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Hydrogen Permeability through Composite Asymmetric Nb Membranes with Metal Barrier Layers

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ABSTRACT

The article discusses the possibility of using various metals to create barrier layers between the niobium membrane and palladium catalytic layers. Such layers are necessary to reduce the degradation of the palladium catalyst layers during membrane operation. For this, the maximum hydrogen permeability of asymmetric niobium foil membranes was determined, on the one hand covered with a W, Re, Mo, Cu, Co, Ni, Ag film, and the maximum hydrogen permeability of the Nb/Me/Pd membranes was determined, where Me is W, Re, Mo, Cu, Co, Ni, Ag. The change in the structure and composition of the palladium catalytic layer on the surface of composite membranes made of niobium after isothermal holding in vacuum at 420 and 520 ° C for 100 h was studied. It has been found that membranes coated only with a Ni or Co layer are comparable in terms of hydrogen permeability to membranes coated with a Pd layer. Membranes coated with layers of W, Re, Mo, Cu, Ag have low hydrogen permeability, which increases with decreasing thickness of these layers. The hydrogen permeability of such membranes after the deposition of a palladium layer increased by an amount in the case of a barrier layer: from W 170 - 760 times; from Mo by 0.5-10 times; from Re by 23-500 times; from Cu 1.6 - 14 times; from Co by 2.7 times; from Ag by 1.1-10 times. When palladium was applied to the surface of the Ni layer, the hydrogen permeability did not increase. When the thickness of the barrier layers of Cu, Mo, Re, W, Ni, Co is from 13 to 400 nm, the hydrogen permeability of the Nb/Me/Pd composite membranes corresponds to the values $3.9\text{-}7.0 \cdot 10^{-5}$ mol/s*m^2*Pa$^{0.5}$. Minimal changes in the structure and composition of the Pd layer were observed upon prolonged heating of Nb/W/Pd membranes.

Keywords: Composite membrane, niobium, barrier layer, catalytic coating, hydrogen permeability, hydrogen

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INTRODUCTION

The use of inorganic membranes for separation of hydrogen-containing gas mixtures formed during the steam conversion of gaseous hydrocarbons is considered as one of the most promising methods for producing ultrapure hydrogen. From [1] it is known that membranes from group V metals such are V, Nb, and Ta are superior to hydrogen permeability to palladium. However, numerous researche evaluating the feasibility of their application in practice have shown that they cannot replace palladium due to their low corrosion resistance to gases generated during the decomposition of hydrocarbons [2-6]. Hydrogen embrittlement is another problem resulting in the destruction of membranes during dilatation caused by dissolution of hydrogen, and when pressure drops. Suzuki et al. [7] pointed out that doping of vanadium, niobium, and tantalum with tungsten, molybdenum, and iron eliminates the problem of hydrogen dilatation, while the hydrogen permeability remains at a fairly high level.

The solution to the problems to increase the corrosion resistance and ensuring the catalytic activity of the surface of composite membranes based on group V metals was their bilateral coating with a thin layer of palladium [8-16]. Meanwhile, despite the high hydrogen permeability of such membranes, they still have not found commercial application. Low thermal stability of the palladium coating is one of the problems standing in the way of using composite membranes from V, Nb, and Ta [17-20]. Over time, this results in a significant decrease in the hydrogen permeability of membranes from niobium [21], vanadium [22]. The reason is the development of reaction diffusion at the interface between palladium and membrane material along with the formation of an area of solid solutions and the intermetallic compound Pd_3Nb, Pd_3V, Pd_3Ta. Edlund et al. [22] indicated that the acceleration of mutual diffusion of palladium into the membrane material is facilitated by hydrogen diffusion.

Development of mutual diffusion between the membrane material and the catalytic layer can be prevented or reduced due to the formation of a barrier layer between them. However, the material of such a layer should provide high hydrogen permeability. At present, the following materials are offered for use for this purpose: perovskites, hydroxy acids and fluorides [23], metal oxides [23], carbides [6], including niobium and tantalum [8- 9], chalcogenides [10- 11] and nitrides [12]. The low ductility of such materials and a significant difference in characteristics will result in the fact that dilation of the membranes upon dissolution of hydrogen will cause cracking and peeling of the barrier layers and destruction of the palladium film. Currently, the effectiveness of ceramic barrier layers has been proven only when paired with porous metal substrates [24-28]. As an alternative to these materials, it was proposed to consider the possibility to use metal films to obtain non-porous barrier layers. The composition and properties of such metal layers should ensure the stability of the characteristics of the membranes, while minimally inhibiting hydrogen flow. The stability of the characteristics can be maintained provided that there is no or minimal interaction of the barrier layer with the membrane material and the catalytic palladium layer. A layer can retain its characteristics provided that it does not form hydrides and oxides. Resistance to the formation of oxides in a hydrogen-containing atmosphere is important when the integrity of the palladium catalyst layer is compromised.

The formation of intermediate phases, hydrides, and solid solutions at the operating temperatures of hydrogen-permeable membranes was taken into account when analyzing the literature data on the interaction in binary Nb-Me, Pd-Me and H-Me systems. In this regard, the oxide film formation temperature and the possibility of its reduction with hydrogen was evaluated. The main criterion for the metals to be selected for the formation of the barrier layer is the minimum interaction with palladium, and the absence of hydrides in the H-Me system both at 600 ° C and at lower temperatures. Based on this information, the following materials were selected as potential candidates for barrier layers: W, Re, Mo, Cu, Co, Ni, Ag.

W and Mo with Nb form a continuous series of solid solutions. Re is sparingly soluble in Nb. W and Re with palladium form a limited solid solution, and molybdenum forms one intermetallic compound $MoPd_2$. W, Mo, and Re do not form hydrides. Meanwhile, the reduction of the lower oxides of these metals with hydrogen at temperatures up to 600°C is possible only in the case of Re. Ag, Cu, Co, and Ni form a continuous series of solid solutions with palladium; they do not form hydrides; they are reduced to a metal state with oxides. However, Co and Ni with Nb form a number of intermetallic compounds, the permeability of which is not available in the literature. Wang et al. [29-31] showed 100% hydrogen selectivity of hollow fibrous nickel membranes and hydrogen permeability at the level of 7.66×10^{-3} mol m^{-2} s^{-1} at 1000°C, indicating the prospects of using this metal as a material barrier layer.

Since W, Mo, and Re are refractory, a low rate of mutual diffusion in Nb-Me-Pd systems at membrane operating temperatures should be expected. However, the low solubility of hydrogen in them can become an obstacle to their use. Ref. [32] shows that the layers of Nb-40 wt.% Mo, Ta-18 wt.% W solid solutions based on niobium and tantalum deposited on the niobium surface in the absence of a palladium layer do not significantly affect the hydrogen permeability of the membranes. Moreover, due to their low corrosion resistance, the hydrogen permeability of Nb membranes decreases over time.

An obvious disadvantage of Ag, Cu, Co, and Ni is their relatively low melting point and accordingly, high atomic mobility at the temperature of hydrogen diffusion through membranes. can result in a gradual change in the properties of the barrier layer due to the formation of solid Pd-based solutions and intermediate Nb-based phases. But Zhang, X. L. et al. showed [33] shows that Pd/5% Ni solid solutions are characterized by high hydrogen permeability of 3.1×10^{-6} mol/m^2 s Pa. Ryi, S. K. et al. [34] successfully used porous substrates made of porous nickel to obtain membranes consisting of a Pd – Cu – Ni solid solution. At the same time, the disadvantage of nickel is its low hydrogen permeability ($\sim2\times10^{-11}$ mol m^{-1} s^{-1} $Pa^{-0.5}$ at 400°C) [35].

It is known that the hydrogen permeability of metals such as Fe, Ni, Cu, Co, Mo increases with temperature [15- 16]. According to the data given in [36], at 500 ° C, the hydrogen permeability in Ni is $7.8 *10^{-11}$, Cu - $4.9*10^{-12}$, that in Fe is $1.8*10^{-10}$ $mol*m^{-1}*s^{-1}*Pa^{-0,5}$, that is significantly lower in comparison with that in tantalum and palladium ($1.3*10^{-7}$ and $1.9*10^{-8}$ $mol*m^{-1}*s^{-1}*Pa^{-0,5}$). However, the flow of hydrogen through the membrane increases in proportion to a decrease in its thickness indicating the fundamental possibility of using it as a material of a barrier or face layer of metals of both the above and even with lower hydrogen permeability.

Yamaura et al. [37] points out that the hydrogen flow for the amorphous $Ni_{40}Nb_{20}Ta_5Zr_{30}Co_5$ alloy with a nickel coating was less than one fourth of the value achieved using the Pd coating. Meanwhile, it is known [20] that the application of a nickel layer on the surface of niobium and vanadium membranes ensures their high hydrogen permeability. Application of a barrier layer of nickel on a mesoporous steel substrate ensured high hydrogen permeability of palladium membranes [38]. Gryaznov et al. [39] described the positive experience of using a 0.8 µm tungsten barrier layer to prevent mutual diffusion between a 10 µm palladium-ruthenium catalyst layer and a stainless-steel porous substrate.

O'Brien et al. indicated [40] a very low hydrogen adsorption on the surface of the Cu layer that is due to the large value of the hydrogen adsorption activation barrier ΔE qads = 0.54 (0.06 eV). At the same time, it was pointed out in [41] that nickel and copper are characterized by a rather high catalytic activity in the steam methane conversion.

Thus, the influence of W, Re, Mo, Cu, Co, Ni, Ag layers on the characteristics of the hydrogen flow through niobium-based membranes, including those with a catalytic palladium layer, is not described in literature. In this regard, work has been done to study the effect of the thickness of the layer of these metals on the hydrogen permeability of Nb/Me and Nb/Me/Pd membranes, where Me- W, Re, Mo, Cu, Co, Ni, Ag. A change in the structure of the palladium layer upon prolonged isothermal annealing of such membranes in vacuum was also investigated. This made it possible to give a general assessment of the possibility of using these metals as barrier layers to prevent mutual diffusion at the Nb / Pd contact boundary. Based on these data, in the future, more in-depth studies can be carried out to determine the characteristics of composite membranes using barrier layers of metals selected in the framework of this study.

MATERIALS AND METHODS

Niobium (total fraction of impurities (Fe, C, Si, N, Ti, O) is < 0.25% and that of Ta < 0.2%) cold-rolled foil with a thickness of 40 µm in the annealed condition was used to obtain membranes. After ion cleaning, films of W, Re, Mo, Ni, Co, Cu, Ag, and Pd of various thicknesses were deposited by magnetron sputtering on the surface of a 120x120 mm foil of one side. In the first series of experiments, only one layer of the listed metals was applied. In the second series of experiments, a Pd layer was deposited on top of the deposited layer of pure W, Re, Mo, Cu, Co, Ni. The thickness of the films was determined both by measuring on transverse sections, using a JEOL

JXA-8230 microprobe analyzer, as well as by calculation based on the experimentally measured deposition rate of layers.

The hydrogen permeability of the obtained membranes was evaluated using a classical design [42] by measuring the rate of hydrogen flow passing through a hermetically sealed membrane. As a gas-permeable substrate, we used a C160 twill weave mesh made of AISI321 stainless steel, the surface of which was preliminarily oxidized to prevent interaction with the membrane. To ensure tightness, aluminum sealing washers were used.

After heating the membrane in vacuum to 580±5°C, argon was inflated from both sides of the membrane to atmospheric pressure. Hydrogen was introduced from the inlet side of the membrane to an overpressure of 500±15 kPa. In this way the side of the membrane coated with a metal film, received a gas mixture Ar/H_2 with a volume ratio of 1/5. Argon injection was necessary in order to exclude the destruction of the membrane, because at the experimental temperature and hydrogen pressure of ~100 kPa, niobium passes into a brittle state. Numerous preliminary experiments have shown that the elimination of argon puffing and the use of hydrogen at the stage of bringing the pressure to atmospheric from the permeate outlet side leads to the destruction of the membrane with a subsequent increase in the hydrogen pressure on the inlet side. This is due to the occurrence of stresses during hydrogen dilatation.

At the beginning of the experiment, the hydrogen passing through the membrane displaced argon from the chamber from the side of the permeate with a volume of 0.5 ± 0.05 cm^3. As a result, the hydrogen pressure at the outlet became equal to atmospheric and the hydrogen pressure drop between the inlet and outlet sides of the membrane in a short period of time changed from ~500 to 400 kPa.

The Ar/H_2 gas mixture ratio at the inlet side of the membrane was maintained by supplying pure hydrogen to the chamber. In experiments used additionally dried (Tp ≈ -40 ° C) argon (99.95%) and grade B hydrogen (99.95%) (GOST 3033-80) was used additionally. The membrane working area was 78.5 cm^2. The fixation of the gas flow rate was carried out using a block of rotameters and gas flow meters RRG12. At a low flow, its rate was measured by fixing the interval of bubble exit. The bubble volume was previously measured. The measurement of the flow rate of hydrogen was carried out before the breakthrough, as judged by a sharp increase in gas flow. Unfortunately, the destruction of membranes with some barrier layers in a series of 3 experiments occurred even before the hydrogen flux reached its maximum. The analysis of the composition of the gas leaving the membrane was not carried out, since it is known that metal membranes provide absolute selectivity to hydrogen. In addition, the numerous preliminary experiments carried out by the authors of the article have shown that the breakthrough of a membrane of such a large area occurs with a well-recorded increase in the gas flow, and when a microcrack occurs, a continuous increase in the gas flow is observed.

Based on the results of measuring the hydrogen flow rate using formula 1, the flux density (flux) - J, mol/s*m^2. was calculated. The hydrogen permeability of membranes was judged by the value of hydrogen permeability (permence) - P, mol/s*m^2*$Pa^{0,5}$, which was calculated using formula 2.

$$J = \frac{\vartheta}{V_M \cdot S} \qquad (1)$$

$$P = \frac{J}{(\sqrt{p_2} - \sqrt{p_1})} \qquad (2)$$

where ϑ - the hydrogen flow rate, dm^3/s; V_M -the molar volume of gas at temperature and pressure of the stream entering the measuring device from the dm^3/mol installation equal to 22.4 dm^3/mol; S - membrane area, m^2; p_2 — gas pressure on the membrane surface at the inlet side inside the chamber, Pa; p_1 is the pressure of the gas entering the measuring device, Pa.

The surface structure of the palladium film on the niobium composite membrane was studied after annealing in vacuum ($3*10^{-1}$ Pa) at 420 and 520°C for 100 h. The surface was studied using a JEOL JXA-8230 microprobe analyzer in COMPO mode. Moreover, due to the small thickness of the barrier and catalytic layers, the microprobe analysis distorted the actual composition, supplementing it with membrane material. For this reason, a change in the composition on the surface was recorded by comparing the results of analysis of the initial samples and annealed ones.

The calculated thickness of the palladium layer in the experiments to determine the hydrogen permeability of the membranes was 0.155 μm, and in the experiments to study the changes in the structure on the surface of the membranes after heat treatment, it was 0.39 μm. The choice of such values is justified by the fact that, at a thickness of 0.155 μm, the highest hydrogen permeability of the Nb membranes/Pd layer was observed. The small thickness of the Pd layer made it possible to reduce the duration of the heat treatment experiment and made it possible to study changes in the structure and composition of the catalytic Pd film directly near the surface of the barrier layer.

RESULTS AND DISCUSSION

Upon contact with the gas mixture of Nb/Me composite membranes without Pd - the catalytic layer, after a relatively short period of time (50-400 s), the hydrogen flux density reaches its peak values, after which its value decreases (Figures 1 and 2). The reduction rate depends on the coating material. An exception is the Nb/ (Re, Mo) membranes, which are destroyed at the stage of increasing the hydrogen flow rate. At a film thickness of Ni, Co, Cu >0.4 μm, after a relatively rapid decrease, the hydrogen fluxof the membranes stabilize and then slowly decreases until it breaks down. The same is observed when testing Nb/Pd membranes. The destruction of the membranes occurs in the places of inflection, due to the formation of bends on a flat membrane with an increase in its linear dimensions due to dissolution of hydrogen and the resulting sharp decrease in ductility.

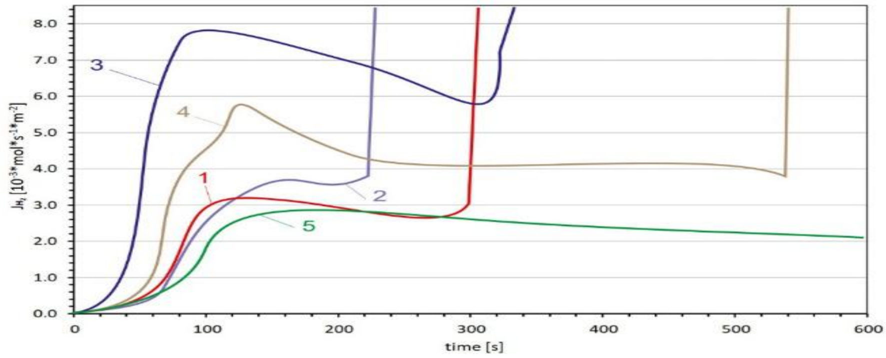


Fig. 1. Effect of Co layer thickness (µm) on the hydrogen flow density of niobium-based membranes (40 µm): 1- 0.049; 2- 0.098; 3 - 0.244; 4 - 0.488; 5 - 0.975.

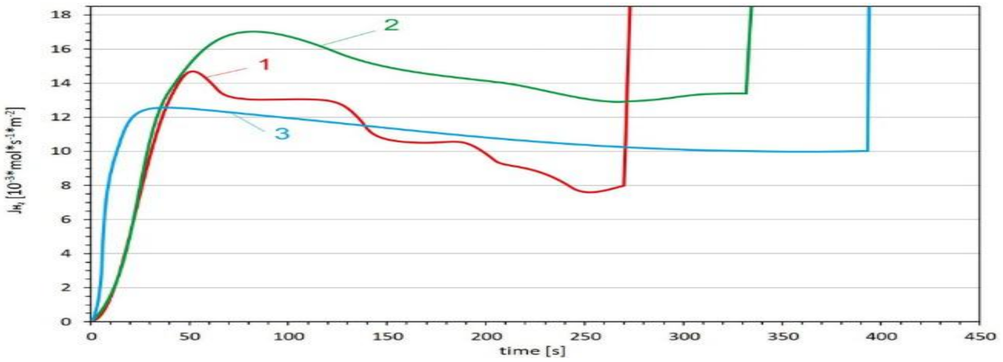


Fig. 2. Effect of Ni layer thickness (µm) on the hydrogen flow density of niobium-based membranes (40 µm): 1 - 0.19; 2 - 0.375; 3 - 0.75.

Membranes coated with a 0.22-1.3 µm film of W, 0.281-0.563 µm film of Re, 0.039-0.078 µm film of Ni, are characterized by a peak hydrogen permeance close to that observed with pure niobium (Figure 3). Membranes with thinner films of W (0.11 µm) and Re (0.028-0.056 µm), and Cu (0.096 - 0.956 µm), Co (0.049 - 0.975 µm), Ni (0.19 - 0.75 µm), have a significantly higher hydrogen permeance as compared to pure niobium-based membranes. At the same time, Ni membranes demonstrate hydrogen permeance at the level of membranes with a Pd layer with a thickness of 0.039 to 0.39 µm, and membranes with Co a 0.244-0.488 µm film only allow hydrogen to pass 2-3 times slower as compared to palladium.

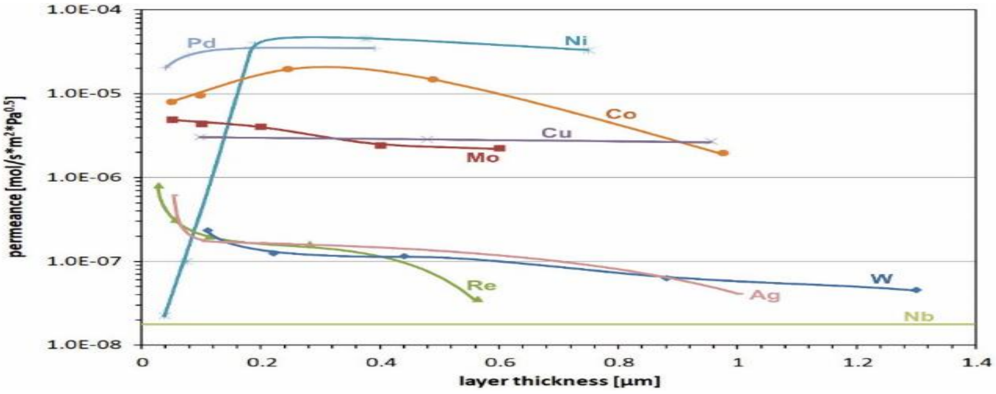


Fig. 3. Effect of the thickness of the metal layer on the surface of niobium-based membranes on their peak hydrogen permeance

Application of a 0.155 µm palladium layer on the surface of niobium-based membranes with a 0.013-0.104 µm W layer (Figure 4), 0.025-0.155 µm Mo layer (Figure 5), 0.048-0.956 µm Cu layer (Figure 6), 0.056-0.282 µm Re layer (Figure 7) can dramatically increase their hydrogen flow density through them. At the same time, the effect of increasing hydrogen permeability in the case of using barrier layers of tungsten, molybdenum and rhenium exceeds that observed when applying palladium without such layers (35.0 * $10^{-6\ mol}$/s*m^2*$Pa^{0.5}$ with a Pd layer thickness of 0.155 µm). In this regard, in the case of applying a 0.1 µm Mo layer and a 0.155 µm Pd layer, the maximum hydrogen permeance of the membrane reaches 42.4 * 10^{-6} mol/s*m^2*$Pa^{0.5}$. Composite membranes with 0.113 µm Re and 0.155 µm Pd layers show maximum hydrogen permeability at the level of 98.6 * 10^{-6} mol/s*m^2*$Pa^{0.5}$, and in the case of 0.013 µm W layer and 0.155 µm Pd layer, the hydrogen permeance reaches 69.7 * 10^{-9} mol/s*m^2*$Pa^{0.5}$. Membranes with a copper layer (0.096 µm), when applying a palladium layer, exhibit a peak hydrogen permeance of 29.0 * 10^{-10} mol/s*m^2*$Pa^{0.5}$. With increase in the thickness of tungsten, molybdenum, silver and copper layers, the hydrogen permeance of the composite membranes decreases. Over time, the hydrogen permeance of such composite membranes decreases, but to a lesser extent than that observed when testing uncoated membranes.

Composite membranes with an Ag barrier layer and a palladium catalytic layer are characterized by the lowest hydrogen flow density. At the same time, the peak hydrogen permeability of membranes with an Ag layer of 0.2 μm reaches 1,88*10^{-6} mol/s*m^2*$Pa^{0.5}$, and with an increase in the Ag layer thickness to 2 μm, it sharply decreases 2,25*10^{-8} mol/s*m^2*$Pa^{0.5}$, which is lower than that of pure niobium. In addition, when the Ag layer is 0.2 μm thick, a clear change in the texture of the membrane surface is observed after experiments, which indicates active diffusion between the barrier layer and the palladium layer.

The hydrogen flow density through composite membranes with barrier layers of 0.375 μm nickel and 0.488 μm cobalt does not significantly decrease after reaching the maximum values and remains relatively stable until the membranes are destroyed. The hydrogen permeability of such membranes reaches 4,06 и 4,64 mol/s*m^2*$Pa^{0.5}$, respectively.

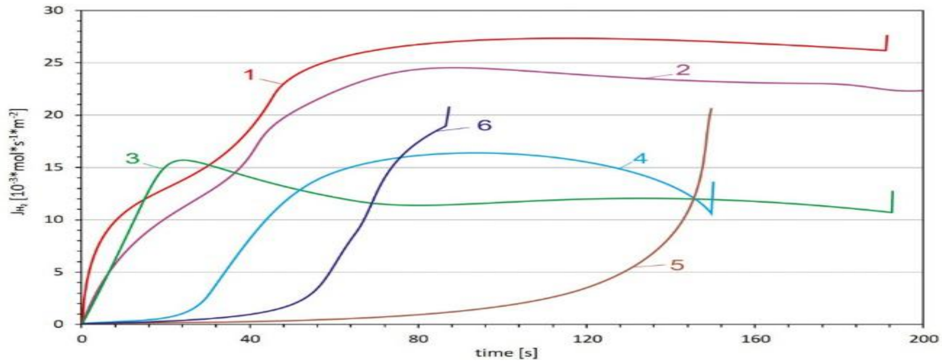


Fig. 4. Effect of the thickness of the barrier layer of W on the hydrogen flow density through niobium membranes with a catalytic Pd layer of 0.155 μm in an Ar/H_2 (1/5) gas mixture at 580°C (μm). 1-0.013; 2 - 0.02; 3 - 0.041; 4- 0.104; 5- 0.208; 6 - 0.416

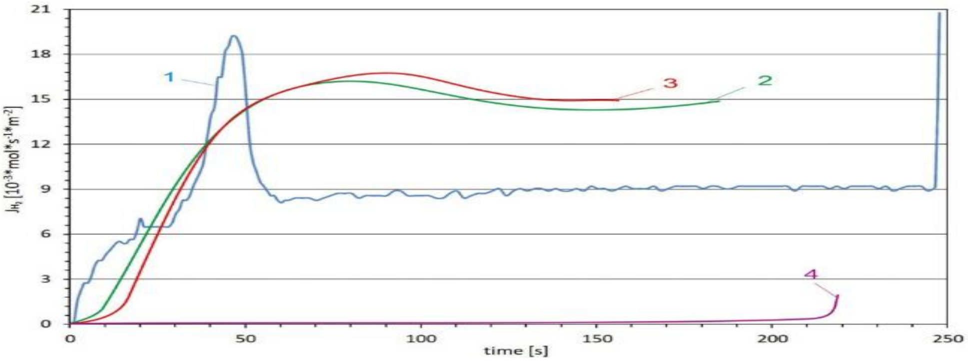


Fig. 5. Effect of the thickness of the barrier layer of Mo on the hydrogen flow density through niobium membranes with a catalytic 0.155 μm Pd layer in an Ar/H_2 (1/5) gas mixture at 580°C (μm). 1-0.025 μm; 2 - 0.05 μm; 3 - 0.1 μm; 4 - 0.2 μm

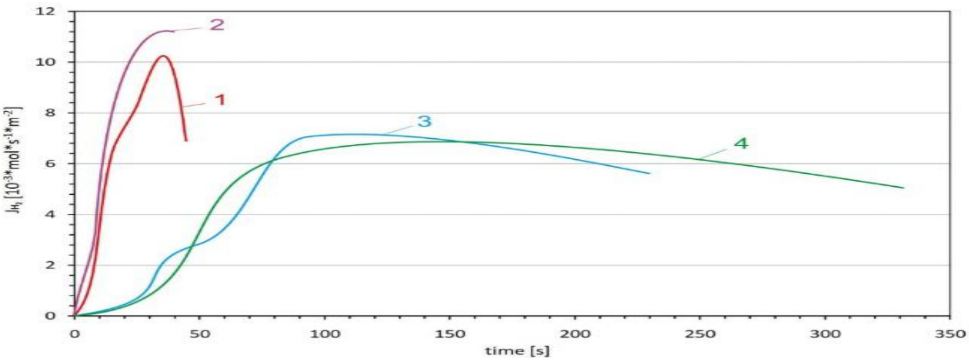


Fig. 6. Effect of the thickness of the barrier layer of Cu on the hydrogen flow density through niobium membranes with a catalytic 0.155 μm Pd layer in an Ar/H_2 (1/5) gas mixture at 580°C (μm). 1- 0.048; 2 - 0,096; 3 - 0.478; 4 - 0.956

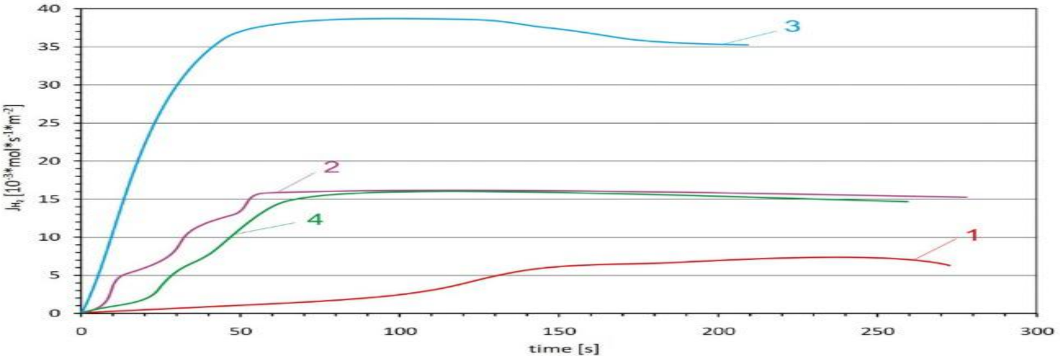


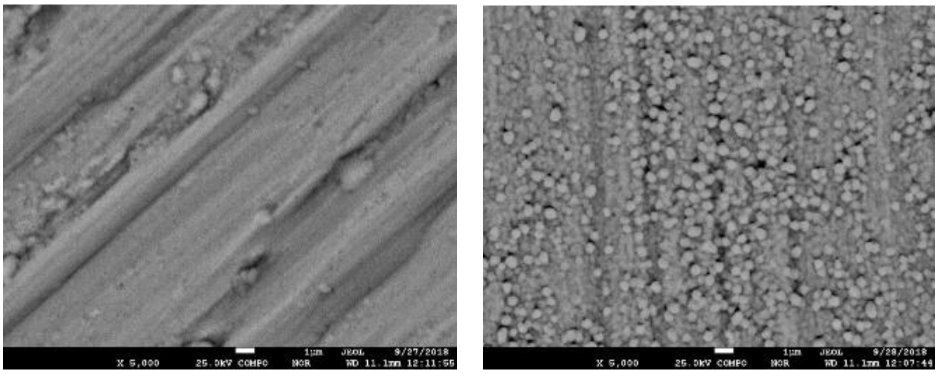
Fig. 7. Effect of the thickness of the barrier layer of Re on the hydrogen flow density through niobium membranes with a catalytic 0.155 μm Pd layer in an Ar/H_2 (1/5) gas mixture at 580°C (μm). 1- 0.028; 2 - 0.056; 3 - 0.113; 4 - 0.282

Changes in the structure and composition of the palladium layer on the surface of composite niobium-based membranes were studied after isothermal exposure at 420C° and 520 C° for 100 hours. W (0.44 μm), Mo (0.4 μm), Cu (0.478 μm), Re (1.125 μm) were used as barrier layers. The thickness of the barrier layers was taken extremely large in order to minimize the diffusion of niobium into the palladium layer. The thickness of the palladium layer was 0.39 μm. A typical structure of a Pd film deposited on the surface of the barrier layer of the initial membrane samples is shown in Figure 8.

The data obtained indicate that, under isothermal exposure at 420° C, the palladium catalytic layer on the surface of the barrier layers of W and Mo practically does not change the composition and structure. On the surface of the barrier layers of Re, separate regions with a changed porous structure are formed, and the palladium content decreases and the content of rhenium and niobium increases. The structure of the Pd film on the surface of a layer of Cu, Co, and Ni practically does not change, while the content of atoms of the material of the barrier layer substantially increases therein. In Pd films, on the surface of Co and Ni layers during electron microscopic investigation, in the study in the COMPO mode, finely dispersed lighter precipitates were weakly manifested.

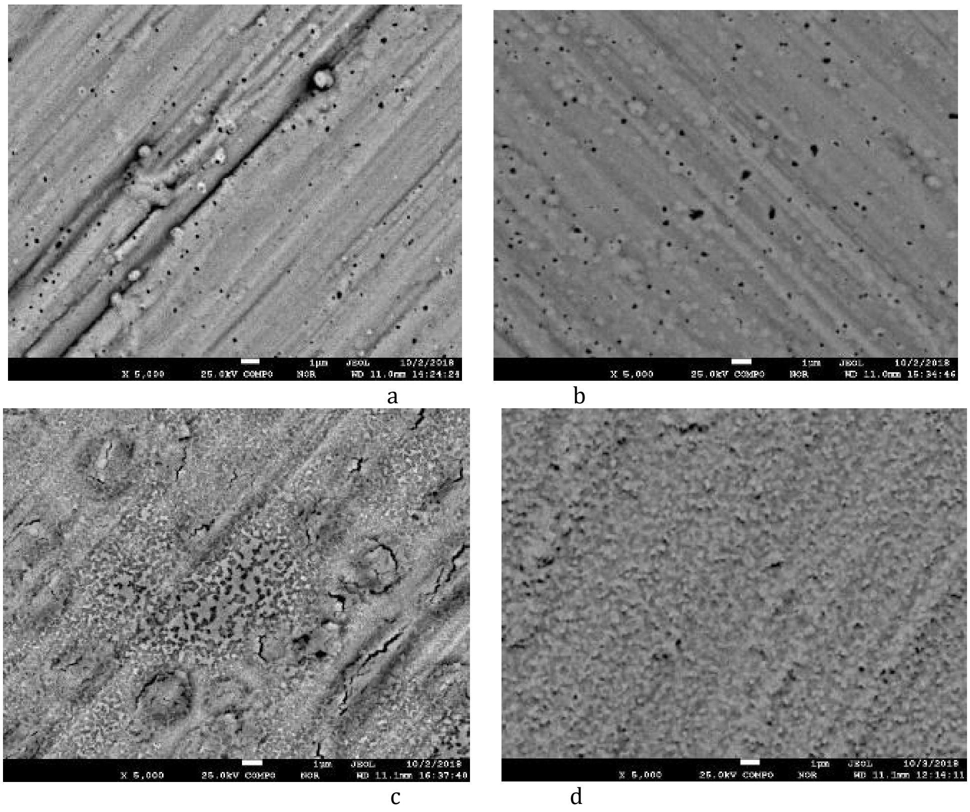
Upon isothermal exposure of the samples at 520°C, the content of the palladium film changed on the surface of all barrier layers except for the layer of W. In the structure of the palladium film on the surface of W, Mo, and Co, numerous holes with a cross section of up to 0.35 μm (Figure 8 a, b) were formed. The Pd film on the surface of the Re barrier layer underwent changes associated with the formation of microcracks, swellings, and the development of recrystallization with the formation of an island structure (Figure 8 c). The Pd film on the surface of the Cu barrier layer had not significant changes in the structure; in particular, the size of the globules decreased from 0.8 to 0.1–0.3 μm. On the surface of a Pd film deposited on a Ni layer, in the study in the COMPO mode, dispersed light precipitates with a size of 0.1 μm or less are detected.

The detected extrema on the curves of changes in the peak hydrogen permeance in dependence to the thickness of the Pd, Co, and, especially, Ni films (Figure 3) are poorly describable in theoretical aspect under the condition of uniform thickness of the sprayed films. This dependence indicates that the processes developing during hydrogen atoms transfer through a catalytic film are not limited only to adsorption, dissociation, hydrogen diffusion and atoms transfer through the metal layer/membrane interface; otherwise, with an increase in thickness, a decrease in hydrogen permeance would be observed as in the case of Re, Mo, Cu and W.



a b

Fig. 8. The initial surface structure of composite membranes. It is a typical structure of a - [Nb/W; Mo; Re (0.4-1.2 μm)/Pd 0.39 μm]; b - [Nb/Cu 0.478 μm/Pd 0.39] μm



a b

c d

Fig. 9 - Change in the structure of the palladium layer (0.39 μm) on the surface of barrier layers of various compositions after isothermal exposure at 520°C for 100 h.
a -W 0,44 μm; b- Mo 0,4 μm; c -Re 1,125 μm; d -Cu- 0,478 μm

Adibhatla et al. [43], it was pointed out that the surface morphology of $Ni_{64}Zr_{36}$ membranes significantly affects their hydrogen permeance. In this regard, the formation of pure nickel microcrystals on the surface of such membranes contributes to a sharp increase in the hydrogen flow. It is possible that the bends observed by us on the hydrogen permeance curves are associated with a change in the texture, continuity, and actual surface area of metal films sprayed onto the surface of niobium-based membranes by magnetron sputtering. This changes the adsorption and catalytic characteristics of the membrane surface, affecting the dissociation of hydrogen molecules. It is most likely that with an increase in the duration of spraying, the inhomogeneity of crystal growth on the film surface increases, which increases the actual surface area and improves the adsorption and dissociation of hydrogen molecules, while the hydrogen flow through the membrane is not constrained by the permeability of the catalytic layer. With a further increase in the thickness of the catalytic layer, the permeability of the catalytic layer begins to play a decisive role in the hydrogen flow density. As a result, there is a decrease in membrane permeability. Such a mechanism is indicated in the works [44]. For example, several studies report that surface phenomena begin to affect when palladium layers are less than 4–5 μm thick [45]. A significant change in the structure of the films with a change in their thickness from 10 to 100 nm is pointed out in a number of papers [46]. However, the results of studies of changes in the surface roughness of a palladium film after heat treatment in air [47-50] indicate that the change in permeability is associated not only with an increase in surface area.

A decrease in the hydrogen permeance of composite membranes after reaching peak values indicates a change in the surface properties of the films, probably due to interaction with water vapor and oxygen dissolved in a hydrogen-containing gas medium. The degree of decrease in the value of this characteristic substantially depends on the film material and hydrogen permeance. In this regard, membranes with a palladium layer over time practically do not reduce the level of hydrogen permeance. Membranes with films with the thickness of $W > 0.11$ μm, for $Re > 0.281$ μm, 0.039-0.078 μm for Ni retain hydrogen permeance for a long time. In other cases, a gradual decrease in the flow of hydrogen was observed.

As the obtained data show, the best catalytic characteristics of the considered metals (W, Re, Mo, Cu, Co, Ni, Ag, Pd) are possessed by layers of Pd (Figure 3), which ensures the highest hydrogen permeance of niobium membranes. Based on the results obtained, to conclude that further studies aimed at the use of Ni and Co films as an alternative to the palladium catalytic layer are promising. Since, while ensuring sufficient stability, such membranes can be used in membrane separation systems for hydrogen evolution from gas mixtures that do not contain aggressive gases. Among obvious advantages of such films, there is the ability to reduce the oxides of these metals with hydrogen in the range of membrane operating temperatures (500-600 °C). The prospect of using Ni as a catalytic layer on the surface of a V membrane was indicated by David M.

Viano et al. [20]. Membranes with Ag, Cu, Mo, Re and W films are characterized by low hydrogen permeance indicating a low catalytic activity of these metals.

Application of a 0.155 μm palladium layer on the surface of niobium-based membranes (40 μm) with a 0.013-0.104 μm W layer, 0.025-0.155 μm Mo layer, 0.048-0.956 μm Cu layer, 0.056-0.282 μm Re layer can significantly increase their hydrogen permeability. Thus, the hydrogen permeability of membranes after the deposition of a palladium layer increased by an amount in the case of a layer: from W by 170 - 760 times; from Mo by 0.5-10 times; from Re by 23-500 times; from Cu 1.6 - 14 times; from Co by 2.7 times; from Ag by 1.1-10 times. When palladium was applied to the surface of the Ni layer, the hydrogen permeability did not increase. This indicates that, in spite of the low catalytic activity, thin films of Re and W are characterized by high conductivity of hydrogen atoms. The nature of this phenomenon, as well as the nonlinear dependence of hydrogen permeance on the thickness of these layers, requires additional research.

The summary of results on the peak hydrogen permeance of composite niobium-based membranes with a barrier layer of Mo, W, Re, Cu and a catalytic palladium layer allows us to reveal a characteristic range of values (Figure 9). With a thickness of the barrier layers of 13 to 400 nm, the hydrogen permeance of such membranes corresponds to 3.9-7.0 $*10^{-5}$ mol/s*m^{2}*Pa$^{0.5}$. Obviously, the barrier layers in this thickness range are characterized by high hydrogen permeance. Moreover, the hydrogen permeance of the composite membrane is generally limited by the processes of association of hydrogen atoms and subsequent desorption of molecules from its opposite side.

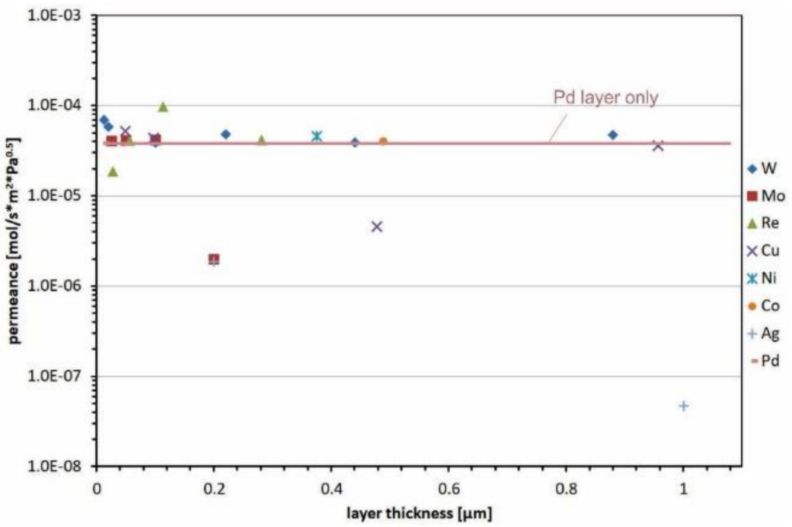


Fig. 10. Effect of the composition and thickness of the metal barrier layer on the surface of niobium-based membranes with a 0.155 μm palladium protective catalytic layer on their peak hydrogen permeance.

The study of the structure and composition of the Pd film (0.155-0.39 μm) after isothermal exposure of the composite membranes made it possible to establish that with increasing temperature from 420 °C to 520°C, the mutual diffusion between the catalytic and barrier layers of Mo, Re, Cu is significantly enhanced. A continuous series of solid solutions is formed between the Cu, Ni, Co layer and catalytic Pd layer, leading to an increase in the concentration of the material of the barrier layer on the surface of the catalytic layer. Moreover, an increase in the concentration of niobium is detected, indicating a counter diffusion of this element. This changes the characteristics of the membrane surface and, as a result, generally reduces the hydrogen permeance of the membranes. The interaction between Mo and Pd is explained by the development of reaction diffusion along with the formation of the intermetallic compound, MoPd$_2$. The formation of pores in this case can be associated with the development of the Frenkel effect, since the diffusion of palladium atoms toward the boundary with molybdenum causes the formation of many vacancies that gradually unite into pores. The change in the structure and composition of the palladium layer on the surface of the rhenium barrier layer can only be explained by the fact that palladium forming limited solid solutions with rhenium diffuses to the niobium surface. It is also possible of the formation of a χ-phase at the boundary between Nb and the Re layer. These processes lead to the the formation of microcracks and swelling of the film.

The Pd film on the surface of W barrier layer in the indicated temperature range does not change the composition, however, at 520 °C, through holes with a cross section of up to 0.25 μm are formed therein. At this temperature, the solubility of Pd in W is less than 0.5 at.%. Therefore, the only explanation for this phenomenon can be the diffusion of palladium along the grain boundaries of the tungsten layer to the membrane surface resulting in the Frenkel effect. However, this requires further research, Sasaki et al.[21] describe the process of pore formation in a palladium film on the surface of Nb membranes was considered as not related to the formation of the Pd$_3$Nb compound.

Based on the data obtained, it can be concluded that it is theoretically possible to use W barrier layers (0.01-0.4 μm) to reduce mutual diffusion between a Nb -based membrane and a Pd catalytic layer. With maintained high level of hydrogen permeance, the tungsten barrier layer provides minimal changes of the composition on the surface of the catalytic layer. Obviously, with an increase in the thickness of the W layer in the indicated interval, the stability of the properties of the Pd layer will increase. The undoubted advantage of W is its high melting point, which guarantees an extremely low rate of mutual diffusion at the Nb / W interface with the formation of solid solutions at a membrane operating temperature of 400-600 ° C. W is the only refractory metal that does not form solid solutions and intermetallic compounds with Pd, which in turn should ensure the absence of bulk diffusion at the W / Pd interface.

Cu barrier layers, due to the development of mutual diffusion with palladium along with the formation of solid solutions, result in a gradual increase in the concentration of this element on the surface of the catalytic layer, while palladium penetrates the membrane surface, where after reaching a certain concentration it combines with Nb to form $NbPd_3$. Despite the high level of hydrogen permeance of membranes with such a layer, this will result in a gradual decrease in this value. A similar situation will be observed on the surface of composite niobium-based membranes with Ni and Co barrier layers.

Membranes with Ag layer are characterized by low hydrogen permeance, as in the case of using only it, and paired with a palladium catalytic layer. It makes the use of pure silver unpromising as a barrier layer.

A change in the composition of the catalytic palladium layer and the transformation of its structure are observed during the long-term isothermal exposure of such membranes despite the high and anomalously high hydrogen permeance of niobium-based membranes with Mo and Re barrier layers. The reason is the development of mutual diffusion between Pd and Mo, followed by the formation of the $MoPd_2$ compound and the diffusion of Pd through the Re layer to the niobium surface and, in turn, the formation of an intermediate compound. Accordingly, an increase in the thickness of the Mo barrier layer cannot solve the problem of maintaining the properties of the catalytic layer. Experiments on isothermal treatment of membranes with a Re barrier layer of the increased thickness revealed the degradation of the catalytic layer and the destruction of the barrier layer over time. It enables us to conclude that Re also cannot be used as a layer to prevent diffusion destruction of the catalytic layer. Considering that dense metal films do not provide the required level of permeability and stability of membrane operation, microporous metal layers can be promising barrier layers. For example, such layers can be obtained by depositing iron oxide nanopowders [51-52].

CONCLUSION

Membranes [Nb / layer of Ni (thickness from 0.039 to 0.39 μm)] are characterized by hydrogen permeance at the level of the membranes [Nb / layer of Pd (0.155 μm)], and membranes [Nb / layer of Co (thickness 0.244-0.488 μm)] only in 2-3 times more slowly pass hydrogen. The use of layers of these metals at the inlet and outlet of hydrogen from the membranes may be promising for replacing the Pd layer in some applications.

Membranes [Nb / layer (Ag; Cu; Mo; Re; W)] are characterized by low hydrogen permeance, which indicates an insufficient catalytic activity of the surface of these metals.

Composite membranes [Nb/Cu; Mo; Re; W; Ni barrier layer; Co/ Pd catalytic layer] are characterized by high hydrogen permeance. With a thickness of the barrier layers of 13 to 400 nm, the hydrogen permeance of such membranes corresponds to 3.9-7.0 $*10^{-5}$ $mol/s*m^2*Pa^{0.5}$. This allows us to conclude that the barrier layers in this thickness range provide a high hydrogen diffusion rate.

During prolonged (100 hours) isothermal exposure (520°C) of composite membranes [Nb / barrier layer (Cu; Mo; Re; Ni; Co) / catalytic layer (Pd)] palladium layer, due to the development of mutual diffusion, changes the composition and structure. With a decrease in the holding temperature to 420 ° C, the intensity of the processes of mutual diffusion significantly decreases, however, a change in the structure and composition still occurs. The use of W for the manufacture of the barrier layer ensures the stability of the composition of the Pd layer during prolonged annealing of niobium membranes at 420°C and 520°C. Meanwhile, in the structure of the palladium layer after heat treatment, micropores of ,2 0.25 μm are detected, which are presumably the result of slow diffusion of palladium through the barrier layer to the membrane surface.

The high hydrogen permeance and the best stability of the structure and composition of the palladium catalytic membrane layer [Nb / barrier layer (W) / catalytic layer (Pd)] allows us to consider Was a promising material for barrier layers to limit mutual diffusion between Nb and Pd. Recommended layer thickness W should be >> 0.2 μm.

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