IRSTI 53.49.15

The effect of the catalytic layer composition on the hydrogen permeability of assymetric tantalum-based membranes

1* Panichkin A.V., 1 Kenzhaliyev B.K., 1 Kenzhegulov A.K., 1 Imbarova A.T., 1 Karboz Zh.A., 2 Shah A.

1 Satbayev University, Institute of Metallurgy and Ore Benefication JSC, Almaty, Kazakhstan
2 Faculty Technical and Vocational, Sultan Idris Education University, 35900 Tanjung Malim, Perak Malaysia

* Corresponding author email: abpanichkin@mail.ru , a.panichkin@satbayev.university

ABSTRACT

The paper offers the measuring results for hydrogen permeability of the membranes made of 40 μm thick tantalum foil covered with a metallic film with different thicknesses on one side. The measurements were performed when the membranes were in contact with a commercial argon and hydrogen gases mixed at the ratio of 1/5 at an overpressure of 500 kPa and at 580-585°C. It is shown that films of Mo, Re, W, Cu, Co, and Ni metals deposited on the tantalum membrane surface from the side facing a hydrogen-containing gas mixture increase its hydrogen permeability. The effect degree of these metals increases in the specified row from left to right. The effect on the hydrogen permeability of tantalum membranes, comparable to and superior to the deposition of a Pd film, exerts the deposition of Cu, Co, and Ni films. It is explained by the high hydrogen permeability level of these metals and the catalytic activity of their surface that results in intense hydrogen dissociation. The value of the hydrogen permeability of the membranes naturally increases with a thickness decrease of metallic films, however, it is obvious that this behavior is not linear. The hydrogen permeability of membranes with Cu, Co, and Ni films decreases over time, that is explained by the oxygen segregation at the Ta membrane/film interface, as well as by the processes on the membrane surface in contact with the gas mixture. The nature of these processes should be studies since the lower oxides of these metals are reduced by hydrogen at this temperature.

Keywords: composite membrane, tantalum, metal catalytic overcoat, hydrogen permeability, dilatation.

Information about authors:	
Panichkin Aleksandr Vladimirovich	*Candidate of Technical Sciences, Head of the National Scientific Laboratory, Institute of Metallurgy and Ore Beneficiation, E-mail: abpanichkin@mail.ru, ORCID ID: 0000- 0002-2403-8949*
Kenzhaliyev Bagdaulet Kenzhaliyevich	*Doctor of technical sciences, General Director - Chairman of the Board of the Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan. Email:: bagdaulet_k@satbayev.university, Orcid ID: 0000-0003-1474-8354*
Kenzhegulov Aidar Karaulovich	*PhD, Researcher of the Laboratory of Metall Science, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan. Email: kazakh_1403@mail.ru, ORCID ID: 0000- 0001-7001-2654*
Imbarova Akerke Talgatkyzy	*Researcher of the Laboratory of Metall Science, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan. Email: akerke_345@mail.ru, ORCID ID: 0000-0002-9366-314X*
Karboz Zhanar Adilbekkyzy	*Engineer of the Laboratory of Metall Science, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan. Email: k.zhanar.a@mail.ru, ORCID ID: 0000-0003-2538-8585*
Shah Arman	*Professor, Dr., Faculty Technical and Vocational, Sultan Idris Education University, 35900 Tanjung Malim, Perak Malaysia. Email: armanshah@ftv.upsi.edu.my, ORCID ID: 0000-0002-4366-9156*

Introduction

One-stage membrane separation with the ultrapure hydrogen production is a promising method to separate hydrogen from gas mixtures formed during steam reforming. Currently, palladium and its alloys are industrially used as a membrane material but their very high cost limits the spread of this method. In respect thereof, the hydrogen industry development requires to develop new highly efficient and inexpensive hydrogen permeable membranes [1- 2]. Group 5 metals are significantly cheaper than palladium and are characterized by high hydrogen absorption capacity.

Under various sources, the hydrogen permeability of tantalum is $6*10^{-8}$-$2*10^{-7}$mol$*$m$^{-1}*$s$^{-1}*$Pa$^{-0.5}$ at 440 °C [1]. However, the tantalum surface is covered with an oxide film as a result of interaction with reactive gases, as well as surface segregation of the oxygen dissolved in the grid, at operating temperatures (> 350°C). Such a film sharply reduces the catalytic dissociation of hydrogen molecules on the membrane surface required to absorb hydrogen [3]. The actual hydrogen permeability of 40 μm thick tantalum membranes upon contact with technical grade hydrogen decreases up to ~1.17-6 $*10^{-10}$mol$*$m$^{-1}*$s$^{-1}*$Pa$^{-0.5}$ [4] when the temperature rises to 500-580°C.

It is believed that double-sided coating with a layer of palladium or palladium alloys up to several microns thick is the most promising to reduce oxidation and improve catalytic dissociation on the tantalum membrane surface [1- 2, 5- 6]. However, this coating when heated is subject to destructive changes in the morphology of its surface [5] and a change in composition due to reactive diffusion at the border with tantalum. These processes rapidly reduce membrane hydrogen permeability. In this regard, the search for effective ways to prevent the degradation of the palladium film properties is of decisive importance to use tantalum as a material for hydrogen-permeable membranes. Replacement of palladium with another metal is even more promising.

It is proposed to use a barrier layer separating the Group 5 metal membranes and the Pd alloy layer to prevent mutual diffusion. The materials used to form barrier layers can be divided into two types: non- porous and porous ones. The hydrogen flux is determined by the hydrogen permeability of the layer material in the first case, and by its gas permeability in the second one. Perovskites, hydroxy acids and fluorides [1], metal oxides [1], carbides [7], including niobium and tantalum [8 - 9], chalcogenides [10 - 11] and nitrides [12] are considered as materials for the barrier layers based on the requirement of hydrogen transfer and inertness with respect to palladium and the membrane material.

Despite certain advances in researches focused on the development of barrier layers made of non-metallic materials, it can be concluded that non-metallic coatings cannot be considered promising due to the fact that they are characterized by a complete absence of plasticity that will result in their inevitable destruction during hydrogen dilatation of membranes, that is shown in the work [12]. Besides,

questions about the magnitude of the adhesion of tantalum and palladium to such films and the problem how to apply these films commercially remain open. Metal-based barrier layers are more promising in contrast to them since they are characterized by plasticity, lack of porosity, and the possibility of using various methods of deposition. Meanwhile, studies focused on use of metal barrier layers are very limited [13- 14].

It is known that the hydrogen permeability of such metals as Fe, Ni, Cu, Co, Mo increases with temperature [15- 16]. The hydrogen permeability is Ni - $7.8 *10^{-11}$, Cu - $4.9*10^{-12}$, Fe - $1.8*10^{-10}$ mol$*$m$^{-1}*$s$^{-1}*$Pa$^{-0,5}$ at 500°C under the data given in [17], that is significantly lower in comparison with tantalum and palladium ($1.3*10^{-7}$ and $1.9*10^{-8}$mol$*$m$^{-1}*$s$^{-1}*$Pa$^{-0,5}$). However, the hydrogen flux through the membrane increases in proportion to the decrease in its thickness that confirms the fundamental possibility to use both the specified metals as a material for the barrier or face layer and with an even lower value of hydrogen permeability.

The stability of the structure and properties of the metal barrier layers on the membrane surface can be maintained only if there is no reaction interaction of the layer material with hydrogen, tantalum and palladium with the formation of hydrides, intermetallic compounds, weak mutual diffusion with the formation of solid solutions, in the temperature range 400-600°C. Analysis of binary phase diagrams Ta-Me, Pd-Me, H-Me (where Me are various metals) enables us to conclude that W is the most inert to Ta and Pd; it forms only solid solutions with them. Re forms solid solutions with Pd but forms χ - phase with Ta. Due to the high melting temperature, W and Re are characterized by low diffusion coefficients that suggests that the layers of these metals are stable in the specified temperature range. Mo and Ta are infinitely soluble in each other but this metal is less promising as a barrier layer due to the formation of one intermetallic compound $MoPd_2$ with Pd. Ni, Co, Cu, Ag form a continuous series of solid solutions with Pd but they form a number of intermetallic compounds with tantalum Ni and Co. The low melting point of Cu, Ag can cause palladium to diffuse into their surface. It can be concluded based on the analysis of the phase diagrams that W and Re are the most suitable metals for use as a barrier layer separating the tantalum membrane from the palladium catalytic layer. Cu and Ag can be considered as promising materials to replace the palladium layer in direct contact with tantalum. The

use of Ni, Co as a material for such layers will be possible only in the case of slow reaction diffusion, or if their intermetallic compounds with Ta will not significantly reduce the hydrogen permeability of the composite membrane.

The literature contains an extremely small number of publications devoted to studies of the hydrogen permeability of composite membranes made of Ta, Nb, V and alloys based on them with a metallic face layer, with the exception of Pd [18]. Earlier [19] it was shown that the deposition of films of solid solutions based on these metals on the front side of niobium and tantalum membranes does not significantly affect the hydrogen permeability in comparison with membranes without coatings. At the same time, the authors of [20] have shown that the deposition of Ta and Nb layers on the surface of membranes made of the $V_{85}Al_{10}Ta_5$ alloy reduces the hydrogen permeability in comparison with similar membranes but with Pd coating by 44 and 48%, respectively. In [21], it is specified that the hydrogen flux for an amorphous $Ni_{40}Nb_{20}Ta_5Zr_{30}Co_5$ alloy with a nickel coating was less than one fourth of the value achieved with the use of a Pd coating.

Thus, to use tantalum as a material of hydrogen permeable membranes to create membrane reactors, it is important to search for metals that can be used as a material:

- a barrier layer to prevent the interaction of the tantalum hydrogen permeable membranes and the palladium catalytic layer;

- face layer, instead of palladium, in cases where the separated hydrogen-containing atmosphere is not aggressive.

There is no information in the literature on the change in the hydrogen permeability of tantalum membranes when layers of such metals as W, Re, Mo, Cu, Ni, Co are deposited on their surface. Due to the fact that these metals are promising for use as a barrier or face layer in a number of their properties, this article presents the study results of the effect of the thickness of the face layer made of these metals on the hydrogen permeability of tantalum membranes.

Experimental part

40 μm thick tantalum (HFC) cold-rolled foil in the annealed state produced at the Ulba Metallurgical Plant JSC were used to obtain the membranes. W, Re, Mo, Ni, Co, Cu, and Pd films of various thicknesses after ionic cleaning were deposited onto

120x120 mm foil surface from one side by magnetron sputtering. Only one layer of the specified metals was applied to the inlet side of the membrane. The thickness of the films was determined both by measuring the transverse sections using a JEOL JXA-8230 microprobe analyzer, and by calculation based on the experimentally measured deposition rate of layers.

The hydrogen permeability of the obtained membranes was determined with a classical design device [22] by measuring the flow rate of hydrogen passing through a sealed membrane. A C160 twill weave mesh made of AISI321 stainless steel with surface preliminarily oxidized to prevent interaction with the membrane was used as a gas-permeable substrate. Aluminum sealing washers were used to ensure tightness.

When the membrane was heated in vacuum up to 580 - 5°C, argon was admitted on both sides of the membrane up to atmospheric pressure. Hydrogen was admitted from the inlet side of the membrane up to an excess pressure of 500 - 15 kPa. Thus, an Ar/H2 gas mixture with a volume ratio of 1/5 was obtained from the membrane side covered with a metallic film. Argon injection was required to exclude the destruction of the membrane, since the plasticity of tantalum sharply decreases at the experimental temperature and hydrogen pressure of ~100 kPa. Numerous preliminary experiments have shown that the elimination of argon admission and the use of hydrogen at the stage of bringing the pressure to atmospheric from the permeate outlet side results in the membrane destruction 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, hydrogen passing through the membrane displaced argon from the chamber from the permeate side with a volume 0.5 ± 0.05 cm^3. As a result thereof, 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/H2 gas mixture ratio on the inlet side of the membrane was maintained by feeding pure hydrogen into the chamber. Additionally dried (Tr ≈ -40°C) argon 99.95% and hydrogen grade B (99.95%) (GOST 3033-80) were used in the experiments. The working area of the membranes was 78.5 cm^2. The gas flow rate was fixed using a block of rotameters and RRG12 gas flow meters. The measurement of its velocity was performed by fixing the interval of the

exit of bubbles from the capillary at low flow. The bubble volume was previously measured. The hydrogen flow rate was measured before the breakthrough that was shown by the sharp increase in the 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 composition analysis of the gas leaving the membrane was not performed, since it is known that metal membranes provide absolute selectivity to hydrogen. Besides, numerous preliminary experiments performed by the authors of the article have shown that a breakthrough of a membrane with such a large area occurs with a well-recorded increase in the gas flow, and a continuous increase in the gas flow is observed when there is a microcrack.

The hydrogen flow density was calculated in J, mol/s*m^2 based on the measurement results for the hydrogen flow rate using Formula 1. The hydrogen permeability of membranes was shown by the hydrogen permeability value - P, mol/s*m^2*Pa^{0,5} calculated by Formula 2.

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

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

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

A test for hydrogen permeability of uncoated tantalum foils was performed for comparison under identical conditions.

Results and Discussion

The experimental results obtained showed that the deposition of thin metallic layers on the surface of tantalum membranes results in an increase in their hydrogen permeability. The deposition of Cu, Co and Ni layers, to a lesser extent Mo, W, and Re, has a significant effect on this parameter.

The time dependence of the hydrogen permeability of a Ta membrane covered with a W layer with a thickness of more than 0.22 μm is close to linear (Figure 1), and the destruction of such membranes occurs before the curve reaches its maximum or a gentle segment. The hydrogen permeability change curve reaches an extremum at a layer thickness of 0.11 μm. With a W layer width increase from 0.11 to 0.44 μm, the maximum membrane hydrogen permeability decreases from 10.8*10^{-7} until 1.8*10^{-7} mol/s*m^2*Pa$^{0.5}$.

The curves of changes in the hydrogen permeability of membranes with a 0.028 - 0.113 μm thick Re layer are concave that confirms an increase in the rate of change in this value and the destruction of membranes until reaching maximum values (Figure 2). The observed change in the hydrogen permeability of the tantalum membrane with time is almost identical with a Re layer thickness of 0.028 and 0.056 μm, and its maximum value is ~5.4 *10^{-7} mol/s*m^2*Pa$^{0.5}$. An increase to 0.113 and 0.281 μm results in a decrease in the rate of change in the hydrogen permeability and a decrease in its maximum value to ~3.2 and ~1.6 *10^{-7} mol/s*m^2*Pa$^{0.5}$. A Ta membrane with a 1.125 μm thick Re layer is characterized by the hydrogen permeability observed in tantalum membranes − 1.8-4.5 *10^{-8} mol/s*m^2*Pa$^{0.5}$.

With an increase in the Mo layer thickness from 0.05 to 0.2 μm, the period until the maximum level of hydrogen permeability of the Ta membrane is reached decreases from ~80 to 40 sec. In this case, the maximum value of the membrane hydrogen permeability practically does not change and is 3.0-3.1 *10^{-7} mol/s*m^2*Pa$^{0.5}$ (Figure 3). An increase in the layer thickness to 0.4 μm results in a decrease in this parameter up to ~1.9*10^{-7} mol/s*m^2*Pa$^{0.5}$ and an increase in the period until it reaches 60 s. The membrane with a 0.6 μm thick Mo layer breaks through until an inflection appears on the curve at a hydrogen permeability value ~1.18*10^{-7}mol/s*m^2*Pa$^{0.5}$.

The maximum hydrogen permeability increases from 2.01 to 4.02 *10^{-6} mol/s*m^2*Pa$^{0.5}$ with a decrease in the Cu film thickness from 1.912 to 0.478 μm (Figure 4). The hydrogen permeability of the membranes decreases after reaching the maximum values, that is explained by a change in the characteristics of the copper layer surface. The most likely reason for it is the formation of a thin oxide layer on the developed film surface since its color changes from pink to bright red.

In the range of Co film thicknesses 0.049-0.488 μm, the maximum hydrogen permeability reaches 8.06-9.5*10^{-6} mol/s*m*Pa$^{0.5}$, and at 0.975 мкм − 3.85*10^{-6} mol/s*m^2*Pa$^{0.5}$ (Figure 5). This value decreases to 5.4-7.5*10^{-6} mol/s*m^2*Pa$^{0.5}$ over time. A membrane with a 0.975 μm film was
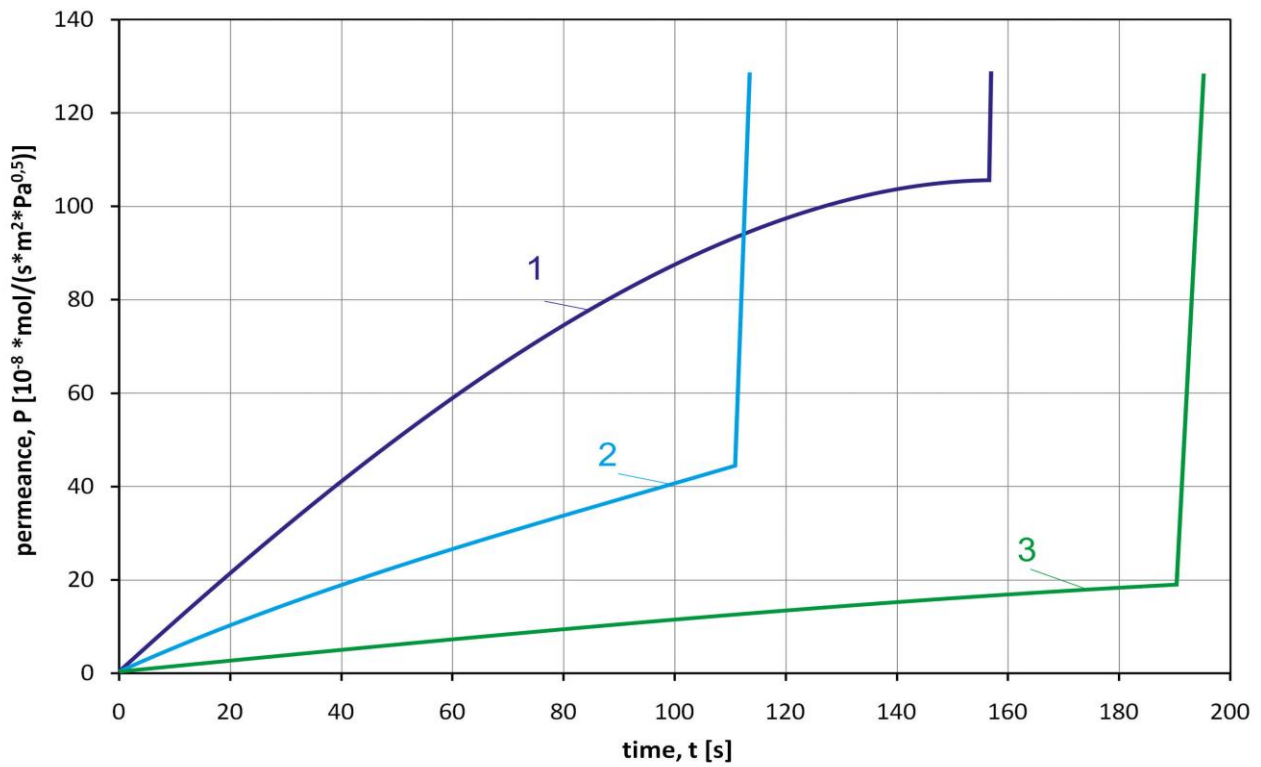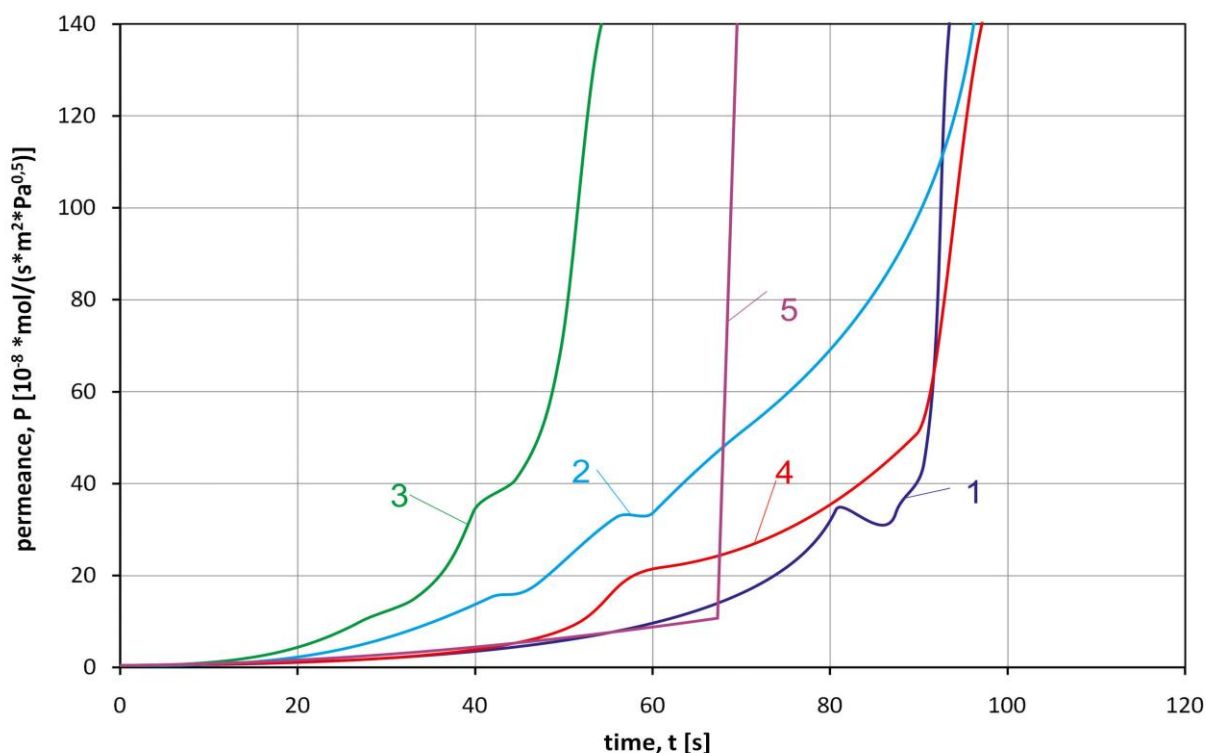
1 - 0.11; 2 - 0.22; 3 - 0.44

Figure 1 Effect of the W layer thickness (µm) on the change in the hydrogen permeability of Ta/W composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C
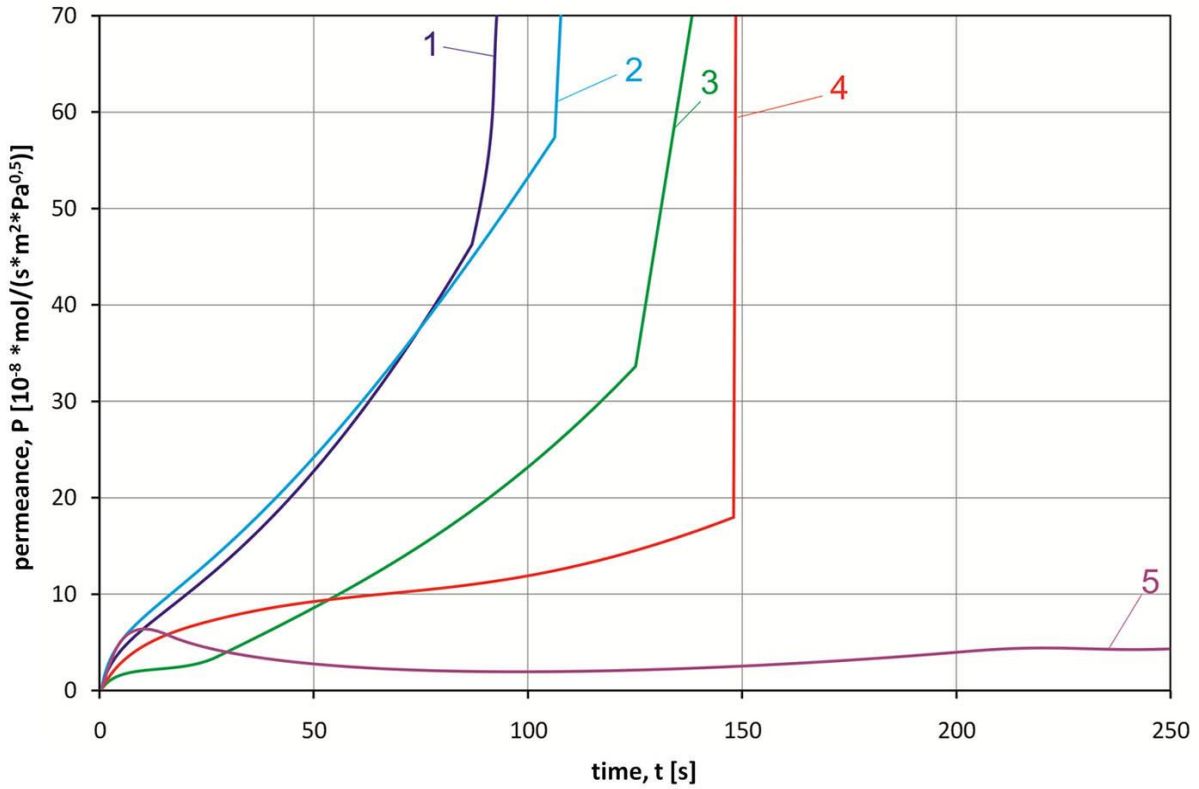

1- 0.028; 2- 0.056; 3 - 0.113; 4 - 0.281; 5 - 1.125

Figure 2 Effect of the thickness of the Re layer (µm) on the change in the hydrogen permeability of Ta/Re composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C
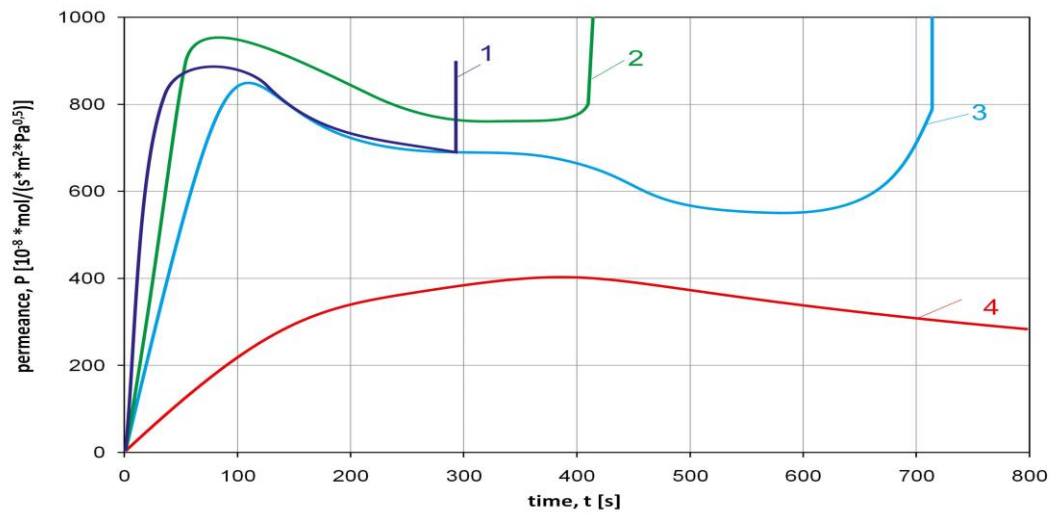
1 - 0.05; 2 - 0.1; 3 - 0.2; 4 - 0.4; 5 - 0.6

Figure 3 Effect of the Mo layer thickness (µm) on the change in the hydrogen permeability of Ta/Mo composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C
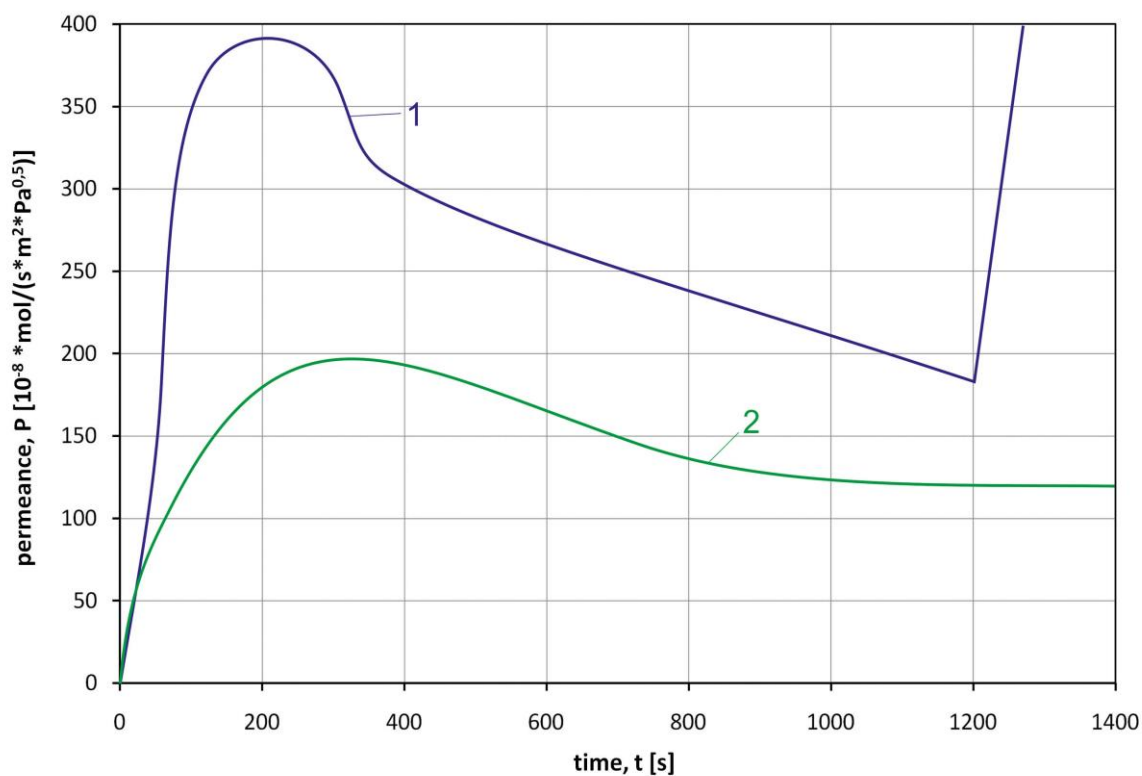
1- 0.478; 2- 1.912

Figure 4 Effect of the Cu layer thickness (µm) on the change in the hydrogen permeability of Ta/Cu composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C
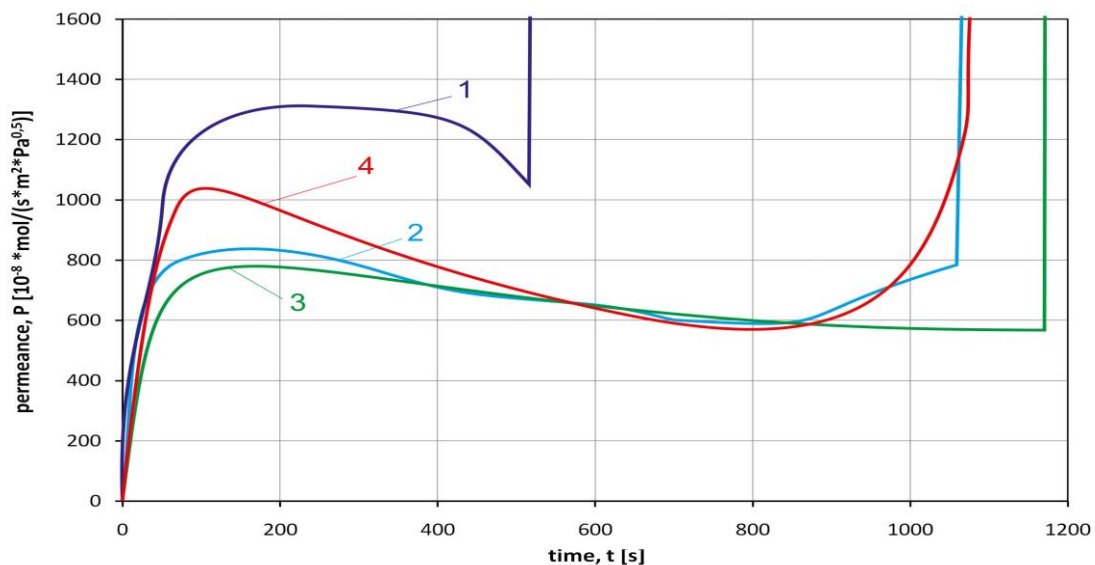
1- 0.049; 2 - 0.244; 3 - 0.488; 4 - 0.975

Figure 5 Effect of the Co layer thickness (µm) on the change in the hydrogen permeability of Ta/Co composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C

operated for the same time until destruction, as did a membrane made of pure tantalum, while the steady-state level of hydrogen permeability exceeded ~100 times and corresponded to $2.48*10^{-6}$ mol/s*m²*Pa^0.5.

At a Ni film thickness of 0.075 µm the Ta membranes demonstrate the maximum hydrogen permeability at the level 13.3 $*10^{-6}$ mol/s*m²*Pa^0.5 (Figure 6). The membranes are destroyed in a short time at 0.038 µm. In the range of thicknesses from 0.19 to 0.75 µm, the maximum value of hydrogen permeability is close and is 7.87-10.6 $*10^{-6}$ mol/s*m²*Pa^0.5. a decrease in hydrogen permeability is observed to 5.77-5.94 $*10^{-6}$ mol/s*m²*Pa^0.5 over the membrane operation time.

The maximum value of the hydrogen permeability of Ta membranes decreases from 14.4 to $9.68*10^{-6}$ mol/s*m²*Pa^0.5 with an increase in the Pd layer thickness from 0.039 to 0.155 µm (Figure 7). There is a smooth decrease in hydrogen permeability to $11.5*10^{-6}$ mol/s*m²*Pa^0.5 over the time, at 0.039 µm and to $8.05*10^{-6}$ mol/s*m²*Pa^0.5 at 0.155 µm. Then the membranes lose their tightness and collapse. The hydrogen permeability of membranes significantly decreases at a Pd layer width of 0.39 µm, and amounts to $1.22-1.35*10^{-6}$ mol/s*m²*Pa^0.5. And the period until the membrane breakdown increases with an increase in the Pd layer thickness. The data obtained correlate well with the results presented in the work. [23].

1- 0.075; 2 - 0.19; 3 - 0.375; 4 - 0.75

Figure 6 Effect of the Ni layer thickness (µm) on the change in the hydrogen permeability of the Ta/Ni composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C
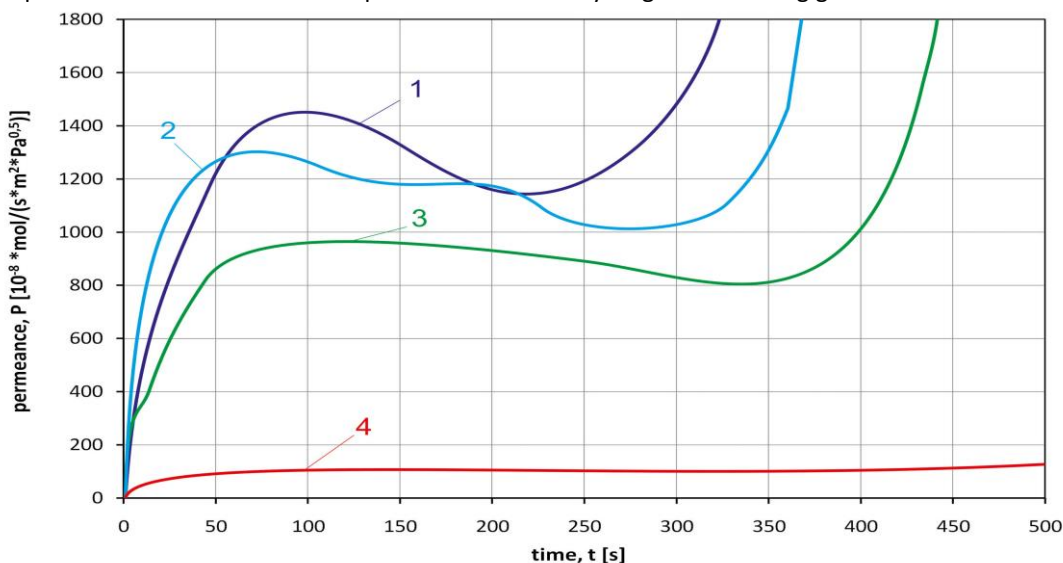
1 - 0.039; 2 - 0.078; 3- 0.155; 4- 0.39

Figure 7 Effect of the Pd layer thickness (µm) on the change in the hydrogen permeability of Ta/Pd composite membranes over time upon contact with a hydrogen-containing gas mixture at 580°C

Study of the W and Mo films structure after the tests showed that cracks and peeling are possible in the surface as a result of dilatation of Ta membranes with a coating thickness of more than 0.4 µm, (Figure 8). It confirms their limited plasticity. Meanwhile, no cracks were found on the surface of thinner films. Films of other metals, such as Re, Cu, Co, Ni and Pd, did not undergo significant changes during the test period.
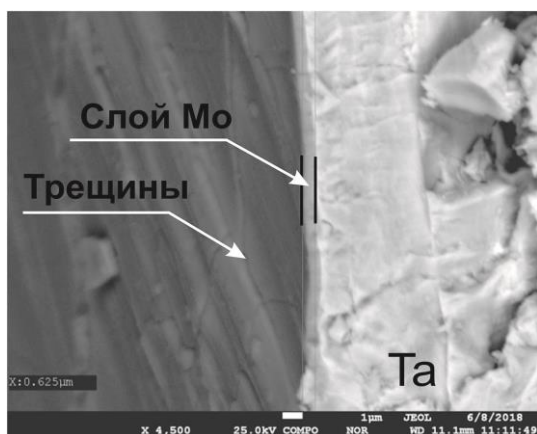
Слой Mo – Mo layer
Трещины – Cracks

**Figure 8** Chipping and formation of microcracks in a 0.625 µm Mo layer after the membrane testing

The experimental results obtained enable us to conclude that the deposition of metallic layers on the tantalum membrane surface allows to increase its hydrogen permeability (Figure 9). This parameter is significantly influenced by both the layer material and its thickness. A decrease in its value with an increase in the layer thickness is explained with the hydrogen permeability value of the layer material [15]. However, such a significant effect of the coating material used on the membrane as a whole is explained primarily by the catalytic properties of the surface that determine the development of dissociative processes on the membrane surface in contact with a hydrogen-containing gas mixture. If we compare the hydrogen solubility in copper, nickel, and palladium at the experimental temperature, under the data given in [24], then the difference in the hydrogen permeability of membranes with a Pd and Cu layer with an identical thickness should be ~10 times, and between membranes with Pd and Ni coating by at least 3 times in favor of palladium coating, and in terms of hydrogen permeability, this difference should be $3.8*10^3$ и $2.43*10^2$ respectively [15]. But in fact, with an equal film thickness, tantalum membranes with a palladium film demonstrate even lower hydrogen permeability. Thus, in the case of Pd - 0.078 µm and Ni - 0.075 µm films, the hydrogen permeability is 12.9 and 13.3 $*10^{-6}$ mol/s*m*Pa$^{0.5}$, and in the case of Pd films - 0.39 µm and Cu-0.478 µm, Co - 0.488 µm: 1.35, 4.0, 9.5a$*10^{-6}$ mol/s*m^2*Pa$^{0.5}$ respectively. All this suggests that the hydrogen dissociation on the surface of nickel, cobalt and copper proceeds more intensively than on the palladium surface. Meanwhile, it cannot be

excluded that the reason for the results obtained can be a significant difference in the value of the

energy barrier during the transition of hydrogen atoms through the Ta/coating interface.
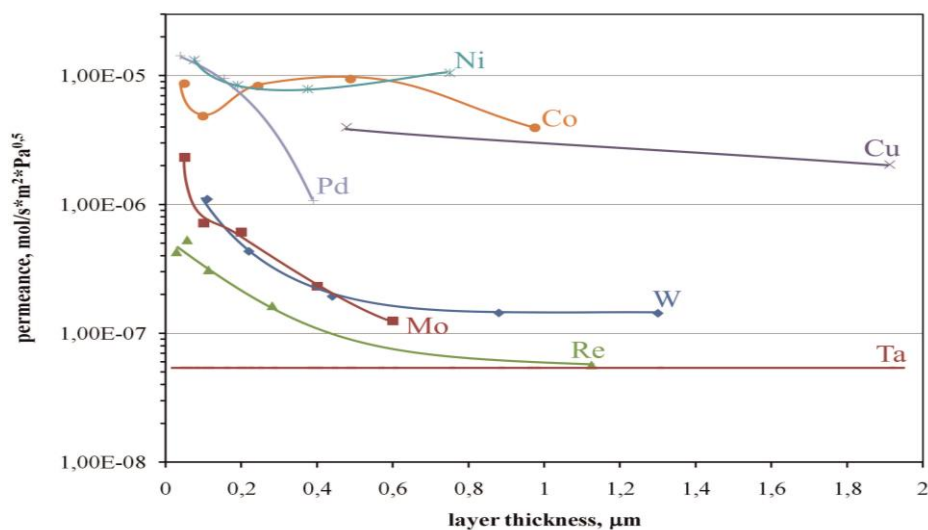
Figure 9 Effect of the composition and thickness of the metallic layer on the tantalum membrane surface on the value of their peak hydrogen permeability

The low hydrogen permeability of Ta membranes with a Mo, W, and Re layer is primarily justified by the extremely poor hydrogen permeability of these metals, since there is a significant dependence of this parameter on the thickness of the films of these metals. Thus, the permeability coefficient of the W films was from 1.1 to $32*10^{-15}$ mol/s*m*Pa$^{0.5}$ after 24 hours at 400°C under the data of [25], meanwhile, this characteristic significantly increases with an increase in temperature due to an increase in the diffusion coefficient of hydrogen [26]. Molybdenum in comparison with tungsten is characterized by a higher hydrogen permeability ~$5*10^{-12}$ mol/s*m*Pa$^{0.5}$[15], however, it does not allow achieving higher hydrogen permeability of the tantalum membrane.

The decrease in the hydrogen permeability value observed in many experiments over time is explained by several reasons. First, the hydrogen concentration behind the membrane increases at the initial stage of diffusion, since this cavity that is not significant in volume (~ 10 cm^3), is initially filled with argon. It causes a decrease in the difference in the partial pressures of hydrogen on the outer and inner surfaces of the membrane. Second, there is a gradual change in the properties of the outer and inner surfaces of the membrane that slows down the intensity of dissociative-associative processes at the hydrogen/membrane interface specified by a change in the membrane surface color, especially facing the inside of the unit chamber. Besides, a

probable reason is the oxygen diffusion to the surface of the tantalum membrane and the formation of an oxide film at the coating/tantalum membrane interface described in [27] but it requires additional researches.

A gradual decrease in the hydrogen permeability of membranes due to the formation of an oxide film on the coating surface in direct contact with the gas mixture is, in principle, possible when Mo and W coatings are used, while the Re, Ni, Cu, and Co lower oxides at these temperatures are reduced by hydrogen to the metallic state. Under the data of [28], even a small H$_2$O content in hydrogen results in a significant decrease in this characteristic in molybdenum that is obviously associated with a decrease in catalytic activity on the surface due to the formation of oxides.

The duration of its operation until destruction increases with an increase in the metallic layer thickness on the membrane surface. Besides, the total operating time of membranes with a copper, nickel, and cobalt layer significantly exceeds the one that is observed for membranes with tungsten, rhenium, and molybdenum films. It is explained by the fact that the diffusion of hydrogen decreases with an increase in the layer thickness, and, as a consequence, the dilation of tantalum membranes decreases resulting in their destruction. The mechanism of increasing the operating time of tantalum membranes in the case of deposition of a layer of hydrogen highly conductive copper, nickel and cobalt can only be explained from the

standpoint of preventing the formation and propagation of cracks on the membrane surface deformed due to dilatation, since these metals retain a high level of plasticity when hydrogen is dissolved in them.

Conclusions

Films of Re, W, Mo, Cu, Co and Ni metals deposited on the tantalum membrane surface from the side facing the hydrogen-containing gas mixture increase its hydrogen permeability. The effect degree of these metals increases from left to right in the specified row. The deposition of Cu, Co, and Ni films has an effect on the hydrogen permeability of tantalum membranes that is comparable to and superior to the deposition of a Pd film. It is explained by the high level of hydrogen permeability of these metals and the catalytic activity of their surface that results in intense hydrogen dissociation. With a thickness decrease of the metallic films, the value of the hydrogen permeability of the membranes naturally increases but it is obvious that this behavior is not linear.

Over time, the hydrogen permeability of membranes with Cu, Co, and Ni films decreases that is explained by the oxygen segregation at the membrane/film Ta interface, as well as by the processes on the membrane surface in contact with the gas mixture. The nature of these processes requires study, since at the hydrogen diffusion temperature, the lower oxides of these metals are reduced by hydrogen. One of the probable reasons is defects in the structure of the deposited films, due to which active gases penetrate to the tantalum surface and interact with it.

It can be concluded based on the data obtained that it is promising to replace the palladium catalytic overcoat on the surface of membranes made of tantalum and its alloys with Cu, Co, Ni films and to use such membranes to extract hydrogen from gas mixtures without aggressive substances.

Considering the increase in the hydrogen permeability of tantalum membranes upon deposition of Re, W, Mo, Cu, Co, and Ni films, it is promising to test them as barrier layers separating the face layer from palladium.

Тантал негізіндегі асимметриялық мембраналардың сутегі өткізгіштігіне каталитикалық қабат құрамының әсері

[1*] Паничкин А.В., [1] Кенжалиев Б.К., [1] Кенжеғұлов А.Қ., [1] Имбарова А.Т., [1] Кәрбоз Ж.Ә., [2] Шах А.

[1] Сәтбаев университеті, Металлургия және кен байыту институты, Алматы, Қазақстан

[2] Техникалық және кәсіптік факультеті, Сұлтан Идрис атындағы білім беру университеті, 35900 Танджунг Малим, Перак Малайзия

[*] Автордың электрондық поштасы: abpanichkin@mail.ru , a.panichkin@satbayev.university

ТҮЙІНДЕМЕ

Мақалада танталдың жұқалтырынан (фольгасынан) жасалған, қалыңдығы 40 мкм, бір жағы әр түрлі қалыңдықтағы металл қабыршығымен қапталған мембраналардың сутегі өткізгіштігін өлшеу нәтижелері келтірілген. Өлшеу мембраналар 580-585°C   500 кПа артық қысым кезінде 1/5 қатынасында техникалық таза аргон мен сутектің газ қоспасымен жанасу кезінде жүргізілді. Тантал мембранасының сутегі құрамды газ қоспасы жағындағы бетіне жалатылған Mo, Re, W, Cu, Co және Ni металдарының қабыршықтары оның сутегі өткізгіштігін жоғарылататыны анықталды. Осы металдардың әсер ету дәрежесі көрсетілген қатарда солдан оңға қарай артады. Тантал мембраналарының сутегі өткізгіштігіне Cu, Co және Ni қабыршықтарын тұндыру әсер етеді. Мұны Pd қабыршығын жалатқанмен салыстыруға болады және одан да асып түседі. Бұл осы металдардың жоғары сутегі өткізгіштігімен және олардың бетінің каталитикалық белсенділігімен түсіндіріледі, нәтижесінде сутегінің қарқынды диссоциациясы жүреді. Металл қабыршықтарының қалыңдығы азайған сайын мембраналардың сутегі өткізгіштігінің шамасы заңды түрде артады, дегенмен бұл заңдылық сызықтық емес. Уақыт өте келе Cu, Co және Ni қабықшықтары бар

мембраналардың сутегі өткізгіштігі төмендейді, бұл Та мембрана / қабыршық бетіндегі оттегінің бөлінуімен, сондай-ақ мембрана бетіндегі газ қоспасымен жанасу процестерімен түсіндіріледі. Бұл процестердің табиғатын зерттеу қажет, өйткені бұл температурада осы металдардың төменгі оксидтері сутегімен тотықсызданады.

Түйін сөздер: композициялық мембрана, тантал, металдық каталитикалық жабын, сутегі өткізгіштік, дилатация.

Авторлар туралы ақпарат:

Паничкин Александр Владимирович
- техника ғылымдарының кандидаты, Металлургия және кен байыту институты, Ұлттық ғылыми зертхана жетекшісі, Email: abpanichkin@mail.ru, ORCID идентификаторы: 0000-0002-2403-8949

Кенжалиев Бағдәулет Кенжәліұлы
- техника ғылымдарының докторы, Бас директор – Басқарма төрағасы, Металлургия және кен байыту институты, Алматы, Қазақстан. Email: bagdaulet_k@satbayev.university, Orcid идентификаторы: 0000-0003-1474-8354

Кенжеғұлов Айдар Қараулұлы
- PhD, Металлургия және кен байыту институты, металтану зертханасының ғылыми қызметкері, Алматы, Қазақстан. Email: kazakh_1403@mail.ru, ORCID идентификаторы: 0000-0001-7001-2654

Имбарова Ақерке Талғатқызы
- Металлургия және кен байыту институты, металтану зертханасының ғылыми қызметкері, Алматы, Қазақстан. Email: akerke_345@mail.ru, ORCID ID: 0000-0002-9366-314X

Кәрбоз Жанар Әділбекқызы
- Металлургия және кен байыту институты, металтану зертханасының инженері, Алматы, Қазақстан. Email: k.zhanar.a@mail.ru, ORCID ID: 0000-0003-2538-8585

Шах Арман
- профессор, Сұлтан Идрис атындағы білім беру университетінің техникалық және кәсіптік факультетінің докторы, 35900 Танджунг Малим, Малайзия, Перак. Email: armanshah@ftv.upsi.edu.my, ORCID идентификаторы: 0000-0002-4366-9156

Влияние состава каталитического слоя на водородопроницаемость ассиметричных мембран на основе тантала

¹*Паничкин А.В., ¹Кенжалиев Б.К., ¹Кенжегулов А.К., ¹Имбарова А.Т., ¹Карбоз Ж.А., ² Шах А.

¹ АО «Институт металлургии и обогащения» при НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан
² Факультет технического и профессионального образования, Университет Султана Идриса, 35900 Танджунг Малим, Перак, Малайзия

* Электронная почта автора: abpanichkin@mail.ru , a.panichkin@satbayev.university

АННОТАЦИЯ

В работе представлены результаты измерения водородопроницаемости мембран из фольги тантала толщиной 40 мкм, с одной стороны покрытых металлической пленкой различной толщины. Измерения проведены при контакте мембран с газовой смесью аргона и водорода технической чистоты в соотношении 1/5 при избыточном давлении 500 кПа при 580-585°C. Показано, что пленки металлов Mo, Re, W, Cu, Co и Ni, нанесенные на поверхность танталовой мембраны со стороны, обращенной к водородсодержащей газовой смеси, повышают ее водородопроницаемость. Степень влияния этих металлов возрастает в указанном ряду слева на право. Влияние на водородопроницаемость мембран из тантала, сопоставимое с нанесением пленки Pd и превосходящее его, оказывает осаждение пленок Cu, Co и Ni. Это объясняется высоким уровнем водородопроницаемости этих металлов и каталитической активностью их поверхности, приводящей к интенсивной диссоциации водорода. С уменьшением толщины металлических пленок величина водородопроницаемости мембран закономерно растет, однако, очевидно, что эта закономерность не линейна. С течением времени водородопроницаемость мембран с пленками Cu, Co и Ni снижается, что объясняется сегрегацией кислорода на поверхности раздела Та мембрана / пленка, а также процессами на поверхности мембраны, контактирующей с газовой смесью. Природа этих процессов требует изучения, поскольку при этой температуре низшие оксиды этих металлов восстанавливаются водородом.

Ключевые слова: композиционная мембрана, тантал, металлическое каталитическое покрытие, водородопроницаемость, дилатация.

Информация об авторах:

Паничкин Александр Владимирович
кандидат технических наук, заведующий Национальным научным Лаборатория Института металлургии и обогащения, E-mail: abpanichkin@mail.ru, ORCID ID: 0000-0002-2403-8949

Кенжалиев Багдәулет Кенжәлиевич	*доктор технических наук, генеральный директор – председатель Правления Института металлургии и обогащения, Алматы, Казахстан. Email: bagdaulet_k@satbayev.university, ORCID ID:0000-0003-1474-8354*
Кенжегулов Айдар Қараулович	*к.м.н., научный сотрудник лаборатории металловедения Института Металлургия и обогащение руд, Алматы, Казахстан. Email: kazakh_1403@mail.ru, ORCID ID: 0000-0001-7001-2654*
Имбарова Акерке Талгатовна	*научный сотрудник лаборатории металловедения Института Металлургия и обогащение руд, Алматы, Казахстан. Email: akerke_345@mail.ru, ORCID ID: 0000-0002-9366-314X*
Карбоз Жанар Аилбеккызы	*инженер лаборатории металловедения Института Металлургия и обогащение руд, Алматы, Казахстан. Email: k.zhanar.a@mail.ru, ORCID ID: 0000-0003-2538-8585*
Шах Арман	*профессор, доктор технического и профессионального факультета Образовательного университета Султана Идриса, 35900, Танджунг Малим, Перак, Малайзия. Email: armanshah@ftv.upsi.edu.my, ORCID ID: 0000-0002-4366-9156*

Литература

[1] Dolan M.D. (2010). Non-Pd BCC alloy membranes for industrial hydrogen separation. // *Journal of Membrane Science*. 362, 12–28. https://doi.org/10.1016/j.memsci.2010.06.068

[2] Sarker S., Chandra D., Hirsche M. and over. (2016). Developments in the Ni–Nb–Zr amorphous alloy membranes. // *Applied physics A. Materials Science Processing.* P. 122-168. https://doi.org/10.1007/s00339-016-9650-5

[3] Ding H. Y., Zhang W., Yamaura S.I., Yao K.F. (2013). Hydrogen permeable Nb-based amorphous alloys with high thermal stability. // *Materials Transactions*. 54 (8), 1330-1334. https://doi.org/10.2320/matertrans.MF201310

[4] Panichkin A.V., Derbisalin A. M., Mamayeva A. A., Dzhumabekov D. M., Imbarova A.T. (2017). Hydrogen permeability of membranes based on niobium and tantalum foils in the atmosphere of technical purity hydrogen. // *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* 3, pp. 42-47. https://doi.org/10.31643/2018/166445

[5] Буснюк А.О., Ноткин М.Е., Григориади И.П., Алимов В.Н., Лившиц А.И. (2010). Термическая деградация палладиевого покрытия водородопроницаемых мембран из ниобия. // *Журнал технической физики*. 80(1), 117-124.

[6] Young S.J ., Chan H.L., Seong Y.K., Kwan Y.L., Chang W.Y., Suk W.N., Jonghee H. (2018). Characterization of a Pd/Ta composite membrane and its application to a large scale high-purity hydrogen separation from mixed gas. // *Separation and Purification Technology.* 200. 221-229. https://doi.org/10.1016/j.seppur.2017.12.019

[7] Лившиц А.И., Ноткин М.Е., Алимов В.Н., Буснюк // Патент РФ 129416. 11.09.2012. Мембрана для выделения водорода из газовых смесей. А.О.

[8] Hatano Y., Ishiyama K., Homma H., Watanabe K. (2007). Improvement of high temperature stability of Pd coating on Nb by intermediate layer comprising NbC and Nb_2C. // *Journal of Alloys and Compounds*. 446 – 447, 539-542.

[9] Hatano Y., Ishiyama K., Homma H., Watanabe K.(2007). Improvement in high temperature stability of Pd coating on Nb by Nb_2C intermediate layer. // *International Journal of Hydrogen Energy.* 32, 615-619. https://doi.org/10.1016/j.ijhydene.2006.06.045

[10] Dye R.C., Snow R. //. Патент. США. 6,214,090. 10.04.2001. Thermally tolerant multilayer metal membrane.

[11] Karthikeyan A., Martindale C., Martin S.W. (2004). Preparation and characterization of new proton conducting chalcogenide glasses. // *Journal of Non-Crystalline Solids*. 349, 215-222. https://doi.org/10.1016/j.jnoncrysol.2004.08.145

[12] Nozaki T., Hatano Y. (2013). Hydrogen permeation through a Pd/Ta composite membrane with a HfN intermediate layer. // *International Journal of Hydrogen Energy.* 38(27), P. 11983-11987. https://doi.org/10.1016/j.ijhydene.2013.07.012

[13] Глазунов Г.П., Ажажа В.М., Андреев А.А., Барон Д.И., Волков Е.Д., Конотопский А.Л., Неклюдов И.М., СвинаренкоА.П. (2007). Кинетика проникновения водорода в двухслойных диффузионных системах на основе циркония и палладия. // *Вопросы атомной науки и техники. Серия: Физика радиационных повреждений и радиационное материаловедение.* 6, 13-17.

[14] Глазуно Г.П. (1995). Исследование влияния тонких металлических пленок на водородопроницаемость палладиевых мембран при низких давлениях. // *Вопросы атомной науки и техники. Серия. Вакуум, чистые металлы, сверхпроводники.* 1, 72-80.

[15] Steward S. A. // Review of Hydrogen Isotope permeability Through Materials. Lawrence Livermore National Laboratory Report UCRL-53441. DE84 007362. Available from: National Technical Information Service, US Department of Commerce, Springfield, VA, USA, 1984. https://doi.org/10.2172/5277693

[16] Robert E. Buxbaum, Terry L. Marker. (1993). Hydrogen transport through non-porous membranes of palladium-coated niobium, tantalum and vanadium. // *Journal of Membrane Science.* 85, 29-38. https://doi.org/10.1016/0376-7388(93)85004-g

[17] Basile A. (2013). Handbook of Membrane Reactors 1st Edition. Reactor Types and Industrial Applications.Woodhead Publishing. 968.

[18] Glazunov G.P., Volkov E.D., Hassanein A. (2000). Hydrogen behavior in bimetallic systems: permeation through thin metal films. // *Problems of Atomic Science and Technology. Series: Plasma Physics (5).* 3. 102-104.

[19] Panichkin A.V., Kenzhaliyev B.K., Derbisalin A.M., Mamayeva A.A., Dzhumabekov D.M. (2017). Hydrogen permeable membranes based on niobium foils coated with layer of tungsten and molybdenum in niobium solid solution characteristics research. // *2nd International Symposium on Mechanical Engineering and Material Science.* 134, 38-41.

[20] Cheol Y.K., Hong S.C., Gu Y., Kyoung W.P., Eric F. (2010). Hydrogen Permeation of Pd-Free V-Based Metallic Membranes for Hydrogen Separation and Purification // *Materials Science Forum.* 654-656, 2831-2834.

[21] Yamaura S., Inoue A. (2010). Effect of surface coating element on hydrogen permeability of melt-spun $Ni_{40}Nb_{20}Ta_5Zr_{30}Co_5$ amorphous alloy // *Journal of Membrane Science.* 138-144.

[22] Panichkin A.V., Derbissalin A.M., Imbarova A.T., Dzhumabekov D.M., Alibekov Zh. Zh. (2017). Improvement of methodology and equipment for determination of hydrogen performance of thin flat metallic membranes // *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* 2, pp. 46-52. https://doi.org/10.31643/2018/166445

[23] Rothenberger K.S., Howard B.H., Cugini A.V., Enick R.M., Bustamante F., Ciocco M.V., Morreale B.D., Buxbaum R.E. (2002). Hydrogen permeability of tantalum-based membrane materials at elevated temperature and pressure. // *Fuel Chemistry Division Preprints.* 47(2), 814-815.

[24] Samhun Y., Ted S.O. (2011). Correlations in palladium membranes for hydrogen separation: A review. // *Journal of Membrane Science.* 375, 28–45.

[25] Vincenc N., Janez K., Cristian L., Porosnicu C. (2014). Characterization of tungsten films and their hydrogen permeability. // *Journal of Vacuum Science & Technology A Vacuum Surfaces and Films.* 32(6):061511.

[26] Keiichiro U.K., Katayama ., Fukada D.S. (2015). Hydrogen gas driven permeation through tungsten deposition layer formed by hydrogen plasma sputtering. // *Fusion Engineering and Design.* 98–99, 1341-1344.

[27] Rothenberger K.S., Howard B.H., Killmeyer R.P., Cugini A.V., Enick R.M., Bustamante F., Ciocco M.V., Morreale B.D., Buxbaum R.E. (2003). Evaluation of tantalum-based materials for hydrogen separation at elevated temperatures and pressures. // *Journal of Membrane Science.* 218, 19–37.

[28] Tanabe T., Yamanishi Y., Imoto S. (1992). Hydrogen permeation and diffusion in molybdenum. // *Journal of Nuclear Materials.* 191–194, 439–443. https://doi.org/10.1016/S0022-3115(09)80083-4

Reference

[1] Dolan M.D. (2010). Non-Pd BCC alloy membranes for industrial hydrogen separation. // *Journal of Membrane Science*. 362, 12–28. https://doi.org/10.1016/j.memsci.2010.06.068 (In Eng.).

[2] Sarker S., Chandra D., Hirsche M. and over. (2016). Developments in the Ni–Nb–Zr amorphous alloy membranes. // *Applied physics A. Materials Science Processing.* P. 122-168. https://doi.org/10.1007/s00339-016-9650-5 (In Eng.).

[3] Ding H. Y., Zhang W., Yamaura S.I., Yao K.F. (2013). Hydrogen permeable Nb-based amorphous alloys with high thermal stability. // *Materials Transactions*. 54 (8), 1330-1334. https://doi.org/10.2320/matertrans.MF201310 (In Eng.).

[4] Panichkin A.V., Derbisalin A. M., Mamayeva A. A., Dzhumabekov D. M., Imbarova A.T. (2017). Hydrogen permeability of membranes based on niobium and tantalum foils in the atmosphere of technical purity hydrogen. // *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* 3, pp. 42-47. https://doi.org/10.31643/2018/166445 (in Eng)

[5] Busnyuk A.O., Notkin M. E., Grigoriadi I.P., Alimov V. N., Livshits A.I. (2010). Termicheskaya degradatsiya palladiyevogo pokrytiya vodorodopronitsayemykh membran iz niobiya [Thermal degradation of the palladium coating of hydrogen permeable niobium membranes]. // *Zhurnal tekhnicheskoy fiziki.* 80(1). 117-124. (in Rus).

[6] Young S.J ., Chan H.L., Seong Y.K., Kwan Y.L., Chang W.Y., Suk W.N., Jonghee H. (2018). Characterization of a Pd/Ta composite membrane and its application to a large scale high-purity hydrogen separation from mixed gas. // *Separation and Purification Technology.* 200. 221-229. https://doi.org/10.1016/j.seppur.2017.12.019 (In Eng.).

[7] Livshits A. I., Notkin M. E., Alimov V. N., Busnyuk // Patent RF 129416. 11.09.2012. *Membrana dlya vydeleniya vodoroda iz gazovykh smesey [Membrane for hydrogen recovery from gas mixtures].* A.O. (in Rus).

[8] Hatano Y., Ishiyama K., Homma H., Watanabe K. (2007). Improvement of high temperature stability of Pd coating on Nb by intermediate layer comprising NbC and Nb_2C. // *Journal of Alloys and Compounds*. 446 – 447, 539-542. (In Eng.).

[9]   Hatano Y., Ishiyama K., Homma H., Watanabe K. (2007). Improvement in high temperature stability of Pd coating on Nb by Nb$_2$C intermediate layer. // *International Journal of Hydrogen Energy.* 32, 615-619. https://doi.org/10.1016/j.ijhydene.2006.06.045 (In Eng.).

[10] Dye R.C., Snow R. //. Патент. США. 6,214,090. 10.04.2001. Thermally tolerant multilayer metal membrane. (In Eng.).

[11] Karthikeyan A., Martindale C., Martin S.W. (2004). Preparation and characterization of new proton conducting chalcogenide glasses. // *Journal of Non-Crystalline Solids*. 349, 215-222. https://doi.org/10.1016/j.jnoncrysol.2004.08.145 (In Eng.).

[12] Nozaki T., Hatano Y. (2013). Hydrogen permeation through a Pd/Ta composite membrane with a HfN intermediate layer. // *International Journal of Hydrogen Energy.* 38(27), P. 11983-11987. https://doi.org/10.1016/j.ijhydene.2013.07.012 (In Eng.).

[13] Glazunov G.P.. Azhazha V. M., Andreyev A.A., Baron D. I., Volkov E.D., Konotopskiy A.L., Neklyudov I. M., Svinarenko A. P. (2007). Kinetika proniknoveniya vodoroda v dvukhsloynykh diffuzionnykh sistemakh na osnove tsirkoniya i palladiya [Kinetics of hydrogen permeation in two-layer diffusion systems based on zirconium and palladium]. // *Voprosy atomnoy nauki i tekhniki. Seriya: Fizika radiatsionnykh povrezhdeniy i radiatsionnoye materialovedeniye.* 6. 13-17. (in Rus).

[14] Glazuno G.P. (1995). Issledovaniye vliyaniya tonkikh metallicheskikh plenok na vodorodopronitsayemost palladiyevykh membran pri nizkikh davleniyakh [Study of the effect of thin metal films on the hydrogen permeability of palladium membranes at low pressures]. // *Voprosy atomnoy nauki i tekhniki. Seriya. Vakuum. chistyye metally. sverkhprovodniki*. 1. 72-80. (in Rus).

[15] Steward S. A. // Review of Hydrogen Isotope permeability Through Materials. Lawrence Livermore National Laboratory Report UCRL-53441. DE84 007362. Available from: National Technical Information Service, US Department of Commerce, Springfield, VA, USA, 1984. https://doi.org/10.2172/5277693 (In Eng.).

[16] Robert E. Buxbaum, Terry L. Marker. (1993). Hydrogen transport through non-porous membranes of palladium-coated niobium, tantalum and vanadium. // *Journal of Membrane Science.* 85, 29-38. https://doi.org/10.1016/0376-7388(93)85004-g (In Eng.).

[17] Basile A. (2013). Handbook of Membrane Reactors 1st Edition. Reactor Types and Industrial Applications.Woodhead Publishing. 968. (In Eng.).

[18] Glazunov G.P., Volkov E.D., Hassanein A. (2000). Hydrogen behavior in bimetallic systems: permeation through thin metal films. // *Problems of Atomic Science and Technology. Series: Plasma Physics (5).* 3. 102-104. (In Eng.).

[19] Panichkin A.V., Kenzhaliyev B.K., Derbisalin A.M., Mamayeva A.A., Dzhumabekov D.M. (2017). Hydrogen permeable membranes based on niobium foils coated with layer of tungsten and molybdenum in niobium solid solution characteristics research. // *2nd International Symposium on Mechanical Engineering and Material Science.* 134, 38-41. (In Eng.).

[20] Cheol Y.K., Hong S.C., Gu Y., Kyoung W.P., Eric F. (2010). Hydrogen Permeation of Pd-Free V-Based Metallic Membranes for Hydrogen Separation and Purification // *Materials Science Forum.* 654-656, 2831-2834. (In Eng.).

[21] Yamaura S., Inoue A. (2010). Effect of surface coating element on hydrogen permeability of melt-spun Ni$_{40}$Nb$_{20}$Ta$_5$Zr$_{30}$Co$_5$ amorphous alloy // *Journal of Membrane Science.* 138-144. (In Eng.).

[22] Panichkin A.V., Derbissalin A.M., Imbarova A.T., Dzhumabekov D.M., Alibekov Zh.Zh. (2017). Improvement of methodology and equipment for determination of hydrogen performance of thin flat metallic membranes // *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* 2, pp. 46-52. https://doi.org/10.31643/2018/166445 (In Eng.).

[23] Rothenberger K.S., Howard B.H., Cugini A.V., Enick R.M., Bustamante F., Ciocco M.V., Morreale B.D., Buxbaum R.E. (2002). Hydrogen permeability of tantalum-based membrane materials at elevated temperature and pressure. // *Fuel Chemistry Division Preprints.* 47(2), 814-815. (In Eng.).

[24] Samhun Y., Ted S.O. (2011). Correlations in palladium membranes for hydrogen separation: A review. // *Journal of Membrane Science.* 375, 28–45. (In Eng.).

[25] Vincenc N., Janez K., Cristian L., Porosnicu C. (2014). Characterization of tungsten films and their hydrogen permeability. // *Journal of Vacuum Science & Technology A Vacuum Surfaces and Films.* 32(6):061511. (In Eng.).

[26] Keiichiro U.K., Katayama ., Fukada D.S. (2015). Hydrogen gas driven permeation through tungsten deposition layer formed by hydrogen plasma sputtering. // *Fusion Engineering and Design.* 98–99, 1341-1344. (In Eng.).

[27] Rothenberger K.S., Howard B.H., Killmeyer R.P., Cugini A.V., Enick R.M., Bustamante F., Ciocco M.V., Morreale B.D., Buxbaum R.E. (2003). Evaluation of tantalum-based materials for hydrogen separation at elevated temperatures and pressures. // *Journal of Membrane Science.* 218, 19–37. (In Eng.).

[28] Tanabe T., Yamanishi Y., Imoto S. (1992). Hydrogen permeation and diffusion in molybdenum. // *Journal of Nuclear Materials.* 191–194, 439–443. https://doi.org/10.1016/S0022-3115(09)80083-4 (In Eng.).