

Measurement of deuterium permeation and diffusion in several stainless steels

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Abstract: It's necessary for safety and circumstance influence evaluation to make sure that the hydrogen isotopes permeate through stainless steel used in tritium system. A dynamic quadrupole mass spectroscopy method was adopted to measure deuterium permeation and diffusion through stainless steel. The background effect, linearity of quadrupole mass spectrometer, calibration method, permeability measurement, diffusivity and measurement, uncertainty evaluation were investigated. It was indicated that this method had many advantages over other methods, such as high sensitiveness (up to 10^{-9} Pa.l.s⁻¹), fast response, and high precision with a combined standard uncertainty of 17.25%. The permeability and diffusivity of deuterium in 1Cr18Ni9Ti, HR1, HR2 stainless steels were measured over the temperature range of 473k ~ 823k. The permeability of deuterium in these stainless steels were expressed as follows, for 1Cr18Ni9Ti stainless steel : $\varphi=3.66 \times 10^{-5} \exp(-50.69/RT)$, for HR1 stainless steel : $\varphi=4.06 \times 10^{-5} \exp(-55.66/RT)$, for HR2 stainless steel : $\varphi=4.73 \times 10^{-5} \exp(-50.81/RT)$.

Key words: Hydrogen permeation, Tritium, Stainless steel, Mass spectroscopy

1. Introduction

The permeation and diffusion of tritium in materials can embrittle materials, pose a health hazard for personnel and lose tritium. Due to the high probability of tritium permeation through the materials during high-temperature operation, the interaction of tritium with structural materials is very important for safety considerations [1~2]. The austenitic steel HR1, HR2, 1Cr18Ni9Ti are generally used for structural material of high –temperature components in tritium- handling systems. A database based on experiment is being formed. The gas permeation method is one of most useful methods to measure the permeation and diffusion of tritium through structural material, which can acquire dynamic parameters of permeation and diffusion [3~4]. The dynamic quadrupole mass spectroscopy method has many advantages over other gas permeation methods, such as high sensitiveness, fast response, visualization, and high precision etc. The details of this method and the results of measurement for stainless steel mentioned above were introduced in this paper.

2. Experiments

The experimental device consisted of sample chamber, charge deuterium system, calibration component, vacuum component, and detection system of deuterium permeation stream (Fig1). Samples of Piece shape or cup shape were adopted with the ends connecting to charge deuterium system and detection system of deuterium permeation stream by welding respectively.

The charge deuterium system which of pressure range is about 0~10 MPa was used to supply high purity deuterium for permeation experiment. It consisted of high-pressure membrane

valves, capacitance membrane gauge, pressure gauge, deuterium bed, standard gas vessel, without-oil vacuum pump. The calibrate system was used to supply standard flows by utilizing diffidence mode and constant conductance mode to decrease detection lower limit and increase upper limit respectively. The quadrupole mass spectroscopy (QMS) with difference evacuator was used to detect deuterium ion current under the dynamic vacuum equilibrium condition for the detection system of deuterium permeation stream. The material of the device was almost austenitic steel. The inner surface of pipe and vessel had polished by electrolysis. The bi-blade seal mode was adopted in flange joint, which use without oxygen copper gasket. Therefore this device sealed excellently with vacuum degree of 10^{-7} Pa.

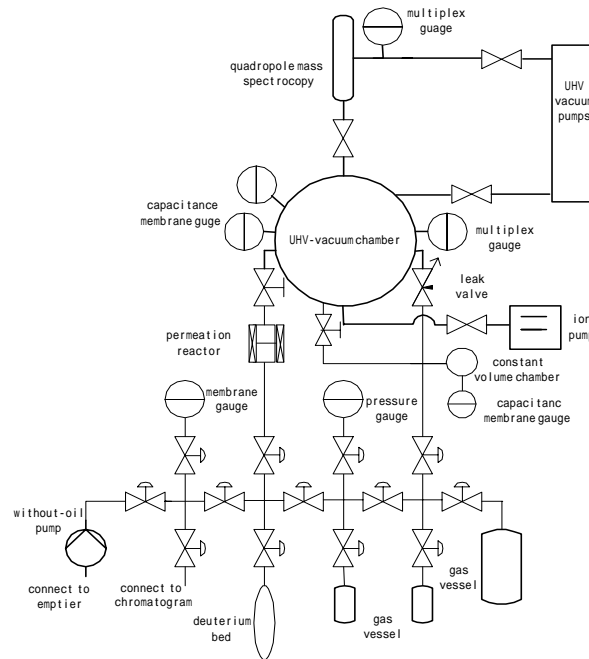


Fig.1. Schematic of experimental devices for measuring permeation of deuterium through steel

Before deuterium permeation experiments were processed, the calibration of deuterium ion current should be carried out. After the vacuum of the system attained to 10^{-6} Pa, and the QMS work stably for a while, the calibration process was started. Tiny deuterium gas stream was introduced to vacuum chamber and QMS from constant volume chamber by adjusting the leak valve. An velocity of flow of the. The ion current of deuterium in QMS should match to the velocity of flow of the deuterium which deduced by the varieties of pressure in constant volume chamber during calibration. Therefore, the relationship between the deuterium permeation flow and deuterium ion current were made sure. The permeation reactor was heated up to 700 in order to remove the gas absorbed on reactor material, then the reactor was cooled down to experimental temperature. The high purity deuterium was imported to the reactor.

The QMS recorded the change of permeation flow versus time, temperature, pressure, etc. The permeability was obtained by formula 1.

$$\phi = J_{\infty} \frac{l}{\sqrt{P}} \quad (1)$$

Where ϕ is permeability ($\text{mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1/2}$), J_∞ is permeation flow under the stabilization permeation status ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), P is gas pressure (Pa), l is the thickness of sample. The diffusivities are defined as

$$D = \frac{l^2}{6t_L} \tag{2}$$

where t_l is time when $J_L=0.617J_\infty$.

In order to test the performance of the device, many experiments were carried on. These experiments included: utmost vacuum test, leak and release gas test, linearity of QMS test, flow out volume test, constant volume test, constant flow conductance test, calibration experiment, etc.

3. Results an discussions

3.1 Residue gas analysis

The residue gases of the system are H_2 and H_2O (Fig2). The cleanliness vacuum environment was suit to calibration and measurement.

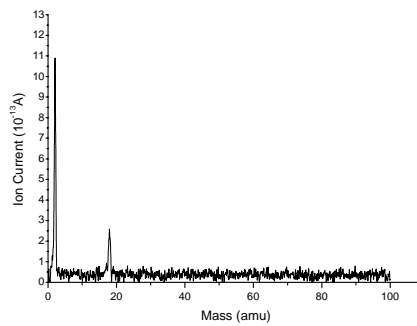
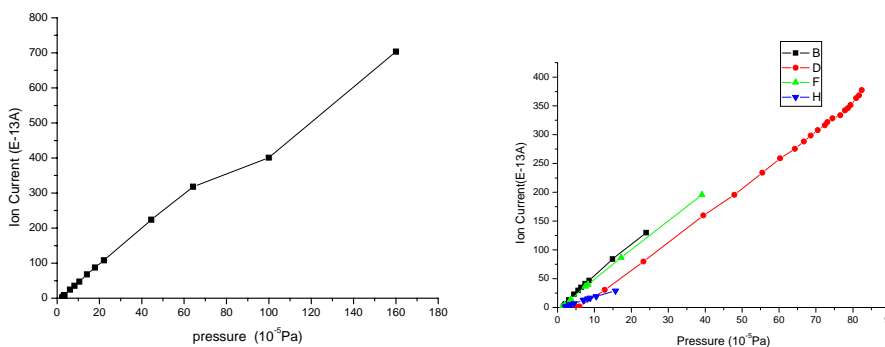


Fig.2. Spectrum of the residue gas

3.2 Linearity of QMS

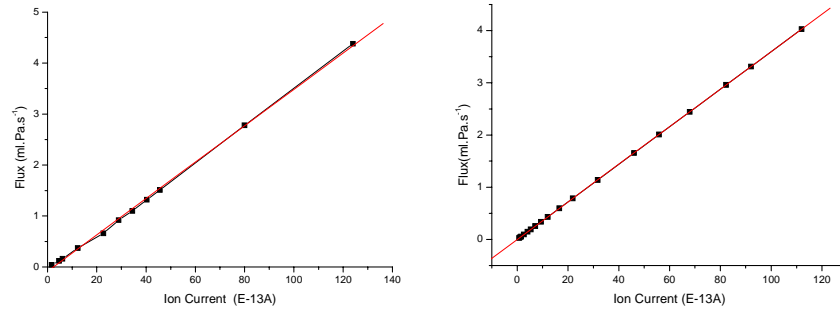


a. Under measure experiment evacuate speed b. Under variety evacuate speed

Fig.3. The deuterium ion current versus pressure

The changes of deuterium ion current in QMS versus vacuum pressure were shown as Fig 3. It showed that the relationship between the deuterium ion current and vacuum pressure were linear when vacuum pressure was superior to 8×10^{-4} Pa.

3.3 Deuterium flow calibration



a. Constant volume method b. Constant flow conductance method
 Fig.4. The curve of calibration

One of the results for calibration was shown in Fig 4, which is indicated that the flow proportioned to ion current of QMS. As for Constant volume method, the formula was defined as

$$Q_c = 3.568 \times I \times 10^{11}, \tag{3}$$

For Constant flow conductance method, the formula was defined as

$$Q_c = 3.595 \times I \times 10^{11}, \tag{4}$$

where Q_c is deuterium flow (ml.Pa.s^{-1}), I is ion current of QMS (A). Detect limit of D_2^+ ion current for QMS using the faraday cup is about 10^{-15}A , which accorded with the deuterium flow about $10^{-7}\text{Pa.l.s}^{-1}$. If the electron amplifier was used, the detect limit of deuterium flow would up to $10^{-9}\text{Pa.l.s}^{-1}$.

3.4 The type spectrum for permeation measurement

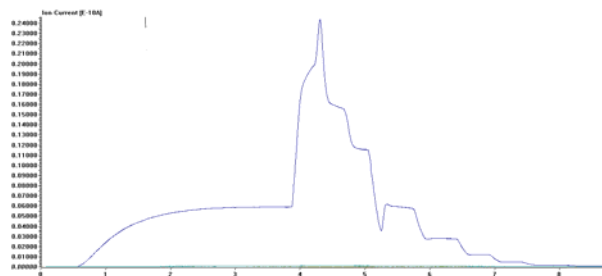


Fig.5. The type spectrum for permeation measurement

The sample was heated to higher temperature for a while after the permeation became stable at set temperature, then the sample was cooled down to lower temperature. After the permeation became stable, the sample was cooled down to lower temperature again.

The deuterium permeation flux increased exponentially at the beginning. Once the stable permeation taken place, the response of permeation flux to temperature became more distinctive and the time to next stable permeation became shorter. The repeatability experiment manifested that deuterium permeation flux would change a little though the cycle of adsorption and desorption. This hinted that the phase transform, impurity, crystal granularity, stress may affect the permeation.

3.5 Pressure experiments

The pressure experiments were carried out for validate the measure method. The results manifested that the square root of pressure of deuterium on upper side was proportioned to the

permeation flux, thus proved the method was effective.

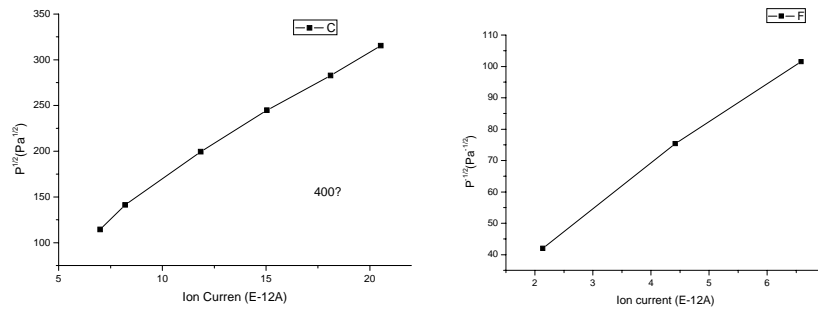


Fig.6. The permeation flux versus the pressure of deuterium on upper side

3.6 Uncertainty evaluation

Basis on Uncertainty evaluation methods, the uncertainty for measure deuterium permeability in stainless steel could be define as

$$\left| \frac{\delta Q_L}{Q_L} \right| = \left| \frac{\delta \left(\frac{I_L - I_0}{I_S} \right)}{\frac{I_L - I_0}{I_S}} \right| + \left| \frac{\delta \left(1 - \frac{I_0}{I_S} \right)}{1 - \frac{I_0}{I_S}} \right| + \left| \frac{\delta V}{V} \right| + \left| \frac{\delta T}{T} \right| + \left| \frac{\delta(\Delta p)}{\Delta p} \right| + \left| \frac{\delta(\Delta t)}{\Delta t} \right| + \left| \frac{\Delta T}{T} \left(\left| \frac{p}{\Delta p} \right| + 1 \right) \right| \quad (5)$$

Each of factor of uncertainty was listed in table 1. The uncertainty of 17.25% would acquired by synthesize each factor.

Table.1 Uncertainty evaluation for measure deuterium permeability

Item	Uncertainty (%)
Volume measurement	0.5
Difference of pressure	1.0
Difference of time	0.05
Fluctuate of temperature	0.5
Temperature measurement	1
Repeatability	8
Fluctuate of evacuate speed	4
Leak and release gas rate	0.1
Ion current measurement	2
Ion background influence	0.1
Synthesized uncertainty	17.25

3.7 The deuterium permeation through stainless steel

The permeability and diffusivity of deuterium in 1Cr18Ni9Ti, HR1, HR2 stainless steels were measured over the temperature range of 473k ~ 823k.. The permeability of deuterium in these stainless steels were expressed as follows, for 1Cr18Ni9Ti stainless steel : $\varphi=3.66 \times 10^{-5} \exp(-50.69/RT)$, for HR1 stainless steel : $\varphi=4.06 \times 10^{-5} \exp(-55.66/RT)$, for HR2 stainless steel : $\varphi=4.73 \times 10^{-5} \exp(-50.81/RT)$. For one kind stainless steel samples, the discrepancy of activation energy and front exponential factor may be caused by the discrepancy of hot removing gas, hydrogen background, residue stress, surface status, etc.

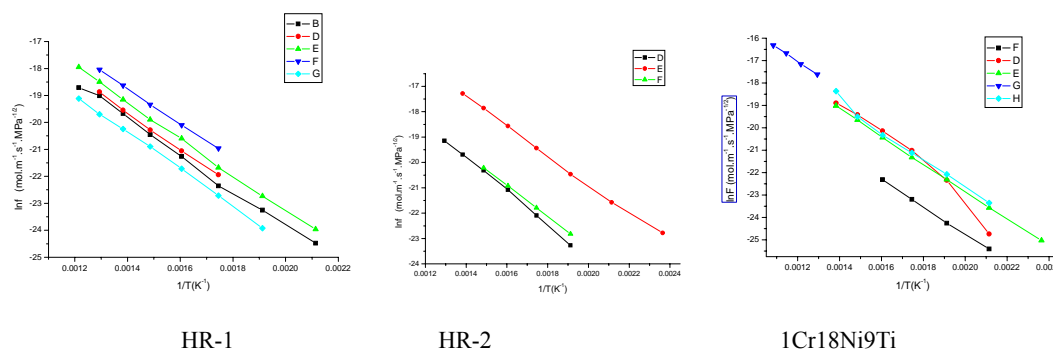


Fig.7. The deuterium permeation versus temperature

The deuterium diffusibility of stainless steel without suffering adsorption and desorption of deuterium treatment was measured (table 4). The logarithm of the diffusibility didn't fit the temperature linearly. These were likely to derive from two aspects factors. Firstly, the hydrogen trap status for each fresh sample was different. This effect could be eliminated by adsorption and desorption of deuterium at high temperature again and again in later experiments. Secondly, The states of oxidation film on surface of stainless steel had changed at temperature range from 400 to 550 .This could be amended by temperature section experiment or plating palladium sample, or cycle inject deuterium method.

Table 2 The deuterium diffusibility for stainless steel (m².s⁻¹)

Temperature (k) Material	823	773	723	573	523
1Cr18Ni9Ti		1.206E-10	6.46E-11		
HR-1	5.60E-10	3.78E-10	9.64E-11	4.62E-11	
HR-2		2.46E-10	1.99E-10	4.25E-11	

4. Conclusion

- 1) The relationships between the deuterium ion current and vacuum pressure were linearity,when vacuum pressure was superior to 8×10⁻⁴Pa. Within the linearity range of QMS, the permeation flux can be calibrated by constant volume and constant flow conductance method.
- 2) The detect limit of deuterium flow of 10⁻⁹Pa.l.s⁻¹ would achieved by this method.
- 3) the uncertainty for measure deuterium permeability in stainless steel was about 17.25%.
- 4)The permeability of deuterium in these stainless steels were expressed as follows, for 1Cr18Ni9Ti stainless steel : $\varphi=3.66 \times 10^{-5} \exp(-50.69/RT)$, for HR1 stainless steel : $\varphi=4.06 \times 10^{-5} \exp(-55.66/RT)$,for HR2 stainless steel : $\varphi=4.73 \times 10^{-5} \exp(-50.81/RT)$.

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