

Hydrogen permeability of surface-modified Pd-Ag membranes at low temperatures

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Abstract. Hydrogen-permeable membranes of the Pd77% Ag33% alloy were obtained. Membranes were modified with a catalytically active coating, which consist of a crystalline nanostructured palladium black. Membranes were obtained by magnetron sputtering using mosaic targets. The surface modification with a catalytically active coating was performed by electrochemical deposition from an aqueous solution of H_2PdCl_4 . The low-temperature kinetic characteristics of the hydrogen permeability of metallic Pd77% Ag23% membranes with a modifying coating of crystallized palladium black were analysed. During the analysis of the obtained experimental data about the kinetic characteristics of the obtained membranes, it was revealed that the surface effects are the limiting stage of hydrogen transport through palladium membranes at low temperatures. It was experimentally confirmed that the high specific surface of the synthesized catalysts causes the acceleration of the kinetic characteristics of hydrogen transport. The possibility of intensifying the processes of hydrogen transport through metallic membranes by creating active centers of chemisorption and dissociation on their surface is shown.

1. Introduction

In recent years the use of hydrogen as energy carrier is a very promising area in the energy sector. High-purity hydrogen (>99,999%) is the most demanded in production of optical fibers, semiconductors, medicaments, and also as an energy source for fuel cells [1]. It is assumed that significant part of hydrogen will be produced due to methane conversion, and also due to its separation other hydrocarbon gases, which are not involved in energy production process nowadays (petroleum production associated gases, petrochemical production discharge gases and other) [2, 3]. For this purpose, palladium-based and palladium-alloy membranes are perfectly fits. Those membranes have almost total hydrogen selectivity, high ability to cleave C-C-bonds, high thermal stability and mechanical strength [4]. Those membranes can be used in membrane reactor, that allows to combine chemical reaction for obtaining hydrogen with purification stage and in hydrogen isotope separation plants for the production of water with a modified isotopic composition [5-9]. For mass integration of metallic membranes into industrial hydrogen separation processes, it is very important to estimate their productivity and stability in working conditions. Since its considered, that those types of membranes are working at relatively high temperatures (300–600 °C) and high pressure (2–50 bar or even higher), and also in transient conditions, in which they can undergo rapid, it is important to understand the nature of changes of the material properties and under the conditions they were made.



Currently the main effort are directed at lowering working temperatures, membranes cost, increasing mechanical strength, durability and catalytic activity. Palladium is rare and expensive material, and its cost is expected to rise because of growing demand for its use in large scales. Minimizing of palladium quantity contributes to lower membrane.

Producing of ultra-thin palladium layers allows to minimize discharge intensity of precious metals. However this entails two problems: limitation of membrane mechanical strength and the difficulty of obtaining films without defects. Therefore, during the deposition of a selective layer, three main tasks must be performed: lowering of the selective layer thickness (the aim is to increase permeability and lower membrane cost while ensuring of complete absence of defects); decreasing the number of defective membranes (the aim is to control the total cost of the production process); producing of Pd-based alloys (the aim is to improve permeability in working conditions, i.e. in thermal cycles or in the sulfur presence). According to this, we further use the electrolytic deposition of finely-divided palladium from H_2PdCl_4 water solution on impulse low-voltage potentiostat-galvanostat P-250I («Elins», Russia).

Hydrogen permeation of membranes is heavily decreasing at the temperatures below 200 °C because equilibrium is achieved very slowly [10]. This condition can be partially overcome by modifying the working surface with palladium-containing film coatings [11]. Usually, pure palladium suffers from hydrogen embrittlement because of the lattice expansion caused by the $\alpha - \beta$ phase transition which occurs when metal is exposed to hydrogen atmosphere at the temperature 298 °C and the pressure 2 MPa [12, 13]. This phase transition generates tensile stress, especially in the case of a tubular geometric shape, which often leads to cracking of the Pd layer and, consequently, to subsequent loss of membrane hydrogen selectivity. This disadvantage can be avoided by working under the conditions of the above critical point, when the membrane is exposed to hydrogen, or by changing the phase diagram of Pd [14]. The last option can be implemented by alloying pure Pd with other metals: silver, copper, ruthenium, gold. Pd-based alloys with specific concentrations of these metals change the metal hydride phase diagram, avoiding the mentioned embrittlement problem [15].

Hydrogen permeation in palladium-silver alloys varies according to the extreme law and reaches a maximum at a 15-25 % content of silver [16]. Phase diagram of the Pd-Ag system presented in Figure 1. A large amount of silver in alloys reduces the purity of the diffused hydrogen, doesn't allow to lower a dew point temperature below -70 °C and poisons the membranes. Relatively frequent in the operation of capillaries and membranes from a complexly doped alloy are most likely associated with unequal distribution of doping elements [16]. We have chosen an alloy of the composition Pd77% Ag23%, the choice of which caused by the most optimal mechanical and catalytic properties [17].

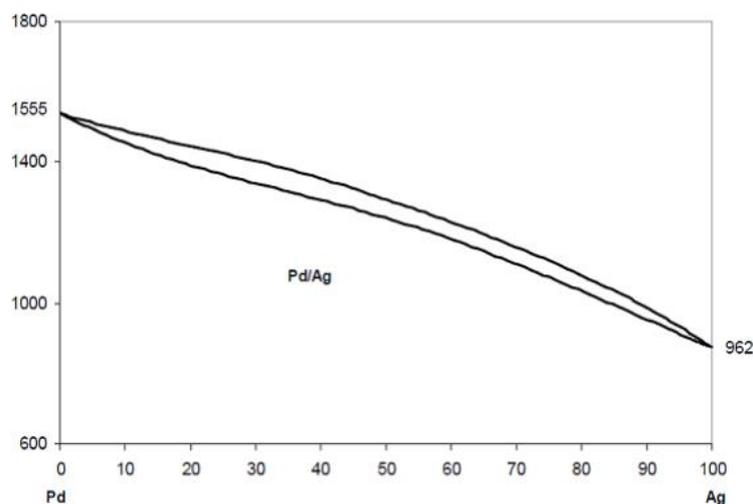


Figure 1. Phase diagram of Pd-Ag system`.

Thus, the aim of this research was to study the efficiency of the modification of the Pd-Ag alloy membrane to increase the kinetic characteristics of hydrogen transport in the low-temperature operating range (25-90°C) for the use of membranes in ultrapure hydrogen and low-temperature electrochemical current sources.

2. Materials and Methods

2.1. Membrane

A magnetron sputtering method for obtaining experimental Pd77% Ag23% alloy membranes was developed based on mosaic targets. The sputtering itself was performed on a Q150T ES sputtering vacuum system (Quorum Technologies, UK). To create a composite target for a magnetron sputtering system, chemically pure refined palladium and silver ingots were rolled on DRM – 130 electromechanical roll mills (Durstun, UK) to a thickness of 25 μm with intermediate annealing in a muffle furnace at the temperature 250 °C. Silver had been previously rough-forged with a wedge-shaped anvil on the anvil along the length of the ingot to a thickness of 3–3.5 mm, followed by smoothing with a flat pane to a thickness of 3 mm and intermediate annealing at 300 °C for 20 seconds. Then, the metal plates were connected into a target packet between the contact pressure plate and the ring with the ratio of the surface areas, which are free for the magnetron sputtering: $S(\text{Ag}) / S(\text{Pd}) = 20.8 / 79.2$. The difference in the areas ratio of the elements to their ratio in the film composition is justified by the difference in the atomization energies of palladium and silver ($\Delta H(\text{Pd}) = 353 \text{ kJ/mol}$, $\Delta H(\text{Ag}) = 251,5 \text{ kJ/mol}$).

2.2. The synthesis of catalyst

To modify the surfaces of the Pd77% Ag23% alloy films, pretreatment in a 6 M concentrated NaOH solution was performed for 30 minutes, followed by etching in a 60% HNO₃ solution for 30 seconds. Then, the films were transferred to an electrolytic cell connected for subsequent electrodeposition through a silver wire (99.99% silver) to a potentiostat / galvanostat P250I («Elins», Russia) Anodic polarization was carried out in 0.1 M HCl at a current density of 10–20 mA / cm². Then, cathodic polarization was carried out in 0.05 M H₂SO₄ at a current density of 10–20 mA / cm². A series of palladium black samples were electrolytically deposited in a 2% H₂PdCl₄ solution at current densities of 2–14 mA / cm² for 0.1 to 1.5 hours, and after the deposition films were washed with bidistilled water and cathodically polarized in 0.05 M H₂SO₄. As a result of surface analysis of the experimental series of surface modifiers synthesis, two types of coating were obtained (with a deposition time of 0.5 hours and 1 hour), which are the most interesting from a scientific and applied point of view. Coatings from these two series are structures that potentially have high catalytic activity values.

The amount of the dispersed phase of palladium was controlled by direct gravimetry using an analytical balance. Samples of films in the holder were weighed with an accuracy of 10⁻⁶ g. The mass difference obtained by this method shows the mass of the deposited palladium, i.e., its discharge intensity. Thus, with a membrane area of 2 cm², the total palladium discharge during electrodeposition at a deposition current density of 10 mA / cm² and a deposition time of 1 hour is about 5.2 mg.

2.3. Hydrogen Permeation

The kinetic characteristics of the obtained samples of palladium black were studied on the installation we developed, which is basing on the microgasvolumetric method (Figure 2).

The amount of hydrogen permeated through the membrane was measured by the microvolumetric method, i.e. by measuring the volume of hydrogen diffused through the membrane at constant pressure. The entering of hydrogen to the lower gas loop through the membrane when the purge valve is closed causes an equivalent enlargement in the total volume of the gas mixture in the gas outlet loop and the meniscus level of the measuring liquid in the capillary moves in time.

The hydrogen permeation process consists of three main stages [18]:

1. dissociation of hydrogen on the input surface of membrane, flowing with velocity v_i ,
2. dissociation of atomic hydrogen through the membrane, flowing with velocity v_D ,

3. atomic recombination of hydrogen into molecules on the output membrane surface, flowing with velocity v_o .

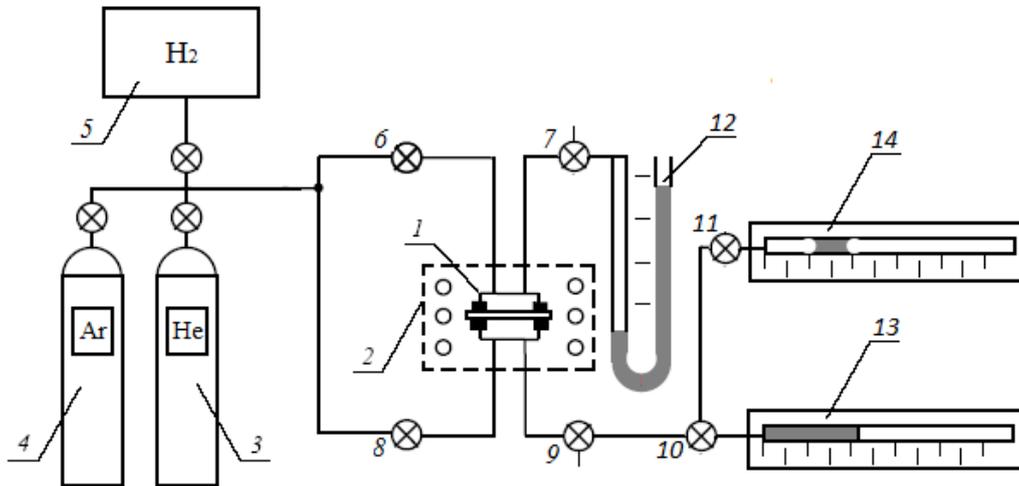


Figure 2. Installation for hydrogen permeation measurement: 1 – permeability cell; 2 – liquid thermostat; 3 – helium cylinder; 4 – argon cylinder; 5 – hydrogen generator «Spektr»; 6-11 – gas valves; 12 – mercurial U-shaped manometer; 13 – gas analyzer; 14 – measuring capillary.

Under the condition of equilibrium between hydrogen in the gas phase and atomic hydrogen in the adsorbed layer:

$$v_i = k_D p_1 - k_P p_{1A}^2; \quad (1)$$

$$v_o = k_P p_{2A}^2 - k_D p_2; \quad (2)$$

$$v_D = D \frac{k_S (p_{1A} - p_{2A})}{h} = D \frac{C_1 - C_2}{h}. \quad (3)$$

k_D and k_P – dissociation rate constant and recombination constant, D – diffusion coefficient of hydrogen in metal, k_S – solubility coefficient of atomic hydrogen in metal, p_1 and p_2 – molecular hydrogen pressure on the input and output membrane surfaces, p_{1A} and p_{2A} – atomic hydrogen pressure on the input and output membrane surfaces, h – membrane thickness,

$C_1 = k_S p_{1A}$ and $C_2 = k_S p_{2A}$ – concentration of dissolved atomic hydrogen to near-surface layer of metal on the input and output membrane surfaces.

Under stationary conditions, these velocities are equal and corresponds to the hydrogen permeation rate:

$$v = v_i = v_o = v_D.$$

From the equations (1) and (2) we can express:

$$p_{1A} - p_{2A} = \frac{k_D (p_1 - p_2) - 2v}{k_P (p_{1A} + p_{2A})},$$

$$C_1 - C_2 = \frac{k_s^2}{2k_p C_{cp}} (k_D (p_1 - p_2) - 2v),$$

where $C_{cp} = (C_1 + C_2)/2$.

Substituting into the expression (3):

$$v = D \frac{k_s^2}{2hk_p C_{cp}} (k_D (p_1 - p_2) - 2v),$$

$$v = k(p_1 - p_2),$$

$$k = \frac{1}{\frac{1}{\alpha_{diff}} + \frac{2}{k_D}}, \quad \alpha_{diff} = \frac{Dk_s^2 K_p}{2hC_{cp}}, \quad K_p = \frac{k_D}{k_p}.$$

Mass transfer of hydrogen through a metal membrane resistance is composed of diffusion (determined by α_{diff}) and “chemical” resistances. Diffusion resistance depends on the membrane thickness δ , diffusion and solubility coefficients, which depend on temperature, and on the concentration of dissolved hydrogen, which depends on pressure. If the limiting stage of the process is diffusion, then k_D is much larger than α_{diff} , and:

$$k = \alpha_{diff} = \frac{Dk_s^2 K_p}{2hC_{cp}}.$$

An equilibrium is established on the surface: $v_i = v_o = 0$, accordingly:

$$p_{1A} = \sqrt{K_p p_1},$$

$$p_{2A} = \sqrt{K_p p_2},$$

$$C_{cp} = \frac{k_s \sqrt{K_p}}{2} (\sqrt{p_1} + \sqrt{p_2}),$$

$$k = \frac{Dk_s \sqrt{K_p}}{h(\sqrt{p_1} + \sqrt{p_2})},$$

$$v = \frac{Dk_s \sqrt{K_p}}{h} (\sqrt{p_1} - \sqrt{p_2}).$$

Thus, the rate of the permeation process is proportional to the square root of the pressure of gaseous hydrogen, which generally corresponds to the Richardson equation [19]:

$$v = k(\sqrt{p_1} - \sqrt{p_2}) e^{-\frac{E_A}{RT}}.$$

If the limiting stage of the process is dissociation, then k_D is much less than α_{diff} , and accordingly:

$$k = \frac{k_D}{2},$$

$$v = \frac{k_D}{2}(p_1 - p_2).$$

Thus, in this case hydrogen permeation rate is to pressure of gaseous hydrogen.

2.4. SEM Image

The surface of the modified membranes was examined using a scanning electron microscope with a field emission cathode JSM-7500F («JEOL», Japan). The surfaces of both coatings were investigated from the permeate side of the membrane and from the retentate side. The coating homogeneity of the applied coatings was confirmed by a series of microphotographs (a sample of at least 10 microphotographs of the surface per cm^2).

3. Results

3.1. Hydrogen permeation

Figure 3 and Table 1 show the hydrogen permeation data for a Pd77% Ag23% alloy with formed palladium black structures and undercrystallized palladium black structures:

- flux density J , $\text{mmol} / \text{c} \cdot \text{m}^2$ – flow through a unit area of a sample;
- hydrogen permeation coefficient P , $\mu\text{mol} / (\text{c} \cdot \text{m}^2) \cdot \text{cm} / \text{Pa}^{0.5}$ - value numerically equal to the flux density through the sample of unit thickness at Δp .

Table 1. Hydrogen permeation data.

Δp , MPa	J , $\text{mmol}/\text{c} \cdot \text{m}^2$	P , $\mu\text{mol}/(\text{c} \cdot \text{m}^2) \cdot \text{cm}/\text{Pa}^{0.5}$
(b) Undercrystallized palladium black structures		
0.1	0.0037	0.00052
0.2	0.0107	0.00107
0.3	0.0173	0.00142
0.4	0.0243	0.00173
0.5	0.0324	0.00204
0.6	0.0393	0.00228
(a) Formed palladium black structures		
0.1	0.006	0.00148
0.2	0.016	0.00253
0.3	0.026	0.00322
0.4	0.037	0.00383
0.5	0.048	0.00438
0.6	0.059	0.00486

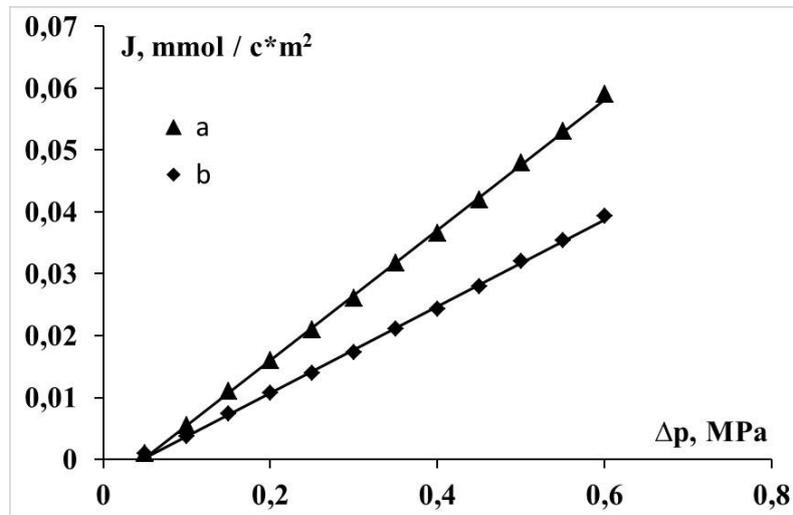


Figure 3. Hydrogen permeation graph for Pd77% Ag23% alloy membranes with two modifying coatings 0.5 h (a) and 1 h (b).

As can be seen from the data presented in Figure 3 and Table 1, the hydrogen flux density in the formed structures of palladium black is 1.5 times higher than hydrogen flux density of undercrystallized at an gauge pressure of 0.6 MPa.

Figure 4 shows that the dependence of the flux density for a membrane with a modified surface is well approximated by a first-order line, which, according to [20] indicates that the hydrogen penetration rate is limited by dissociation of hydrogen on the surface.

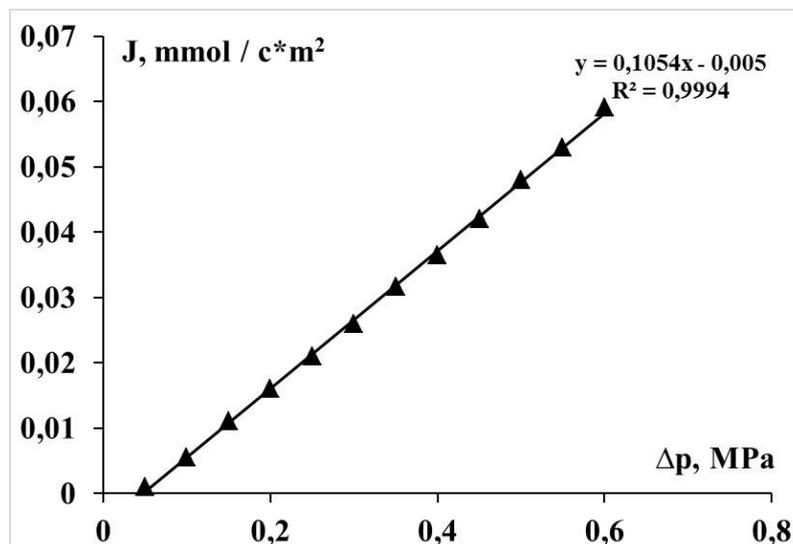


Figure 4. Dependence of flux density on gauge pressure on the input membrane surface for membrane with modified surface.

Figure 5 shows the data on the measurement of the hydrogen flux density through a palladium-silver membrane (Pd 77% Ag 23%) with electrochemically modified surfaces at different temperatures.

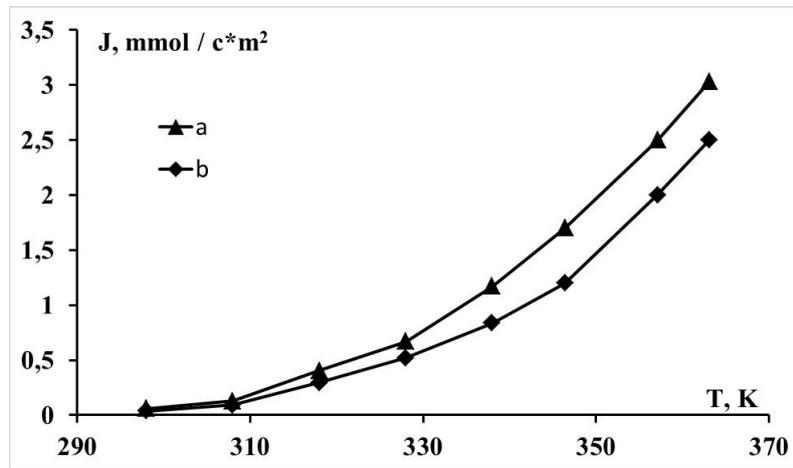


Figure 5. Dependence of hydrogen flux density on the temperature for Pd77Ag23 alloy membranes with two types of modifying coatings 0.5 h (a) and 1 h (b).

As can be seen from the data presented in Figure 5, the flux density of the palladium black structures increases by 1.2–2 times for every 10 K. In the formed palladium black structures, the hydrogen flux density at a temperature of 363 K is 1.2 times higher than of hydrogen flux density undercrystallized structures at an excess pressure of 0.6 MPa.

Figure 6 shows the data on measuring the dependence of hydrogen permeability on pressure for membranes with formed palladium black structures and undercrystallized palladium black structures.

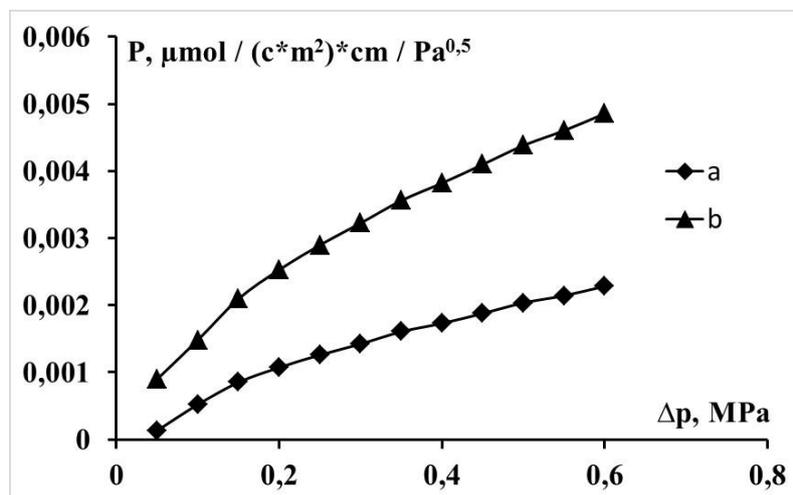


Figure 6. Dependence of hydrogen permeation on pressure for Pd77Ag23 alloy membranes with two types of modifying coatings 0.5 h (a) and 1 h (b).

As can be seen from the data presented in Fig. 6, the hydrogen permeation of the formed structures of palladium black is 2.1 times higher than hydrogen permeation of undercrystallized structures at an excess pressure of 0.6 MPa.

Figure 7 presents the data of measuring the hydrogen permeability of the formed palladium black structures and undercrystallized palladium black structures with temperature change.

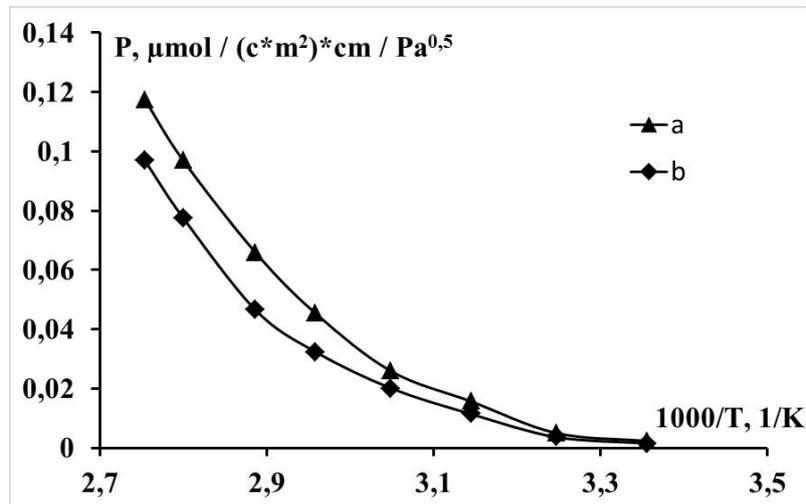


Figure 7. Dependence of hydrogen permeation on temperature pressure for Pd77Ag23 alloy membranes with two types of modifying coatings 0.5 h (a) and 1 h (b).

3.2. SEM Image

Micrographs of coatings on Pd77% Ag23% alloy membranes were obtained by the method, described in paragraph 2.4 SEM-Images of the formed palladium black structures and undercrystallized palladium black structures are shown in Figure 8 and Figure 9 at magnifications of x5000 and x50000.

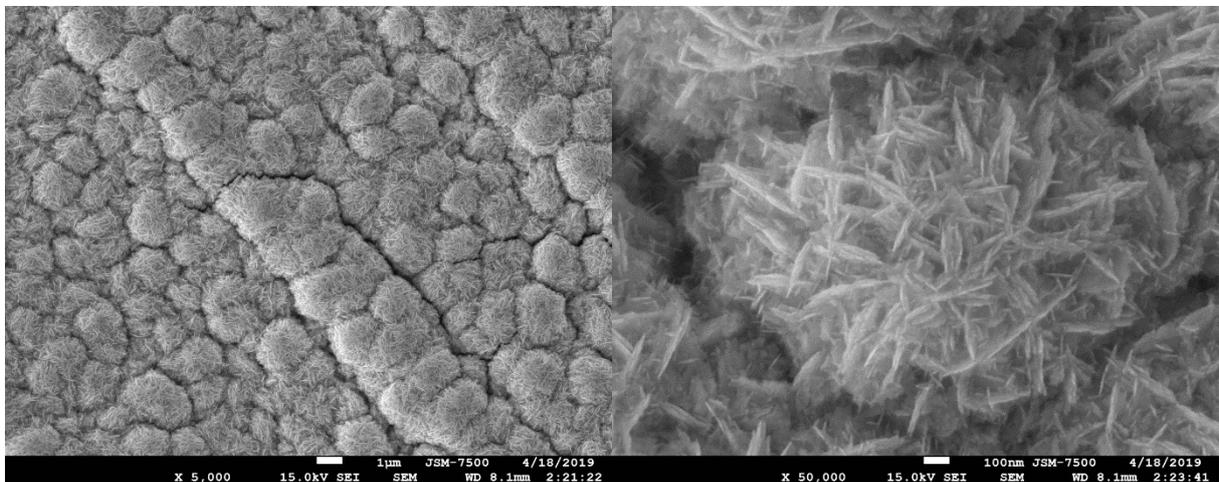


Figure 8. SEM Image of undercrystallized palladium black structures (a - x5000, b - x50000).

Undercrystallized palladium black structures are nanoparticles with a size of 30-120 nm in length and 15-20 nm in width. The average sizes of spherical ensembles of palladium black particles in undercrystallized structures are 1-3 μm^2 . Completely formed palladium black structures have the form of crystallites with a size of 200-800 nm. The average size of the ensembles of the formed palladium black structures is 4-6 μm^2 .

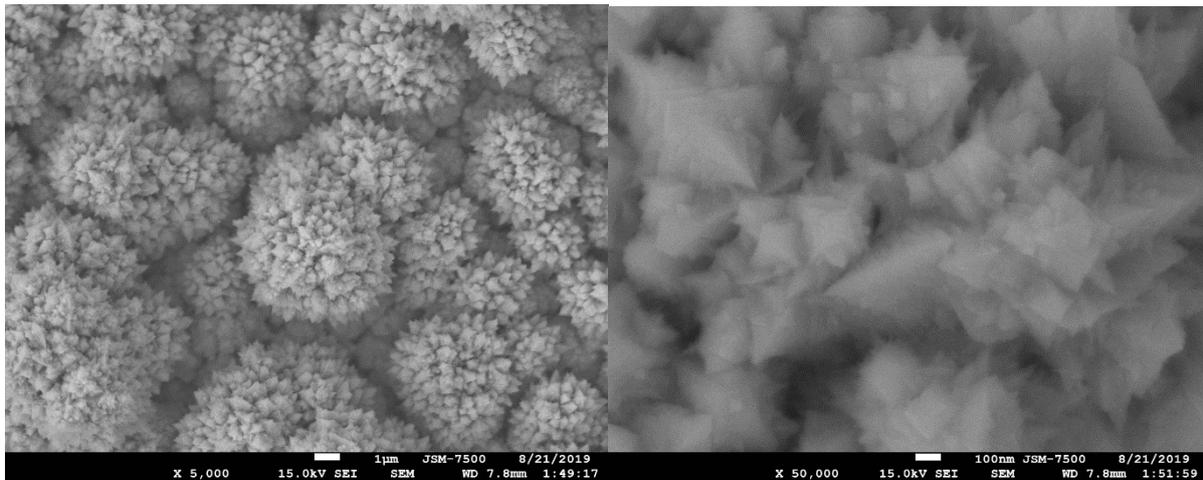


Figure 9. SEM Image of formed palladium black structures (a - x5000, b - x50000).

4. Discussion

The investigation of the correlation between the structure of the modifying coating and the deposition parameters provides an understanding of the evolution of microstructures during the growth and recrystallization of surface modifiers. Further, this makes it possible to synthesize surface modifiers for specific technological conditions, for example, under transient conditions of working temperatures and pressure, membranes selectivity for various compositions of hydrogen-containing mixtures of gases and toxic impurities.

In this research, the low-temperature kinetic characteristics of the hydrogen permeability of metallic Pd77% Ag23% membranes with a modifying coating of crystallized palladium black were analyzed. During the electrolytical deposition of the modifying coating, a different spectrum of microstructures was obtained. The structures differed not only in the grain size of palladium black, but also in surface morphology, expressed by crystallographic orientation and structural defects. In order to develop low-temperature, high-performance membranes and to understand the correlation between the kinetic characteristics of the hydrogen transport process and the microstructure of surface modifiers, further researches will be carried out.

5. Conclusion

The Pd77% Ag23% alloy was obtained on the Quorum Q150TS / E / ES sputtering system by the developed method of magnetron sputtering using mosaic targets. Catalysts in the form of finely dispersed palladium were synthesized on the surface of prepared substrates by electrolytical deposition — two series with different deposition times. A comparative investigation of the kinetic characteristics of hydrogen transfer in modified membranes in the low temperature range was carried out. Samples, obtained at a 1 hour deposition time, have a hydrogen flux density and hydrogen permeability coefficient of almost two times higher than a hydrogen flux density and hydrogen permeability coefficient of undercrystallized palladium black structures, obtained at a 0.5 hours deposition time at the same current density. The dependence of the hydrogen flux density on the gauge pressure is approximated by a first-order line, which indicates the limitation of the hydrogen transport process through modified membranes by surface phenomena. The analysis of microphotographs of the obtained films surface using a JEOL JSM-7500F scanning electron microscope allowed us to conclude, that the acceleration of chemisorption processes caused by the finely dispersed coating. The active centers of the surface processes are the angles and faces of palladium black crystallites, which provide high activity and selectivity of the membrane surface in relation to hydrogen. Has been proposed a method for intensifying hydrogen transport through Pd77% Ag23% alloy membranes by developing the surface by creating chemisorption centers.

Acknowledgments

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