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IMPROVEMENT OF METHODOLOGY AND EQUIPMENT FOR DETERMINATION OF HYDROGEN PERMEABILITY OF THIN FLAT METALLIC MEMBRANES

Abstract: The paper describes an improved technique for determining the hydrogen permeability of flat thin metal membranes, which makes it possible to exclude the use of mass spectrometry during measurements. The technique is distinguished by the use of large-area membranes (78.5 · 10-4 m²), which makes it possible to measure both large and small gas flows using a combined method. The method of thermal conversion of the mass flow of gas into an electrical signal using calibrated flowmeters with an error of ± 0, 9 % measures limiting flows with a velocity of 0.36 dm³/h or more. By the volumetric method, by determining the interval for the escape of hydrogen bubbles from the capillary, the limiting fluxes up to 30 mm³/s are determined. The advantage of using a large area membrane is the ability to determine the life of the membrane and the nature of its deformation during dilatation. The paper describes the developed equipment for determination of hydrogen permeability at temperatures up to 650 °C and pressure up to 1 MPa. The equipment includes a furnace with a retort and a heated membrane holder, a module for vapor conversion of gaseous hydrocarbons and a gas drying module. It is equipped with safety systems that ensure the release of excess pressure and shut off the electric power supply of the furnace in the event that the temperature exceeds a predetermined value. The equipment is universal and allows measuring hydrogen permeability using both pure hydrogen and various gas mixtures under conditions of isothermal maintenance, smooth reduction and cyclic temperature change. It is characterized by the convenience of mounting the membrane in the holder and holder in the camera. The sequence of work with the developed equipment is resulted.

Key words: hydrogen permeability, thin metal membranes, chamber furnace, modular plant, gas mixtures, niobium and tantalum membranes, diffusion-alloyed, composite membranes

Introduction. Hydrogen permeable membranes are a rapidly developing field of science and technology. They are widely in demand both in the composition of single hydrogen separators and as part of a catalytic membrane reactor. The introduction of technologies based on membrane separation of hydrogen-containing gas mixtures obtained as by-products in industry or in the steam conversion of gaseous hydrocarbons will depend on their productivity and economic efficiency. This technology becomes attractive only when the membrane separators can achieve the required flow of hydrogen, operating temperature, cost, durability and resistance to contamination. The standards for these characteristics were established by the US Department of Energy [1], and membrane designers around the world are striving to meet these criteria. The most important of which are: temperature ((250–500 °C), flow (150 $cm^3/cm^2 \cdot min$ with dP (H_2) 100 psia (0.69 MPa), cost (~ $ 1000/m^2) membrane service life (5 years). At present, only the membranes of palladium-based alloys correspond to the requirements for stability and temperature range of operation, however, their extremely high cost and insufficient hydrogen permeability require the search for new materials and membrane designs.

Hydrogen permeability is measured by volumetric, mass spectrometric, sorption, desorption, radiographic or potentiostatic methods [2-9]. Predominantly in the study of composite, i.e. consisting of 2 or more layers, membranes are used methods of microgasovolumetric and mass spectrometric determination of the hydrogen flow passing through the membrane [2, 10-11]. When measuring the flow of hydrogen by a volumetric method, capillaries of different diameters are used, in which the volume of gas released at a particular time is determined from the displacement of the water droplet. This complicates the measurement procedure, since it requires the selection of the capillary section. In addition, the volume of the capillary limits the measurement period. The minimum reliably measured amount of hydrogen passed through the sample by the method of measurement is $1 \cdot 10^{-4}$ cm^3/c [9]. The mass spectrometric method is more accurate, but it is expensive and requires the use of more sophisticated equipment. This makes it promising to further simplify and improve the methodology and

equipment for measuring the hydrogen permeability of membranes.

The purpose of this work is to improve the methodology and improve equipment for determining the hydrogen permeability of flat membranes at different temperatures and pressures.

Experimental part. *Development of methodology. Measurement of the flow rate of hydrogen*. The developed methodology should provide for the possibility of using simple measuring equipment. Thus, the rejection of the mass spectrometer in the measuring circuit makes it possible not only to simplify the measurement process, but also to reduce the cost of equipment for conducting experiments ten times. However, to determine the flow of hydrogen, its value should be sufficient to measure using electronic flowmeters, or by visually observing the flow of hydrogen. The latter is proposed to be determined by measuring the period of the escape of hydrogen bubbles from the capillary, dropped into water at a fixed depth.

The most acceptable for the price and accuracy of measuring the gas flow is the method of thermal conversion of the mass flow of gas into an electrical signal. Thus, the regulators of mass flow rate RRG-10 and RRG-12 offered on the market have an upper limit of gas regulation in nitrogen of 0.36 dm^3/h (100 mm^3/s) and can be calibrated to a higher flow rate. At the same time, the systematic component of the above basic error of gas flow conversion for RWG-10 is ± 1.1%, and for RWG - 12 ± 0.9%. The time to establish the readings of these flowmeters is 2 sec [12].

Determination of the interval of bubble outflow from a capillary immersed in a vessel with water allows measuring smaller flows. For example, with a hole diameter of Ø 1 mm and a slope of 45° , the volume of 1 bubble averages 30 mm^3, and can be determined fairly accurately by calibration. Accordingly, fixing the bubble outlet at intervals of 1 or more seconds allows the flow to be measured less than 30 mm^3/s with great accuracy. When the frequency of the formation of bubbles more than 1 time per second there is a measurement error. It consists of both the error of measuring the period and increasing the volume of a single bubble. The latter is due to the fact that the bubble detachment requires a time of the order of 0.2 s and in the case of a large gas flow, until it is separated from the surface of the capillary, its overflow occurs. Consequently, when bubbles exit with an interval of less than 1 s, this method can not be used.

The calculation of hydrogen permeability P, $mol/s{\cdot}m{\cdot}Pa^{0.5}$ when measuring the period of the appearance of hydrogen bubbles is made by the formula 1.

$$P = \frac{V \cdot \delta \cdot 10^{-6}}{V_M \cdot t \cdot S \cdot (\sqrt{p_2} - \sqrt{p_1})}, \quad (1)$$

where V – the volume of the bubble, mm^3; d - membrane thickness, m; VM – the molar volume of gas at the temperature and pressure of the flow entering the measuring device from the dm^3/mole unit; T – the bubble release time, s; P_2 – gas pressure on the membrane surface inside the chamber, Pa; P_1 – pressure of gas entering the measuring device, Pa; S – the area of the membrane, m^2.

Thus, the two methods for measuring hydrogen flow can be used as the basis for the method for determining the hydrogen permeability of membranes. They can be used in combination or separately.

Area of the test membrane. The increase in the area of the membrane in determining the hydrogen permeability of the material from which it is made allows not only to increase the accuracy of the measurement, but also to simultaneously evaluate the effect of dilatation on the duration of membrane operation prior to failure. It is obvious that when testing membranes from expensive palladium this will increase the cost of the experiment, however, in the case of testing the membranes from niobium, tantalum, vanadium, etc. The increase in material costs will not be significant. By comparing the hydrogen permeability of niobium, vanadium, tantalum, and a gas stream, which can be measured by determining the interval between gas bubbles, it has been found that for a circular membrane the optimal working diameter is 80-100 mm. The circular shape of the membrane is dictated by the use of standard flanges and sealing rings to ensure a sealed connection of the membrane to the measuring unit.

Temperature and pressure. Equipment for determining the hydrogen permeability of thin flat metal membranes should provide the ability to conduct measurements in the range of 250-650 °C and pressure from atmospheric and up to 1 MPa. In these intervals, as a rule, the hydrogen permeability of palladium, niobium, vanadium and tantalum membranes is measured, while covering the recommended interval for industrial use [1].

Gas permeable substrate. Upon contact with hydrogen, membranes based on niobium, tantalum, and vanadium become brittle at temperatures above 400 ° C for a short period of time (several dozen seconds) as a result of the dissolution of hydrogen in their crystal lattice. When a gas membrane with a thickness of 40-200 μm is applied to the surface of the gas pressure, in the absence of a base on which the membrane

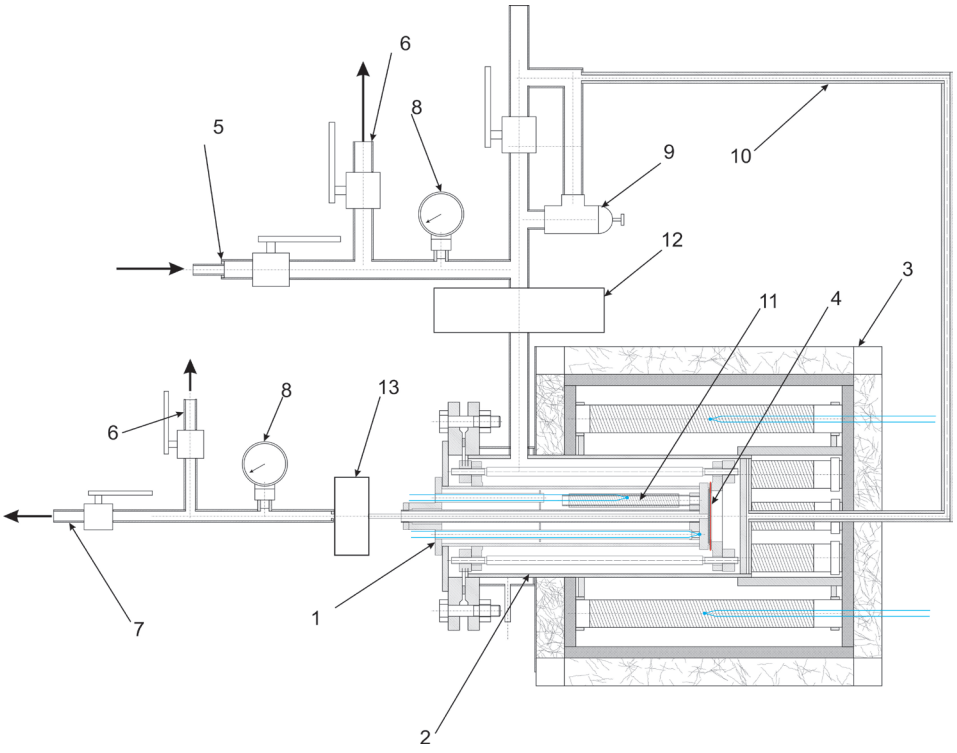
"breaks", its destruction will occur instantly, even if its area is not large. At the same time, the base to which the membrane adheres must ensure a stable removal of the filtered hydrogen from its outer surface, i. E. Should be characterized by sufficient porosity. The material from which a gas permeable substrate can be made should be characterized by inertness with respect to hydrogen in the indicated temperature range and minimally dissolving it in itself. A series of search experiments on the selection of various materials from which the substrate can be made led to the conclusion that chromium-nickel steel is optimal. From its powdered sintering, it is possible to produce gas permeable membrane substrates for industrial installations. For a laboratory installation for the determination of hydrogen permeability, the use of a stainless woven filter cloth, a plain weave with a mesh size of 80-200 microns (GOST 3187-76), is optimal. When conducting experiments in this pressure range, this grid does not deform and stably ensures gas permeability at a high level.

Results and its discussion. *Development of equipment. Materials for the manufacture of the chamber, pipelines and other units of equipment for determining the hydrogen permeability of metal membranes.* Analysis of literature data [13] showed that for the manufacture of parts of the plant in contact with hydrogen at high temperatures and pressures, the most suitable for such parameters as hydrogen solubility, hydrogen embrittlement, strength, heat resistance, price, manufacturability are chromium-nickel steels AISI 304, AISI 321, AISI 316, AISI 310, etc. At a relatively low price, they are characterized by heat resistance, low hydrogen dissolution, are well welded and processed by cutting, seamless pipes of various assortment, flanges, bends, etc. are manufactured industrially.

To seal the membrane tightly to the installation using pressure flanges, the gaskets can be made of copper or aluminum. These materials used in similar equipment, during numerous tests have shown the promise of further application. To prevent damage to the membrane, the gaskets must be in an annealed condition.

The sealing of the retort cover to prevent extrusion when hydrogen is injected into the retort cavity and its heating is suggested to be made from a fluoroplastic sheet F-40 of grade "P", which is an inert, non-porous, heat-resistant material.

The design of the apparatus for determining the hydrogen permeability of thin flat metal membranes. The main unit of the unit for determining the hydrogen permeability of flat membranes is a heated retort with a heated membrane holder (Figure 1), equipped with piping systems for gas supply, evacuation and discharge of purified gas, and an emergency gas discharge system. In the design of the Institute of Metallurgy and Ore Benefication, the retort has an internal diameter of 208 mm with a wall thickness of 6 mm and is made of steel AISI 316L. To prevent the release of hydrogen, in the event of a breach of the integrity of the welded seams of the bottom, it has an additional bottom with a branch pipe to divert gas from the furnace. The pipes used, the bottom, the flanges are designed for a maximum working pressure of up to 1.6 MPa, while



1 – holder of a membrane; 2 – retort; 3 – the furnace; 4 – metal membrane; 5 – a branch pipe of hydrogen (argon); 6 – branch pipe for evacuation of the system; 7 – branch pipe for extraction of purified hydrogen; 8 – a manometer (a vacuum gauge); 9 – protective valve; 10 – system of emergency removal of gaseous products; 11 – membrane heater; 12 – gas cooling system; 13 – electronic gas flow meter RRG-12

Figure 1– Installation for testing flat thin metal membranes for hydrogen permeability

in the case of excess of 1 MPa, a safety valve 9 is triggered, which releases the pressure by withdrawing gas to the discharge line 10.

To mount the membrane a holder has been designed (Figure 2), in which the sealing of the membrane with a gas permeable substrate is achieved by using spacers of flat aluminum washers 0.5 mm thick. They are pressed against the body of the holder by a flange with the help of pins. The holder is designed for fastening membranes with dimensions 120x120 mm, after which the working part of the membrane has a diameter of 100 mm.

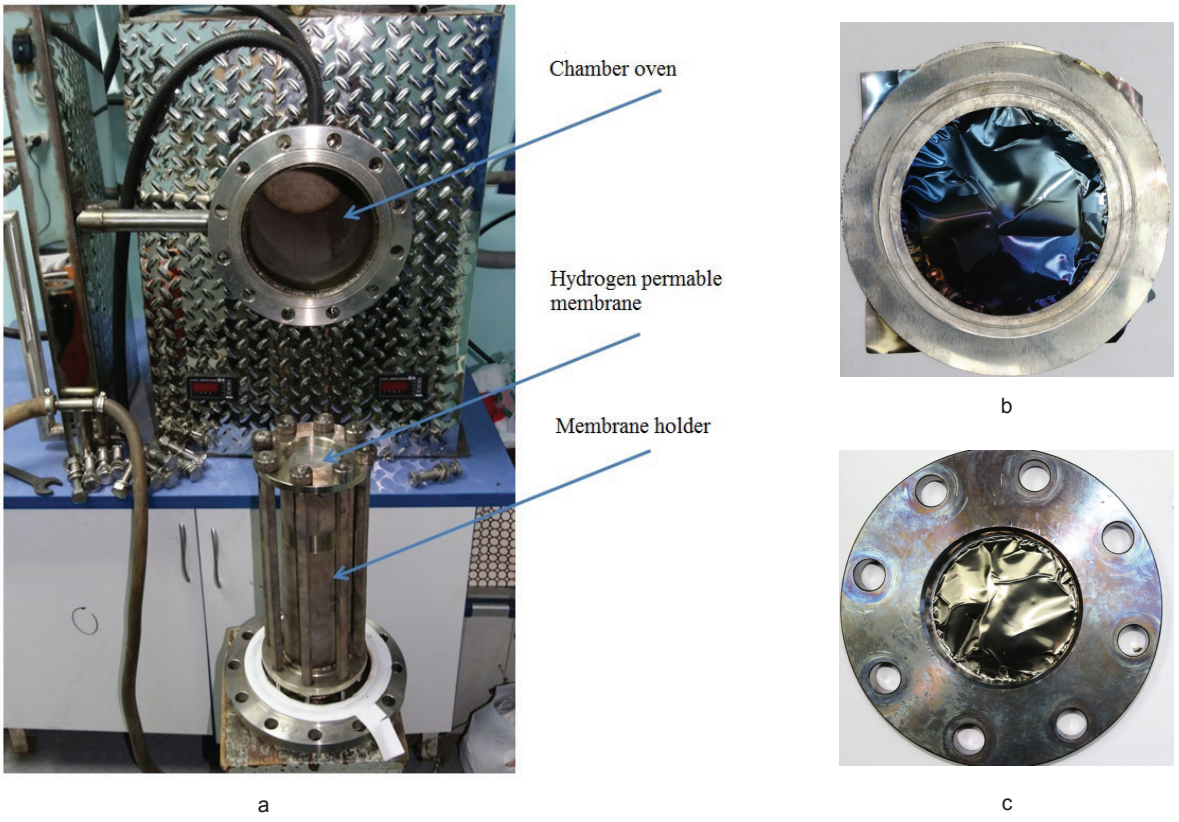
By selecting the materials of the diaphragm holder parts, during heating, additional flange clamping is provided due to the difference in the temperature coefficients of the linear thermal expansion of the attachment body and the studs that tighten the flanges. Since hydrogen is characterized by high thermal conductivity, which increases with pressure, it was necessary to equip the holder with an additional heater designed to meet the requirements of safe operation in order to maintain the specified temperature of the metal membrane. Heat from the heater is fed through a thick copper plate directly to the wall to which the membrane adheres, which ensures a uniform temperature field across the entire plane of the membrane.

To evaluate the actual temperature of the membrane, a chromel-alumel thermocouple is inserted into the inner cavity of the holder, contacting the wall to which a metal membrane adheres via a gas permeable substrate. Maintenance of the pre-set temperature of the heater and furnace is carried out with the aid of the OWEN TRM-10 PID controllers controlling solid-state relays. The temperature is measured by means of chromel-alumel thermocouples located in the furnace cavity and preheater.

The hydrogen or hydrogen-containing gas mixture system, controlled by manually operated valves, includes a pressure gauge (vacuum gauge) for monitoring the pressure, a tap for connecting the fore-vacuum pump, a valve for the controlled pump and a valve for emergency pressure relief.

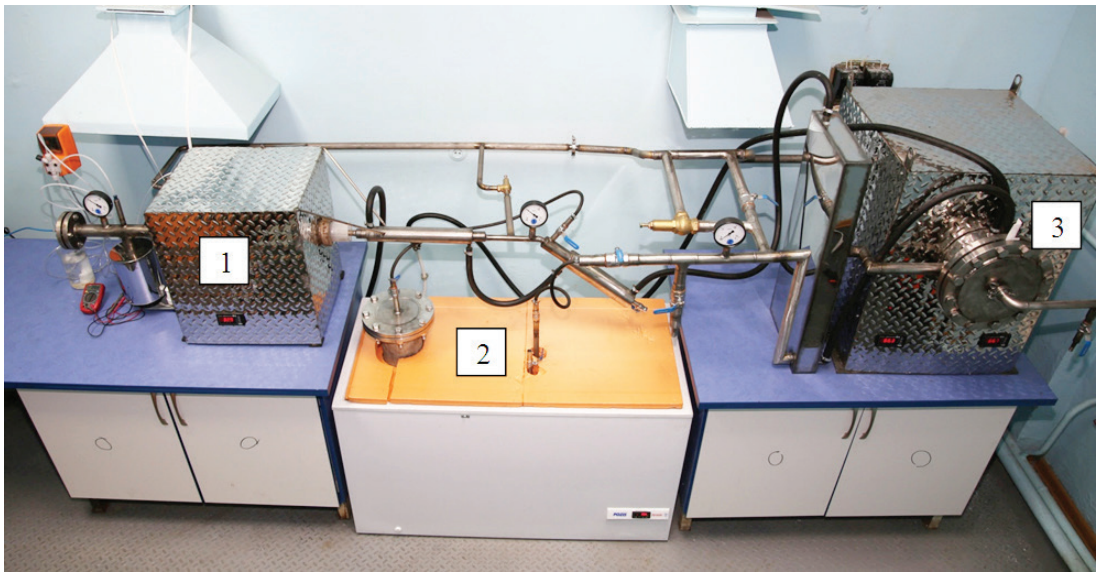
From the furnace, the hydrogen inlet system is separated by a cooler to cool the discharged gases, in order to prevent their self-ignition and damage to the seals in the valves. The refrigerator is cooled by running water from the cooling system of the furnace.

To dehydrate the incoming hydrogen or hydrogen-containing gas mixture, a special module is pro-



a - furnace with a membrane holder; b - membrane with sealing rings; c - diaphragm between flanges

Figure 2 – Installation for determining the hydrogen permeability of thin membranes



1 - argon purification module, 2 - hydrogen dehydration module, 3 - membrane module

Figure 3 - Membrane modular plant for production of ultrapure hydrogen from gas mixtures

vided in the device for determining hydrogen permeability (Figure 3). It is a cylindrical vessel whose outer walls are cooled by a freezer to -35 to -40 °C. The inner cavity of the vessel is filled with aluminum shavings, on the surface of which, when the gas is inflated, condensation of moisture occurs.

To study the operation of hydrogen permeable metal membranes under real conditions, a vapor conversion system for gaseous hydrocarbons was created, the principle of which is based on the industry-applied method of passing a vapor-gas mixture through a nickel catalyst. As a result of the catalytic reaction, a mixture of hydrogen with mono- and carbon dioxide is formed. The most intensive process occurs at 850-900 °C and pressure ~10 bar. The laboratory installation for the vapor conversion of gaseous hydrocarbons is designed for a capacity of ~2 dm^3/min at 10 bar (Figure 3). The installation for the precise proportions of the vapor-gas mixture uses a dosing pump and a flow meter. It provides protection systems that include a double wall of the reactor for venting gases to the emergency discharge system in the event of a burnout of the working pipe and safety valves to reduce the pressure of the gases in the installation when it exceeds 1 MPa. The external walls of the reactor are heated in a tubular resistance furnace controlled by the OWEN TRM-10 PID regulator. The gas obtained as a result of steam conversion is passed through the dehumidification module and can be stored in it as in a receiver. When replacing the nickel catalyst with titanium chips, this block can be used to purify argon used in experiments on hydrogen permeability.

Procedure for conducting experiments to determine the hydrogen permeability of flat metal membranes. After fixing the diaphragm, the holder with the cover is mounted on the furnace, the heater and thermocouples are installed. Vacuuming the cavity with the membrane to be separated, and then the chamber of the furnace, is performed. This pumping sequence is necessary to prevent the membrane from breaking through. Further, the furnace chamber is disconnected from the vacuum pump and argon is poured into it to flush the pipelines, after which the furnace chamber is again evacuated. When the vacuum pump is switched on, the oven is turned on and the chamber is heated to the set temperature, after which the heater power is connected and the temperature stabilizes. Then, the furnace chamber is disconnected from the vacuum pump and argon is introduced into the system to atmospheric pressure, the membrane tightness is checked according to the vacuum gauge. In the case of the integrity of the membrane and the tightness of its connection, in the cavity separated by a membrane, hydrogen or argon is added to atmospheric pressure. The branch pipe emerging from this cavity is switched to a gas flow meter. Hydrogen or a hydrogen-containing gas mixture is introduced into the chamber up to a given pressure. By means of a gas flowmeter or, in the case of a small gas flow, by measuring the gas bubble exit interval, a flow of hydrogen is measured. At the same time, the change in the wall temperature to which the membrane adheres is fixed. The experiment is carried out before the membrane breaks, which can be judged by a sharp increase in the flow of hydrogen.

According to the obtained data from formula 1, the hydrogen permeability of the membrane is calculated.

At present, more than 120 experiments have been carried out to determine the hydrogen permeability of niobium tantalum homogeneous cross-section diffusion-doped and composite membranes with a thickness of 40 μm. The conducted experiments showed high efficiency of measurements using an electronic flowmeter and a volumetric method. In addition to hydrogen permeability, the period before failure was determined, deformations on the membrane surface caused by dilatation were recorded.

The developed installation made it possible to carry out measurements under conditions of isothermal maintenance, smooth reduction and cyclic temperature change. It is characterized by the convenience of mounting the membrane in the holder and holder in the camera, reliability.

Conclusions. Thus, the proposed technique and the developed equipment allow, without the use of mass spectrometry, to effectively measure the hydrogen permeability of thin flat metal membranes. The design of the equipment meets the safety requirements for working with hydrogen and hydrogen-containing gases and allows measurements in a wide range of temperatures and pressures.

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ТҮЙІНДЕМЕ

Бұл жұмыста өлшеу кезінде масспектрометрді пайдаланап, жұқа жазық мембраналардың сутегі өткізгіштігін анықтаудың жетілдірілген әдістемесі келтірілген. Бұл әдістеменің өзгелерден айырмашылығы, көлемі жағынан үлкен мембраналарды пайдаланып, аралас әдіс көмегімен аз және көп көлемдегі газ ағынын өлшеуге мүмкіндік береді. 0,3л және одан да көп жылдамдықтағы, шекті ағынға дейінгі шамадағы шығымды өлшеу электр сигналмен калибрлеу арқылы газдың массалық шығымын жылулық түрлендіру әдісімен өлшенеді. Түтікшеден шыққан көпіршік шарлардың 30мм^3/с дейінгі шекті ағымының шығу интервалы анықталады. Үлкен көлемдегі мембрананы пайдаланудың артықшылығы, мембарананың сипаттамасы мен оның жұмыс жасау ресурсын және ұлғаю кезіндегі деформациясын анықтауға мүмкіндік береді. Жасалған сутегі өткізгіштікті анықтайтын қондырғы 650°С температураға және 10 Бар дейін жұмыс жасауы жазылған. Құрылғы мынадай бөлшектерден тұрады: пеш, ретorta, мембарананы жылыту ұстағышы, газ тәрізді булы конверсия модулі және қауіпсіздік жүйесі. Қондырғы әмбебап болып жасалған. Онда таза сутегі және басқа газ қоспаларын қолданып, изотермиялық температура жағдайында еркін және циклді түрде өзгерте отырып сутегі өткізгіштікті анықтауға болады. Бұл қондырғыда мембрананы бекіткішке, бекіткішті камераға орнату үшін қолайлы жағдай жасалған. Ұсынылған қондырғының жұмыс жасау реті келтірілген.

Түйінді сөздер: сутегіөткізгіштік, әдістеме, өлшеу, қондырғы, жұқа мембрана

РЕЗЮМЕ

В работе описана усовершенствованная методика определения водородопроницаемости плоских тонких металлических мембран, позволяющая исключить использование масс-спектрометрии при проведении измерений. Методика отличается использованием мембран большой площади (78,5·10^{-4} м^2), что делает возможным при помощи комбинированного метода измерять как большие, так и малые потоки газа. Методом теплового преобразования массового расхода газа в электрический сигнал с использованием калиброванных расходометров с погрешностью ±0, 9% измеряются предельные потоки со скоростью от 0,36 дм^3/ч и более. Волюмометрическим методом путем определения интервала выхода пузырьков водорода из капилляра определяются предельные потоки до 30 мм^3/с. Преимуществом применения мембран большой площади является возможность определения ресурса работы мембраны и характера ее деформации при дилатации. В работе дано описание разработанного оборудования для определения водородопроницаемости при температурах до 650 °С и давлении до 1 МПа. Оборудование включает печь с ретортой и подогреваемым держателем мембраны, модуль паровой конверсии газообразных углеводородов и модуль осушения газов. Оно оснащено системами безопасности, обеспечивающими стравливание избыточного давления и отключение электрического питания печи в случае превышения температуры заданной величины. Оборудование универсально и позволяет проводить измерение водородопроницаемости с использованием как чистого водорода, так и различных газовых смесей, в условиях изотермического поддержания, плавного снижения и циклического изменения температуры. Оно характеризуется удобством монтажа мембраны в держатель и держателя в камеру. Приведена последовательность работы с разработанным оборудованием.

Ключевые слова: водородопроницаемость, тонкие металлические мембраны, печь камерная, модульная установка, газовые смеси, ниобиевые и танталовые мембраны, диффузионнолегированные, композиционные мембраны

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