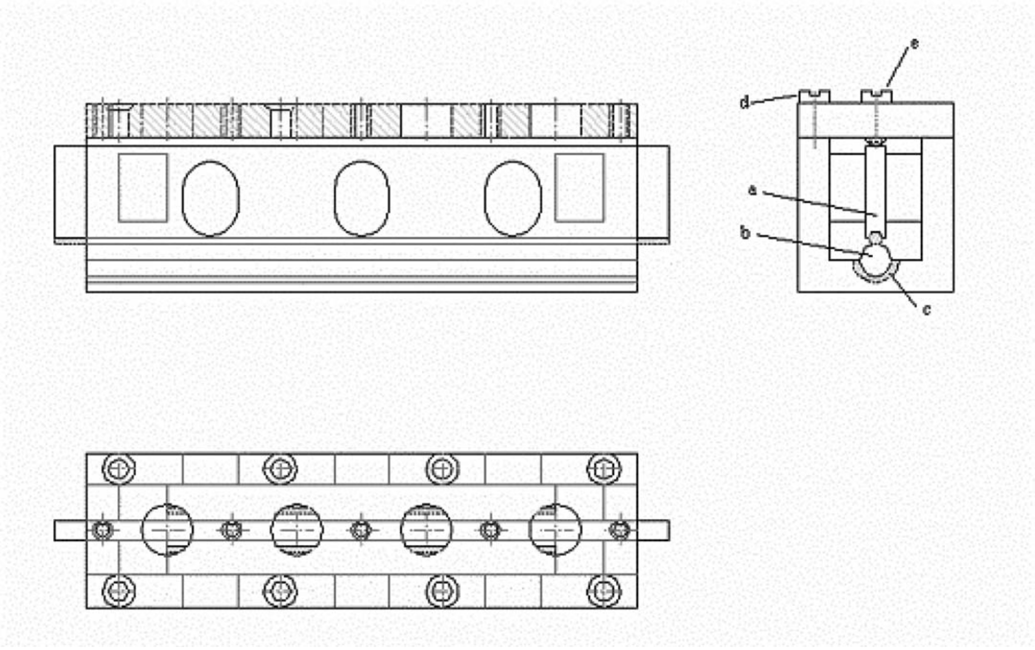


Figure 1 Scheme of the device used for welding the Pd-Ag tubes.

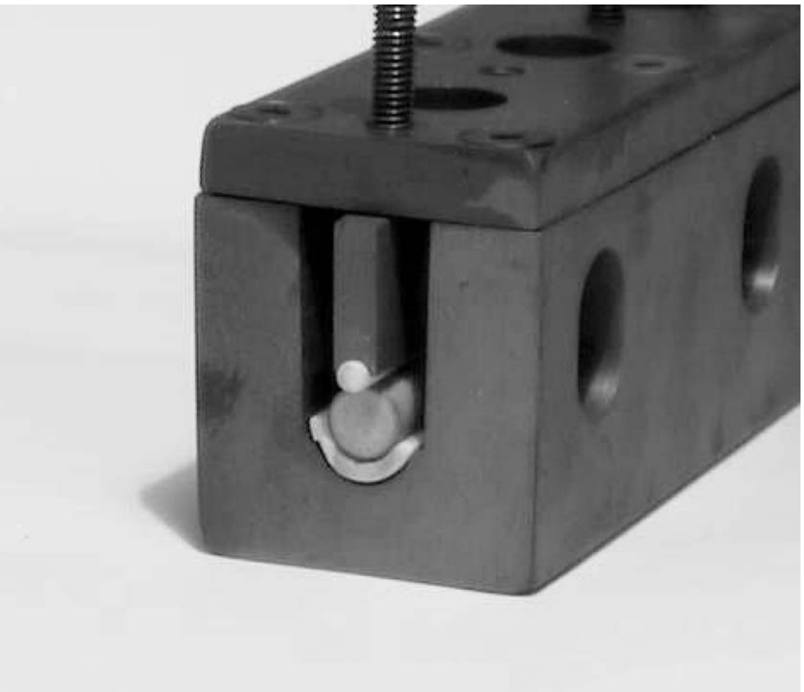


Figure 2 Picture of the device used for welding the Pd-Ag tubes.

order to obtain slices wide enough to cover the tube surface. The edges of the slice are overlapped and joined by using the device shown in Figs 1 and 2. Particularly, with reference to Fig. 1 the device consists of the following elements:

(a) steel blade with an alumina bar,
(b) Pd-Ag tube wrapped around an alumina cylinder,
(c) alumina bearing shell,
(d) screws for cope closing,
(e) pressure screw.

By means of the alumina bar the steel blade applies a controlled pressure on the overlapped limbs of the Pd-Ag tube to be assembled, Fig. 3. The pressure value can be adjusted by means of the screws.

The diffusion bonding process has been carried out in an oven at 100 kPa under a reducing atmosphere (Ar-5%H_2) in order to avoid palladium oxidation and tarnishing.

The heat treatment consists of the following steps:

- heating up to a temperature of 720°C at a ramp rate of 0.1°C s^{-1},
- heating up to a temperature of 1100°C at a ramp rate of 0.2°C s^{-1},
- (holding) dwell at 1100°C for 1 h,

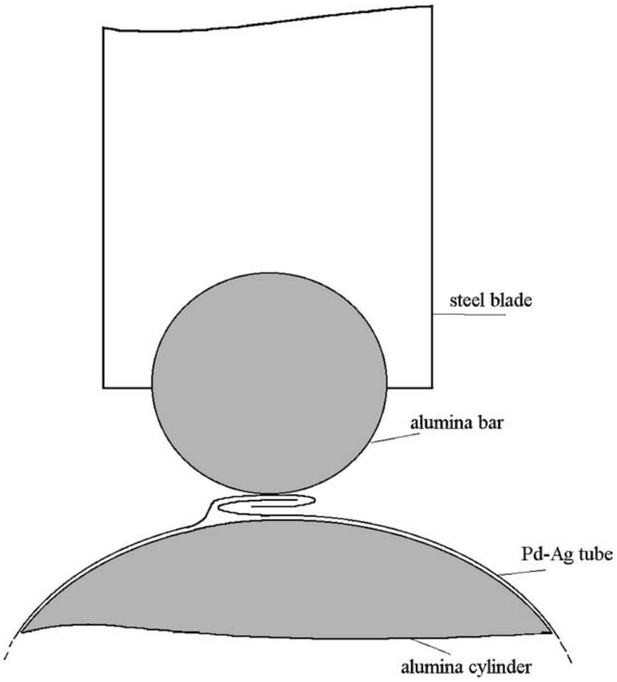


Figure 3 (a) and (b), schemes with details of the device used for welding the Pd-Ag tubes.

- free cooling down to the room temperature (in about 3 h).

The diffusion bonding is due to the high mobility of Ag atoms in the solid phase of the Pd-Ag alloy: from literature data [6] the self-diffusion coefficient of silver D, $m^2\ s^{-1}$, has been found in the temperature range 640–955°C:

$$D = D_o \exp(-E/RT) \qquad (1)$$

where D_o = frequency factor = $6.7 \times 10^{-5}\ m^2\,s^{-1}$; E = activation energy = 45.2 kcal mol^{-1}; R = gas constant, kcal $mol^{-1}\ K^{-1}$; T = temperature, K.

The value of the diffusion coefficient calculated by the formula (1) is used to estimate the diffusion welding time for a given thickness of the membrane. In fact, an assessment of the time required for joining thin Pd-Ag foils has been carried out by calculating the diffusion time of the Ag atoms through metal layers of thickness 35 and 50 μm under the following hypotheses:

- use of self-diffusion coefficient of silver instead of diffusion coefficient of silver in the Pd-Ag alloy,
- negligible dependence of the diffusion coefficient versus the solute concentration,
- extrapolation of the formula (1) beyond the temperature range of 640–955°C,
- negligible mobility of the palladium atoms.

In Table I, as a result of the analysis, the calculated time is reported versus the temperature and the thickness of the metal foils to be joined.

The analysis shows that a thermal treatment for 1 h in the range 1000–1100°C represents the optimum operating conditions in order to weld tubes of thickness around 50 μm.

TABLE I Diffusion bonding operating conditions

	Time (h) required for joining foils of thickness	
T (°C)	35 μm	50 μm
800	8.81	17.97
900	1.44	2.93
1000	0.31	0.64
1100	0.08	0.17
1200	0.03	0.06

Due to the high vapor pressure of silver, during the heat treatment neither higher temperatures nor the vacuum have been applied in order to avoid silver evaporation and the resulting change in the Pd-Ag alloy composition.

2.2. Pd Membrane to metallic support joints

The above described procedure has been furthermore modified to produce reliable and durable joints between palladium membranes and metallic supports (stainless steel, nickel, etc.). In fact, in order to produce membrane devices (i.e., membrane modules) it is necessary to assure the joining of Pd-Ag to stainless steel. To do it, the stainless steel support has to be coated with a silver thin layer (1–2 μm) before carrying out the described diffusion welding procedure. The silver layer can be deposited by electroless plating, electrochemical deposition, chemical vapor plating or sputtering; in Figs 4 and 5, two example schemes of the joints between Pd-Ag

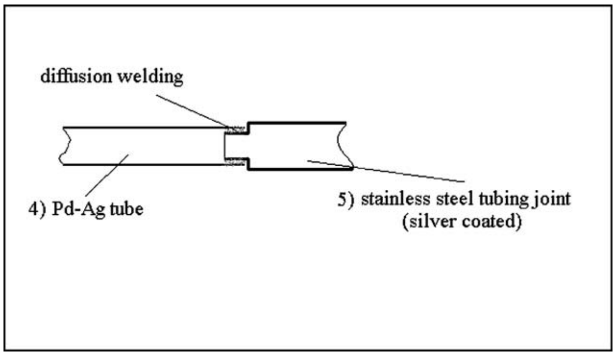


Figure 4 Scheme of a connection between a Pd-Ag tube and a stainless tubing joint.

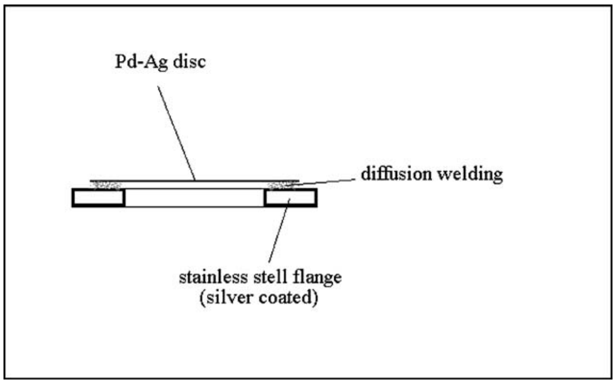


Figure 5 Scheme of a joint between a Pd-Ag disc and a stainless flange.

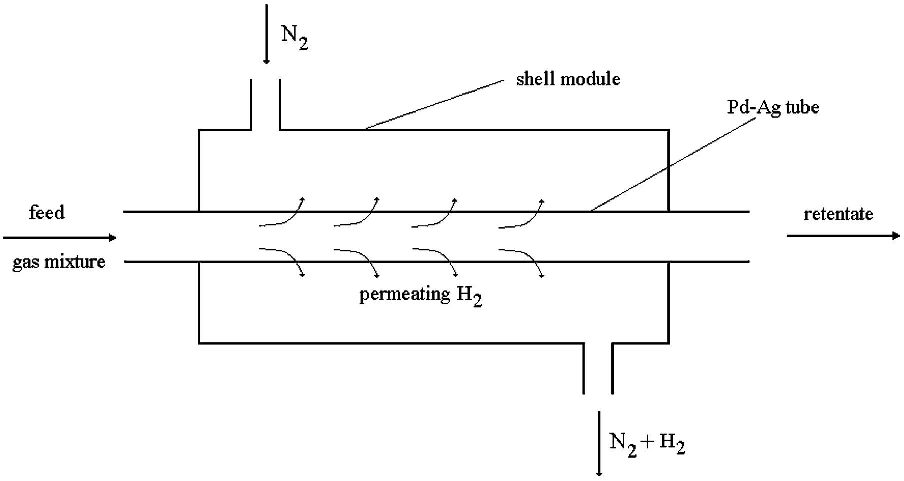


Figure 6 Scheme of a Pd permeator for hydrogen separation.

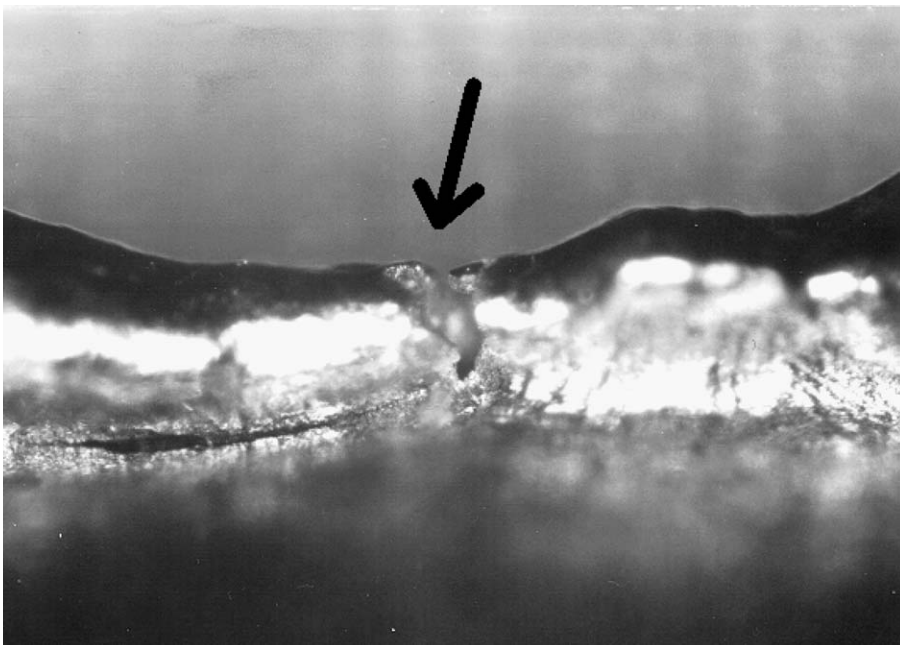


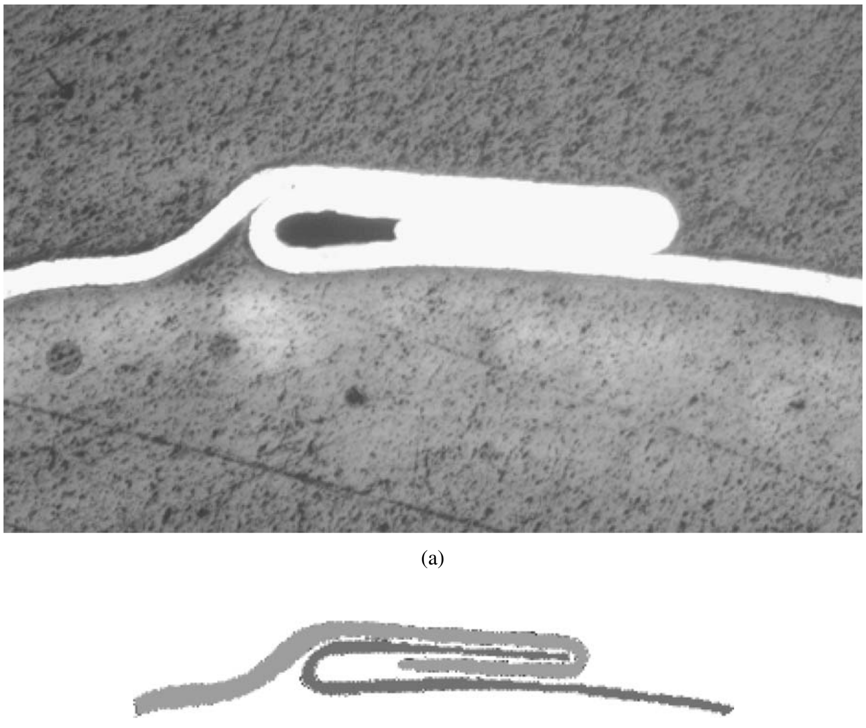
Figure 7 Details of a arc-welded tube after thermal and hydrogenation cycling (100×).

membranes (tube and flat geometry, respectively) and stainless steel are reported.

3. Results and discussion

Pd-Ag membrane tubes are currently used as permeators for separating hydrogen from other gases: in fact, palladium and palladium alloys are able to separate hydrogen selectively because of the high solubility and diffusivity of this gas in their lattice. A schematic view of a hydrogen permeator tube is given in Fig. 6: the gas mixture (feed stream) enters the tube, the hydrogen gas passes through the palladium tube wall because of an adsorption-diffusion mass transfer mechanism. The hydrogen permeated is finally collected in the shell side of the permeator by purging with nitrogen (or alternatively by vacuum pumping) while the retentate stream (poor in hydrogen) leaves the permeator tube. In these applications, the membranes operate under thermal cycling (from ambient temperature up to 400°C) and different hydrogen pressures: for this, the metal embrittlement could take place as a consequence of the hydrogen loading cycles. We have studied and produced Pd and Pd-Ag tubes of thickness 50 μm and diameter 10 mm by joining the cold-rolled and annealed thin metal foils.

Previously, TIG welding (arc welding using tungsten electrode under inert gas atmosphere) has been used for producing the Pd-Ag thin tubes. However, this welding technique requires particular procedures to be applied to very thin foils and produces thermally stressed zones around the welding line. Permeation tests on these tubes have shown the formation of defects and cracks: in Fig. 7, an arc-welded specimen is shown after thermal and hydrogenation cycles that has produced the rupture in the zones embrittled by the arc welding. Particularly, the formation of cracks across and along the welding line can be observed. As an alternative, heat treatments aimed at recovering the thermally stressed zones have been avoided in order to maintain the required mechanical proprieties (yield strength, hardness) of the thin tube which has to be able to withstand operating pressures up to 500 kPa.



(a)

(b)

Figure 8 (a) Cross section of the diffusion bonding joint (32×). (b) Scheme of the overlapping method used for the diffusion bonding joint.

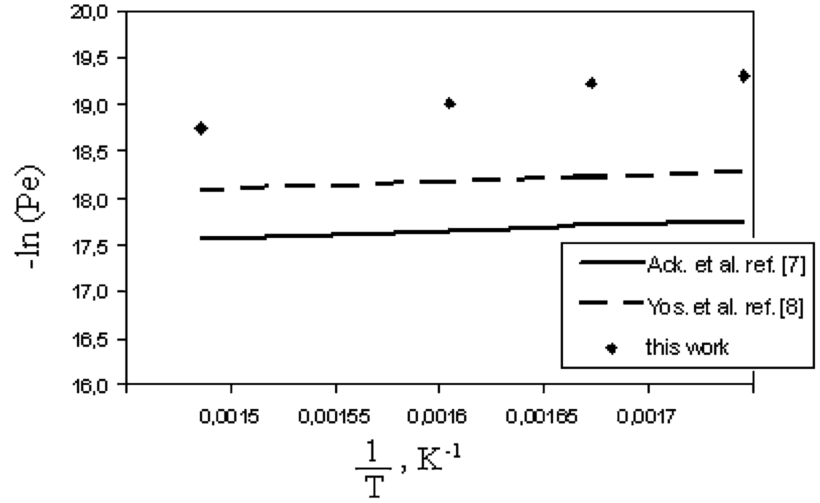


Figure 9 Arrhenius plot of the hydrogen permeability *Pe*, mol m^{-1} s^{-1} Pa-0.5.

To overcome these drawbacks, the diffusion bonding procedure described in the previous section has been developed and applied for welding the Pd-Ag thin metal foils. The presence of silver in the alloy assures the formation of diffusion bonding under an appropriate thermal treatment. In the Fig. 8a and b, the cross-section of the tube in the welded zone can be observed.

A membrane tube, thickness 51 μm, diameter 10 mm, and length 150 mm, produced in this way has shown good chemical, physical, and mechanical stability. This membrane has been characterized in a long-term permeation test (2 months) in the temperature range of 300–400°C with a feed hydrogen pressure ranging from 60 to 140 kPa. The permeated hydrogen has been collected in the shell side by purging with a nitrogen flow rate of 7.44×10^{-4} mol s^{-1} at atmospheric pressure. Under the hypothesis of a Sievert's solubility mechanism, the hydrogen permeation through the metal lattice of a membrane is expressed by the Richardson's law:

$$F = \frac{Pe}{t}(\sqrt{p_{\text{up}}} - \sqrt{p_{\text{down}}})A \qquad (2)$$

where F is the hydrogen permeation flow rate, mol s^{-1}; Pe is the hydrogen permeability, mol m^{-1} s^{-1} $Pa^{-0.5}$; t is the membrane thickness, m; p_{up} and p_{down} are the hydrogen partial pressure in the upstream and downstream side of the membrane, respectively, Pa; A is the membrane area, m^2.

As a result of the permeation test, the following expression of hydrogen permeability (Pe in mol m^{-1} s^{-1} $Pa^{-0.5}$) has been obtained:

$$Pe = 1.85 \times 10^{-7} e^{-\frac{2236.1}{T(K)}} \qquad (3)$$

These values agree with the data reported in the literature for these Pd-Ag alloys [7–11]: in Fig. 9 the comparison is shown with the data from references [7] and [8].

Similar tests have been carried out on Pd-Ag membranes joined by gas tungsten arc welding: typically, a loss of hydrogen selectivity has been observed after 2–3 weeks due to cracks formation in the welding zone [12].

On the other hand, the observed chemical and physical stability of the diffusion welded membranes can be considered as a consequence of the fact that diffusion bonding involves neither melting nor micro structural degradation of the material [13, 14].

4. Conclusions

Pd-Ag permeator tubes of thickness 50 μm have been produced starting from cold-rolled metal foils welded by a diffusion bonding procedure. These Pd-Ag permeator tubes used for hydrogen separation and production have the main characteristics of complete hydrogen selectivity (i.e., absence of defects) and chemical and physical stability. Among the welding procedures studied, the diffusion bonding one, based on high mobility of the silver atoms present in the alloy, consists of a heat treatment at 1100°C for 1 h at 100 kPa of Ar-5% H_2. Due to the high silver vapor pressure and in order to avoid the silver evaporation, the heat treatment has not been carried out under vacuum conditions.

The main advantages of the diffusion bonding process applied to the Pd-Ag permeator tubes are the following:

- welding is defect-free (absence of micro-holes), thus assuring a complete hydrogen selectivity of the permeator tubes,
- there are no heat-affected zones: this fact reduces the embrittlement of the Pd-Ag alloy under thermal and hydrogenation cycling, thus assuring chemical and physical stability.

These qualities have been verified in long-term tests where prototype membrane tubes for high purity hydrogen separation and production have been characterized. Because of their complete hydrogen selectivity, these membranes find potential application in the fusion reactor fuel cycle for the separation of hydrogen from its isotopes [15, 16] and in other energy applications, such as production and separation of pure hydrogen for PEM fuel cells [17, 18].

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Received 24 June
and accepted 30 December 2003