

# *Hydrogen permeable membranes based on niobium foils coated with layer of tungsten and molybdenum in niobium solid solution characteristics research.*

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**Abstract** - Paper presents the results of measuring the hydrogen permeability of 40  $\mu\text{m}$  niobium foil membranes, on one side coated with a layer of a solid solution of tungsten in niobium or molybdenum in niobium. The measurements were carried out in a hydrogen atmosphere of technical purity with a smooth temperature decrease followed by isothermal aging and under conditions of cyclic temperature variation. It is shown that the degree of purity of argon used for magnetron sputtering has the greatest influence on the hydrogen permeability of composite niobium membranes. As a result of 1  $\mu\text{m}$  thick molybdenum in niobium (Nb - 15 wt% Mo) and tungsten in niobium (Nb-10 wt% W) solid solution deposition on the surface of a niobium membrane, the average value of their hydrogen permeability decreases, while a number of samples demonstrated a significant increase of durability. When the Nb - 15 mass% Mo layer is deposited in purified argon, the hydrogen permeability of the membranes increases by 15-20 times compared to pure niobium and up to 30 times in comparison with the membranes deposited in technical purity argon and reaches 68  $\text{mol/s}\cdot\text{m}\cdot\text{Pa}^{0.5}$ , however, lifetime of membranes before destruction is dramatically reduced and ranges from 13 to 280 s., with a rapid decrease in hydrogen permeability due to their oxidation. In case of Nb - 10 wt.% W films deposition using additionally purified argon, the hydrogen permeability of membranes rises more than 20-times and reaches a level of 30  $\text{mol/s}\cdot\text{m}\cdot\text{Pa}^{0.5}$ , however, the membrane operation time is shortened to 25-320 s. The hydrogen "superconductivity" effect found in niobium composition membranes requires further studies. The use of films of solid solutions of molybdenum or tungsten in niobium, as buffer layers between the membrane and palladium layer, is proposed.

**Keywords**—*composite membrane; niobium; solid solution; coating; hydrogen permeability; dilatation*

## I. INTRODUCTION

One of the most promising ways to extract hydrogen from gas mixtures formed during steam conversion is a one-step membrane separation to produce ultrapure hydrogen. However, palladium and its alloys are industrially used as membrane material, but very high cost limits the spread of this method. In this regard, development of the hydrogen industry requires the development of new highly efficient and inexpensive hydrogen permeable membranes. Metals of the 5-th group, in particular niobium, are substantially cheaper than palladium and are characterized by high hydrogen-absorbing capacity [1-4]. This makes it possible to manufacture membranes for hydrogen purification from them, however, due to the high hydrogen embrittlement and activity with such gases as CO, O<sub>2</sub>, H<sub>2</sub>O at the hydrogen diffusion temperatures, characteristics of such membranes deteriorate rapidly. As a result of interaction with reactive gases, as well as surface segregation of oxygen dissolved in the lattice, at the operating temperatures (> 520 K), niobium surface is covered with an oxide film, which hampers the catalytic dissociation of hydrogen molecules necessary for hydrogen absorption [1-5].

It means, it's necessary to protect the membrane surface from oxidation. It is believed that the most promising coating for niobium membrane is palladium or its alloys up to several microns thick [6-14], performing both protective and catalytic functions. However, problems facing the use of niobium composite membranes are: low thermal stability of the palladium coating, insufficient obstacle to transition to brittle condition of niobium membranes at operating temperatures. Thus, it is necessary to search for other ways to increase the

corrosion resistance of niobium membranes and to prevent their destruction during the transition to a brittle state.

As follows from the experimental data presented in [15], thin layer of solid solutions of tungsten and molybdenum in niobium (Nb-18 at% Mo, Nb-16.5 at% W) are magnetron sputtered on the niobium surface, it's increases its corrosion resistance at 550°C in the ordinary atmosphere at a residual pressure of ~100 Pa in 110 and 38 times, respectively. In this case, the study of the hydrogen permeability of such membranes and their behavior upon contact with hydrogen is promising.

**II. EXPERIMENTAL METHOD**

To prepare the membranes, 40 μm thick JSC Ulba Metallurgical Plant, niobium (NbW0) foils were used. After ionic cleaning, thin films of solid solutions, based on niobium were applied to the 120x120 mm foil surface by magnetron sputtering. For this purpose, a magnetron sputtering device equipped with an ion source APEL-IS-21CELL and magnetrons APEL-MRE100 was used. Ionic purification was carried out with argon at an operating voltage 3.00 kV, current 60-80 mA, pressure 3\*10<sup>-1</sup> Pa, and 20 minute duration. Magnetron sputtering was carried out for 20 minutes using a sectional target Ø100 mm at a work current 2.01 A, 300 V, pressure 2-4.5\*10<sup>-1</sup> Pa. The distance between the substrate and the target was 200 mm. Magnetron sputtering was carried out using 99.993% purity argon and after additional purification by passing through a layer of a titanium sponge heated up to 800°C. Composition and thickness of the obtained tungsten and molybdenum solid solutions in niobium were determined on a JEOL JXA-8230 microprobe analyzer.

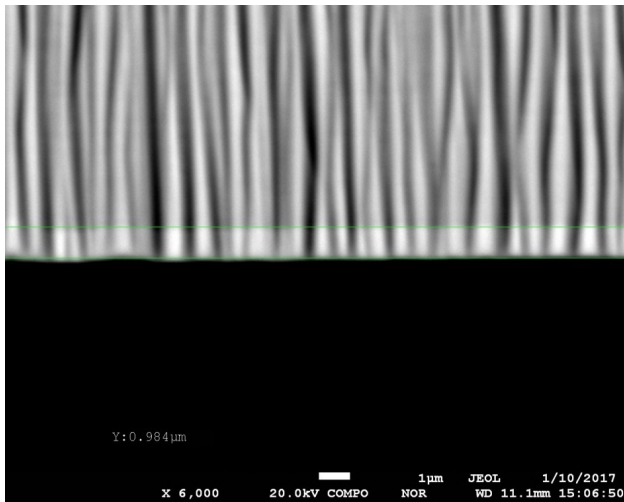


Fig. 1. A layer of a solid solution of tungsten in niobium on the surface of a niobium foil. (Cross section).

Experiments to determine the hydrogen permeability of Ø100 mm niobium-based composite membranes were carried out using the method and on the equipment described in [16]. Measurement of hydrogen permeability was carried out at an excess pressure of hydrogen of grade B (99.95%) at 300, 400, 500, 700 kPa and at the beginning of the experiment at 550, 565, 575, 585 °C under conditions of uniform temperature

decrease followed by isothermal aging and under cyclic temperature changes with oscillations up to ~±20° with a period of ~600 s. The choice of experimental conditions is based on the optimal operating conditions found for membranes based on niobium foils [17]. Simultaneously with the value of the gas flow, the temperature of the base was fixed, to which the membrane adhered. The tests were carried out before the membrane burst. Hydrogen was additionally subjected to purification from moisture by passing it through chilled to -40 ° C aluminum chips.

**III. EXPERIMENTAL PART**

With the selected modes of magnetron sputtering of the sectional targets, layers of Nb-10 wt% W, Nb-15 wt% Mo were deposited on the surface of the niobium foils. Their thickness was 1 ±0.1 μm.

The results of measuring the hydrogen permeability of the resulting composite membranes are presented in Tables I and II. Under the experimental conditions, with a smooth temperature decrease, the hydrogen permeability of the membranes first increases, reaching a maximum in 100-300 s. from the moment of membrane contact with hydrogen. In the future, it decreases to certain values, the value of which under isothermal holding conditions does not significantly decrease with time. In some cases, the destruction of the membrane occurs even before the stabilization of hydrogen permeability.

TABLE I - HYDROGEN PERMEABILITY OF COMPOSITE MEMBRANES Nb - 15 WT% MO

№	H <sub>2</sub> pressure, KPa	Temp. change mode	T <sub>st.</sub> , °C	T <sub>set.</sub> , °C	H-permeability, mol/s·m·Pa <sup>0.5</sup>	Period, sec
Magnetron sputtering in Ar 99,993%						
1	700	Cyclic	560	537-545	from 0,2 to 1,3	1800
2	300		575	555-575	from 0,05 to 2	8200
3	400		575	555-576	from 1,2 to 3,6	3800
4			575	545-574	5,8 after 200 s, 1,8-3,1	1600
5	500		575	545-575	от 0,2 до 1,3	1800
6	500	Smooth cooling reaching isotherm	575	539	300 from max. 1,9, then 1,4	2400
7			585	550	280 from max 3,1, then 1	2700
Magnetron sputtering in additionally purified argon						
8	500	Smooth cooling reaching isotherm	585	572 break	reduce from 18 to 8	610
9			550	536 break	120 from max. 68, break 28	325

TABLE II - HYDROGEN PERMEABILITY OF COMPOSITE MEMBRANES Nb-10 WT.% W

№	H <sub>2</sub> pressure, KPa	Temp. change mode	T <sub>st.</sub> , °C	T <sub>set</sub> , °C	H-permeability, mol/s·m·Pa <sup>0.5</sup>	Period, sec
Magnetron sputtering in Ar 99,993%						
1	500	Cyclic	550	510-528	From 0,2 to 1,3	1700
2	500	Smooth cooling reaching isotherm	550	510	300 from max. 2,7, then 0,5	3600
Magnetron sputtering in additionally purified argon						
3	500	Smooth cooling reaching isotherm	575	572 (break)	210 from max 14,8, then smooth reduce 3,6	610
4	500	Cyclic	575	538-552	150 from max 24,5, then oscillating from 2,5 to 10,3	2550
5				585	547-567	60 from max. 8,8, then smooth reduce to 2.1 and increase to 3,1

In the conditions of cyclic tests, at the initial stage, an increase in hydrogen permeability is observed. Then, after the reduction, it begins to oscillate, while the period of change in hydrogen permeability coincides with the period of change in the temperature of the membrane with a slight shift of the curves relative to each other (Fig. 2). Almost in all the cases considered, the active evolution of hydrogen occurs during the heating of the membrane and slowed down during cooling. A gradual decrease in the average value of hydrogen permeability with time has been observed. With an increase in the excess pressure of hydrogen, especially above 500 kPa, there is a tendency to reduce the duration of the membrane until it breaks down. The increase of temperature has less effect on this value. In a number of cases, tests under identical conditions lead to different results on hydrogen permeability and the duration of membrane operation prior to its destruction.

The most significant difference in the value of hydrogen permeability and the duration of membrane operation prior to failure was observed in the case of using additionally purified argon in the magnetron sputtering of solid solution layers. The tables show only those experiments in which the membranes have been operating for a long time. However, during the first 20 seconds more than 70% of the membranes obtained using purified argon were destroyed. In such membranes, the flow of hydrogen passing through them from the first seconds of the experiment reached 20-70 mol/s·m·Pa<sup>0.5</sup>, then, as a rule, there was a gradual increase in the flow followed by an instantaneous breakthrough. Only a small fraction of the membranes managed to overcome the peak value of hydrogen permeability, after which the decrease in its value began (Fig. 2b).

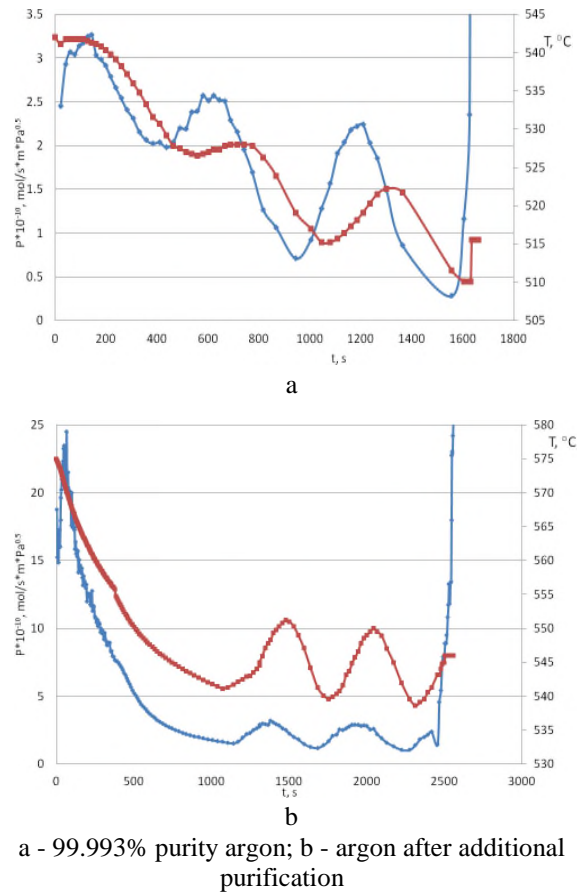


Fig. 2. Magnetron sputtering argon purification effect on hydrogen permeability of 40 μm thick niobium membranes, deposited with a layer of ~1 μm solid solution of Nb-10 wt% W.

A comparison of the obtained data with the results of a change in the hydrogen permeability of 40 μm thick niobium foil, given in [17], was made. It follows from the comparison that, as a result of the deposition of layers of a solid solution of 1 μm thick molybdenum in niobium (Nb - 15 wt% Mo) and tungsten in niobium (Nb - 10 wt% W) on a niobium membrane surface using non-purified argon, decrease in the average value of their hydrogen permeability, with a number of samples demonstrating a significant increase in resistance to destruction. When the Nb-15 mass% Mo layer is deposited in purified argon, the hydrogen permeability of the membranes increases by 15-20 times compared to pure niobium and up to 30 times in comparison with the membranes obtained by depositing in un-purified argon and reaches 68 mol/s·m·Pa<sup>0.5</sup>, however, the period of membrane operation before destruction is dramatically reduced and it's from 13 to 280 s, while a rapid decrease in hydrogen permeability is observed. In case of deposition of Nb-10 wt% W films in additionally purified argon, the hydrogen permeability of the membranes rises more than 20-times and reaches a level of 30 mol/s·m·Pa<sup>0.5</sup>, however, the membrane operation time is shortened to 25-320 s

A visual examination of the surface of membranes after experiments showed that in all cases the cause of their destruction was dilatation caused by diffusion of hydrogen.

However, under conditions of cyclic temperature change, the membranes show a significantly longer duration of operation prior to failure in comparison with that observed under conditions of smooth temperature decrease followed by isothermal aging. It was assumed in [17] that this is a consequence of the redistribution of the folds arising during the oscillation of the folds formed during the expansion of the niobium foil as a result of hydrogen dissolution.

Considering the essential dependence of hydrogen permeability of membranes on the presence of impurities in the surface layer, probably oxygen, it can be concluded that the decrease in hydrogen permeability of the developed niobium-based composite membranes over time is mainly a consequence of oxidation of their surface as a result of reaction with active gases contained in hydrogen of technical purity, used in experiments.

#### IV. CONCLUSION

Thus, studies of 40  $\mu\text{m}$  thick niobium foil membranes coated with layers of solid solutions of Nb-15 wt% Mo or Nb-10 wt% W have been carried out. It was shown that the value of their hydrogen permeability changes significantly, depending on the impurities deposited in passing with the films of solid solutions during magnetron sputtering. The presence of small impurities leads to a decrease in the hydrogen permeability of the membrane as a whole to values lower than that observed for pure niobium. Films deposited on the surface of a niobium membrane using purified argon transform it into a state of hydrogen "superconductivity". The increasing flow of hydrogen through the membrane leads to its dilatation and, as a rule, to its rapid breakthrough. This raises the task of developing methods for hardening flat membranes to improve their resistance to fracture. Since hydrogen permeability of the investigated composite membranes is rapidly reduced by contact with hydrogen of the investigated composite membranes, due to oxidation, it is promising to use such films, possibly with a higher concentration of molybdenum or tungsten, as buffer layers between the membrane and the palladium layer.

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