Materials selection and design of a hydrogen measurement device in Pb–17Li

A. Ciampichetti [a,*], I. Ricapito [b], G. Benamati [c], M. Zucchetti [a]

[a] *EURATOM/ENEA Fusion Association, Politecnico di Torino, DENER, Corso Duca Degli Abruzzi 24, 10129 Torino, Italy*
[b] *RSI Sistemi, Via A. De Togni 2, 20123 Milano, Italy*
[c] *ENEA FIS ING, C.R. Brasimone, 40032 Camugnano (BO), Italy*

Abstract

In the helium cooled lithium lead (HCLL) and water cooled lithium lead (WCLL) blanket concepts for DEMO correct and reliable management of tritium is of basic importance, both for safety and fuel cycle reasons. To develop a sensor for measurements of hydrogen (and its isotopes) concentration in liquid Pb–17Li, a permeable capsule of niobium was chosen. Different simulations with a mathematical model have been performed, and then the sensor was designed, constructed and tested. The first experimental results in gas phase showed a permeating flux much lower than the predicted one, probably due to the formation of an oxide layer on the capsule surface or to the formation of niobium hydrides. To solve this problem different solutions are presented.
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1. Introduction

In the helium cooled lithium lead (HCLL) and water cooled lithium lead (WCLL) blanket concepts for DEMO, where a molten lithium lead alloy is used as a breeder material, correct and reliable management of tritium is of basic importance for the correct operation of the blanket tritium cycle.

As a consequence, the main processes for tritium extraction, removal and recovery from the blanket must be developed and optimised. In this regard, the tritium extractor from flowing lithium lead (TES, Tritium Extraction System) is a critical system and the determination of the hydrogen isotopes concentration in the liquid metal is mandatory for its correct design.

Therefore, the need for a reliable sensor with quick response for the measurement of hydrogen isotopes concentration in the liquid breeder is evident and its conceptual design is just the aim of this work. Among different possibilities, the choice of a sensor based on the principle of hydrogen isotopes permeation into a capsule of a suitable material seems to be, at least in principle, the simplest and the most reliable one. Moreover, many data on hydrogen isotopes permeability through different materials – and their compatibility in a liquid metal environment – are available in literature. On the other side, as it will be clarified below, the measurement of the hydrogen isotopes concentration in Pb–17Li by a permeation sensor requires knowledge of the Sieverts' constant at the foreseen operating conditions.

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

In its 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 pressure P_{eq}. The capsule is connected, through a

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* Corresponding author. Tel.: +39-0534 801277; fax: +39-0534 801225.

E-mail address: andrea.ciampichetti@brasimone.enea.it (A. Ciampichetti).

small tube, to an external pressure gauge or to a vacuum pumping system, depending on its mode of operation.

The tube connecting the capsule to the gauge measurement has to be made of a suitable material not permeable to hydrogen. The reason for this requirement is the need of local hydrogen concentration measurement in liquid metal. This can be obtained using a steel tube covered by an Al-based permeation barrier. It consists of a double layer with an Al_2O_3 top coat and a Al–Fe substrate, the permeability of which is several orders of magnitude lower than that of the capsule material.

The measurement of the hydrogen isotopes partial pressure in the capsule or hydrogen permeation flux through the capsule walls has to be correlated with the hydrogen concentration C_L in the liquid metal, once fundamental laws of gas permeation through the capsule walls and hydrogen solubility in liquid metal are applied.

The permeation sensor can be operated in equilibrium or in 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, is reached. Then, the hydrogen equilibrium pressure measured inside the capsule is related to C_L by the Sieverts' law constant for H/Pb–17Li system:

$$C_{L,H} = K_{S,L} P_{eq}^{0.5}. \tag{1}$$

In the case of the dynamic operation mode, the situation of the sensor is different because the inner volume of the capsule is continuously evacuated under the action of vacuum pump. Considering a pure diffusion regime through the membrane, the hydrogen flux at steady state is given by

$$J_{out,ss} = K_{S,M} D_m P_{eq}^{0.5}/s, \tag{2}$$

where $K_{S,M}$ and D_m are the Sieverts' constant and diffusivity, respectively, for the system hydrogen/material, while s is the thickness of the capsule.

From the experimental value of $J_{out,ss}$ the equilibrium pressure P_{eq} is determined and, through the Sieverts' law for H–Pb/17Li system (Eq. (1)), the hydrogen concentration in liquid metal is found.

Therefore, in the equilibrium mode the hydrogen concentration in the liquid metal is measured through the equilibrium pressure inside the capsule, while in the dynamic mode the hydrogen concentration in the liquid metal is determined by the steady state flux of the permeated hydrogen.

From a simple theoretical point of view, the correct operation of a sensor working in equilibrium mode depends only on a reliable determination of the hydrogen Sieverts' constant $K_{S,L}$ in the liquid metal. Only the rate of the capsule pressurisation is affected by the perme-

ation 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 correct determination of $K_{S,M}$ and D_m for the system H-solid membrane.

3. Candidate materials and technological requirements for application in Pb–17Li

The main constraints in designing a hydrogen permeation sensor in a liquid metal like Pb–17Li for the application in the blanket of DEMO reactor can be summarised as follows:

(a) The sensor must be able to quickly follow rapid changes of the hydrogen concentration in the liquid metal. This means that the capsule material should have a high permeability. This permits high permeating fluxes to be obtained and then a fast pressurisation of the inner volume of the sensor, up to the equilibrium pressure, if the sensor is operated in equilibrium mode. The same applies also to the sensor operated in dynamic mode. In order to obtain reasonable time constants (e.g. some minutes), materials with permeation values (in DEMO-relevant operating conditions) higher than 10^{-12} mol m^{-1} s^{-1} Pa$^{-0.5}$ have to be selected.

(b) Among different materials with similar permeability values, those ones with higher diffusivity and lower Sieverts' constants are the most suitable. In this way, the hydrogen inventory in the capsule wall is minimised because of the lower Sieverts' constant. Furthermore, for materials with the same permeability, higher hydrogen diffusivity allows to reach more quickly the steady state flux and pressure equilibrium. So, whatever is the selected operation mode, materials with high hydrogen diffusivity are more suitable for this kind of application.

(c) The capsule material must be chemically compatible, particularly from the point of view of corrosion, with Pb–17Li in the temperature range of 450–550 °C. Therefore, any pure metal or alloy containing Ni, Al, Ti, Zr, Cu in relevant percentage has to be avoided [1].

(d) The capsule volume should be as small as possible, because the hydrogen inventory in the sensor must be negligible when compared to the hydrogen inventory in the liquid metal. In the perspective of a possible application to DEMO, this means to avoid significant perturbations of the tritium concentration in the liquid metal during transients.

(e) The dead volume of the permeation sensor must be as small as possible, in order not to increase too much time necessary to obtain the hydrogen

pressure equilibrium between the capsule and liquid metal phase.

In the light of points (a)–(c), Nb, Ta, V seem to be possible candidates for the permeable capsule chamber walls, considering that, despite their high Sieverts' constant, they have a relatively high hydrogen diffusivity. Use of pure Iron (Fe ARMCO) is also a possible solution, especially if one takes into account the easier welding and machining of this material.

4. Simulation of the permeation behaviour of the sensor

A first evaluation of the performance of the H-sensor has been carried out, taking into account the permeation characteristics of niobium and ARMCO iron. This assessment was carried out by a general permeation model that has been set up for this study [2].

As far as the geometry of the sensor is concerned, the parameters that have been considered are:

- capsule external diameter: 1.3 cm
- capsule thickness: 1 mm
- capsule height: 3 cm
- tube height: 30 cm
- tube external diameter: 1.3 cm
- tube thickness: 1.5 mm.

Concerning the permeation parameters for niobium and ARMCO iron, the following values, taken from literature [3], have been used for the simulation:

K_S (Nb, 500 °C) = 25 mol m^{-3} Pa$^{-0.5}$
D (Nb, 500 °C) = 7×10^{-9} m^2 s^{-1}
K_r (Nb, 500 °C) = 1×10^{-29} m^4 s^{-1}
K_S (Fe, 500 °C) = 10^{-2} mol m^{-3} Pa$^{-0.5}$
D (Fe, 500 °C) = 1.5×10^{-8} m^2 s^{-1}
K_r (Fe, 500 °C) = 1×10^{-25} m^4 s^{-1}.

The temperature of the system has been fixed at 500 °C and the external hydrogen pressure at 50 mbar. This is a realistic hydrogen isotopes partial pressure in the liquid breeder of the HCLL DEMO blanket.

It must be pointed out that with the above recombination coefficients the hydrogen mass transport through the capsule wall is limited by the bulk diffusion. This is equivalent to assume that the kinetics of adsorption and recombination reactions at the capsule wall surface are very fast and no oxide layers are present.

In the mathematical modelling, it has also been assumed that the connecting tube is a kind of dead volume, which is not permeable to hydrogen isotopes.

In Fig. 1 the pressurisation rate of the sensor with a Nb capsule is shown, with all the parameters listed above. As one can see, the pressurisation rate is fast and
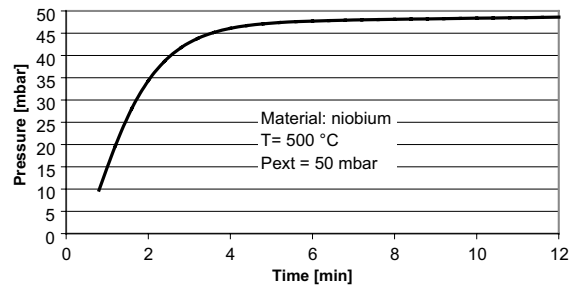

Fig. 1. Pressurisation rate of the sensor with the Nb capsule: theoretical results.
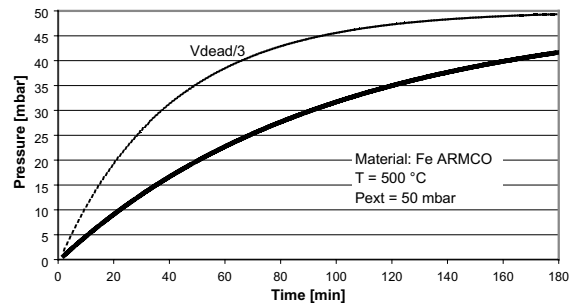

Fig. 2. Pressurisation rate of the sensor for two different values of dead volumes (V_{dead} and $V_{dead}/3$).

the equilibrium pressure is reached in about 5 min. The reason of this high pressurisation rate is the unusual high value of the Sieverts' constant K_S, about three orders of magnitude higher than in a ferrite matrix. The simulation showed that with such a high value of K_S and, as a consequence, of permeability, the pressurisation rate is not particularly sensitive to the dead volume of the sensor.

In Fig. 2 the same type of simulation is shown for the same sensor with an ARMCO Fe capsule. In this case, two dead volumes are considered, the first one referring to the assumed normal dead volume of the impermeable connecting tube, the second one being decreased of a factor 3. In this case, the pressurisation rate and, as a consequence, the time necessary to reach equilibrium pressure is strongly dependent on the dead volume, differently from the previous case, because of the much lower permeability.

5. Design of the sensor and its first characterisation

The final version of the sensor operating in equilibrium mode was designed to construct the first prototype. It consists of (see Fig. 3):

- a permeable capsule with the connecting tube. The capsule is made of niobium (external diameter: 13
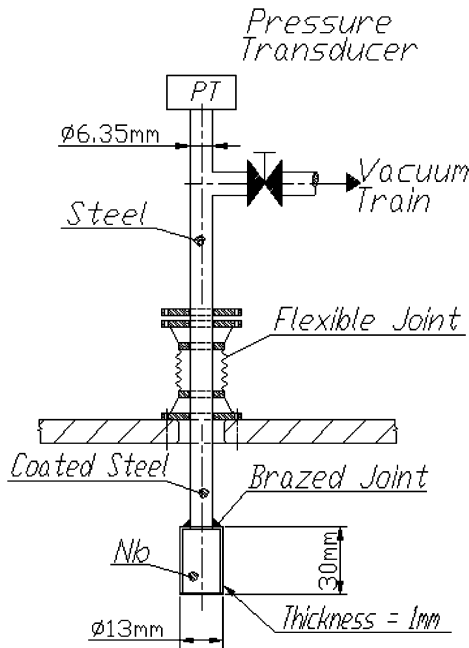
Fig. 3. The hydrogen permeation sensor.

Fig. 4. Experimental result obtained with the Nb sensor in gas phase.

mm, height: 30 mm, thickness: 1 mm), the tube is made of stainless steel coated with a layer of alumina (external diameter: 6.35 mm). The connection between the capsule and the tube is a brazed joint;

- a flexible joint to allow the vertical movement of the capsule;
- a capacitance pressure gauge (Baratron supplied by Varian) placed at the top of the sensor;
- a ultra high vacuum valve to isolate the sensor from the vacuum pumping system.

Because during the tests the brazed joint is not in contact with Pb–17Li, it was chosen silver as brazing material. Anyway, if this condition is not respected, it is necessary to adopt a mechanical joint (Swagelok type, as an example).

The experimental campaign is being carried out using the device VIVALDI, that it is available at ENEA-Brasimone and suitable for testing the permeation sensor in DEMO-relevant conditions. A detailed description of the VIVALDI facility is reported in [4].

In the first phase of the experimental campaign, the sensor performances were studied in gas phase. The temperature was fixed at 450 °C, while the hydrogen partial pressure was in the range 1–2 bar.

The first results (see Fig. 4) showed an hydrogen permeating flux much lower than the predicted one, probably due to the formation of an oxide layer on the capsule surface. Moreover, the permeation flux shows, after an initial rise, a rapid decrease similar to that re-
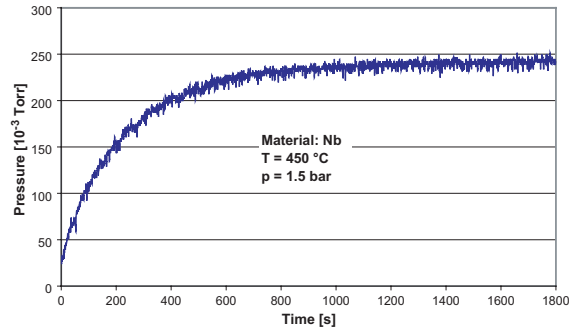
ported in [5]. In this recently published work, the permeation of hydrogen through tantalum, which a negative heat of solution such as niobium has, was thoroughly investigated. In this case the conclusion was that hydrogen permeation is limited by surface processes and it decreases during the experiment due to changes on the membrane surfaces. Similar conclusions are probably correct also in the case under study.

Therefore, the influence on the permeation of lower recombination coefficients, with respect to the one assumed above, was considered, and their impact on the steady state permeation flux has been investigated. Results are reported in Fig. 5. As one can see, the permeation flux is strongly dependent on K_r, if low values on the low pressure side of the capsule, are assumed.

It must be pointed out that in the mathematical simulation, assuming low values of the recombination coefficient the formation of oxide layers on the metal surface is already taken into account.

In parallel the possibility that this low permeating flux is due to the formation of niobium hydrides is under further investigations.
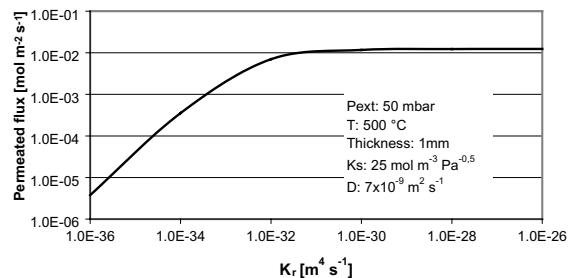

Fig. 5. Influence on the steady state permeation flux of the recombination coefficient for the system H–Nb: theoretical results.

6. Conclusions

The possibility to develop a permeation sensor to determine the hydrogen isotopes concentration in liquid Pb–17Li for WCLL or HCLL blanket modules has been investigated and first results presented and discussed.

Among different solutions, it appeared that, at least in the first phase of the experimental campaign, a permeable capsule of niobium should be tested as the most attractive material, because of the good compatibility with liquid Pb–17Li and the very high hydrogen permeability which could make possible the use of this sensor in real-time application.

After different simulations performed by a mathematical model set in diffusion limited regime, which showed that with a permeable capsule of niobium the pressurisation time is very short, the sensor was designed and constructed. However, the first results in gas phase showed a value of the hydrogen permeating flux much lower than the predicted one, probably due to the formation of an oxide layer on the capsule surface. In the light of these results and a recently published study [5], it appears very likely that hydrogen permeation takes place in surface limited regime, with a very low recombination coefficient. In fact, by decreasing in the mathematical model the recombination coefficient, much lower permeation fluxes were obtained.

However the possibility that this low permeating flux is due to the formation of niobium hydrides is now under further investigations.

The possible solutions to solve the problem are:

- to operate the sensor with the niobium capsule in dynamic mode;
- to deposit on the niobium surface a thin platinum layer in order both to prevent oxidation and to increase the hydrogen adsorption kinetics on the capsule walls;
- to select a different permeable material for the sensor.

Before selecting the most suitable solution for the further development of the activity, the tests will be extended in liquid metal phase.

Acknowledgements

References

[1] H. Feuerstein, H. Gräbner, J. Oschinski, J. Beyer, Forschungszentrum Karlsruhe GmbH, Report FZKA 5596, 1995.
[2] A. Ciampichetti, I. Ricapito, M. Zucchetti, Politecnico di Torino Report, PT DE 569 IN, February 2003.
[3] E. Serra, PhD thesis, Department of Pure and Applied Physics, University of Salford, England, 1996.
[4] A. Aiello et al., ENEA Report LB-A-R-012, July 2001.
[5] A. Pisarev et al., J. Nucl. Mater. 317 (2003) 195.