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HYDROGEN PERMEABILITY OF MEMBRANES BASED ON NIOBIUM AND TANTALUM FOILS IN THE ATMOSPHERE OF TECHNICAL PURITY HYDROGEN

Abstract: The paper presents the results of measuring the hydrogen permeability of membranes from niobium and tantalum foils with 40 μm of thickness. The measurements were carried out in a hydrogen atmosphere of technical purity with a smooth decrease in temperature followed by isothermal aging and under conditions of cyclic temperature variation. It is shown that the temperature and the magnitude of the excess pressure influence the hydrogen permeability of the niobium and tantalum membranes. A decrease in temperature causes a reduction in hydrogen permeability. The increase in hydrogen pressure shortens the period until the maximum of hydrogen permeability is reached. This indicates that an increase in the gas pressure loss accelerates the saturation of the membrane with hydrogen. The values of hydrogen permeability and the duration of the membrane before destruction are interrelated. The more hydrogen flow through the membrane, the faster it breaks down. When membranes function under cyclic temperature fluctuations, the period before their destruction is longer compared to that observed in membranes with a smooth temperature decrease followed by isothermal aging. This phenomenon is explained by a significant change in the solubility of hydrogen in niobium and tantalum in the range of 500-600 °C. Probably, a cyclic change in temperature leads to a decrease in the average concentration of hydrogen in niobium and tantalum and, as a result, increases their plasticity. Under conditions of cyclic temperature change, the optimal hydrogen permeability and the period before destruction of the niobium membrane show in the range of 535-555 °C at a pressure of 500 kPa, and membranes from tantalum in the range of 555-568 °C and 300-500 kPa. Investigation of the surface of membranes after contact with hydrogen showed that the main cause of their breakthrough are microcracks, which arise when crossing folds formed during membrane dilatation. It is assumed that the creation of conditions to prevent the crossing of folds and their more orderly formation will significantly increase the service life of hydrogen permeable membranes. Upon contact with technical grade hydrogen, the surface of the membranes of tantalum and niobium is coated with a thin oxide film. This leads to a decrease in hydrogen permeability over time.

Key words: hydrogen permeability, thin membranes, niobium, tantalum, dilatation, hydrogen

Introduction. Analysis of literature data shows that today in the world the most promising way to produce ultrapure hydrogen is the process of separation of gas mixtures H_2+CO+CO_2, formed during the steam conversion of hydrocarbons. The separation of hydrogen is carried out using inorganic membranes based on palladium and its alloys. The high cost of such membranes and the relatively short period of their operation significantly increases the cost of hydrogen. In this regard, the development of the hydrogen industry requires the development of new highly efficient and inexpensive hydrogen permeable membranes. Metals of the 5th group, in particular tantalum and niobium, are substantially cheaper than palladium and are characterized by high hydrogen-absorbing ability [1-4]. This allows them to make membranes for hydrogen purification, however, due to high hydrogen embrittlement and activity against such gases as CO, O_2, H_2O at hydrogen diffusion temperatures, the membranes from these metals change their characteristics and fail. As a result of interaction with reactive gases, as well as surface segregation of oxygen dissolved in the lattice, the surface of these metals is covered with an oxide film, which extremely hinders the catalytic dissociation of hydrogen molecules necessary for the absorption of hydrogen on the surface [1-5]. At operating temperatures (> 520 K) in contact with the components of a gas mixture containing hydrogen, the thickness of the oxide film increases [5]. However, if the pressure of the chemically active gases is sufficiently low, and the temperature of the membrane is high enough, such a film is practically not formed on its surface. Moreover, it is known that a thin oxide film leads the membrane to a superconductivity state along atomic hydrogen and more energy hydrogen particles [1].

In view of the fact that in typical gas mixtures, the pressure of such chemically active components as H_2O, CO_2, O_2, C_nH_m is large, it is required to protect the surface of the hydrogen permeable membrane from oxidation. It is believed that the most promising is a coating of palladium and its alloys, up to a few microns thick. Composite membranes based on metals of the 5 th group, coated with a thin layer of palladium, have been developed for a number of years [6-14], but they have not yet found commercial application. One of the problems facing the use of composite membranes from niobium and tantalum is the low thermal stability of the palladium coating, an insufficient obstacle to embrittlement of niobium and tantalum membranes at operating temperatures. Thus, it was found [9] that even at T> 723 K, membranes from palled niobium become brittle if the concentration of dissolved hydrogen H / Nb exceeds 0.25-0.3. In order not to exceed this maximum allowable concentration at the required pressures, the temperature should be sufficiently high, for example, at a pressure of 10 atm. T> 1100 K for niobium.

The problem of using niobium and tantalum as a material of hydrogen permeable membranes is very acute. Its solution can have a significant impact on the development of hydrogen energy in the world. This makes it necessary to conduct more in-depth studies of the behavior of membranes based on niobium foils and tantalum under various conditions.

Experimental part. *Experimental techniques and procedure.* Experiments on the determination of the hydrogen permeability of niobium and tantalum foils were carried out by the method and on the equipment described in [15]. The niobium foil (99.5 wt% Nb) and tantalum (99.92 wt% Ta) foil thickness 40 ± 4 μm produced by Ulba Metallurgical Plant JSC were subjected to testing. The foil was supplied in a roll of 120 mm wide tape. The area of the membrane subjected to the study had a round shape of ø 80 mm.

Measurement of hydrogen permeability was carried out at an excess pressure of hydrogen of grade B (GOST 3022-80) at 300, 400, 500, 600, 700 kPa and at the beginning of the experiment 550, 565, 580 °C under conditions of uniform temperature decrease followed by isothermal aging and under cyclic conditions temperature changes with oscillations up to ~±20°. Simultaneously with the value of the gas flow, the temperature of the base was fixed, to which the membrane adhered. The tests were carried out before the membrane burst. Hydrogen was additionally subjected to water purification by passing it through chilled to -40 °C aluminum chips.

Results and discussion. The results of measuring the hydrogen permeability of membranes from niobium and tantalum under conditions of modulated temperature decrease followed by isothermal aging and cyclic temperature fluctuations are presented in Tables 1 and 2. As follows from the data obtained, with a modulated temperature decrease, hydrogen permeability first increases, reaching a maximum after 200-500 s from the moment of contact of the membrane with hydrogen, and then decreases to certain values, the value of which under isothermal holding conditions does not significantly decrease with the course of time. In a number of cases, the destruction of the membrane occurs even before the stabilization of hydrogen permeability.

The period before destruction depends insufficiently on the temperature of the start of the experiment and the pressure.

Table 1 – Hydrogen permeability of membranes under conditions of modulated temperature decrease followed by isothermal section

Excess hydrogen pressure, kPa	Temperature of experiment start and isothermal section, °C	Maximum of hydrogen permeability $P \cdot 10^{-10}$, $mol/s \cdot m \cdot Pa^{0.5}$	Time of reaching the maximum of hydrogen permeability, sec	Hydrogen permeability P · 10-10 under isothermal conditions, $mol/s \cdot m \cdot Pa^{0.5}$	Time to destruction of membrane, sec.
Niobium foil 40 micron					
500	575; 525	1,35	700	0,55 - 0.62	4200
500	578; 561 (destruction)	3,4	400	3 at the time of destruction	680
600	585; 552 (destruction)	3,1	350	2,35	950
Tantalum foil 40 micron					
500	480; 350	1,17	750	0,02	Has not destructed to 12,300
700	565;527 (destruction)	6	200	2,7	1100
500	585; 557	3,3	420	2,4	1530

Under conditions of cyclic tests, the period of change in hydrogen permeability coincides with the period of temperature change of the membrane with a slight shift of the curves relative to each other. Obviously, this is due to the inertia of the temperature measurement. Practically in all the cases considered, active hydrogen evolution occurs at the stage of membrane heating and slowed down upon cooling. In some cases, hydrogen cooling completely stops when the membrane is cooled. Advantageously, after the expiration of ~2000 s from the moment of contact of the membrane with hydrogen, the average value of hydrogen permeability decreases slightly. With increasing temperature, there is a tendency to decrease the duration of the membrane operation until the moment of destruction, and an increase in the excess pressure of hydrogen practically does not affect this. In a number of cases, tests under identical conditions lead to different results on the duration of the membrane operation prior to its destruction.

An analysis of the data obtained indicates that the temperature and pressure are influenced by the hydrogen permeability of the niobium and tantalum membranes. A decrease in temperature causes a reduction in hydrogen permeability. In this case, the hydrogen pressure has an indirect effect on the actual temperature in the chamber. Since the value of the thermal conductivity of gases directly depends on the pressure, then with increasing hydrogen pressure, heat transfer increases when it contacts the water-cooled units of the installation. This leads to a decrease in the temperature inside the chamber in comparison with the preset.

Table 2 – Hydrogen permeability of membranes under cyclic temperature changes

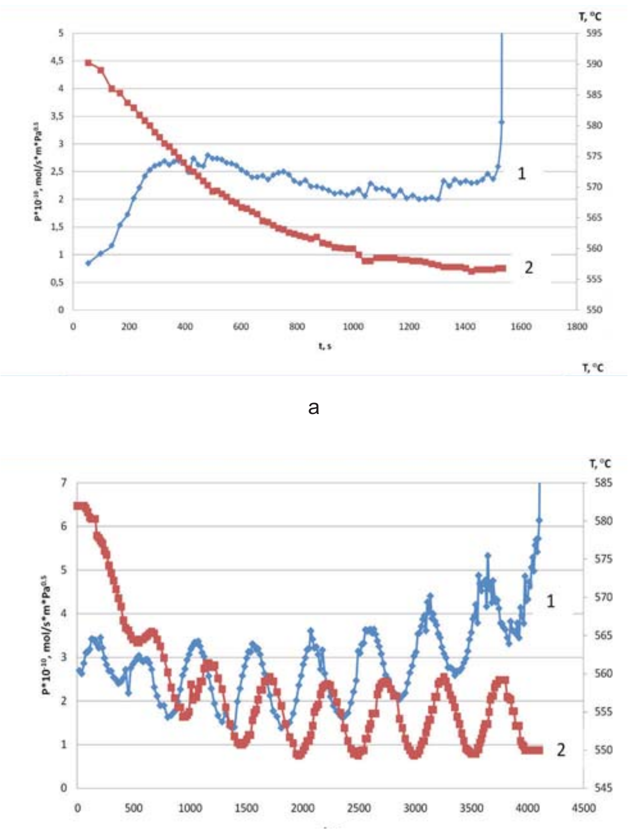
Excess hydrogen pressure, kPa	The temperature of the experiment start, °C	Interval and period, temperature fluctuations, °C and sec	Interval of vibration of hydrogen permeability $P \cdot 10^{-10}$, mol/ $s \cdot m \cdot Pa^{0.5}$	Time to membrane destruction, s	hydrogen permeability change characteristics
Niobium foil 40 microns					
500	545	510-520; ~500	from 0.2 to 1.7	3700	Cyclic change in hydrogen permeability with a period similar to the cycle of temperature change. Growth in the heating stage and decrease with cooling. Stabilization after 400-500 s from the moment of contact with hydrogen
600	550	512-533 ~500	from 1 to 2.3	1500	
300	565	537-552; ~500	from 0.3 to 2.5	2350	
500	565	525-540; ~500	from 0.6 to 4.2	2100	
700	565	512-525 ~250	from 0.05 to 1.3	7000 (Has not destructed)	
300	585	569-576; ~500	from 2 to 3.7	1050	
400	585	560-570; ~300	from 3.5 to 4.8	850	
600	585	558-568; ~500	from 1.1 to 2.7	1350	
700	585	555-558; ~350	from 2.7 to 3.5	900	
Tantalum foil 40 microns					
500	530	510-537; ~650	from 0.2 to 2.3	8300	Cyclic change in hydrogen permeability with a period similar to the cycle of temperature change. Growth in the heating stage and decrease with cooling. Stabilization after 400-500 s from the moment of contact with hydrogen
300	565	538-548; ~500	from 0.4 to 3	2400	
400	565	549-560; ~500	from 0.3 to 2.25	1600	
500	565	525-537; ~500	from 0.18 to 1.5 with a decrease to 0.1	Разрушение не произошло через 7000 с	
300	585	555-568; ~500	from 1.7 to 4.3	2200	
400	585	555-568; ~500	from 2.2 to 4.3 from 1.2 to 3.6 from 1.3 to 3.4	900, 1750, 4400	
500	585	548-562; ~500	from 1.3 to 3.3 from 0.2 to 1.6	4000 8300	
600	585	547-565; ~500	from 0.8 to 2.7	2400	
700	585	540 –557; ~550	from 0.2 to 1.7	3400	

On the temperature curves, this manifests itself in the form of a drop in the temperature in the chamber immediately after the hydrogen inlet and its subsequent stabilization at a lower level (Figure 1 a). During cyclic temperature fluctuations, after the hydrogen is introduced, the mean temperature and the amplitude of the oscillations decrease (Figure 1 b).

Increasing the hydrogen pressure shortens the period until a maximum of hydrogen permeability is reached, at which the membranes are smoothly cooled (Table 2). This indicates that an increase in the pressure drop of the gas accelerates the saturation of the membrane with hydrogen.

When comparing the values of hydrogen permeability and the duration of the membrane before destruction, their direct dependence is observed. The more hydrogen flow through the membrane, the faster it breaks down.

The membranes under conditions of cyclic temperature fluctuation demonstrate a significantly longer duration of operation prior to destruction, in comparison with those observed under conditions of smooth temperature decrease followed by isothermal aging. At the same temperature range, the average hydrogen flow rate is practically independent of the type of heating. The increase in the membrane operating time before destruction in conditions of temperature fluctuations can be explained by the significant dependence of hydrogen solubility in tantalum and niobium on temperature. Thus, according to the state diagram of the Ta-H system, the solubility of hydrogen at 500 °C is 22 at.%, And at 600 °C, 12 at.%. Such a significant change in solubility, apparently, helps to reduce the concentration of hydrogen in tantalum and niobium during thermal cycling, which provides a higher level of their plasticity.



a

b

a – gradual cooling and isothermal aging, b – thermocycling
1 – hydrogen permeability, 2 – temperature

Figure 1 – Dependence of the hydrogen permeability of a tantalum membrane on the type of heating at a hydrogen pressure of 500 kPa

In this case, the optimal hydrogen permeability and the period before destruction of the niobium membrane show in the range of 535-555 °C at a pressure of 500 kPa, and membranes from tantalum in the range of 555-568 °C and 300-500 kPa.

Investigation of the surface of membranes after extraction from the installation by definition of hydrogen permeability showed that as a result of dilatation they acquire a network of folds that form cells of various sizes (Figure 2). At the same time, the greater the pressure of hydrogen, the more acute folding tips were observed in the membranes. Revealing the causes of breakthroughs of membranes showed that in the overwhelming majority of them microcracks appeared at the intersection of folds (Figure 2). Since the dissolution of hydrogen in niobium and tantalum sharply reduces their plasticity, the formation of a crack will occur at the point of concentration of stresses, which can be both intersecting folds and the area of contact with the sealing rings. The appearance of such folds at a pressure of 300 to 700 kPa indicates the occurrence of very high stresses in the crystal lattice of the membranes causing the foil portions to shift relative to the gas permeable substrate. Obviously, the compressive stresses that arise under such conditions prevent rapid destruction of the membrane. Since the direction of the formation of folds under such conditions is not predictable, it is impossible to predict the occurrence of foci of stress concentration. The creation of conditions to prevent the crossing of folds and their more orderly formation will significantly increase the life of hydrogen permeable membranes.

The difference in hydrogen permeability of membranes revealed under the same experimental conditions is due primarily to the difference in the properties of the membrane surface. The main reason for this is the formation of an oxide layer that slows the diffusion of hydrogen into the membrane. This reduces the flow of hydrogen through the membrane, which keeps its plasticity at a sufficiently high level. The stresses arising during the formation of folds are not sufficient for the initiation of a crack. The oxide layer on the surface of the membrane can occur both in the factory environment and directly on contact with hydrogen contaminated with oxygen. The latter is confirmed by a decrease in hydrogen permeability with time, and by a change in the color of the surface of the membranes from tantalum.

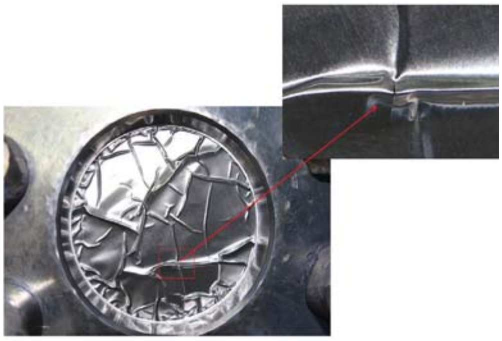


Figure 2 – Formation of a crack in hydrogen permeable membranes as a result of dilatation

Conclusions. As can be seen from the above, an increase in the service life of membranes from foils of tantalum and niobium can be achieved by a set of measures. Providing an increase in the corrosion resistance of the membrane surface facing the hydrogen-containing gas mixture will ensure the stability of the properties during their operation. The creation of conditions for controlled deformation of membranes during dilatation will reduce the probability of formation of foci of internal negative stresses that cause cracks in the low-plastic membrane material. Cyclic temperature changes can significantly increase the service life of the membrane in comparison with the isothermal conditions of their operation. This makes it promising to use this method to increase the service life of membrane modular plants for the production of ultrapure hydrogen made from metals with a sharply varying hydrogen solubility as a function of temperature.

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ТҮЙІНДЕМЕ

Бұл жұмыста 40 мкм қалыңдықтағы тантал және ниоби фольгаларынан жасалған мембраналардың сутегіөткізгіштігін өлшеу нәтижесі көрсетілген. Өлшеулер температураның үздіксіз төмендеумен техникалық таза сутегі атмосферасында изотермиялық ұстау және циклдік температураның өзгеруі бойынша жүргізілді. Онда ниобий және тантал мембраналарының сутегіөткізгіштігіне температура мен артық қысымының мөлшерін әсері деп көрсетілген. Температураның төмендеуі сутегі өткізгіштігінің төмендеуін туғызады. Сутегі қысымының өсуі сутегіөткізгіштің максимум деңгейіне дейін мерзімін азайтады. Бұл газ қысымының артуы мембрананың сутегімен қанықтыру деңгейін тездететінін көрсетеді. Мембраналардың сынуға дейінгі жұмыс жасау ұзақтығы мен сыну мәндері бір-бірімен байланысты. Мембрана арқылы сутегі ағыны үлкен көлемде өткен сайын, оның бұзылуы жиілейді. Ол, мембраналар изотермиялық әсерінен кейін температураның тегіс төмендету бақылау жағдайымен салыстырғанда циклдық вариация температура жағдайында сутегі өткізгіштігінің сынғанға дейін жұмыс жасау уақытының едәуір көп ұзақтығын және сутегіөткізшткіктің ұзақтығын көрсететіні анықталды. Бұл құбылыс қатты 500-600°С диапазон аралағындағы температурада тантал және ниобийда сутегінің еруінің әртүрлі өзгеруі арқылы түсіндіріледі, бәлкім сутегі диффузия ықпал етеді, тантал және ниобиде сутегінің орташа концентрациясының төмендеуіне алап келеді нәтижесінде олардың пластикалық қасиетін арттырады. Температураны циклды өзгерту жағдайнда ниобий мембраналардың сутегіөткізштігінің оңтайлы режимі және мембрананың сыуға дейінгі аралығы 500 кПа қысымда 535-555°С , ал тантал бойынша 555-568°С және 300-500 кПа. Мембрананың сутегімен байланысынан кейін бетін зерттеу, олардың жарылуының негізгі себебі мембрананың кеңеюі кезінде түзілетін қатпарлардың қиылысында туындайтын микрожарықтар екенін көрсетті. Ол қатпарлардың қиылысын және одан ұтымды нысанын болдырмау үшін жағдай жасау айтарлықтай сутегі-өткізгіштігіне мембраналар қызмет мерзімін ұлғайтуға мүмкіндік береді деп күтілуде. Тантал мен ниобий мембраналарының бетінің техникалық тазасутегімен байланысында, жұқа тотықты пленкамен жабылады. Бұл ұзақ уақыт бойы сутегі өткізгіштігінің азаюына әкеледі.

Түйін сөздер: сутегіөткізгіштік, жұқа мембрана, ниобий, тантал, кеңею, сутегі.

РЕЗЮМЕ

В работе представлены результаты измерения водородопроницаемости мембран из фольг ниобия и тантала толщиной 40 мкм. Измерения были проведены в атмосфере водорода технической чистоты при плавном снижении температуры с последующей изотермической выдержкой и в условиях циклического колебания температуры. Показано, что на водородопроницаемость ниобиевой и танталовой мембраны влияние оказывают температура и величина избыточного давления. Уменьшение температуры вызывает снижение водородопроницаемости. Повышение давления водорода сокращает период до достижения максимума водородопроницаемости. Это указывает на то, что увеличение перепада давления газа ускоряет насыщение мембраны водородом. Величины водородопроницаемости и продолжительности работы мембраны до разрушения являются взаимосвязанными. Чем больше поток водорода через мембрану, тем быстрее происходит ее разрушение. При функционировании мембран в условиях циклического колебания температуры период до их разрушения больше в сравнении с наблюдаемым у мембран при плавном снижении температуры с последующей изотермической выдержкой. Это явление объяснено существенным изменением растворимости водорода в ниобии и тантале в интервале 500-600 °С. Вероятно, циклическое изменение температуры приводит к снижению средней концентрации водорода в ниобии и тантале и как следствие повышает их пластичность. В условиях циклического изменения температуры оптимальные водородопроницаемость и период до разрушения мембраны из ниобия демонстрируют в интервале 535-555 °С при давлении 500 кПа, а мембраны из тантала в интервале 555-568 °С и 300-500 кПа. Исследование поверхности мембран после контакта с водородом показало, что основной причиной их прорыва являются микротрещины, возникающие при пересечении складок, образующихся при дилатации мембраны. Предположено, что создание условий для предотвращения пересечения складок и их более упорядоченного формирования позволит существенно увеличить ресурс работы водородопроницаемых мембран. При контакте с водородом технической чистоты поверхность мембран из тантала и ниобия покрывается тонкой оксидной пленкой. Это приводит к снижению водородопроницаемости с течением времени.

Ключевые слова: водородопроницаемость, тонкие мембраны, ниобий, тантал, дилатация, водород

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ПОЛУЧЕНИЕ TiN/Al_2O_3 ПОКРЫТИЙ МЕТОДОМ МЕХАНИЧЕСКОГО СПЛАВЛЕНИЯ

Резюме: Представлены результаты исследования морфологии поверхности и механические свойства покрытий TiN/Al_2O_3, полученных методом механического сплавления (МС). Установлено, что формирование морфологии поверхности покрытий из порошковых материалов на подложке зависит от эффективности пребывания компонентов порошка в зоне динамической нагрузки удара шаров. Рентгенофазовое исследование TiN/Al_2O_3 покрытий показало уширение дифракционных пиков, что