

HYDROGEN ISOTOPES PERMEATION THROUGH FUSION ORIENTED MATERIALS

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ABSTRACT

The evaluation of hydrogen and its isotopes permeability and solubility in fusion oriented materials is a key issue in fusion technology concerning safety, fuelling and reliability. Different devices have been designed and constructed at ENEA Brasimone Centre, with the aim to characterize hydrogen isotopes transport and inventory phenomena in structural and breeding materials, in the temperature range between 473 K – 1073K and in liquid metal and gas phase.

Several materials were examined, martensitic steels, tungsten, Tritium Permeation Barriers (TPB), and the main results, together with a brief description of experimental devices and procedure, are herein presented and discussed.

1 INTRODUCTION

In considering materials for fusion reactors a detailed understanding of the transport and inventory parameters of hydrogen and its isotopes through these materials is an important issue concerning safety, fuelling and reliability. A large R&D effort has been done in the frame of EU Fusion Technology programme to select and develop structural materials for the first wall and internal components of DEMO, and to reduce tritium permeation through structures. Numerical codes have been developed for the calculation of recycling, inventory and permeation of deuterium and tritium in fusion reactor design concepts in non steady state conditions. Essential input data for these codes are the permeability, diffusivity and solubility of hydrogen isotopes in the structural material involved. Hydrogen related problems for fusion applications are been studied since several years in the ENEA Brasimone Centre.

Different experimental devices have been developed in ENEA, with the aim to fully characterise hydrogen and its isotopes transport and solubility in different materials, in a wide range of temperatures, in gas and liquid metal phase.

The experimental activities are focused on the determination of hydrogen/deuterium transport parameters in the temperature range 473÷723K using a time dependant permeation technique in gas

phase with hydrogen and deuterium driving pressures in the range 10-10⁵ Pa. Recently a new experimental device was designed and constructed to reach temperatures up to 800°C.

Several materials and deposition processes were selected to act as Tritium Permeation Barriers (TPB). The most promising candidate material resulted alumina, deposited on steels using Chemical Vapour Deposition (CVD) and Hot Dipping (HD) pack aluminisation. The qualification of TPB has been conducted using different devices. The latest generation is represented by *Vivaldi*, an apparatus in which two different specimens can be directly compared in terms of permeability, in the temperature range between 573 K and 723 K, in gas and liquid metal phase.

The main results, together with a description of the experimental devices and methodology, are herein presented and discussed.

2 EXPERIMENTAL

2.1 Hydrogen isotopes permeation at high temperature in gas phase: PERI and PERI 2 devices

The PERI (PERmeation of hydrogen) device was developed in the ENEA Brasimone laboratories, in order to evaluate hydrogen transport and inventory parameters. The permeation device “PERI” is described elsewhere^[1,2] and a schematic view appears in fig. 1.

The specimen divides the apparatus in two sides: the high pressure side and the low pressure side. High pressure deuterium gas, with a nominal purity of 99.7 %, was taken from a cylinder, although hydrogen gas had also been used. The hydrogen had an impurity content less than 1 vppm of H₂O and O₂, and was produced by a hydrogen electrochemical generator connected to a hydrogen purifier.

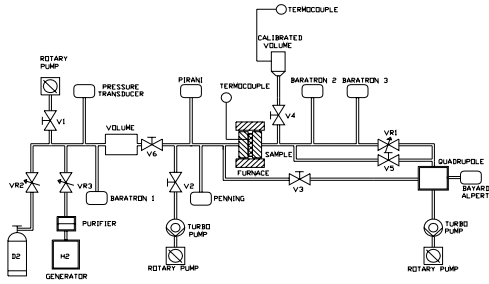


Fig. 1: Schematics of the permeation apparatus PERI for the gas-phase measurements.

The hydrogen/deuterium gas is admitted to the sample via a control valve which, together with a pressure transducer and a Baratron, enables the pressure to be set at any value between $100\text{-}1.5 \cdot 10^5$ Pa. The sample is heated by a resistance furnace. Gas permeates through the sample causing a rise in pressure in the outlet volume. For each run, an analysis of the high pressure and permeated gas is carried out by a quadrupole mass spectrometer in order to check for possible contaminants. A National Instruments system (Labview) is used for data acquisition.

2.2 Liquid metal/gas phase method: Corelli (I and II) and Vivaldi devices

The experimental installation CORELLI I was constructed with Ultra High Vacuum (UHV) components [3]. The test section was a cylindrical container, which hosted a cylindrical hollow specimen. The geometry of the specimen was chosen in response to the WCLL design requirement. The container was joined to a feed tank for its filling up with the lead alloy. Further on the test section a UHV line with a calibrated volume for the measurement of the hydrogen pressure inside the specimen was foreseen as well as a UHV line for measuring hydrogen in the test section and a UHV line to supply hydrogen to the test section. The hydrogen gas was admitted in the test section using a pressure controlled valve with a full scale reading of $1.3 \cdot 10^5$ Pa. All the UHV lines were connected with a turbo-molecular pumping group.

The measurements performed on the CORELLI I device were both in a gas – gas phases and a liquid – gas phases conditions. In the first case after bake out and evacuation the cylindrical test section was filled with hydrogen gas. The hydrogen that permeated through the specimen was released inside, where it caused a pressure rise in the calibrated volume. This pressure rise was measured with a capacitive vacuum gauge with a full scale

reading of $1.3 \cdot 10^2$ Pa. Analogously to the PERI device the pressure rise detected in the calibrated volume was converted in amount of hydrogen mole permeated per unit of area and time, the results obtained were compared with those of PERI. The gas – liquid phases condition was realised by filling the test section with the liquid lead alloy and the hydrogen gas was admitted with a continuous flow. The experimental procedure was the same under both the conditions and a detailed description of the experimental procedures is given in [3]. The main difference between Corelli I and II [4] is represented by the test section design. Since in CORELLI I the sample was welded to the holders with the consequence of a higher permeation area, in CORELLI II the sample was designed to make possible a direct welding to the test section and the holders were eliminated. In order to confirm the results obtained with CORELLI II and to evaluate the TPB effectiveness directly by testing coated and a not coated specimens in the same operating conditions the VIVALDI apparatus was designed and constructed (fig. 2) [5].

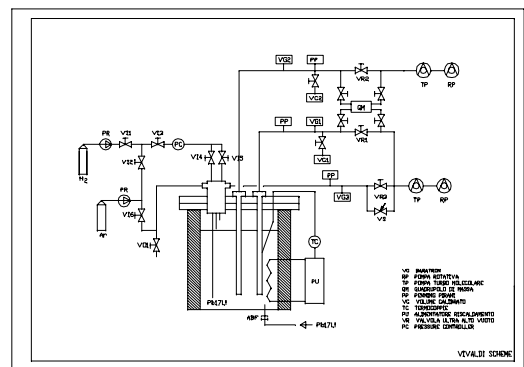


Fig.2: schematic of Vivaldi apparatus

In VIVALDI it is possible to perform comparative evaluation of permeation fluxes, determining directly the TBP. The gas lines of the VIVALDI installation were the same as those of CORELLI. Two hollow cylinder specimens were sealed with a standard CF 16 flange, realised with the same material of the specimen. The coupling between the samples and the upper and lower counter flanges was realised with standard Cu O-ring. As for CORELLI, in VIVALDI experimental tests were performed in gas – gas and in liquid – gas phases. The measurement lines and the pressure transducers of the two specimens were perfectly symmetric to guarantee the same measurement accuracy.

With regard to the experimental procedure, it was the same applied in CORELLI in gas phase, while in liquid metal phase a small continuous flow of hydrogen gas was bubbled through the liquid maintaining constant the pressure in the section.

3 THEORY

It is possible to obtain an expression for the permeation flux J (moles of gas $\text{m}^{-2} \text{s}^{-1}$) of hydrogen atoms through a membrane of uniform thickness d (m), in the case where the driving hydrogen pressure is increased instantaneously from zero to p (Pa) (always very much higher than the pressure on the low pressure side), and where the initial concentration throughout the solid is zero (i.e. the experimental conditions used for the present work). Here $J(t)$ is given by the one-dimensional solution of Fick's law and can be expressed as:

$$J(t) = \frac{D \cdot K_s \cdot p^{1/2}}{d} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left[-D \frac{n^2 \pi^2}{d^2} t \right] \right] \quad (1)$$

where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the membrane and K_s ($\text{mol m}^{-3} \text{Pa}^{-1/2}$) its Sieverts' constant. It is also assumed that the diffusion coefficient D is independent of concentration within the experimental range and no surface effects are present, i.e. the rate limiting process is diffusion through the material rather than surface reactions. At steady-state (i.e., $t \rightarrow \infty$) eq. (1) becomes: $J = P/d p^{1/2}$, where $P = DK_s$ ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1/2}$) is defined as the permeability of the material. To calculate the permeated flux through a cylindrical hollow sample, at steady state condition, the formula for hollow cylinder is used:

$$J = \frac{P \sqrt{p}}{R_{\text{out}} \ln \frac{R_{\text{out}}}{R_{\text{in}}}} \quad (2)$$

The total amount of gas, $Q(t)$ moles of gas, which has permeated after time t , in the one-dimensional case, is given by:

$$Q(t) = \int_0^t J(t') dt' = \frac{P p^{1/2}}{d} t - \frac{P p^{1/2} d}{6D} - \frac{2P p^{1/2} d}{\pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left(-D \frac{n^2 \pi^2}{d^2} t \right)$$

In the Pressure Rise Method (PRM), $Q(t)$ is obtained experimentally from the pressure rise data, using the ideal gas law. The values of P and D can be obtained by fitting the experimental data for each permeation run. Then, having obtained the permeability P and the diffusivity D , the Sieverts' constant is determined directly from the relationship $K_s = P/D$.

4 RESULTS AND DISCUSSION

4.1 Permeation tests in gas phase

The data that could be obtained with the PERI device are the amounts of hydrogen gas that permeates through a disc sample at a given

temperature. As described in paragraph 2 the amount of permeated hydrogen versus time allows evaluating the permeation flux, the permeability, the diffusivity and the solubility of the tested material. With the PERI device austenitic and martensitic steels [6], also with an interlayer of copper [7], W and W-Re [8] were qualified in terms of hydrogen permeability and diffusivity. Moreover, at low temperature the onset of hydrogen trapping effects on martensitic steels was evaluated too [9,10]. The hydrogen trapping behaviour in steels is of great interest because of its relation with the resistance to hydrogen embrittlement.

As example the hydrogen/deuterium permeabilities through and diffusivities in Eurofer 97 steel samples are reported in the Arrhenius plot of figure 3 and 4.

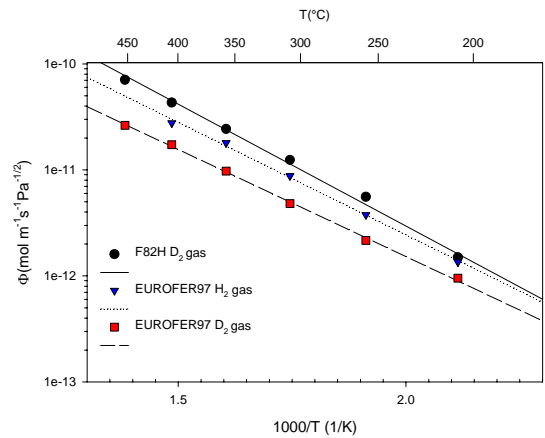


Fig. 3: Permeability of hydrogen/deuterium through **Eurofer 97** compared to F82H

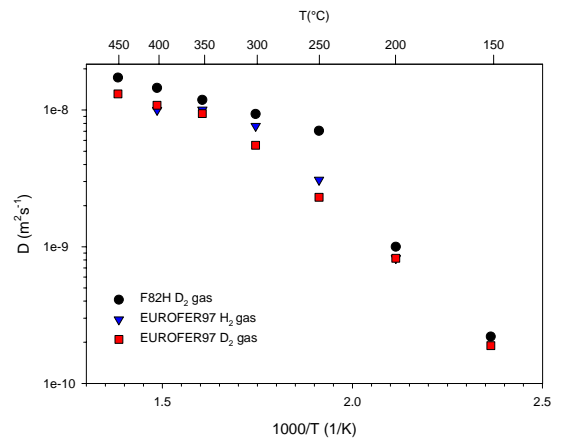


Fig. 4 Diffusivity of hydrogen/deuterium in **Eurofer 97** compared to F82H

In figure 4 is clearly evident the effect of trapping, with a marked decrease of diffusivity at low temperatures. The measurements were performed

with the PRM technique and more details are given in [10].

In the case of W and W-Re, the results obtained in terms of permeability with Peri installation in the temperature range 573÷773K, compared with literature data, are reported in fig. 5.

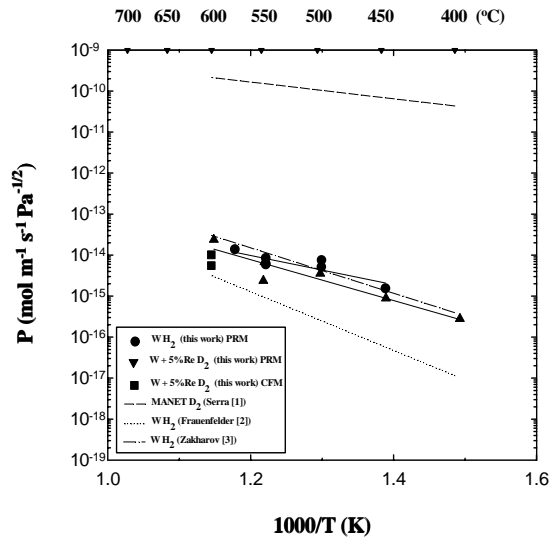


Fig. 5: W and W-Re permeabilities compared with literature data

The maximum temperature reached with PERI was 773 K, too low to obtain a complete set of data on W and W-Re permeabilities. For that reason the PERI II apparatus was developed in which the specimen housing is realised in TZM, a molybdenum alloy, and a different furnace allows to reach temperatures up to 1073K.

The first results, obtained with a 1 mm of thickness specimen, are reported in the Arrhenius plot of fig. 6, compared with literature data.

The agreement with previous experimental results can be considered good.

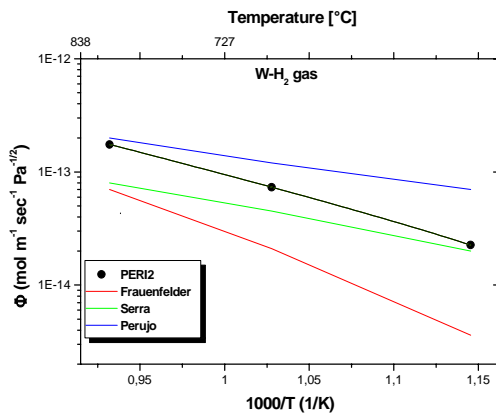


Fig. 6: W permeabilities (PERI 2 apparatus)

4.2 Permeation tests in liquid metal phase

The qualification of TPB was performed using different permeation devices, as mentioned in the previous paragraphs. The first apparatus used was Corelli I, in which a CVD coated sample was tested^[3]. Experimental tests were performed in gas phase and in liquid metal phase, using a gas driving pressure of 10^5 Pa. When operating in liquid metal the gas was bubbled through the liquid. The hydrogen permeated fluxes were measured in the temperature range between 523 and 773K increasing and decreasing the temperature with a step of 50K. Experimental results in terms of fluxes are reported in fig. 7, in comparison with bare materials.

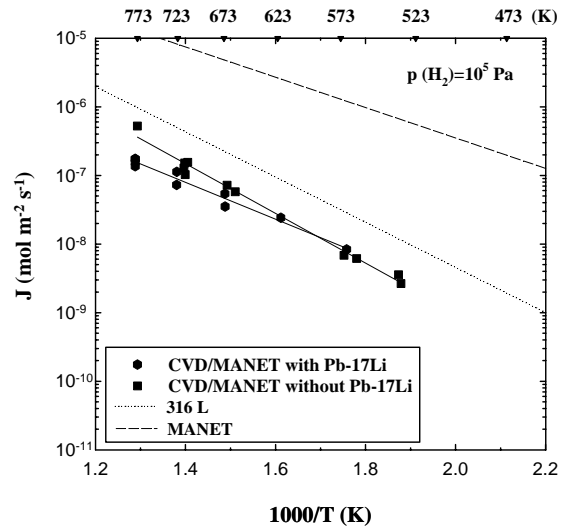


Fig. 7: Hydrogen permeated fluxes through CVD coated and bare specimens in gas phase and liquid metal phase

It is evident that the Permeation Reduction Factor (PRF), defined as the ratio between flux in the bare specimen and in the coated one, in gas and liquid metal phase is about 20, very far from the expected results. For this reason it was supposed the presence of hydrogen leaks through the structure, with an increase in the measured fluxes.

In the second generation apparatus, named Corelli II, the specimen was directly welded to the permeation chamber, reducing the non coated surface in contact with gas. In Corelli II an Hot Dipping coated sample was tested. The gas pressure and test temperatures were the same adopted in Corelli I device.

In this case the PRF in gas phase was similar to that obtained on disk shaped sample^[4], while in liquid metal phase it decreased of more than one order of magnitude (fig. 8).

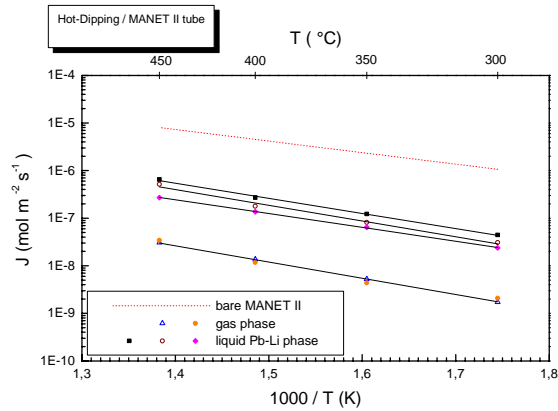


Fig. 8: HD cotad sample: permeated flux in gas and liquid metal phase compared with bare material

In fig. 9 the SEM micrograph of the HD coated sample is reported. The presence of surface microcracks, probably produced by a chemical interaction between a not transformed intermetallic Fe-Al phase and lead lithium, can be observed.

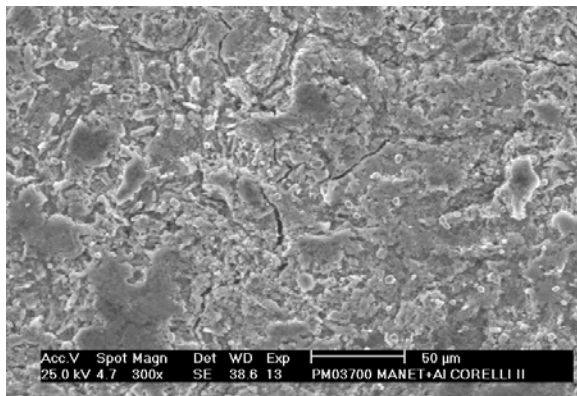


Fig. 9: Surface of HD sample tested in the Corelli II device

Vivaldi apparatus was designed to perform comparative tests between coated and bare cylindrical specimen in gas phase and liquid metal phase, with the aim to directly determine the PRF in the same operative conditions simply comparing the permeated fluxes^[5].

The apparatus was used to characterise CVD and HD coated samples, to obtain a complete set of data to be used in the final coating selection. In fig. 10 are reported the hydrogen permeabilities obtained on two CVD coated samples, compared in the same experimental conditions with bare Eurofer 97 specimens.

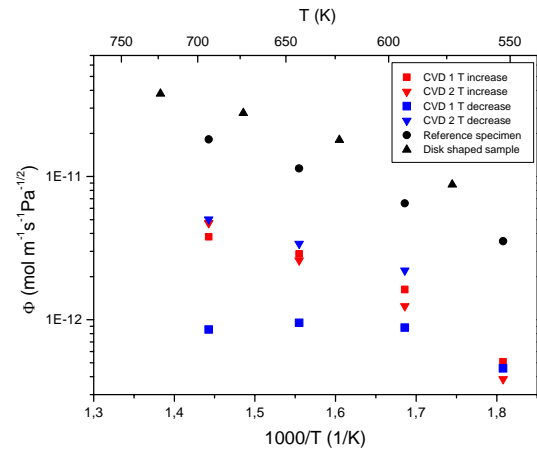


Fig. 10: Hydrogen permeabilities through Eurofer 97 bare and CVD coated specimens

The PRF obtained on the CVD coated samples was in the range between 3 and 8, demonstrating the presence of unrecoverable coating defects. Considering that the minimum acceptable value of PRF foreseen in the WCLL blanket design is 75, it was decided not to perform permeation experiments on these samples in liquid metal.

In fig. 11 the SEM micrograph of the transversal section of the first tested CVD coated specimen, shows the low quality of the coating, with large detachments.

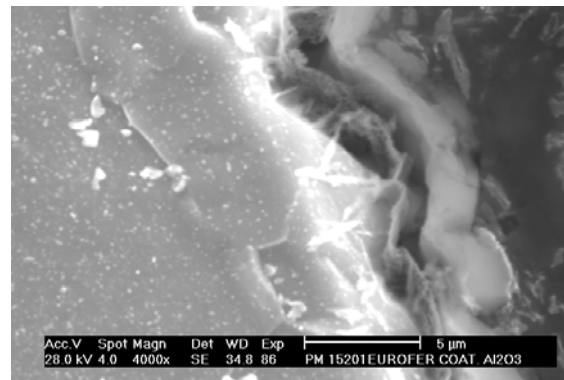


Fig. 11: Cross section of CVD coating (Vivaldi experiment)

Next, permeation experiments were carried out on HD coated sample in gas phase and, considering the good PRF obtained, also in liquid metal phase. The hydrogen permeabilities in gas phase and liquid metal phase compared with those of the bare specimen are shown, as Arrhenius plot, in fig. 12.

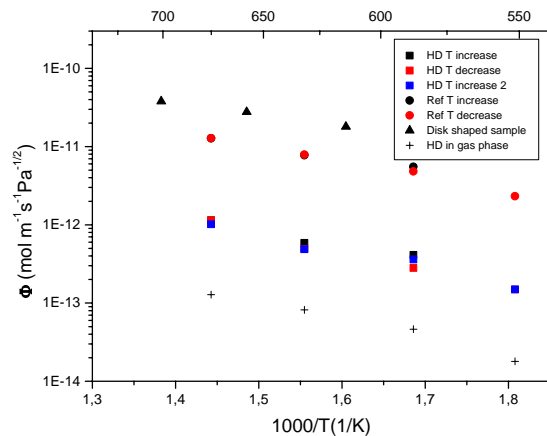


Fig. 12: Arrhenius plot of HD coated sample Permeabilities in gas phase and liquid metal phase compared with those of the reference specimen

Comparing the permeated flux measured in gas-phase and in liquid metal phase, it appears clearly that the permeated fluxes increase in liquid metal. This phenomenon could be related to a chemical interaction between coating and liquid metal as proposed by literature. Considering that the specimen was dipped into liquid metal four days before permeation tests, it could be assumed that any kind of coating damage was produced during this period, reaching a steady state condition before starting the permeation tests.

Also in this case SEM examinations were performed after extraction the specimen from the test section. In fig. 13 the micrograph of the transversal section is shown.

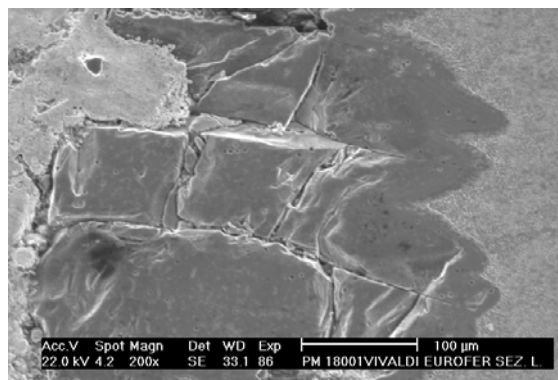


Fig.13: Cross section of HD coating

The morphology and microstructure of the coating is not comparable to the usual one obtained with this deposition technique. On the basis of the metallographic analysis performed it could be reasonably supposed that the usual procedure for producing this type of coating was not adopted. Further investigations are in progress to explain the phenomenon.

4 CONCLUSIONS

Relevant R&D activities were done in ENEA Brasimone centre on material permeability qualification in terms of:

- Hydrogen isotopes permeability behaviour through steels (PERI)
- Hydrogen isotopes permeability behaviour through refractory metals (PERI 2).

Testing procedure and experimental devices to perform permeation measurements in gas and liquid metal phase were improved in terms of flexibility and reliability, starting from Corelli I since Vivaldi, now in use for coating qualification.

The coating qualification procedure elaborated and adopted in Vivaldi can be considered as the 'recommended' procedure, and Vivaldi is now the reference apparatus for coating qualification as TPB in Europe.

The devices available in ENEA Brasimone r.c. make it possible to fully qualify different materials in terms of gas permeation in a wide temperature range (473-1073K).

Gas-permeability measurements in liquid metal phase are also possible using Vivaldi, in which a direct comparison between bare and coated materials or different materials is possible, in the same operative conditions.

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