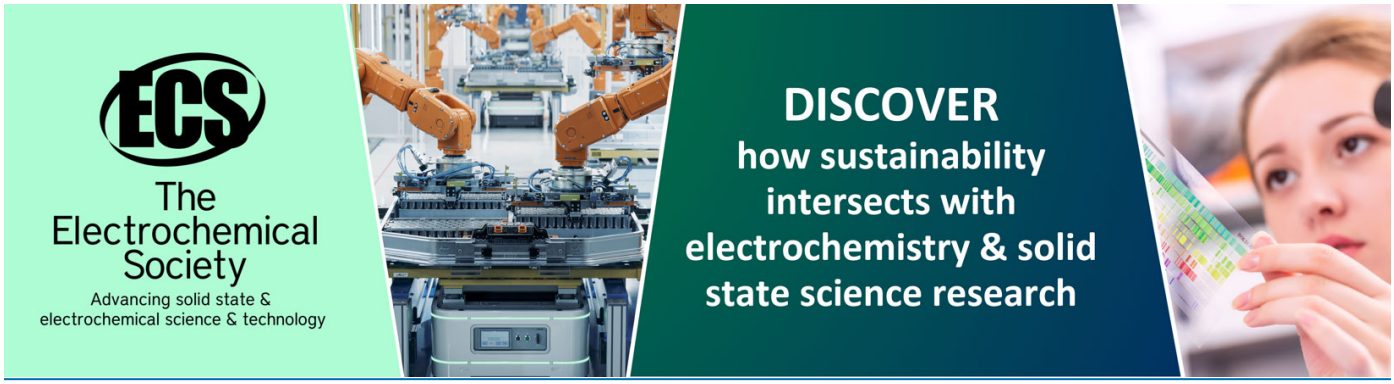
Apparatus and method for determining the gas permeability and flux of helium through the materials and coatings



Apparatus and method for determining the gas permeability and flux of helium through the materials and coatings

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Abstract. Apparatus and method for measuring flow of helium through the materials and coatings, obtained by ion-plasma technologies, are developed and tested. The apparatus for the measurement is designed on the basis of a helium leak detector TI1-14, produced by JSC "Zavod Izmeritel", that provides a minimum detectable flow of helium 7.10-13 Pa.m3/s. The purpose of the study is the creating apparatus and method to determine gas permeability and helium flux through new materials and coatings to create the hermetic devices with special properties. This devices are made from polymer coated with metals, and they should replace full metals device analogues in the field of aerospace engineering.

1. Introduction

The study of gas permeability trough new materials and coatings is important to create the devices of these materials. It is necessary to determine polymer type to create a sealed devices which has minimized gas permeation during operation. Helium is selected as a tracer gas in such tests, because of the high value of its diffusion coefficient through the solid body relative to other gases.

Apparatus and method for measuring flow of helium through the materials and coatings, obtained by ion-plasma technologies, are developed and tested in the laboratory of the electronic instruments and devices department Petersburg State Electrotechnical University.

2. Theory of the gas permeability through the materials and coatings

Permeation is commonly viewed as a three-step process. First, gas dissolves into the solid's surface; then it diffuses through the solid; and finally, it desorbs from it. The time dependence of the permeation rate is determined by the diffusion process because the solution and desorption occur on much shorter timescales than the diffusion through the solid [6]. The concentration c of the diffusing species in the solid's surface is given by Henry's law

$$c = S \cdot p, \tag{1}$$

where S is the solubility coefficient and p is the gas pressure. Diffusion of the dissolved gas into the interior is governed by Fick's second law,

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c, \tag{2}$$

where D is the concentration-independent, isotropic diffusion coefficient. If we consider a planar membrane with a large area-to-thickness ratio, equation (2) can be reduced to a one-dimensional form

$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{d^2 c}{dx^2}\right), \tag{3}$$

where *x* is the coordinate perpendicular to the membrane. Assuming that the membrane is initially free of gas and that the concentrations of gas at the two surfaces are fixed at c_1 and c_2, respectively, the initial and boundary conditions are

$$c(x,\ t=0) = 0 \tag{4a}$$
$$c(x=0,\ t) = 0 \tag{4b}$$
$$c(x=d, t) = c_2 \tag{4c}$$

where *d* denotes the membrane thickness. The solution of equation (3) consistent with equations (4a), (4b), and (4c) is [7]

$$c(x,t) = c_1 + (c_2 - c_1)\frac{x}{d} + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{c_2 \cdot \cos(n\pi) - c_1}{n} \sin\left(\frac{n\pi x}{d}\right) \exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right). \tag{5}$$

The flux of diffusing species is given by Fick's first law,

$$Q = -D\nabla c. \tag{6}$$

The gas flux through the low-pressure surface of the wall can then be calculated from equations (5) and (6):

$$Q(x=d,t) = \frac{D(c_2 - c_1)}{d} + \frac{2D}{\pi}\sum_{n=1}^{\infty} [(-1)^n c_2 - c_1] \exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right). \tag{7}$$

For large values of *t* one obtains the steady state flux

$$Q(x=d, t\to\infty) = \frac{D(p_2 - p_1)}{d}. \tag{8}$$

The product

$$K = DS \tag{9}$$

is the permeation coefficient. It has, like the diffusion and solubility coefficient, a strong dependence on temperature. Finally, the steady state permeation flux *Q* of a gas exposed with a partial pressure difference ($p_1 - p_2$) to a membrane of thickness *d* and surface area *A* is

$$Q = A \cdot Q(x=d, t\to\infty) = K\frac{A(p_2 - p_1)}{d}. \tag{10}$$

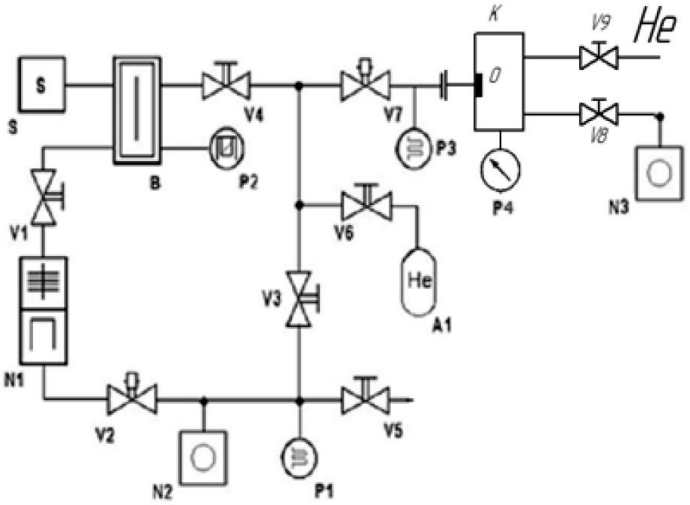
3. The apparatus for the gas permeability measurement

The apparatus for the measurement is designed on the basis of a helium leak detector, which is implemented, in accordance with OST 5.0170-81 [1], the method of the helium chamber. The helium mass spectrometer leak detector TI1-14, produced by JSC "Zavod Izmeritel" (Saint-Petersburg), provides a minimum detectable flow of helium $7 \cdot 10^{-13}$ Pa·m^3/s [5], which corresponds to the first class of tightness according PNAEG-7-019-89 [2].

The measurement stand is equipped with a vacuum testing chamber for the polymer object installation, its pre-drainage and creating a pressure gradient of helium relative to the outer and inner side of the test object. The vacuum circuit of the measurement stand is shown in Figure 1.

Test object, placed in a vacuum testing chamber, is connected to the leak detector and evacuated from the outside and the inside with a leak detector vacuum system. Helium is supplied into the chamber with continuous pumping of the opposite side of the object.

Quantitative value of the helium flux is measured by leak detector signal after stabilization of the helium diffusion through the test object. The appearance of the stand for gas permeability measurement of materials and products on helium is shown in Figure 2. 3D-model of vacuum chamber for installation the test object is shown in Figure 3. The verification of the samples parameters shall be carried out under normal climatic conditions unless otherwise specified.



where S – the mass spectrometry analyzer; V1, V3, V4, V6, V8, V9 – manual valve; N1 – turbomolecular pump; V2, V5, V7 – solenoid valve; N2, N3 - rotary vane pump; A1 – helium standard leak; B – cold trap; K – vacuum chamber; O – test object; P1, P3 – Pirani pressure sensor; P2 – ionization pressure sensor; P4 – mechanical manometer.

Figure 1. Vacuum circuit of the apparatus for measuring the flux of helium through the materials and coatings.

Figure 2. The appearance of the stand for measuring the flux of helium through the materials and coatings.

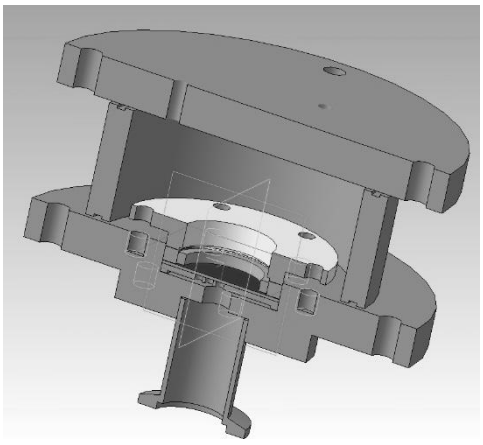


Figure 3. 3D-model of vacuum chamber for installation the test object.

Samples for the measurement should have a disk shape with the following dimensions:
- diameter $44.0_{-0.2}$ mm;

- thickness of 1,00 ± 0,05 to 8,00 ± 0,05 mm;
- surface roughness is not less than Ra = 2.5.

According to GOST 28517-90 [3], the test conditions (pressure drop, the direction of the gas load and others) should be established identical as operation conditions of the material or the device. Test conditions other than the operating conditions may be given in a technically and economically justified cases.

4. Testing procedure

The authors developed a technique of testing to determine the flux of helium through the material. Methods of measurement are made according to OST 11-0808-92 [5]. The key points of testing procedure allows to describe in detail the principles of measurements and the apparatus operation.

1 Preparation of the vacuum chamber.
1.1 Clean the inner surface of the chamber, using calico and ethyl alcohol.
1.2 Dry the chamber for 2 minutes.
2 Preparation of the material sample.
2.1 Measure the wall thickness of the sample *d*.
2.2 Install the sample in position for measurement in vacuum chamber.
2.3 Fix the presser cover bolts.
3 Setting up the leak detector.
3.1 Turn on the leak detector in accordance with the instruction manual [4].
3.2 Perform the leak detector preparation to work according to the instruction manual [4].
4 The assembling of the vacuum system.
4.1 Attach the hollow cylinder and the cap of the vacuum chamber to the inlet flange of the leak detector with mounting bolts.
5 Determination of the system sensitivity threshold.
5.1 Determine the sensitivity threshold Q_{min} by a test helium leak, according PNAEG-7-019-89 [2].

The sensitivity threshold of the helium chamber measurement method depends on the magnitude of the signal background oscillations $\Delta\alpha_f$ and is given by:

$$Q_{min}=2\Delta\alpha_f \cdot S_Q, \tag{11}$$

where $\Delta\alpha_f$ is the maximum amplitude of the background signal oscillations, mV; S_Q is the scale interval of the leak detector (Pa·m^3/s)/mV, calculated by the equation:

$$S_Q=Q_T/\Delta\alpha_T, \tag{12}$$

where Q_T is the value of the test helium leak, Pa·m^3/s; $\Delta\alpha_T$ is the signal output from the test helium leak, mV.

5.2 Record the measured values into protocol: Q_T, Pa·m^3/s; α_f, mV; α_r, mV; $\Delta\alpha_f$, mV; S_q, (Pa·m^3/s)/mV; Q_{min}, Pa·m^3/s.
6 The leak detector pipeline evacuation.
6.1 Open the valve V7 “Input protection”.
6.2 Pump down the vacuum chamber to a residual pressure 7 - 8 Pa.
7 The evacuation of the vacuum chamber. The operation is performed for degassing of the measurement object to remove dissolved helium.
7.1 Open the valve V8 for pumping the vacuum chamber.
7.2 Start the stopwatch.
7.3 Make the evacuation by vacuum system at least for 5 hours to achieve the pressure not more than 700-1400 Pa.
7.4 Close valve V8 to stop pumping vacuum chamber.

8 Measuring the helium flow.
8.1 Turn on the measure mode of the leak detector in accordance with its instruction manual [4].
8.2 Open the valve V9.
8.3 Create a pressure differential of 1 atm. from the inner and outer sides of the object, using helium reducer.
8.4 Register the start of the measurements by the stopwatch.
8.5 Record the start time of the leak detector output signal growth.
8.6 Record the signal α_{he} and time in the protocol with measurement interval no more than 5 minutes. The measurement time is not less than 120 minutes.
9 Completion of measurements.
9.1 Close the helium reducer at the end of the measurement time.
9.2 Pump out the helium from vacuum chamber by opening valve V8.
9.3 Turn off the leak detector according to its instruction manual [4].
9.4 Remove the vacuum chamber.
9.5 Remove the presser cover.
9.6 Take away the sample.
10 Determination of flux of the helium through the material, depending on the time.
The determination of the helium flux through the sample is carried out in accordance PNAEG-7-019-89 [2].
10.1 Calculate the value of the helium flux through the sample Q (Pa·m^3/s) by formula:

$$Q = S_Q \cdot \alpha_{he.} \tag{13}$$

Record Q, Pa·m^3/s results to the measurement protocol.
10.2 Calculate the specific flux helium through the sample material Q_{sp}, [Pa·m^3/s]·[m/(m^2·atm)].

$$Q_{sp} = \frac{Q \cdot d}{A \cdot \Delta P_{he}}, \tag{14}$$

where h is the thickness of the sample, A ≈ 1·10^{-3} m^2 – surface area of the sample. Record Q_{sp} results to the measurement protocol.
11 Processing of the measurement results.
Draw the curves of the time dependence:
– the helium flux through the sample Q (Pa·m^3/s),
– the specific flux helium through the sample Q_{sp}, [Pa·m^3/s]·[m/(m^2·atm)].

5. Verification of the measurement of time-dependent permeation rate

The test sample of a polymer material with a known value for the permeability for helium was investigated on the measuring instrument. PTFE was selected as a material for the measurement of permeability for helium.

Permeation coefficient K for helium and PTFE combination is 7.5·10^{-11} m^2/s [8]. The steady state permeation flow Q of a gas exposed with a partial pressure difference 10^5 Pa (1 atm.) to a membrane of thickness d = *1.5* mm and surface area A ≈ 1·10^{-3} m^2, in accordance with the equation (10), is

$$Q = K\frac{A(p_2 - p_1)}{d} = 7.5 \cdot 10^{-11}\,\frac{\mathrm{m}^2}{\mathrm{s}}\,\frac{1\cdot10^{-3}\ \mathrm{m}^2\cdot10^5\mathrm{Pa}}{1.5\cdot10^{-3}\mathrm{m}} = 5 \cdot 10^{-6}\,\frac{\mathrm{Pa}\cdot\mathrm{m}^3}{\mathrm{s}} \tag{15}$$

The comparison of the calculated data with the experimental values, obtained on the device, confirms the accuracy of the measurement apparatus and method. The results are shown in figure 4.

6. Measuring the flux of helium through the polymer materials with metal coatings

Two polymer samples with metal coatings were selected for the measurement:

- Polyethylene. The high molecular weight modified plastelastomer with copper coating 100 nm.
- Low pressure polyethylene HDPE 209-07 with copper coating 100 nm.

The previously evacuated vacuum chamber had been filled to 10^5 Pa with helium, and the flow through the polymer materials was subsequently measured by the leak detector system.
The curves of the time dependence of the specific flux helium through the sample Q_{sp} are shown at the figure 5.

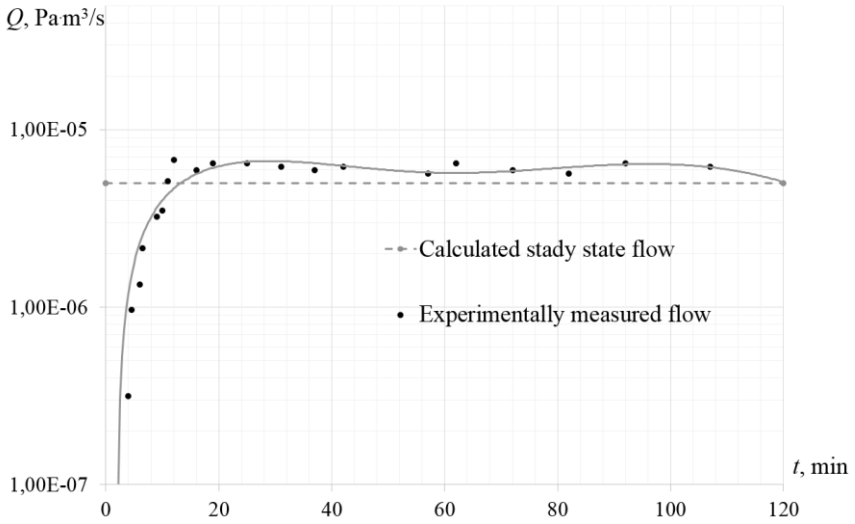


Figure 4. Helium permeation through PTFE sample. Verification of the measurement.

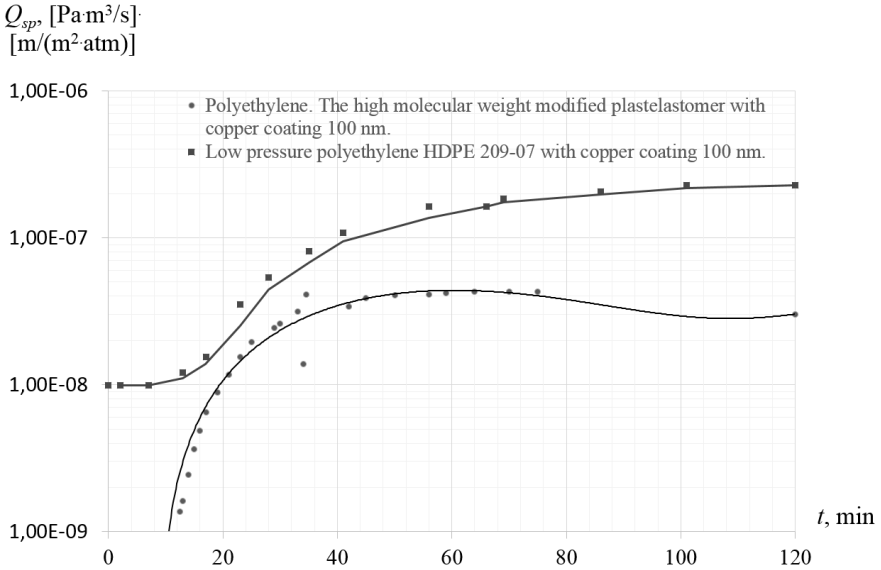


Figure 5. Time dependence of the specific flux helium through the polymers.

It is better to use polyethylene (the high molecular weight modified plastelastomer with copper coating 100 nm.) to create the hermetic devices, in accordance with results of comparison.

7. Conclusions

Apparatus and method for measuring flow of helium through the materials and coatings, obtained by ion-plasma technologies, are developed and tested. The apparatus for the measurement is designed on the basis of a helium leak detector TI1-14, produced by JSC "Zavod Izmeritel", that provides a minimum detectable flow of helium $7 \cdot 10^{-13}$ $Pa \cdot m^3/s$. Research work in the field of diffusion of helium through modern polymer materials with metal coatings are held at this measurement system.

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