Available online at www.sciencedirect.com
ScienceDirect
Fusion Engineering and Design 82 (2007) 153–161
Fusion Engineering and Design
www.elsevier.com/locate/fusengdes

Mechanical design of a PERMCAT reactor module

S. Tosti [a,*], L. Bettinali [a,1], F. Borgognoni [b,2], D.K. Murdoch [c,3]

[a] *Associazione ENEA Euratom sulla Fusione, C.R. ENEA Frascati, Via E. Fermi 45, Frascati, Roma I-00044, Italy*
[b] *Tesi Sas, Via Bolzano 28, Roma, Italy*
[c] *EFDA CSU, Boltzmannstr. 2, D-85748 Garching bei Munchen, Germany*

Received 8 June 2006; received in revised form 9 August 2006; accepted 29 August 2006
Available online 11 October 2006

Abstract

The PERMCAT is a membrane reactor proposed for processing fusion reactor plasma exhaust gas: tritium removal is obtained by isotopic swamping operating in counter-current mode. In this work, a membrane reactor using a permeator tube of length about 500 mm produced via diffusion welding of Pd–Ag thin foils is described. An appropriate mechanical design of the membrane module has been developed in order to avoid any significant compressive and bending stresses on the very long and thin wall permeator tube: two expanded bellows have been applied to the Pd–Ag tube, so that it has been pre-tensioned before operating.

The elongation of the metal permeator under hydrogenation has been theoretically estimated and experimentally verified for properly designing the membrane reactor.

Keywords: Tritium; Pd membrane

0. Introduction

Palladium–silver permeators were developed for separating hydrogen isotopes in plasma exhaust clean-up processing: in fact, palladium alloys dense membranes are characterized by a complete hydrogen selectivity and are applied in continuous processes.

A preliminary study of a fuel clean-up system based on a Pd–Ag diffuser was designed by Yoshida et al. [1]. Other works were presented in the literature concerned with the technological solutions of the fusion fuel cycle process by means of membranes [2–4].

Since 1990, at the Tritium Laboratory of Karlsruhe (TLK) Pd–Ag permeators were operated at the technical PETRA facility in presence of small amounts of tritiated impurities: especially, the experiment was aimed at investigating the effect of helium concentration inside the membrane [5].

After that, a membrane reactor, the PERMCAT, was developed at Tritium Laboratory of Karlsruhe to the

* Corresponding author. Tel.: +39 06 94005160; fax: +39 06 94005374.
E-mail address: tosti@frascati.enea.it (S. Tosti).
[1] Tel.: +39 06 94005160; fax: +39 06 94005374.
[2] Tel.: +39 06 97273277; fax: +39 06 97273277.
[3] Tel.: +49 89 3299 4235; fax: +49 89 3299 4198.

0920-3796/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.fusengdes.2006.08.003

purpose of detritiating plasma exhaust gases in a continuous process [6].

The PERMCAT reactor has been proposed for decontaminating gases containing up to 1% of tritium in forms of water, hydrocarbons or molecular hydrogen isotopes. This reactor has been studied in order to reduce the amount of protium necessary, and to minimize the memory effects by segregating the contaminated parts from non-contaminated parts of the membrane unit [6,7]. In this reactor, the tritiated species are sent to a catalyst bed while H_2 is sent in counter-current mode inside a Pd–Ag tube selectively permeable to the hydrogen isotopes. On the catalyst, tritium is exchanged with protium by isotopic swamping; as an example, the swamping reactions of tritiated methane and tritiated water are reported:

$$2H_2 + CQ_4 \Leftrightarrow CH_4 + 2Q_2 \quad (1)$$

$$H_2 + Q_2O \Leftrightarrow H_2O + Q_2 \quad (2)$$

However, the mechanical design of the PERMCAT reactor has to take into consideration the axial expansion of the Pd–Ag tube: in fact, the hydrogen loading of palladium involves the elongation of the permeator tube which can be prevented by improper mechanical constraints.

The PERMCAT reactor permitted to attain a high decontamination factor in the final step of the CAPRICE (catalytic purification experiment) facility [6]. The finger-type configuration was adopted in order to let the membrane tube free in its elongation, due to hydrogen loading and thermal expansion. The same configuration, consisting of 21 finger-type Pd–Ag tubes with an outer diameter of 3.3 mm and a wall thickness of 0.100 mm, was applied to a PERMCAT reactor proposed for impurity processing in the JET Active Gas Handling [7]. This reactor was designed to cope with a tritiated gas flow rate of at least 1.5 mol h^{-1}, containing up to 1% of tritium in different chemical forms, such as water, methane or molecular hydrogen. Finally, the PERMCAT was applied in the third step of the CAPER process developed at TLK for the final clean-up of ITER exhaust gases: the results from preliminary tests demonstrated that an overall tritium removal efficiency of the CAPER process of about 10^8 can be reached [8].

1. Thin wall Pd–Ag permeator tube

A procedure of cold rolling and diffusion welding of thin Pd–Ag foils has been developed at the ENEA Frascati laboratories for producing thin wall tubes [9]. These permeators have a thinner wall thickness (0.050 mm) compared with the commercial ones (0.100 mm) and, therefore, exhibit a higher hydrogen permeance: however, the reduced thickness needs a particular design in order to ensure a long life also in presence of thermal and hydrogenation cycling [10].

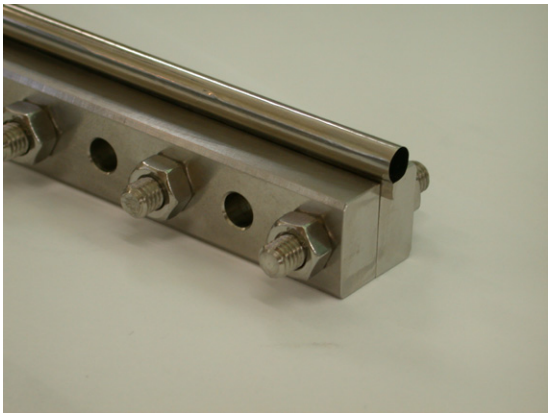

Fig. 1. Thermo-mechanical press used for joining the permeators via diffusion welding.

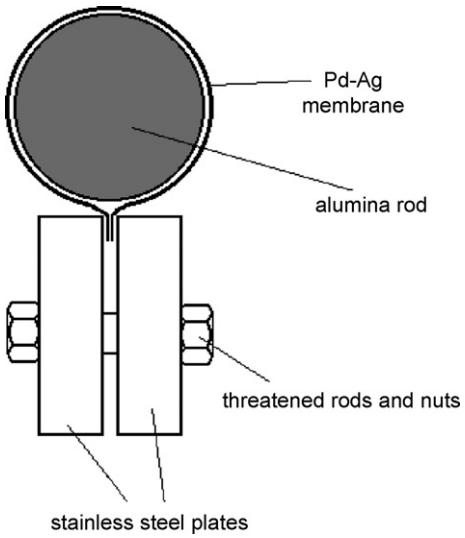

Fig. 2. Scheme of the thermo-mechanical press.

The thin wall permeator tube used in the PERMCAT has been prepared by starting from a commercial Pd–Ag foil (Goodfellow™) of thickness 0.125 mm. The metal foil has been cold rolled by a four-high mill: two strips of thickness about 0.050 mm have been produced. After annealing at 900 °C for 1 h under a vacuum atmosphere, the Pd–Ag foils have been joined by diffusion welding to form two thin wall tubes of diameter 6 mm. The thermo-mechanical press shown in the picture of Fig. 1 and in the scheme of Fig. 2 has been used to perform the welds in an oven operating under vacuum at 900 °C for 2 h. Then, the two membrane tubes have been joined by brazing in order to form a permeator of overall length 516 mm.

2. Assessment of the permeator elongation

An important problem arising in the mechanical design of the PERMCAT reactor originates from the axial expansion of the Pd–Ag tube as a consequence of both heating and hydrogenation of the metal. In order to correctly design the reactor module, the elongation of palladium alloy permeators has to be assessed: this evaluation has been carried out both theoretically and experimentally.

Under thermal and hydrogenation cycling, depending on the temperature Pd–Ag tubes can significantly expand or contract as a consequence of the hydrogen sorption or desorption. The following interpolated formula was obtained from published data [11,12] for the thermal strain of hydrogenated Pd–Ag:

$$\varepsilon_{\mathrm{H/Pd-Ag}} = aT^6 + bT^5 + cT^4 + dT^3 + eT^2 + fT + g \quad (3)$$

where $\varepsilon_{\mathrm{H/Pd-Ag}}$ is the thermal strain of the hydrogenated Pd–Ag, T the absolute temperature (K), a, b, c, d, e, f and g are coefficients whose values are reported in Table 1.

By using the formula (3), starting from a non-hydrogenated Pd–Ag tube, it has been calculated that thermal and hydrogenation cycles in the temperature range from ambient temperature to 400 °C yield a maximum elongation of 1.5% or, alternatively, a hydrogenated Pd–Ag tube reduces by about 1.5% its length after cooling from 350 °C. In fact, at the beginning of its life, a Pd–Ag tube is assembled inside the membrane module in non-hydrogenated form at ambient temperature: therefore, the hydrogenated tube at ambient temperature has to be considered in order to assess the most severe case (i.e. maximum expansion).

Table 1
Coefficients of the expression (3)

	Temperature range (K)	
	293–530	530–713
a (K^{-6})	2.316×10^{-16}	-1.376×10^{-15}
b (K^{-5})	-6.160×10^{-13}	5.166×10^{-12}
c (K^{-4})	6.801×10^{-10}	-8.051×10^{-9}
d (K^{-3})	-3.989×10^{-7}	6.666×10^{-6}
e (K^{-2})	1.306×10^{-3}	-3.092×10^{-3}
f (K^{-1})	-2.256×10^{-2}	7.615×10^{-1}
g	1.601	-7.774×10^{-1}

In order to verify this calculation, an experimental test has been carried out on a standard thin wall tube of diameter 10 mm, wall thickness of 58 μm and length 133 mm produced via diffusion welding according to the technique described above.

2.1. Testing apparatus

The Pd–Ag membrane has been joined at its two ends to a steel tube and a steel plug by a brazing procedure: the resulting permeator has been tested by using the membrane module and the measurement apparatus described in Fig. 3. The experimental apparatus consists of a hydrogen generator producing the gas by electrolysis of distillated water, a nitrogen cylinder providing the sweep gas, two mass flow controllers (MFC) at the inlet of the membrane tube (feed side) and shell side, three pressure gages (PI) at inlet and outlet of the membrane tube and at shell outlet, two thermocouples (TI) on the membrane and Pyrex shell, a heating system for controlling the membrane tube temperature.

The permeator has been inserted into a Pyrex shell module where the permeating gas (hydrogen) is collected by a sweep gas stream (nitrogen). To evaluate the axial expansion of the tube, a finger-type assembly of the permeator has been applied: in this way, the membrane tube is let free in its elongation under thermal and hydrogenation cycling.

2.2. Experimental results

Preliminarily, the tube has been operated at high temperature for activating the surface and allowing the

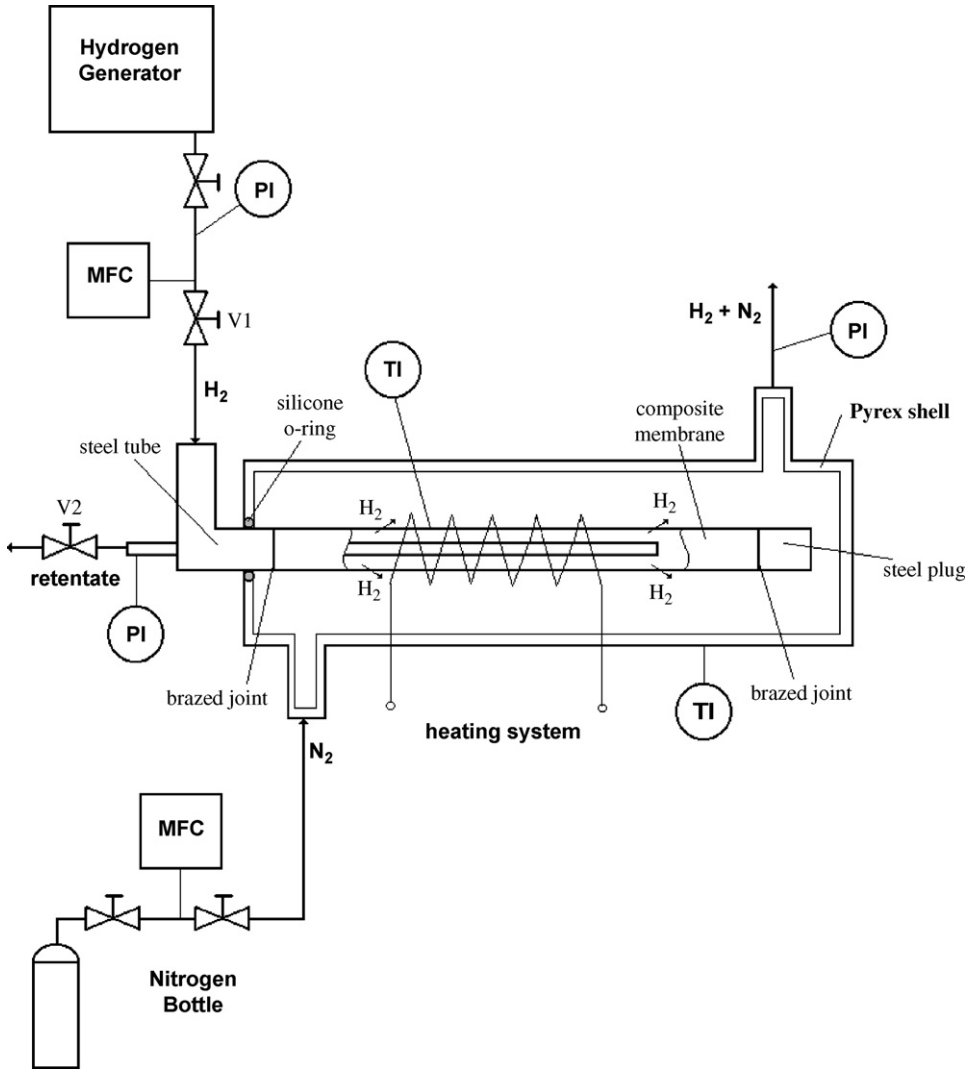

Fig. 3. Scheme of the membrane module and the experimental apparatus.

hydrogen take-up. Then, the Pd–Ag membrane has been continuously tested during 20 days. A typical daily test consisted of cyclic heating and hydrogenation: starting from ambient temperature and low hydrogen internal pressure (<50 kPa), the tube was operated at 300–400 °C and at hydrogen pressures in the range 100–150 kPa, see Fig. 4. Finally, in order to maximize the elongation, the tube has been exposed to hydrogen pressure of 100 kPa at ambient temperature for 24 h: as compared to the initial length of 133 mm, the elongation measured has been of 1.2 mm. During

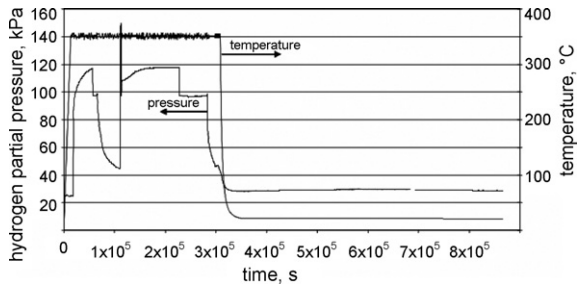

Fig. 4. Graph of a hydrogen loading and permeation test.

the experimental campaign, the membrane tube has been characterized in terms of hydrogen permeability by measuring the transmembrane differential pressure under a controlled hydrogen permeating flux: the permeability coefficient evaluated by the Siervert's law agreed the literature data [13,14].

3. Membrane reactor design

The PERMCAT reactor uses the isotopic swamping for final clean-up of tritium containing gases [7]. The general principle of the reactor has been described in Introduction: its scheme is shown in Fig. 5. The tritiated gases are fed into the shell side of a Pd–Ag membrane reactor where the isotopic swamping with pure hydrogen sent in counter-current and permeated through the membrane takes place. However, the Pd–Ag permeator tube cannot be fixed to the module at both its ends: in fact, the hydrogen loading of the palladium involves the elongation of the permeator tube that can be prevented by improper mechanical constraints. Particularly, the combined compression and bending stresses of the very long and thin wall tube may cause its failure.

Accordingly, the design of the PERMCAT proposed for JET and ITER [7,8] considers a finger-type Pd–Ag tube of wall thickness 0.100 mm. To remove the retentate stream, a stainless steel tube inserted inside the permeator tube is used. The shell side annulus of the membrane unit is filled by catalyst and has an internal/external diameter of 3.3/5 mm: such a small dimension is essential to keep the diffusion pathways perpendicular to the gas stream short and, simultaneously, to provide sufficient linear gas velocity in order to avoid back diffusion of tritium. Protium is introduced into the Pd–Ag tube, and the gas stream to be detritiated is fed in the shell side in counter-current mode: the protium stream permeates the Pd–Ag and decontaminates the stream in the shell side by isotopic exchange. Simultaneously, tritium permeates into the Pd–Ag tube: as a result, an exponential tritium concentration profile along the reactor axis is achieved under steady state conditions, and the outlet stream of the shell side has a very low contamination with tritium.

3.1. New PERMCAT design

The mechanical design of a membrane reactor housing the thin wall permeator tube produced by diffusion welding at ENEA laboratories and complying the principles of the PERMCAT reactor has been studied.

In this configuration the Pd–Ag tube of length 516 mm, diameter 6 mm and wall thickness 0.050 mm contains the catalyst bed while the swamping gas is sent into a shell side annulus of internal/external diameter 6/8 mm. The reactor module has two Conflat^{TM} flanges connections in the membrane lumen side, while shell side connections are two VCR^{TM}. In order to comply

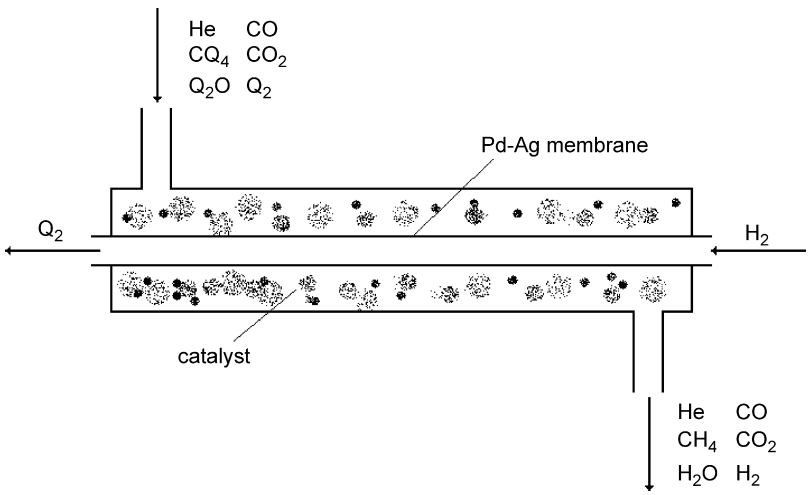

Fig. 5. Basic scheme of the PERMCAT reactor.

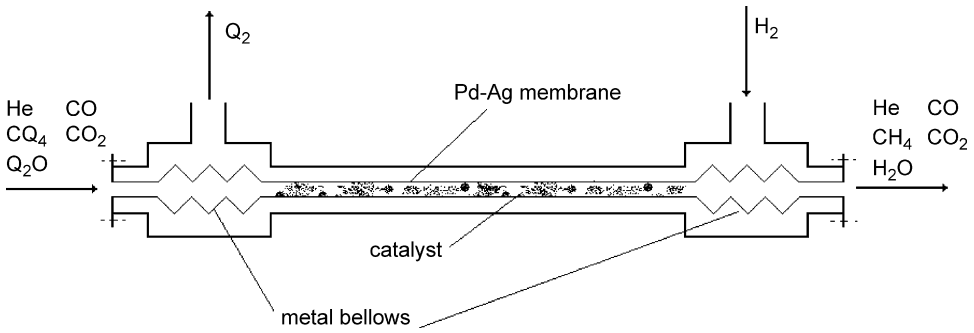

Fig. 6. Scheme of the reactor.

with the safety requirements of tritium operation, the minimum wall thickness of the 316 LN stainless steel module is 3 mm and the external parts have been TIG welded and qualified by radiography and eddy currents method. In Fig. 6, a scheme of the designed reactor is shown, while Fig. 7 reports the mechanical drawing of the module.

As shown in Fig. 6, both ends of the membrane tube are fixed to the module. To ensure the reliability of the device, a new mechanical configuration has been approached: the use of two metal bellows as well as an assembling procedure that maintains the permeator tube always tensioned during operation have been foreseen [15].

In fact, being fixed to the reactor module on both its two ends, the very long and thin wall Pd–Ag tube may be stressed by a particularly harmful situation as a consequence of the hydrogen uptake: the constraints, applied to the two ends of the tube by the module, prevent its free elongation from taking place and produce buckling due to the combined bending and compressive stress.The assembling procedure of the permeator tube inside the module and its behavior under operating conditions are shown in Fig. 8:

(1) The permeator tube, consisting of the Pd–Ag membrane joined to the two metal bellows and two stainless steel ends, is inserted into the module where one end is TIG welded. The permeator length is shorter than the module length: the gap has been calculated to be 7.5 mm (1.5% of the Pd–Ag total length) by taking into account the assessment of the membrane elongation described in Section 2.

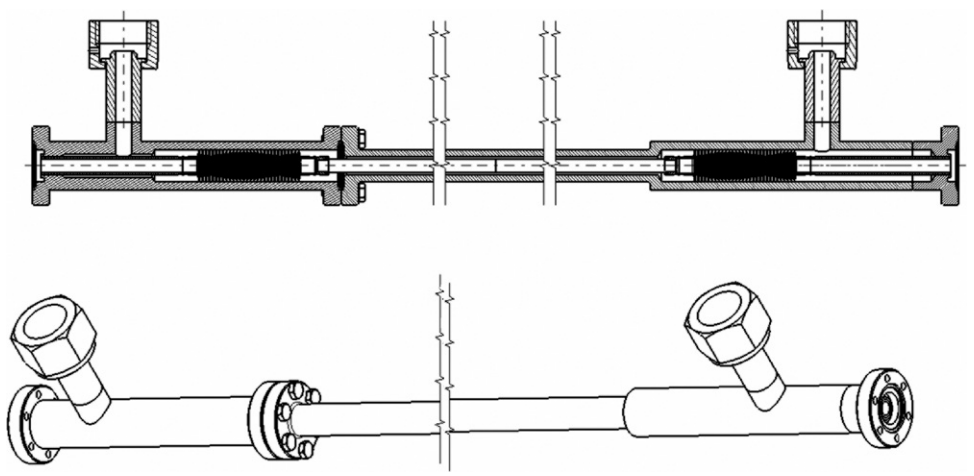

Fig. 7. Mechanical drawing of the PERMCAT module.

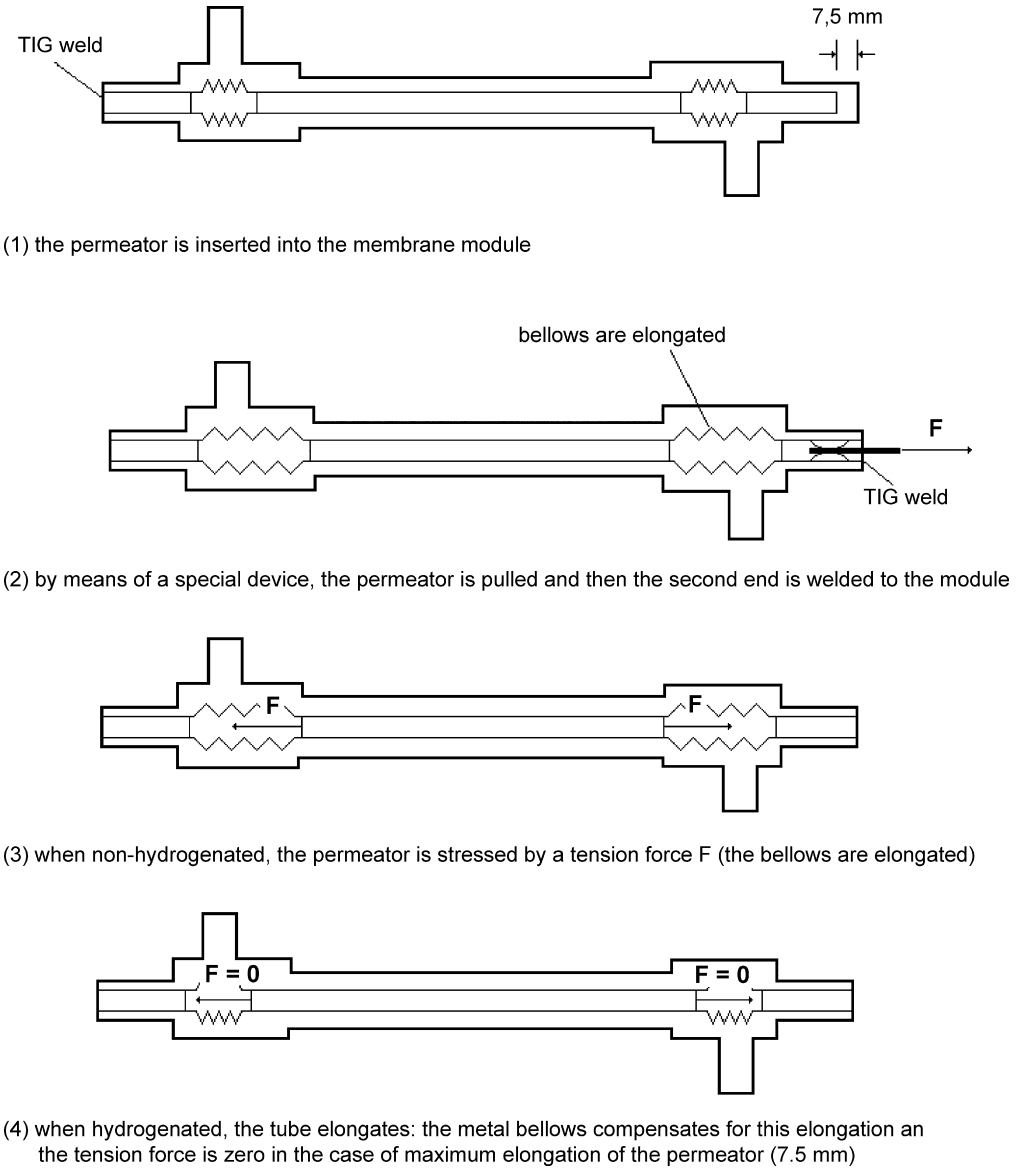

Fig. 8. Scheme of the procedure for assembling the permeator inside the module.

(2) By means of a special device, the permeator tube is pulled so that its second stainless steel end is TIG welded to the module: the metal bellows are thereby elongated.
(3) The metal bellows apply a tension force F to the non-hydrogenated Pd–Ag membrane tube.
(4) The hydrogenated Pd–Ag elongates under operation: the contraction of the metal bellows compensates for this expansion by reducing the tension force applied to the membrane (F is zero in the case of the maximum estimated elongation of the permeator, 7.5 mm).

3.2. Evaluation of the Pd–Ag membrane axial stresses

The difference between the thermal expansion of Pd–Ag and stainless steel is very small: in particular, it

becomes negligible if compared to the expansion due to the hydrogenation of the palladium alloy [11]. Therefore, in this calculation the thermal expansion of the stainless steel housing has been neglected.

In the case of a rigid assembly (i.e. absence of bellows) of the permeator fixed at both its ends to the module, the compressive stress applied to the Pd–Ag membrane is evaluated by the formula:

$$\sigma = E\varepsilon \tag{4}$$

where σ (MPa) is the axial stress, E (MPa) the Young module and ε is the Pd–Ag strain.

When the Pd–Ag tube is hydrogenated, the estimated elongation of 1.5% is prevented and a resulting compressive stress of 1680 MPa can be assessed by using, for the Young module, the value of 112 GPa obtained from literature for pure Pd [16]. This compressive stress is very large, particularly if applied to a very long and thin wall tube.

When the bellows are introduced between the permeator and the module, the static scheme of the apparatus is modified: under the hypothesis of a permeator tube infinitely stiffer than the bellows, the maximum axial stress of the Pd–Ag membrane can be evaluated by the formula:

$$\sigma_{\max} = \frac{F}{S} \tag{5}$$

where F (N) is the force applied by the bellows to the Pd–Ag membrane and S (m^2) is the cross-section of the Pd–Ag tube.

The force F can be calculated by the expression:

$$F = \frac{k}{2L} \tag{6}$$

where k ($N\,m^{-1}$) is the spring rate of each of the two bellows and L (m) is the overall stroke of the two bellows (i.e. the elongation of the Pd–Ag membrane to be compensated, 7.5 mm). By using the spring rate of $1.43 \times 10^3\,N\,m^{-1}$, a force F of 5.38 N and an axial stress of 5.71 MPa result. In the case of a standard assembly of the permeator fixed to the module through two metal bellows, this stress value is considered as a compressive stress applied to the membrane when hydrogenated: even though modest, this compressive stress can result in damage at the membrane tube, especially considering the combination of bending and the presence of cyclic stresses and fatigue rupture. Alternatively, by adopting the procedure described in Section 3.1, a tension stress of 5.71 MPa is applied to the permeator at the beginning of its life when, non-hydrogenated, it is assembled inside the module. During operation, as a consequence of the hydrogen uptake the Pd–Ag membrane elongates, the bellows contract and the axial stress decreases, thus becoming negligible in the case of maximum hydrogenation.

This stress analysis has been performed by taking into account a vertical position of the reactor: in this case, the weight of the Pd–Ag tube filled with the catalyst (about 20 g = 0.2 N) is negligible in comparison to the tension force applied by the bellows (5.38 N). Alternatively, when the reactor should be placed horizontally, the permeator tube bending, due to the weight of the catalyst and the weight of the tube itself, involves mechanical stresses (about 10 MPa) that cannot be neglected as compared to the axial stresses (5.71 MPa) resulting by applying the tension force of 5.38 N via the bellows. So, in the case of an horizontal position of the PERMCAT, a higher tension force has to be applied by the bellows, in order to avoid any compressive stress of the thin wall tube.

4. Discussion and conclusions

The PERMCAT reactor studied for processing the plasma exhaust gas of JET and ITER uses a Pd–Ag membrane tube selectively permeable to hydrogen and its isotopes. Its design has to take into account the chemical-physical properties of Pd–Ag alloy under the operating conditions. Especially, the hydrogen uptake involves the elongation of the membrane tube and, therefore, harmful stresses are applied by the module. In order to overcome these drawbacks, previous applications have used finger-type permeators, as well as the use of metal bellows, for compensating the membrane elongation.

In this work, a new mechanical design has been investigated in order to use the Pd–Ag permeator tubes produced at ENEA. These tubes have a wall thickness (0.050 mm) reduced in comparison with commercial ones (0.100 mm), and present higher hydrogen permeance. However, also a modest compressive stress combined with the bending of these very thin wall permeators of length over 500 mm (for the PERMCAT application) may produce the failure of the membrane.

For this reason, two pre-tensioned metal bellows have been inserted between the permeator and the module in order to maintain the membrane tube always tensioned or at least unstressed during operation. This new design of the PERMCAT reactor has been applied to Pd–Ag thin wall tubes produced via diffusion welding: however, it can be also appropriated in case of different palladium permeators produced via other techniques or having higher thickness.

This PERMCAT design can be easily scaled up to the throughputs required for ITER by inserting several Pd–Ag tubes in parallel into one stainless steel housing where two opposite rigid flanges will be connected to the pre-tensioned bellows of the permeator tubes. The mechanical stresses scheme of this multi-tube reactor remains similar to the one tube solution: as an advantage, both the heating and the gas flow supply systems are applied to the overall reactor module.

The design proposed may also be applied to Pd membrane reactors used for producing pure hydrogen from reforming and/or partial oxidation of hydrocarbons and alcohols in small-medium size energetic applications, such as polymeric fuel cell systems. In fact, at present, the cost and the poor durability of Pd reformers prevent their wide-spread use, while the reactor design proposed in this work for the PERMCAT uses low-cost thin wall Pd–Ag permeators, and seems to be promising in terms of increased reliability.

Acknowledgments

This work, supported by the European Communities under the contract of Association between EURATOM/ENEA, was carried out within the framework of the European Fusion Development Agreement. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

References

[1] H. Yoshida, S. Konishi, Y. Naruse, Preliminary design of a fusion reactor fuel cleanup system by the palladium-alloy membrane method, Nucl. Technol. Fusion 3 (1983) 471–484.

[2] R.D. Penzhorn, R.D. Rodriguez, M. Glugla, A catalytic plasma exhaust purification system, Fusion Technol. 14 (1988) 450–455.

[3] R.A.H. Edwards, G. Modica, Reduction of tritiated water on a regenerable iron reactant: Pilot Plant, Fusion Technol. 28 (1995) 586–590.

[4] V. Violante, A. Basile, E. Drioli, Membrane separation technologies: their application to the fusion reactor fuel cycle, Fusion Eng. Design 22 (1993) 257–263.

[5] R.D. Penzhorn, U. Berndt, E. Kirste, W. Hellriegel, W. Jung, R. Pejsa, et al., Long term permeator experiment PETRA at the tritium laboratory Karlsruhe: commissioning tests with tritium, Fusion Technol. 28 (1995) 723–731.

[6] M. Glugla, J. Miller, P. Herrmann, M. Iseli, R.D. Penzhorn, Tritium tests with a PERCAT reactor for isotopic swamping. Fusion Technology, Proceedings of the 19th SOFT, Lisbon, Portugal, September 16–20, 1996, pp. 1193–1196.

[7] M. Glugla, A. Perevezentsev, D. Niyongabo, R.D. Penzhorn, A. Bell, P. Herrmann, A PERMCAT reactor for impurity processing in the JET Active Gas Handling, Fusion Eng. Design 49/50 (2000) 817–823.

[8] B. Bornschein, M. Glugla, K. Gunther, R. Lasser, T.L. Le, K.H. Simon, S. Welte, Tritium tests with a technical PERMCAT for final clean-up of ITER exhaust gases, Fusion Eng. Design 69 (2003) 51–56.

[9] S. Tosti, L. Bettinali, D. Lecci, F. Marini, V. Violante, Method of bonding thin foils made of metal alloys selectively permeable to hydrogen, particularly providing membrane devices, and apparatus for carrying out the same, Eur. Patent EP 1184125 (2001).

[10] S. Tosti, L. Bettinali, Diffusion bonding of Pd–Ag membranes, J. Mater. Sci. 39 (2004) 3041–3046.

[11] D. Fort, I.R. Harris, The physical properties of some palladium alloy hydrogen diffusion membrane materials, J. Less-common Met. 41 (1975) 313–327.

[12] S. Tosti, L. Bettinali, S. Castelli, F. Sarto, S. Scaglione, V. Violante, Sputtered, electroless, and rolled palladium–ceramic membranes, J. Membr. Sci. 196 (2) (2001) 241–249.

[13] E. Serra, M. Temali, A. Perujo, D.K. Ross, Hydrogen and deuterium in Pd–25% Ag alloy: permeation, diffusion, solubilization, and surface reaction, Metall. Mater. Trans. A 29A (1998) 1023–1027.

[14] R.S. Dickson, Tritium interaction with materials, in Basic Tritium Safe Handling Course notes, CFFTP Report I-9471, AECL, Ontario, Canada, 1994.

[15] S. Tosti, L. Bettinali, F. Marini, Dispositivo per la rimozione di trizio da correnti gassose, Italian Patent n. RM2005U000165 (2005).

[16] ASM Metals Handbook, vol. 2, Formerly Tenth Edition, October 1995, ASM International.