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Evaluation of Niobium and Tantalum-Based Materials of the Hydrogen-Permeability Membranes for the Degree of Deformation and the Optimal Temperature Range of Exploitation

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ABSTRACT

The data are presented for the dilatation of 10 μm Nb and 80 μm Ta foil samples with a double-sided 0.15 μm Pd catalytic coating in a hydrogen atmosphere at d temperature of 400-900 °C and a pressure of 100-1000 kPa. These results were obtained with the help of direct measuring the extension of the foil strips under isothermal exposure at a given hydrogen pressure. Based on the data obtained on dilatation and previously published data on the concentration of hydrogen in the α-solid solution at 400 °C, the values of the dilatation coefficient. $\Delta\upsilon\Omega$ were calculated. Using the results of dilatation measurements and dilatation coefficients, the isobars of temperature dependence of hydrogen concentration in Nb and Ta were calculated and constructed. These data made it possible to estimate the limiting change in concentration and linear dimensions over the cross section of a hydrogen permeable membrane of Nb and Ta at various temperatures and operating pressures at the inlet and outlet of the membrane. According to Fick's 1st law and previously published data on the hydrogen concentration value at which solid solutions of Group V metals turn into a brittle state, based on the results obtained, it was concluded that operating conditions of the composite membranes based on Nb and Ta, when used for the release of ultrapure hydrogen, are optimal.

Keywords: Hydrogen dilatation, niobium, tantalum, composite hydrogen permeable membrane, barrier layer, catalytic coating

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INTRODUCTION

Membrane separation of hydrogen-containing gas mixtures is one of the most promising methods for producing ultrapure hydrogen. However, the industrial use of this method is extremely limited due to the use of expensive palladium and palladium-based alloys as a membrane material. From [1- 5] write that hydrogen transport through Group V metals (V, Nb, Ta) is by orders of magnitude faster as compared to palladium This is due to the fact that the rate of transcrystalline hydrogen transfer in these metals is an order of magnitude higher than that in palladium and palladium-based alloys, that is explained by a low barrier and a high hydrogen diffusion coefficient was written by [6].

Relatively low cost that is by orders of magnitude less in comparison with palladium is also an undeniable advantage of such metals. However, a number of disadvantages of membranes made of these metals do not to make it possible to use such membranes. [4] and [7- 13] note that some significant problems have been relatively well resolved enabling us to expect practical applications of membranes based on such metals in the future. In that way, a double-sided deposition of layers of palladium or palladium alloys solved the problem of protecting the membrane surface from oxidation and improving its catalytic activity in order to increase the rate of dissociative-associative processes [7] and [9-13] state that the effect of hydrogen embrittlement was eliminated by developing alloys based on Group V metals having reduced hydrogen solubility, but the hydrogen permeability was maintained at a sufficient level However, even these technical solutions require further improvements.

High hydrogen dilatation complicating the connection of membranes with structural elements of membrane modules made of heat-resistant steels is one of the problems limiting the use of membranes based on these metals. This phenomenon, combined with a sharp decrease in ductility during the dissolution of hydrogen, causes membrane destruction. Thus, it must be taken into account when designing membrane separation systems based on vanadium, niobium, and tantalum.

Upon dissolution, hydrogen atoms in metals with a body-centered cubic lattice occupy tetrahedral pores, causing lattice distortion resulting in a change in crystal volumes was substantiated in works [14-19] and crystal lattice parameters, accordingly [20-21]. It is known that the relative change in the $\Delta V/V$ volume of a metal crystal due to the dissolution of hydrogen with the atomic concentration $c = H/M$, is described as follows:

$$\frac{\Delta V}{V} = c \cdot \frac{\Delta\vartheta}{\Omega} \qquad 1.$$

where $\Delta\upsilon$ is the change in volume per hydrogen atom; and Ω is the average volume per metal atom. $\Delta\upsilon / \Omega$ is the dilatation coefficient independent of concentration (c). For metals with a cubic crystal lattice, a change in one of the dimensions of the sample (e.g., length, $\Delta L/L$) is described as the following ratio:

$$\frac{\Delta L}{L} = \frac{1}{3} \cdot c \cdot \frac{\Delta\vartheta}{\Omega} \qquad 2.$$

According to the results of experimental studies summarized by [22], the change in the volume of niobium upon dissolution of hydrogen reaches 15% at an equiatomic concentration of hydrogen, and in the case of tantalum this value reaches 6% upon dissolution of ~40 at. % hydrogen. A generalization of the experimental data on the hydrogen dilatation of single-crystal samples allowed the authors of [22] to point out the most probable values of the relative change in $\Delta \upsilon / \Omega$ upon dissolution of hydrogen in Nb and Ta, which are 0.174 ± 0.005 and 0.155 ± 0.005, respectively. This is lower than that of Pd and V (0.19 ± 0.01), however, Nb, Ta and V, in contrast to Pd, dissolve significantly larger amounts of hydrogen and, as a result, are more prone to embrittlement.

As the experimental data summarized in [6] show, with an increase in the hydrogen pressure from 0.001 to 0.1 MPa, there is a significant increase in its solubility in V, Nb, and Ta at high temperatures. At the same time, with an increase in temperature from 400 to 800 ° C, a sharp decrease in solubility is observed.

The P-C isotherms given in [23] for the Nb-H system indicate that in the range of 300–450 ° C at a hydrogen pressure of 700 kPa, the ratio of hydrogen to metal atoms (H/M) is ~ 0.7. In the Ta-H system at a temperature of 400°C and H_2 pressure of 80 kPa, the H concentration reaches 30% (0.43) [24]. The expected [7] ratio of H/M atoms for this system at 700 kPa is approximately 0.67, corresponding to a hydrogen concentration of 40 at.%. According to the data of [25] , the H/M ratio measured for V, using the Sievert method at 400°C in the pressure range of 100 to 700 kPa varies from 0.46 to 0.6. The dilatation of these metals can be calculated using the expression 1 and the above values $\Delta\upsilon/\Omega$. In that way, at 400°C and 7 bars, it will be 0.12 for Nb, 0.1 for Ta and 0.114 for V. Accordingly, the linear dimensions of the membrane of these metals falling into the hydrogen-containing atmosphere, when reaching the equilibrium content of H, should increase by 3.3-4%. However, on the opposite side, e.g., at a hydrogen pressure of 100 kPa, the dilatation of the membrane from V will reach 0.087. Respectively, favorable compressive stresses arise from the high-pressure side and unfavorable tensile stresses arise from the opposite side of the membrane. The difference of 0.9% for V and 1.24% for Ta should be compensated with plastic deformation of the membrane from the low-pressure side. The plasticity level of the membrane material in this layer should be high enough so that no cracks occur. However, cracks are more likely to form if plasticity is insufficient. We cannot exclude the development of the plastic flow of the metal due to the occurrence of the Gorsky effect resulting in a gradual stress relief. But this process will obviously proceed at a low speed.

The highest stresses in the membrane will occur at its junction with the substrate which does not undergo deformation in a hydrogen atmosphere. In this region, bulk plastic deformation of Ta, V, or Nb membranes by 3.3–4% should occur. In the case of insufficient plasticity of the membrane, this must inevitably lead to rapid membrane destruction. Meanwhile, in practice, in the article [26] flat membranes predominantly collapse at relatively high temperatures (550-600 ° C) due to the formation of folds which, if intersected, lead to substantially larger deformations. This indicates a certain margin of plasticity under these conditions.

The significant effect of pressure on the solubility of hydrogen and the non-linear nature of the change in the lattice parameters of the α -phase at high hydrogen concentrations indicates the inability to accurately calculate the linear dimensions of membranes based on Group V metals for various operating parameters. In addition, there is practically no information in the literature on the ultimate solubility of hydrogen in V, Nb, and Ta in the temperature range of 400–800 ° C and at a hydrogen pressure of more than 0.1 MPa. In this regard, in order to expand prospects of developments in the field of membrane technologies, it is important to obtain experimental data on changes in the linear dimensions of V, Nb and Ta at a hydrogen pressure of up to 1 MPa and a temperature of up to 900°C.

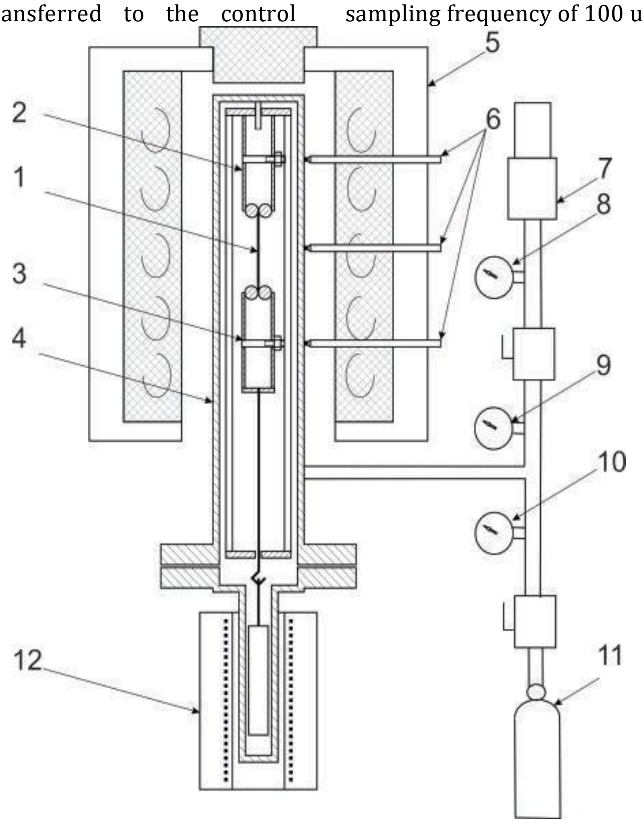
MATERIALS AND METHODS

The tests were carried out by directly measuring the change in the length of a flat sample under isothermal exposure at a certain pressure. Nb 120x12x0.01 mm and Ta 120x12x0.08 mm foil strips were used as samples. Table 1 shows the information on the composition of the materials used in the experiments. To ensure the dissociation of hydrogen molecules and reduce the effect of the oxide film on hydrogen diffusion, a 0.15 µm palladium layer was applied on both sides of the foil. Deposition was carried out by magnetron sputtering after ion surface cleaning. The hydrogen used in the experiments contained 99.99% of the basic substance.

Table 1. The content of impurities in the materials used in the experiments

	W+Mo	Ti	Fe	Ta	Si	C	N	H	O	Nb
Nb	0.0071	<0,001	<0,001	0,034	0,0011	0,0045	0,0045	0,0002	0,023	-
Ta	<0,0003	<0,00008	<0,0003	-	<0,0007	<0,002	0.0028	<0,0002	0.001	<0,003

The measurements were carried out on a setup developed on the basis of Shimadzu AG 100kNx, an electromechanical testing machine. Figure 1 schematically shows the design of the test chamber with a sample placed therein. One end of the sample was clamped into cylindrical jaws in the holder, then a suspension was fixed to it on the other side; at the end of the suspension there was a hook for the core of the measuring instrument. The measuring base of the fixed sample was 100 mm. The holder was rigidly mounted inside the chamber. The upper part of the chamber was heated using a three-zone split furnace of the test machine. Such a furnace provided a temperature difference of not more than ±3°C along the sample length. Vacuum pumping and gas puffing were carried out through a pipe in the lower part of the chamber. Gas pressure was monitored using a digital monometer OVEN PD200-DI1.0-315-0.1-2-N and a vacuum gauge Meradat-VIT12T4. To measure the deformation of the sample, a DT-10S Shinko Electric extensometer with a measurement accuracy of ±5 µm was used. An analog signal from the sensor was amplified with the electronics of the testing machine and converted to digital signal, and then transferred to the control computer program TRAPEZIUMX1.5.0c. As a result, the dependences of the sample deformation on time with a sampling frequency of 100 u/s were obtained.



1 - sample; 2 - sample holder; 3 - suspension; 4 - high pressure chamber; 5 - three-zone furnace; 6 - thermocouples; 7 - vacuum pump; 8 - vacuum gauge Meradat-VIT12T4; 9 - control pressure gauge; 10 - digital monometer OVEN PD200-DI1,0-315-0,1-2-N; 11 - cylinder with hydrogen and a control gear; 12 - extensometer DT-10S Shinko Electric

Figure 1. Diagram of an experimental setup for studying the dilatation of metals in a hydrogen atmosphere.

The chamber with the installed sample, upon sealing, was evacuated to a residual pressure of 10^{-2} Pa and heated during continuous pumping to a set temperature. After stabilization of the temperature, the vacuum channel was closed, and hydrogen was injected to a set pressure. The pressure was modified in the range from 0.1 to 1 MPa in increments of ~ 0.1 MPa and maintained at a level no worse than ±0.003 MPa. The measurements were carried out until the sample length stabilized (Figure 2). After completing the measurement cycle at one temperature, the chamber was evacuated, and the residual deformation of the sample was measured. Then, the sample was replaced with a new one, and measurements were carried out at a different temperature.

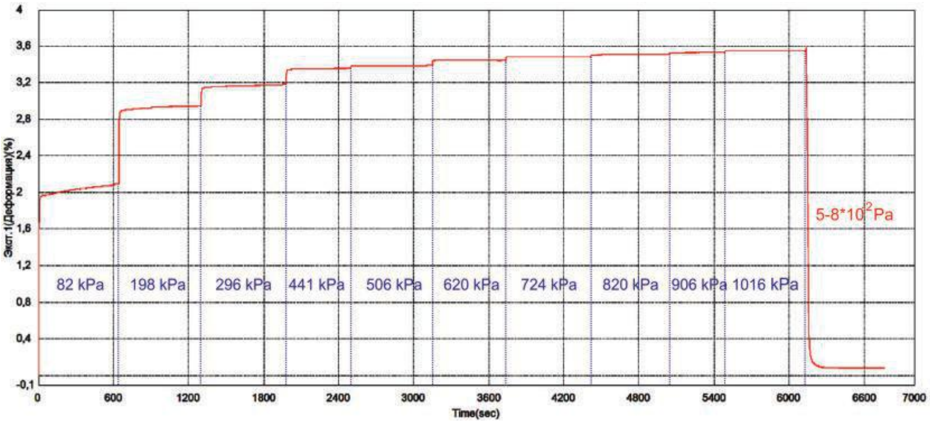


Figure 2. Sample extension curve for Pd 0.15 μm/Nb 10μm/Pd 0.15 μm, obtained with a stepwise increase in pressure at 500°C

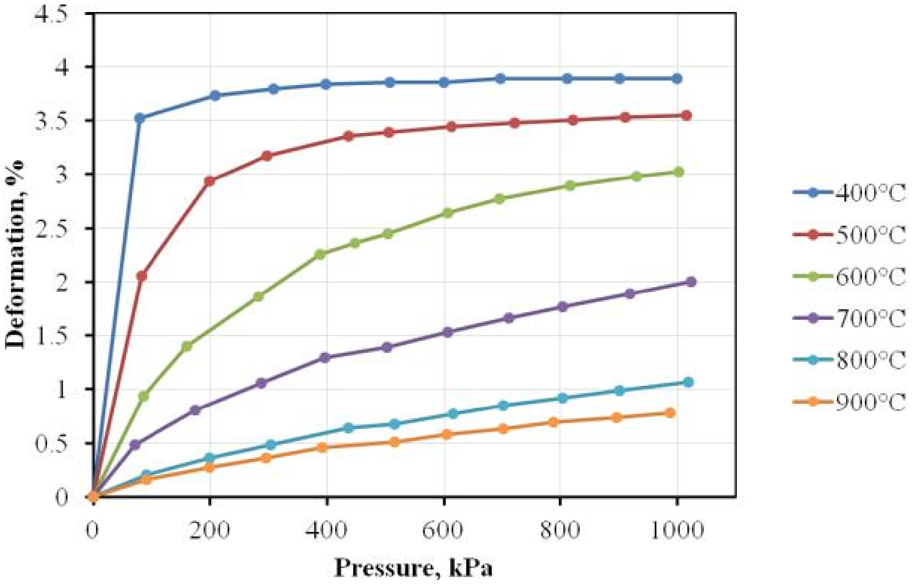
The resulting isotherms of pressure dependence of the sample deformation were recalculated by expression 2 into isobars of the temperature dependence of the ratio of H/M atoms, using $\Delta\upsilon/\Omega$ values known for V, Nb, and Ta.

RESULTS AND DISCUSSION

The pressure dependences of niobium and tantalum are shown in Figure 3. The analysis of the obtained isotherms shows that if pressure increases, the ΔL/L of Ta and Nb samples increases appropriately. The highest Δ L/L is observed at 400 ° C and 1000 kPa, and if temperature increases, the dilatation value decreases appropriately. In the range of 400-500 °C, the most significant increase in ΔL/L is observed if pressure increases from 0 to 200 kPa. With a further increase in P, the growth of dilatation decreases significantly. At a temperature of 400 °C and a pressure of > 800 kPa, dilatation reaches $3.89 * 10^{-2}$. Similarly, at 500 °C the increment of ΔL/L in the range of 910-1100 kPa is $2.2*10^{-4}$, indicating that the dilatation curve goes to a plateau when this value reaches $\sim 3.6*10^{-2}$. As the temperature rises above 500 ° C, the increase in ΔL/L with increasing pressure decreases to a lesser extent. Isotherms at 800 and 900° C in the range from 0 to 1000 kPa take the form of straight lines indicating a close-to-linear dependence of the function f (ΔL/L) on P.

When pressure changes, the obtained isotherms of deformation of Nb and Ta samples are directly related to the change in the solubility of hydrogen in the crystal lattice of these metals according to equation 2. This provides an opportunity to calculate the change in the concentration of hydrogen in niobium and tantalum when pressure and temperature change, as well as to estimate the limiting change in the concentration of H over the cross section of the membrane during filtration.

The experimental data presented in the literature on the solubility of hydrogen in Group V elements are very limited and contradictory. This is due to a significant change in the limiting concentration of hydrogen with a change in temperature and pressure complicating the study. Fromm (1976) et. al. presented the generalized results of the studied solubility of H in a α-solid solution of Group V elements at high temperatures and hydrogen concentration in the form of an equation. Hydrogen solubility isobars were calculated for pressures of 100 and 1000 kPa, using equations 3 and 4 for Nb and Ta, respectively.



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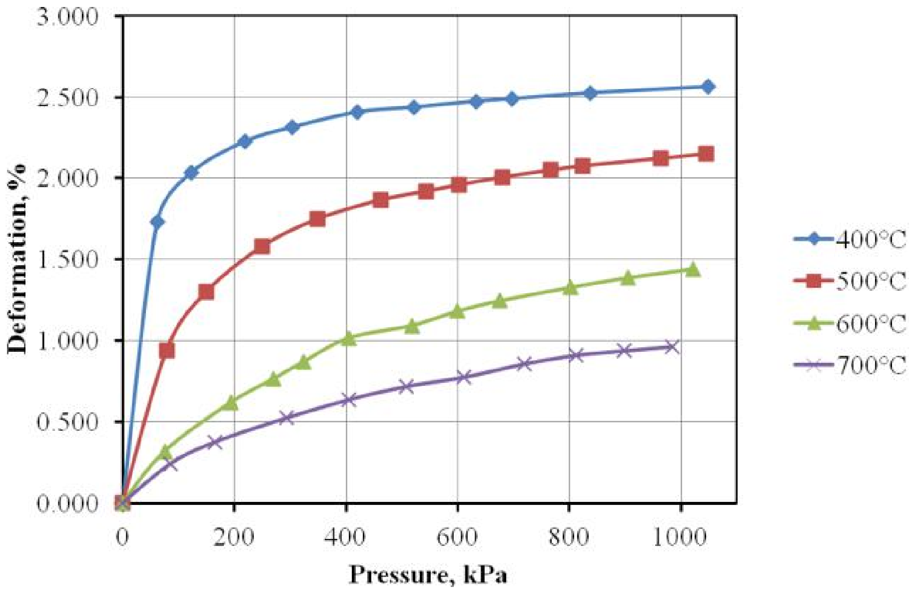


b

a - Nb; b – Ta

Figure 3. Isotherms of deformation of Nb and Ta samples upon pressure modification

$$T=(1843+1738*r-3847*r^2+8395*r^3-7039*r^4)/\ (\lg r-\lg\ (0.904-r)\ +4.45-0.5*\lg P) \qquad 3.$$

$$T=(1760+1447*r-3629*r^2+7411*r^3-7367*r^4)/\ (\lg r-\lg\ (0.702-r)\ +4.33-0{,}5*\lg P) \qquad 4.$$

where r = c/(100-c), T is the temperature K, P is the hydrogen pressure, mmHg

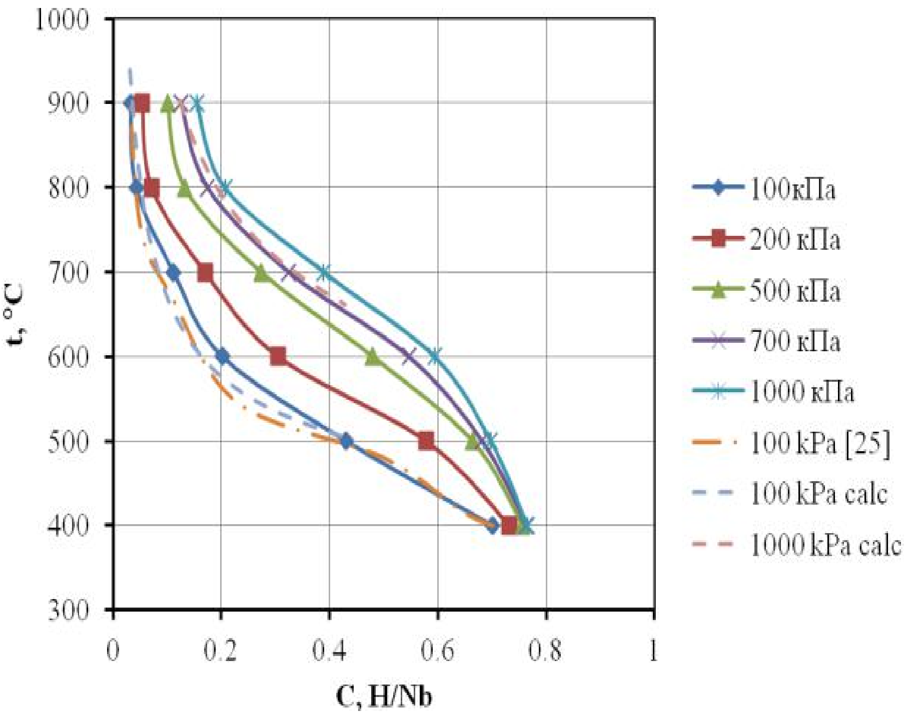
Figure 4 shows these results and experimental solubility data obtained in [27-28] at a hydrogen P of 100 kPa. A comparison of these data with isobars of the temperature dependence of the ratio of C H/M atoms (where M is Nb or Ta), obtained by measuring the dilatation at P = 100 kPa, showed that at $\Delta \upsilon / \Omega$ = 0.174 for Nb and 0.155 for Ta, there is a significant deviation of the curve towards lower concentrations. Since the data summarized in [27] et. al. indicates that the value of $\Delta \upsilon / \Omega$ for polycrystalline samples is lower, this value was recalculated based on the known concentrations of ultimate solubility at a temperature of 400°C and a pressure of 100 kPa shown in articles [28-29]. The data obtained suggest the value of $\Delta \upsilon / \Omega$ is 0.153 for Nb and 0.126 for Ta. Using these coefficients and the obtained dilatation data, isobars were calculated for the temperature dependence of the ratio of C H/M atoms (Figure 4). The plotted curves are in good agreement with previously obtained experimental materials and calculation results by [6] and [27-28].

The limiting gradient of hydrogen concentration arising over the membrane cross section at hydrogen inlet pressure of 500, 700 and 1000 kPa and at the outlet of 100 kPa at various temperatures was calculated based on the obtained data. As the data obtained (Figure 5) show, in Nb and Ta membranes, with an increase in temperature from 400 to 900 ° C, a significant increase in the limiting concentration gradient will be observed with a maximum of ~600°C in the case of Nb and ~500°C in the case of Ta. This, in accordance with Fick's 1st law (formula 5), will provide the greatest value of the hydrogen flux through Nb and Ta membranes in the region of 600 ° C. However, such a large difference in concentration will lead to the greatest internal stresses due to the heterogeneity of dilatation along the membrane cross section (Figure 5).

$$J = D \cdot \frac{|\Delta C|}{d} \qquad 5.$$

According to [29], the transition of Nb from a plastic state to a brittle state occurs when the concentration of hydrogen dissolved in it (H/M > 0.25–0.3) is exceeded and does not depend on temperature up to 500°C. [31] is consistent with these results to a certain extent, however, it indicates that with an increase in temperature above 300°C, the hydrogen concentration at which the transition of Nb to the brittle state occurs is substantially increased, and at 400 ° C it reaches 0.7. The difference in the results can be explained by the difference in the deformation patterns of the samples. Since it was also established for V [29] write that the transition from the plastic state to brittle one occurs when the hydrogen concentration exceeds 0.22, similar values of the concentration should be expected in the case of Ta. Considering the fact that according to the Ta-H state diagram, the decomposition of α-solid solution occurs at a temperature more than 100 degrees lower in comparison with the Nb-H system, a lower transition temperature from the brittle state to plastic one of tantalum upon hydrogen dissolution should be expected.

It can be concluded that composite Pd/Nb/Pd membranes should be operated at temperatures above 670 ° C at a hydrogen pressure of 500 kPa at the inlet and 100 kPa at the outlet based on the temperature and hydrogen concentration at which Nb embrittlement occurs [30-32] gah, as well as on the obtained isobars (Figure 4) and concentration gradient (Figure 5),. Similarly, for Pd/Ta/Pd membranes, this temperature should be more than 570°C. At the same time, an obvious decrease in the ductility of Nb and Ta with an increase in the hydrogen content in them can lead to the destruction of membranes even at these temperatures in the case of a rapid increase in hydrogen pressure at the inlet. This is associated with the high diffusion rate of hydrogen and, as a consequence, with a high dilatation rate. Thus, to clarify the operating temperatures of membranes at which their brittle fracture will not develop, it is necessary to more accurately study the ductility of α-solid solutions of hydrogen in Nb and Ta depending on the concentration, temperature, and deformation rate. The results of these studies will likely make it possible to use Nb and Ta membranes as material, rather than Nb and Ta alloys which are less technologically advanced. In context of the decrease in thermal stability of the palladium catalyst layer with increasing temperature in work [33-40], this problem can be solved either by developing a barrier layer that reduces mutual diffusion, or by replacing palladium with a more thermostable material.



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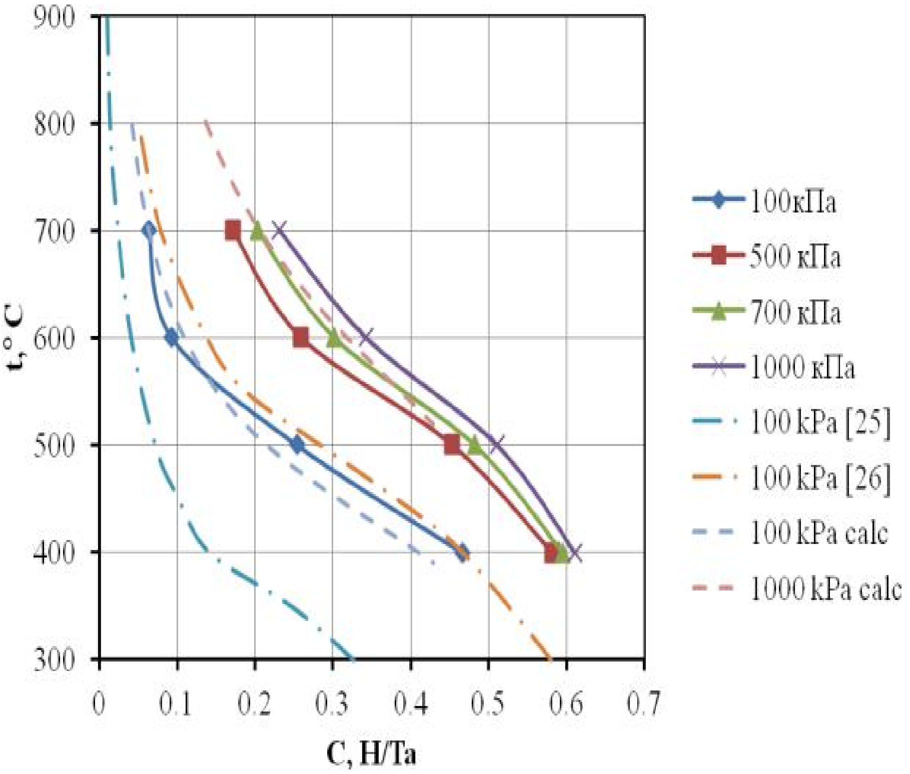
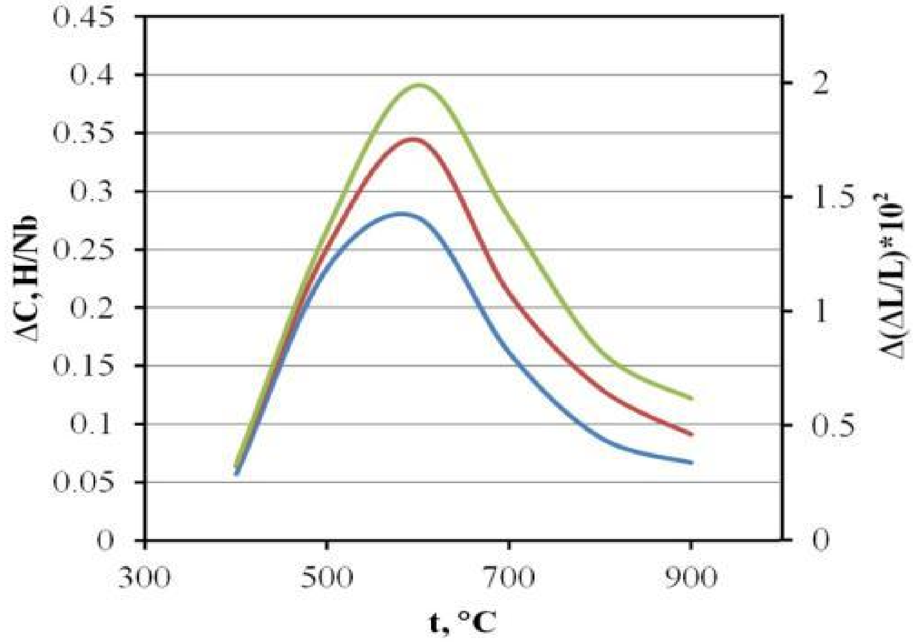


b

a - Nb; b – Ta

Figure 4. Isobar effects of temperature on the change in the H/M ratio of atoms



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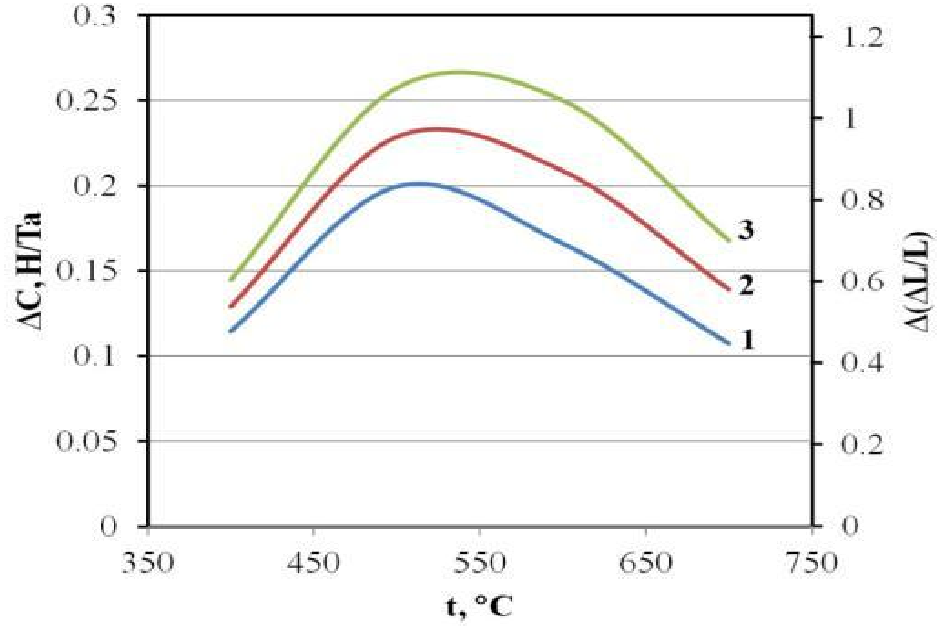

b

a - Nb-H; b - Ta-H

Figure 5. Limiting concentration gradient over the membrane cross section for various hydrogen pressures on the external surface (1 - 500/100 kPa; 2 - 700/100 kPa; 3 - 1000/100 kPa)

CONCLUSION

1. On the basis of direct measurement of the extension of 10 μm Nb and 80 μm Ta foil samples with a double-sided 0.15 μm Pd catalytic coating, data on their dilatation in a hydrogen atmosphere at a temperature of 400-900 ° C and a pressure of 100-1000 kPa was obtained. It has been established that with increasing temperature, dilatation decreases, and with increasing hydrogen pressure, its growth increases.
2. The values of the dilatation coefficient. $\Delta \upsilon \Omega$ were calculated based on the obtained data on dilatation and previously published data on the concentration of hydrogen in the α-solid solution at 400°C,. I is 0.153 and 0.126 for polycrystalline Nb and Ta, respectively. These values are lower than preset values for single-crystal samples of these metals in the case of the formation of diluted solutions.
3. The isobars of temperature dependence of hydrogen concentration in Nb and Ta were calculated and constructed using the results of dilatation measurements and dilatation coefficients. These data made it possible to estimate the limiting change in concentration and linear dimensions over the cross section of a hydrogen permeable membrane of Nb and Ta at various temperatures and operating pressures at the inlet and outlet of the membrane.
4. According to Fick's 1st law and previously published data on the hydrogen concentration value at which solid solutions of Group V metals turn into a brittle state, based on the results obtained, it is concluded that operating conditions of the membranes based on Nb and Ta. At hydrogen pressure 500 kPa at the inlet and 100 kPa at the outlet, composite Pd/Nb/Pd membranes should be operated at temperatures above 670 ° C. Similarly for Pd/Ta/Pd membranes, this temperature should be more than 570°C.

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