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HYDROGEN DILATATION OF V-BASED COMPOSITE MEMBRANES

One of the problems limiting the use of vanadium as hydrogen permeable membranes is its high dilatation upon hydrogen dissolution in it. The information available for the dilatation coefficient value ($\Delta v/\Omega$) is contradictory, experimental information on the hydrogen solubility in vanadium within 100-1000 kPa at from 250 to 700°C is very limited. It does not enable to calculate the membrane dilatation. The article contains the measuring results for dilatation of strips made of vanadium foil 100 μm thick in a hydrogen atmosphere in the pressure range from 75 to 1000 kPa, temperatures from 250 to 700°C. The dilatation coefficient ($\Delta v/\Omega$) of polycrystalline vanadium was calculated based on the data obtained for dilatation and data previously published for the hydrogen concentration in the α -solid solution at 400°C. It is 0.165. Isobars for the temperature dependence of the hydrogen concentration in vanadium are calculated and constructed using the dilatation measuring results and the dilatation coefficient values. These data are agreed with theoretical and experimental data published previously. The limiting change in concentration and linear dimensions over the cross section of a hydrogen-permeable membrane from V was estimated at various temperatures and operating pressures at the membrane outlet based on the isobars plotted for temperature dependences of the $C_{H/V}$. The conclusions are made on the optimal working conditions of Pd/V/Pd membranes when hydrogen is released from hydrogen-containing gas mixtures in accordance with Fick's 1st law and data published previously for hydrogen concentration value at which solid hydrogen solutions in vanadium become brittle.

Keywords: hydrogen dilatation; vanadium; composite hydrogen permeable membrane; concentration gradient; deformation

1. Introduction

The ultrapure hydrogen consumption volume in industry has been growing steadily in recent decades, and the development of the semiconductor and chemical industries, a significant increase in its consumption is expected in the future, with the increase in the use of solid fuel elements. Non-porous metal hydrogen-conducting membranes enable us to separate ultrapure hydrogen from gas mixtures in a single processing step due to their absolute hydrogen selectivity. This makes the development of membranes and membrane modules to produce ultrapure hydrogen promising. However, currently used membranes based on palladium alloys are extremely expensive that greatly limits their distribution. Membranes based on 5th group metals (V, Nb, Ta) and their alloys can become an alternative in the future, since the hydrogen transport through such membranes occurs more than 10 times faster than through palladium ones [1-5]. This is explained by a low barrier and a high diffusion coefficient of hydrogen in these metals [6]. But the main advantage of V, Nb, Ta is tens and hundreds of times lower price in comparison with

palladium. Vanadium and alloys based on it are considered as the most promising to create hydrogen-permeable membranes. It is justified by the availability, relatively low melting point and lower temperature to observe an extreme flow of hydrogen.

Meanwhile, the surface low catalytic activity, the tendency to dilatation and embrittlement when hydrogen is dissolved in these metals do not enable the practical use of membranes obtained from them. Currently, the problem of low catalytic activity of the membrane surface is relatively well solved with the use of layers made of palladium and palladium alloys [3,4,7-13]. Hydrogen embrittlement is reduced through development of the alloys based on the 5th group metals, where the hydrogen solubility is reduced but the hydrogen permeability is maintained at a sufficient level [7,9-13].

High hydrogen dilatation remains problematic resulting in the formation of folds in flat membranes and complicating their connection with structural elements of membrane modules made of heat-resistant steels. The dilatation phenomenon in combination with a sharp decrease in ductility during the hydrogen dissolution causes the membrane destruction. Accordingly,

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it should be taken into account when designing the membrane separation systems based on the 5th group metals. However, there is no experimental information on these metals dilatation in the literature and, in particular, on vanadium within the hydrogen temperatures and pressures at which hydrogen-permeable membranes function. It is also problematic to obtain this information by calculation, since data on the hydrogen solubility under various conditions are either absent or very different.

It is known that hydrogen atoms dissolving in metals with a bcc lattice occupy tetrahedral pores, causing lattice distortions, which leads to a change in the volume of crystals [14-17] and as a consequence, the parameters of the crystal lattice [18,19]. The relative change in the volume $\Delta V/V$ of a metal crystal upon dissolution of hydrogen in it to an atomic concentration $c = H/M$ is described by the following quantity:

$$\frac{\Delta V}{V} = c \cdot \frac{\Delta g}{\Omega} \quad (1)$$

where Δv – is the change in volume per hydrogen atom and Ω – is the average volume per metal atom. The $\Delta v/\Omega$ value is a dilatation coefficient independent of the concentration c . For metals with a cubic crystal lattice, a change in one of the sample dimensions, for example, the length $\Delta L/L$, is described by the following relationship:

$$\frac{\Delta L}{L} = \frac{1}{3} \cdot c \cdot \frac{\Delta g}{\Omega} \quad (2)$$

According to various studies [20-24], the vanadium dilatation coefficient for hydrogen dissolution is from 0.149 to 0.2. The experimental data generalized on the hydrogen dilatation of single-crystal samples enabled the authors of [25] to single out the most probable values of the relative change in volume $\Delta v/\Omega$ during the hydrogen dissolution of vanadium – 0.19±0.01. This corresponds to that observed for Pd – 0.19±0.01. However, V-based membranes due to significantly greater solubility of hydrogen, are subject to greater deformation and a decrease in ductility under identical operating conditions. This contributes to the formation of cracks, both in places where folds are formed, and in places where there is a connection with the substrate.

As follows from the experimental data summarized in [6], a significant increase in hydrogen solubility in V occurs at high temperatures with an increase in its pressure from 0.001 to 0.1 MPa. A sharp decrease in solubility is observed at the same time with increasing temperature from 400 to 700°C.

Under the data of [26], the atomic concentration of H/V measured with the help of the Sievert method at 400°C in the pressure range from 100 to 700 kPa varies from 0.46 to 0.6. We can calculate the relative change in volume using Expression 1 and the above $\Delta v/\Omega$ values. So, it will be – 0.114 at 400°C and a pressure of 7 bar for V . Accordingly, the linear dimensions of the membrane made of these metals in the atmosphere containing hydrogen should increase by 3.3-4% when reaching the equilibrium content of H. However, on the opposite side, the membrane dilatation from V reaches 0.087, for example, at a hydrogen pressure of 100 kPa. Accordingly, favorable compressive

stresses arise from the high pressure side in the membrane, and unfavorable tensile stresses appear from the opposite side. The difference of 0.9% for V should be compensated by membrane plastic deformation from the low pressure side. The membrane material plasticity level in this layer should be high enough so that no cracks occur. But the formation of cracks is most likely with insufficient plasticity. And with insufficient plasticity, cracks are most likely to form. However, one cannot exclude the development of the metal plastic flow due to the occurrence of the Gorsky effect resulting in a gradual stress relief. But, obviously, this process will proceed at a low speed, and cracks can occur in the presence of a stress concentrator. It is observed in practice when testing flat membranes mainly destroyed at the intersection of the folds formed [24], or along the top of the folds, where a large deformation develops.

The highest stresses in the membrane will occur at its junction with the substrate that does not undergo any deformation in a hydrogen atmosphere. Volume plastic deformation of vanadium membranes by 3.3-4% should occur in this region. If the membrane has insufficient plasticity it must irreplaceably result in their rapid destruction.

The significant pressure effect on the hydrogen solubility and the non-linear nature of the change in the parameters of the crystal lattice of the α -phase at high hydrogen concentrations, the difference in the previously measured values of the dilatation coefficient indicates the absence of the possibility to make accurate calculations of the linear dimensions of vanadium membranes for their different functioning parameters. Besides, there is practically no information on the hydrogen solubility limit in vanadium in the temperature range 400-700°C and at a hydrogen pressure of more than 0.1 MPa in literary sources. In this regard, it is important to obtain experimental data on changes in the linear dimensions of vanadium at a hydrogen pressure of up to 1 MPa and a temperature of up to 700°C to expand the development prospects in the field of membrane technologies.

2. Experimental

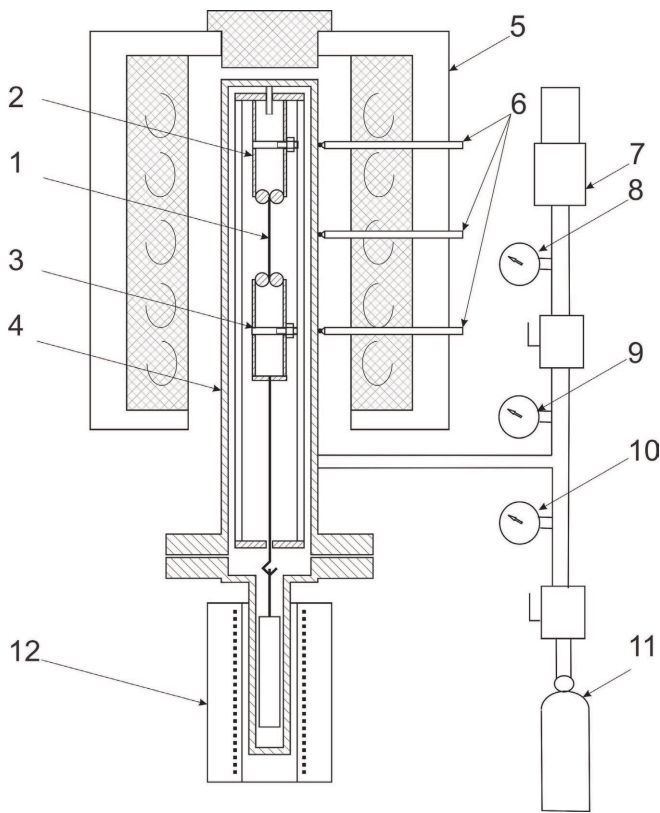
The tests were carried out by directly measuring the change in the length of a flat sample under conditions of isothermal holding at a certain pressure. Strips of cold-rolled vanadium foil 120×12×0.1 mm were used as samples. Information on the composition of the materials used in the experiments is presented in TABLE 1. To ensure the dissociation of hydrogen molecules and reduce the effect of the oxide film on the diffusion of hydrogen, a palladium layer 0.15 μm thick was applied to the foil surface on both sides. The deposition was carried out by the method of magnetron sputtering after ionic cleaning of

TABLE 1
Content of impurities in the materials used in the experiments

V	W+Mo	Al	Fe	Ta	Si	P	S
The basis	—	0.512	0.179	0.034	0.363	0.003	0.004

the surface. The hydrogen used in the experiments contained 99.99% of the basic substance.

The measurements were carried out on a setup developed on the basis of a Shimadzu AG100kNx electromechanical testing machine. Fig. 1 schematically shows the design of the test chamber with a sample placed in it. One end of the sample was clamped into cylindrical jaws in the holder, and on the other side a suspension was fixed to it, at the end of which there was a hook for installing the core from the measuring device. 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 oven of the testing machine. Such a furnace provided a temperature drop along the length of the sample of no more than $\pm 3^\circ\text{C}$. Vacuum evacuation and admission of gases was carried out through a branch pipe in the lower part of the chamber. Gas pressure control was carried out using a digital monometer OVEN PD200-DI1,0-315-0,1-2-N and a vacuum meter Meradat-VIT12T4. To measure the deformation of the sample, a DT-10S Shinko Electric extensometer was used, which provides a measurement accuracy of $\pm 5 \mu\text{m}$. By the electronics of the testing machine, the analog signal from the sensor was amplified and converted into digital, and then transmitted to a personal computer in the TRAPEZIUMX1.5.0c control program. As a result, the dependences of the sample deformation on time were obtained with a sampling frequency of 100 units/s.



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

Fig. 1. Schematic of an experimental setup for studying the dilatation of metals in a hydrogen atmosphere

After sealing the chamber with the installed sample, it was evacuated to a residual pressure of 10^{-2} Pa, and with continuous evacuation, it was heated to a predetermined temperature. After stabilization of the temperature, the vacuum channel was closed and hydrogen was poured in to a given pressure. The pressure was varied in the range from 75 to 1000 kPa with a step of ~ 100 kPa. Its value was maintained at a level not worse than ± 3 kPa. Measurements were performed until the sample length stabilized (Fig. 2). After the completion of the measurement cycle at one temperature, the chamber was evacuated. This caused hydrogen desorption from the bulk of the sample metal, which led to a decrease in its linear dimensions. 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.

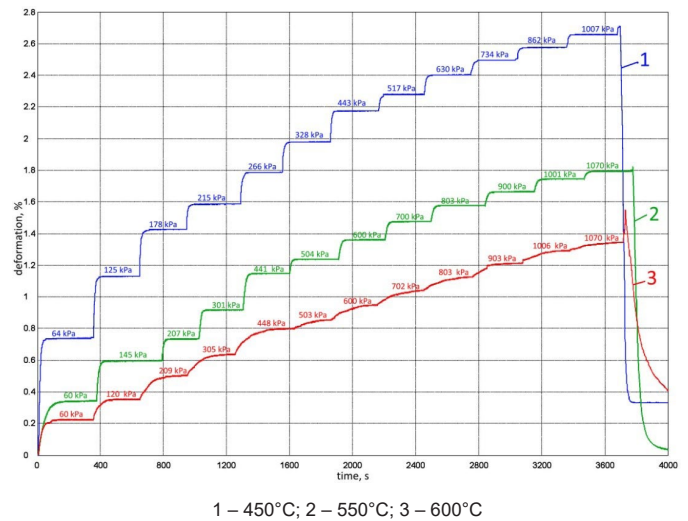


Fig. 2. Curve of elongation of a sample of Pd 0.15 $\mu\text{m}/\text{V}$ 100 $\mu\text{m}/\text{Pd}$ 0.15 μm , obtained at a stepwise increase in pressure at different temperatures

The isotherms of the pressure dependence of the sample deformation obtained in this way were recalculated according to expression 2 into isobars of the temperature dependence of the ratio of H/M atoms using the values of $\Delta v/\Omega$ known for V .

3. Results and discussion

The analysis of the elongation curves of vanadium samples under pressure changes, some of which are shown in Figure 2, shows that when hydrogen is poured into the chamber at 250–550°C for a short period of time (10–60 s), it elongates, and then the sample size stabilizes. At 600–700°C, the elongation curves of the samples become flat when the pressure changes, for this reason the exposure time was increased to stabilize the length of the samples, especially at 700°C. This elongation type indicates that the hydrogen adsorption rate at 600–700°C decreases sharply. This may be due to the intense interaction of the palladium layer with vanadium impairing its catalytic characteristics.

The $\Delta L/L$ value naturally increases with increasing pressure as follows from the isotherms shown in Figure 3. The maximum $\Delta L/L$ is observed at 250°C and 1000 kPa – 3.765%. When the temperature increases, the dilatation value decreases. Up to 350°C, the most significant elongation increase is observed in the pressure range from 0 to 100 kPa, at 400 and 450°C up to 200 and up to 300 kPa, respectively. The increase in dilatation decreases significantly with a further increase in hydrogen pressure, however, the curve does not reach a plateau up to 1000 kPa. This indicates that when the hydrogen pressure increases above 1000 kPa, the vanadium sample elongation will continue. The isotherms take the form of gentle curves at 500-700°C within from 0 to 1000 kPa indicating function f close to linear dependence ($\Delta L/L$) on P .

The resulting vanadium samples deformation isotherms are directly related to the change in the hydrogen solubility in the crystal lattice of this metal in accordance with equation 2 with pressure change. It enables to calculate the change in the hydrogen concentration in vanadium with a change in pressure and temperature, and to estimate the limiting change in the hydrogen concentration over the cross section of the membrane during filtration.

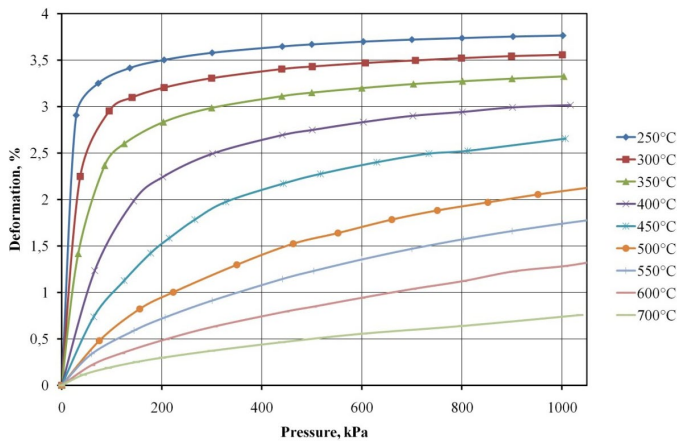


Fig. 3. Isotherms of V samples deformation with pressure

The experimental data on the hydrogen solubility in vanadium presented in the literature are very limited and contradictory [6,25,28-30]. This is due to a significant change in the limiting hydrogen concentration with a change in temperature and pressure complicating the study. In the work [6] the generalized results of studying the solubility of H in a α -solid solution of the V^{th} group elements at high temperatures and hydrogen concentration are presented in the equation form. Hydrogen solubility isobars were calculated for pressures of 100 and 1000 kPa using equation 3 for V .

$$T = \frac{\left(\begin{array}{l} 1515 + 1421*r - 1112*r^2 + \\ + 330*r^3 - 2092*r^4 \end{array} \right)}{\left(\lg r - \lg(0.779 - r) + 4.34 - 0.5*\lg P \right)} \quad (3)$$

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

These results, as well as experimental solubility data obtained by Veleckkis (Veleckkis et al.) [28] at P hydrogen of 100 kPa are shown in Figure 4. A comparison of these data with the temperature dependence isobars for the atomic concentration of $C_{H/V}$, obtained by measuring the dilatation at $\Delta v/\Omega = 100$ kPa, showed that a significant deviation of the curve towards lower concentrations is observed at a value of $\Delta v/\Omega = 0.19$ for V . Since the data summarized in [25] specify that the value of $\Delta v/\Omega$ is lower for polycrystalline and powder samples, it was recalculated based on the known concentrations of ultimate solubility at 400°C and a pressure of 100 kPa [29,30]. As follows from the data obtained, the value $\Delta v/\Omega$ for V is 0.165. The isobars were calculated for the temperature dependence of the atomic concentration $C_{H/V}$ using these coefficients and the dilatation data obtained (Fig. 4). The curves made are agreed with experimental materials previously obtained [29] and the results of calculations according to equation 3.

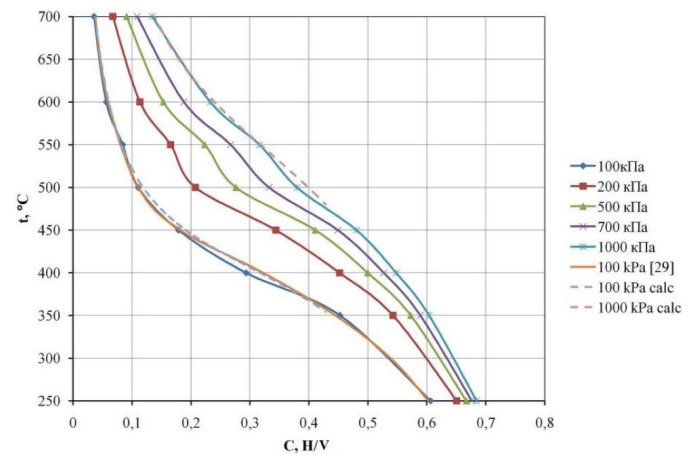


Fig. 4. Isobars of the effect of temperature on the change in atomic concentration H/V

Based on the data obtained, the limiting hydrogen concentration gradient arising along the cross section of the vanadium membrane was calculated at a pressure of 500, 700, and 1000 kPa and at a pressure of 100 kPa at various temperatures. As follows from the data obtained (Fig. 5), there will be a significant increase in the limiting concentration gradient with a maximum of ~450°C in these pressure ranges in the membranes, with an increase in temperature from 250 to 700°C. This will provide the greatest value of the hydrogen flow through the membrane made from vanadium within 400-500°C in accordance with the Fick's 1st law (formula 5). However, such a large difference in concentration will result in the greatest internal stresses due to the dilatation heterogeneity along the membrane cross section (Fig. 5).

$$J = D \cdot \frac{|\Delta C|}{d} \quad (5)$$

According to Yukawa's data [31], vanadium transition to the brittle state occurs already at a concentration of $H/V \approx 0.22$ and does not depend on temperature up to 400°C. Based on these data and the isobars shown in Figure 4, it follows that $Pd/V/Pd$

membranes planned to be operated at an inlet pressure of 500 kPa and an outlet of 100 kPa, can be in a plastic state only at temperatures above 550°C. It should also be noted that the transition to a brittle state is preceded by a decrease in ductility that should also be taken into account when designing the membrane structure. Besides, an magnitude analysis of the residual deformation of vanadium samples (Fig. 6) after hydrogen desorption indicates that the metal plastic deformation development is possible during hydrogen diffusion. This is explained by the fact that when the sample surface comes into contact with hydrogen due to the formation of a gradient of diffusion of hydrogen concentration over the thickness, its outer layers of the membrane expanded more than the inner ones. This led to the appearance of tensile stresses in the inner layers of the sample and compressive stresses in the outer ones. As a result, and as a consequence, their plastic deformation occurred. Accordingly, with cyclic use of membranes, this can become another reason for their destruction.

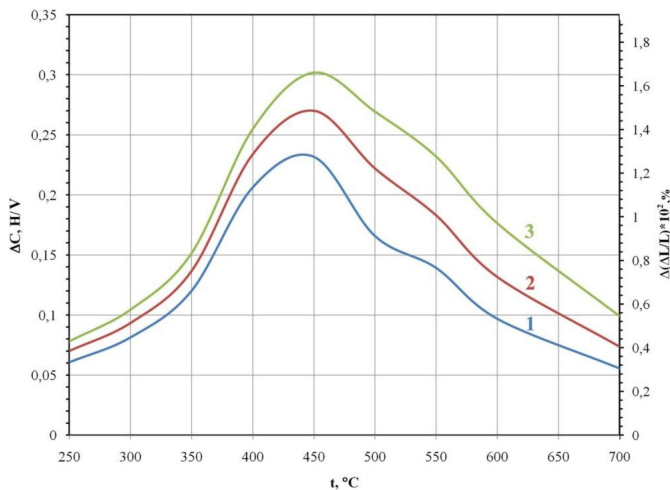


Fig. 5. Maximum concentration gradient over the vanadium membrane cross section at various hydrogen pressures on the external surface (1 – 500/100 kPa; 2 – 700/100 kPa; 3 – 1000/100 kPa)^o

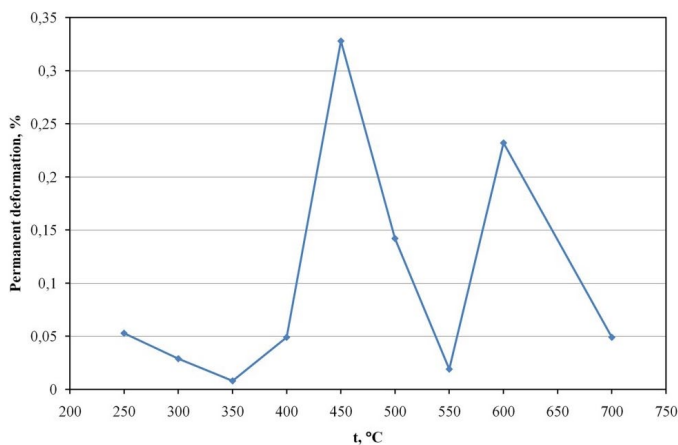


Fig. 6. Residual deformation

The tubular construction of hydrogen-permeable membranes is most often considered at present [32-37]. This form eliminates the formation of folds but does not exclude the

accumulation of deformations at the junction with the supply pipes usually made of heat-resistant steel. In some cases, [32], the design of the membrane modules involves passing a gas-containing hydrogen mixture under pressure through the inner cavity of the tubular membrane and removing purified hydrogen through the outer walls. It causes the expansion of the membrane metal near the inner surface of the walls, in accordance with the data shown in Fig. 6. As a result, it results in a significantly greater deformation of the outer walls in comparison, for example, with a flat membrane. For this reason, the module constructions are more correct, where the external walls of the tubular membrane are in contact with the gas-containing hydrogen mixture under pressure, and the removal of purified hydrogen is performed through the internal cavity.

It is necessary to study more accurately the ductility of α -solid hydrogen solutions in vanadium depending on the concentration, temperature, and deformation rate to clarify the operating temperatures of membranes at which their brittle fracture will not develop. The need for such studies is justified by the fact that during the tests described herein, there were no vanadium samples destroyed when they were hydrogenated at a pressure of up to 1000 kPa even at 250°C, where the H/V hydrogen concentration reached ~ 0.68 . At the same time, our preliminary experiments with Ta and Nb where the hydrogen solubility is close to V showed that they come into contact with hydrogen at a pressure of 100 kPa and a temperature of 250 and 350°C, respectively. This suggests that the destruction of vanadium foils described in [31] is a consequence of a decrease in their plasticity upon dissolution of hydrogen but not a transition to a brittle state.

4. Conclusions

The data were obtained on their dilatation in a hydrogen atmosphere at temperatures of 250-700°C and a pressure of 75-1000 kPa based on direct measurement of the elongation of vanadium foil samples 100 μm thick with a double-sided catalytic Pd coating 0.15 μm thick. It has been established that dilatation decreases with temperature increase, and its magnitude increases with increase in hydrogen pressure.

The dilatation coefficient ($\Delta l/l$) of polycrystalline vanadium was calculated based on the data obtained for dilatation and data previously published for the hydrogen concentration in the α -solid solution at 400°C. It is 0.165. This value is lower than previously established for single-crystal samples of this metal in the case of the formation of solid solutions with a low concentration.

Isobars for the temperature dependence of the hydrogen concentration in vanadium are calculated and constructed using the dilatation measuring results and the dilatation coefficient values. These data are agreed with theoretical and experimental data published previously.

The limiting change in concentration and linear dimensions over the cross section of a hydrogen-permeable membrane

from V was estimated at various temperatures and operating pressures at the membrane outlet based on the isobars plotted for temperature dependences of the $C_{H/V}$. The conclusions are made on the optimal working conditions of $Pd/V/Pd$ membranes in accordance with Fick's 1st law and data published previously for hydrogen concentration value at which solid hydrogen solutions in vanadium become brittle. So, the membranes should be operated at temperatures above 550°C with a hydrogen pressure at the inlet of 500 kPa and at the outlet of 100 kPa, to prevent the destruction of such a membrane due to dilatation.

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