

Performance of a hydrogen sensor in Pb–16Li

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Abstract

To develop a sensor for measurements of hydrogen (and its isotopes) concentration in liquid Pb–16Li, two permeating capsules made with niobium and pure iron have been tested. The experimental results demonstrated that the Nb-sensor is not suitable for the foreseen application. The Fe-sensor cannot be operated in equilibrium mode because of the very long time necessary to reach the hydrogen pressure equilibrium. However, the equilibrium mode cannot be definitively excluded. In fact, by means of a substantial optimisation of the sensor geometry, the pressurisation rate could be fast enough to reach acceptable response times. In this context, different optimised solutions have been developed and good performance demonstrated by simulations. The present Fe-sensor can be successfully operated in dynamic mode, since it is possible to link reliably the permeation fluxes to the hydrogen concentration in the liquid metal.

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1. Introduction

In the HCLL (Helium Cooled Lithium Lead) blanket for ITER and DEMO fusion reactors, an efficient tritium management operation is required in order to minimise the environmental tritium release and to improve the economy of the overall tritium reactor balance.

In this framework, the optimisation of techniques for the measurement of tritium in the different steps of the reactor fuel cycle has to be carried out in parallel with the R&D activities on tritium processing

systems. For instance, the tritium extractor from flowing lithium lead (TES, Tritium Extraction System) is a critical system and the determination of the hydrogen isotopes concentration is mandatory for its correct design [1]. Therefore, the need for a reliable and fast sensor for the measurement of tritium concentration in the liquid breeder is well established. For this application, a sensor based on the principle of tritium permeation into a capsule made of a suitable material seems to be, at least in principle, the simplest and most reliable one. Moreover, much data on tritium permeability through different materials and their compatibility in a liquid metal environment are available, thanks to the experimental studies carried out for the selection of structural materials for the blanket modules. A summary and a complete list of references of the existing data of hydrogen transport parameters for

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several materials is reported in [2]. Results on compatibility studies between Pb–16Li and different metals and alloys are available in [3–5].

A permeation sensor is being developed as a component of a whole measurement system able to distinguish the amounts of the different hydrogen isotopes (especially tritium). The permeation sensor will be used to determine the total pressure of hydrogen isotopes while a mass spectrometry or a tritium detector will be deputed to measure tritium partial pressure.

After the screening of candidate materials, the simulation of the performance and the final design, the first sensor prototypes made with a niobium and a pure iron capsule have been constructed and tested. The results of this activity, as well as the preliminary design of different optimised iron sensors, are presented and discussed in this paper.

2. Basic concepts of a hydrogen permeation sensor in liquid metal

In the simplest architecture, a hydrogen permeation sensor can be seen as a hollow capsule, permeable to hydrogen, immersed in a liquid metal where hydrogen is dissolved at a certain concentration C_L in equilibrium with a partial pressure P_{eq} . The capsule is connected, through a small tube, to an external pressure gauge or to a vacuum pumping system depending on its mode of operation [6,7].

A measurement of the hydrogen partial pressure in the capsule or hydrogen permeation flux through the capsule walls can be correlated with the hydrogen concentration C_L in the liquid metal. This requires applying fundamental laws of gas permeation through the material of the capsule walls and hydrogen solubility in liquid metal.

The permeation sensor can be operated in two modes: the equilibrium mode and the dynamic mode. In the first one, starting from vacuum conditions, the pressure increases inside the capsule because of hydrogen permeation until the pressure P_{eq} , in equilibrium with the hydrogen concentration in liquid metal C_L , is reached. Then, the hydrogen equilibrium pressure measured inside the capsule is related to C_L by the Sieverts' law for a H/Pb–16Li system

$$C_{L,H} = K_{S,L} P_{eq}^{0.5}, \quad (1)$$

where $K_{S,L}$ is the Sieverts' constant. Only knowledge of $K_{S,L}$ is required in this case.

In dynamic mode, the H concentration is measured by the rate of its permeation through the capsule walls. Considering a pure diffusion regime through the membrane, the hydrogen flux at steady state is given by

$$J_{ss} = K_{S,M} D P_{eq}^{0.5} / s, \quad (2)$$

where D is the bulk diffusivity and s the thickness of the permeable walls.

If the equilibrium at the interface between hydrogen in gas phase and hydrogen in the lattice is not achieved instantaneously, the phenomena of dissociation and recombination between hydrogen molecules and atoms have to be taken into account.

In this case, the relationship between hydrogen concentration (or P_{eq}) and the steady state permeation flux is $J_{ss} = f(P_{eq}, D, K_s, K_{r1}, K_{r2})$, where K_{r1} and K_{r2} are H-recombination coefficients on the side walls of the capsule [8].

The correct operation of the sensor working in equilibrium mode depends only on a reliable determination of the Sieverts' constant $K_{S,L}$ in the liquid metal. Only the rate of the capsule pressurisation is affected by the permeation characteristics of the capsule, not the final pressure which is just the required measurement.

On the contrary, in the dynamic mode the same kind of measurement is also affected by the hydrogen permeation characteristics of the capsule material.

3. Design of the sensor and experimental campaign

The main constraints in designing a hydrogen permeation sensor for use in a liquid metal like Pb–16Li for application in the ITER and DEMO blankets, have been found during a previous study [9]. Niobium and pure iron were selected as the most promising materials because they have high hydrogen diffusivity and their chemical compatibility with the lead lithium alloy is very good [3,4].

The final design of the sensor used to construct the first prototypes consists of [8]:

- a permeable capsule made from niobium or Armco iron (external diameter: 13 mm Nb – 12 mm Fe, height: 30 mm, thickness: 1 mm Nb – 0.5 mm Fe) and the connection tube made of stainless steel (external diameter: 6.35 mm);
- a flexible joint to allow the vertical movement of the capsule;

- a capacitance pressure gauge (Barocell) placed at the top of the sensor;
- an ultra-high vacuum valve to isolate the sensor from the vacuum pumping system.

The experimental campaign has been carried out using VIVALDI device (for details see Ref. [10]), which is available at ENEA – Brasimone.

3.1. Experimental campaign on the Nb-sensor

The results of the tests carried out in gas phase at 450 °C were already presented in [9]. Initially, a high hydrogen testing pressure (range 1–2 bar) was chosen in order to obtain, with an easier operation of the testing device and a faster time response of the sensor, the first information on the behaviour of this capsule. Because a hydrogen permeating flux much lower than the predicted one was detected, it was concluded that permeation is limited by surface processes due to the formation of an oxide layer on the capsule surface. For this reason, it was decided to stop experiments and do not continue with lower testing pressure.

The experimental campaign was repeated in liquid metal phase, with the Pb–16Li temperature fixed at 450 °C and the hydrogen partial pressure in equilibrium with the liquid metal at 1.1 bar. These tests showed similar results to the tests in gas phase (see Fig. 1, where the numbers near the curves are the calendar days of the year in which the experiment was performed). Moreover, in this

case, it is evident that the permeation flux decreases during each test, and also from one experiment to the next.

The observed low permeation fluxes show the impossibility of operating the Nb-sensor in equilibrium mode, while the differences obtained performing tests in the same conditions prove the impossibility of operating the sensor in dynamic mode. In other words, because of the unstable conditions over time, uncoated niobium appears not to be suitable for the foreseen application.

A possible solution to solve the problem of oxidation could be to deposit a thin platinum layer on the niobium surface. This coating could prevent oxidation and reduce the activation energy of the hydrogen adsorption process increasing the hydrogen permeation flux [11].

3.2. Experimental campaign on the iron sensor

Experiments both in gas and liquid metal phases have been carried out to test the Fe-sensor in the temperature range 350–550 °C, with a hydrogen partial pressure between 200 and 1100 mbar. These tests demonstrate that, in the present conditions, the operation of the iron sensor in equilibrium mode is not feasible, because of the very long time (several hours) necessary to reach the hydrogen pressure equilibrium. Moreover, a slower pressurisation has been detected during the tests in liquid metal. In spite of these results the equilibrium mode cannot be definitively excluded. In fact, by means of a

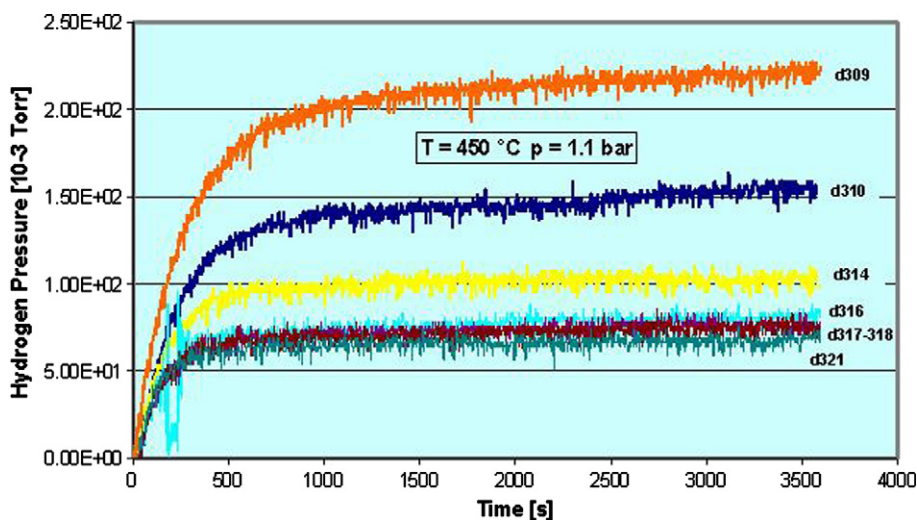


Fig. 1. Experimental results obtained with the Nb-sensor in liquid metal phase. (The numbers near the curves are the calendar days in which the experiment was performed.)

substantial optimisation of the sensor geometry (see next section), the pressurisation rate could be fast enough to reach equilibrium pressure in a relatively short time.

On the other hand, the results show that the sensor could be successfully operated in dynamic mode. Looking at Fig. 2, where the permeation fluxes are shown as a function of the hydrogen pressure for the tests carried out in liquid metal, it is possible to see that all points at each temperature can be satisfactorily correlated using the same exponent in the equation that links the steady state permeation flux to the hydrogen driving pressure.

From a theoretical point of view, an exponent between 0.5 and 1 means that permeation through the membrane is not governed by pure diffusion, but it is in an intermediate regime where surface effects also have a role in the process.

However, taking into account these results, it seems possible to correlate the hydrogen experimental permeation fluxes to the test pressure, even if the reliability of the sensor operation depends on the steadiness of the permeation characteristics of the capsule material (in particular the surface conditions). Regarding this point it has to be emphasized that the experiments have been repeated many times during a period of several months and the results obtained are reproducible. In fact, a decrease of only few percent has been observed in the permeation flux from the beginning to the end of the whole experimental campaign.

In addition, the results showed that:

- the time lag (i.e. the time necessary for the sensor to reach the steady state permeation flux)

observed experimentally during each pressure rise is very short (a few seconds);

- the permeation flux remains practically constant until the pressure on the low pressure side becomes negligible.

This means that the Fe-sensor, operated in dynamic mode, should have a fast response and therefore be able to follow rapid changes of the hydrogen concentration on the high pressure side.

4. Development of optimised permeation sensors

The improvement of the performance of a permeation-based hydrogen sensor operating in equilibrium mode is strictly connected to the ability of increasing the hydrogen permeation flow-rate through the capsule wall as much as possible. This objective can be reached by a combination of:

- decreasing the ‘total sensor volume/permeation surface’ ratio;
- decreasing the capsule wall thickness;
- preventing oxidation of the wall surface.

The first conceived optimisation of the iron sensor involved strongly reducing the dead volume of the present *T* joint placed at the top of the sensor and of the connecting tube (see Fig. 3 of Ref. [9]). Furthermore, the capsule wall thickness has been reduced from 0.5 to 0.1 mm.

Then, three preliminary designs of the sensor capsule, devoted to reduce the ‘total sensor volume/permeation surface’ ratio have been developed and are shown in Figs. 3 and 4. In the left option of

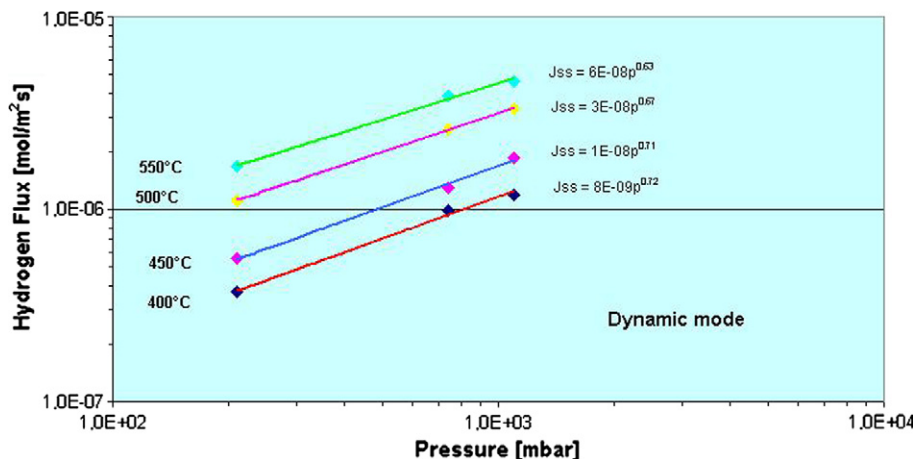


Fig. 2. The permeation flux at the steady state as a function of the test pressure for the Fe-sensor.

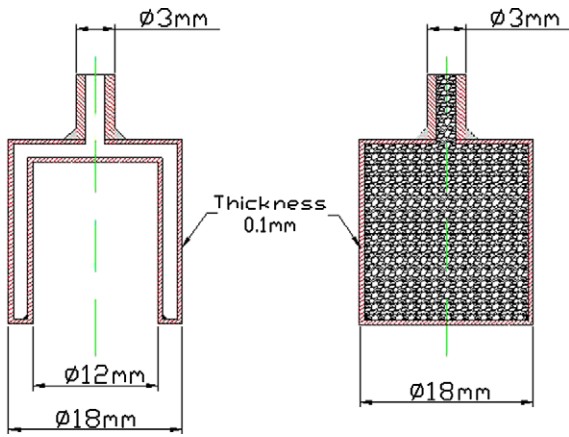


Fig. 3. Design of two optimised H permeation capsules.

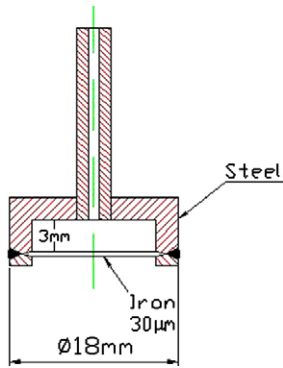


Fig. 4. Design of an optimised capsule having an ultra-thin membrane.

Fig. 3, the internal volume reduction is obtained using an annular geometry for the capsule. The same result is obtained in the right one by filling the capsule with an adequate material (for example, alumina or quartz in form of powders with a suitable grain dimension or in form of an internal cylinder) in which hydrogen is not soluble. The advantage of the first case consists of having a bigger surface available for permeation.

The solution presented in Fig. 4 foresees the use of an ultra-thin permeable membrane. Based on the fact that the minimum thickness that guarantees the absence of pin holes and the resistance to the vacuum is about 20 µm, the thickness has been fixed to 30 µm.

For all these designs the capsule material is still pure iron.

In order to assess the effects of the proposed optimisation on sensor performance, simulations have been carried out by means of an ad hoc developed code [9].

In Fig. 5 the pressure evolution in the sensors having a cylindrical and annulus permeable capsule, with and without filling, is shown. Results for iron capsules with a wall thickness of 0.1 mm and the case of the ultra-thin membrane are shown. The hydrogen pressure was fixed at 10 mbar and the temperature at 500 °C.

Less than 20 min are required, in all cases except the last one, to reach the pressure equalization. In particular, 10 min should be enough for the annulus capsule with filling in these conditions.

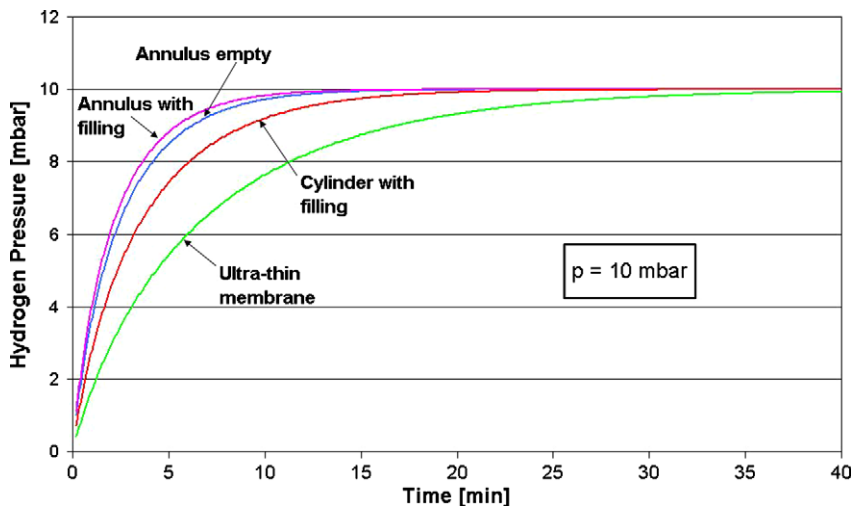


Fig. 5. Simulations of the performance of the optimised sensor solutions.

As far as the permeation properties of the pure iron walls, the following set of parameters, identified during the experimental campaign carried out in the range 200–1100 mbar, has been adopted for these simulations:

$$K_s(500\text{ }^\circ\text{C}) = 3 \times 10^{-3} \text{ mol m}^{-3} \text{ Pa}^{-0.5},$$

$$D(500\text{ }^\circ\text{C}) = 1.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1},$$

$$K_r(500\text{ }^\circ\text{C}) = 1 \times 10^{-29} \text{ m}^4 \text{ s}^{-1}.$$

It has to be pointed out that the reliability of the presented results is affected by the pressure dependence of the materials properties (in particular the adsorption and recombination coefficients).

5. Conclusions

The performance and the possible optimisation of a permeation sensor to determine hydrogen isotopes concentration in liquid Pb–16Li for HCLL blanket modules and their ancillary circuits have been investigated. Niobium and pure iron permeable capsules have been tested so far.

Unfortunately, the observed low permeating fluxes have shown the impossibility of operating the Nb-sensor in equilibrium mode, while the differences obtained in repeated tests under the same conditions prove the impossibility of operating the sensor in dynamic mode.

The results with the Fe-sensor demonstrate the impossibility of operating in equilibrium mode, at least under the present conditions, because of the very long time (several hours) necessary to reach the hydrogen pressure equilibrium. However, this problem could be solved by optimising the sensor geometry, with the reduction of the ratio ‘total sensor volume/permeation surface’ and of the membrane wall thickness. In this context, the preliminary designs of different possible solutions have been presented. They involve the use of a permeable capsule having an annulus section or an ultra-thin membrane and the filling of the sensor with an ade-

quate material. Good results in terms of the performance of these optimised solutions have been demonstrated by simulations.

As far as the dynamic mode of operation is concerned, it has been verified that it is possible to link the permeation fluxes to the test pressure at each temperature by means of a simple power equation. The Fe-sensor quickly reaches the steady state condition of the permeating flux (a few seconds are necessary) and, therefore, if operated in dynamic mode, it could exhibit a fast response and the ability to follow rapid changes of the hydrogen concentration on the high pressure side.

The development of the activity foresees the final design, construction and testing of the optimised iron sensor. Moreover, an innovative sensor consisting of a capsule with permeable walls fabricated with a bilayer of a porous material and a thin metallic coating, will also be developed.

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