Investigation of Properties of Multilayered Film Structure for Creation of Hydrogenselective Membrane[1]

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Abstract – The paper presents the investigation results of an opportunity of creation of a new type membrane with increased characteristics for the pure hydrogen release from hydrogenous gas mixtures. A multilayer coating formed from alternating layers of Nb–Ti and Ti/TiNi on the substrates was used to create hydrogenselective membranes. The substrates of two types were used: plates of porous metal with submicron pore sizes and nickel plates with submicron columnar structure grown on its surface by means of nickel synthesis via a template. Columnar submicron structures will considerably increase the membrane efficiency. The investigation of strength properties and characteristics stability was carried out to create high-permeability membrane structure resistant to hydrogen embrittlement.

1. Introduction

The industrious development of membrane technologies of gas separation refers to 40–50 years of the last century, i.e., to the period of creation of a technology for uranium enrichment on the basis of membrane gas-diffusion installations.

The membrane technologies differ in high selectivity, low power inputs, simplicity of instrumental design and serve a basis of nonwaste technology creation [1]. At that, the catalysts and conventional fluid systems of gas distribution are excluded.

The metal membranes based on palladium and alloys on its basis are most efficient and widely investigated in the world practice. However, the membranes based on palladium are very expensive and their operation resource is limited by the processes of structure and phase transformations, especially in conditions of a dynamic change in temperatures. That is why the metal membranes based on palladium are rarely used in industry, primarily due to shortage and high costs of membranes, as well as due to irreversible "poisoning" of palladium.

At the same time, membranes of metal alloys seem to be promising [2, 3]. In this connection, a new technology of vacuum-plasma deposition of thin multicomponent membrane of Nb–Ti–Ni type is promising to accomplish the tasks of a hydrogen filter creation.

This composite is attractive because Nb–Ti–Ni alloys are highly resistant to hydrogen embrittlement and have a high hydrogen permeation [2, 3].

The authors [3] showed, that $Nb_{56}Ti_{23}Ni_{21}$ alloy consisted primarily of the main bcc-phase (Nb, Ti) of a solid solution and eutectic phase {bcc-(Nb, Ti) + + B2-TiNi} is mostly efficient in hydrogen permeation and makes $3.47 \cdot 10^{-8}$ (mole H_2 $m^{-1} \cdot s^{-1} \cdot Pa^{-0.5}$) at 673 K, which is 1.8 times higher, than at $Nb_{40}Ti_{30}Ni_{30}$, which was considered the highest in Nb–Ti–Ni system. $Nb_{56}Ti_{23}Ni_{21}$ alloy also shows high resistance to hydrogen embrittlement.

Crack formation on thin films due to cyclic temperatures and hydrogen embrittlement is one of the obstacles which is necessary to overcome. The coating resistance increases if they are formed multilayered on porous or fundamentally new substrates with submicron columnar structure [4]. In such coatings, the layers of various chemical compositions perform the functions of crack deceleration and adhesion increase with the substrate surface [5].

2. Substrates for multicomponent multilayered hydrogen-filtering membranes

Two types of substrates served as a basis: of porous stainless steel and massive nickel with submicron columnar structures grown on it.

The porous stainless steel of USA production of 1 mm thickness and pore sizes of 5 and 2 μm and of Russian production of 1.3 mm thickness and pore sizes of 3 and 5 μm was used. The workpieces were additionally rolled with the purpose of decreasing the pore sizes to 1–2 μm.

The porosity of a workpiece was defined by the "bubble" method. The substrate surface after polishing was investigated on the optical 3D-profilometer Micro Measure 3D Station (STIL).

It was discovered that the roughness on Rz makes 0.5–1 μm. On the basis of these investigations it was concluded that the minimal thickness of the coating which will be able to close the pores on the surface makes 10 μm.

The substrates were washed in acetone, wiped with coarse calico moistened in spirit, washed in the ultrasound bath "TYPE UM-2" in the solution of carbon tetrachloride and dried in the drying box during 15–20 min before their placement into the vacuum chamber.

[1] The work has been supported in part by the Russian Foundation for Basic Research (Grant No. 07-08-12192-ofi).

Later on the substrate surface preparation was carried out in the vacuum chamber. The preparation included the stages of ion cleaning, warming and surface activation by gas ions.

3. Formation of substrates with submicron columnar structures of nickel

Metal columnar submicron nanopointed structures created on the massive basis can become a promising material for hydrogen-selective membranes. Such structures can be obtained using track membranes as a template possessing homogeneous cylindrical or conical statistically distributed pores in the polymer film.

In order to obtain submicron columnar structure on the substrate of nickel, a template synthesis was applied which is based on the method of growing various nanostructures. The columnar structure was formed by means of electrodeposition in pores of the track template.

The track membrane (TM) based on polyethylene terephtalate produced in Nuclear Physics Institute with pores of 450 and 200 nm and in the United Institute of Nuclear Research (Dubna) with pores of 50 nm was used as a template.

The pores in the membrane were created by means of irradiation of polyethylene terephtalate by heavy ions with the subsequent chemical etching [6].

The substrates, on which the columnar submicron structures were grown, were produced of Ni plates with the thickness of 200÷1000 μm. The regimes of the base surface preparation and regimes of electrolytic Ni deposition in TM pores, at which there is no intensive release of hydrogen on the substrate, have been studied. The following optimal regimes for the formation of a columnar submicron crystal structure of Ni have been chosen, namely: anode voltage 0.6–0.8 V, average current density – 5 mA/cm^2, pH – 5–6, and electrolyte temperature – 50 °C. The investigations showed that at template synthesis with the template help, it is very important to have a close contact of a template with the substrate surface. A system enabling to provide a close contact of a track template with the surface of a nickel substrate during metal deposition on pores has been created. For this purpose a wire metal mesh with big cells of very thin wire of magnetic metal (iron) was placed on the track template located on the surface of a substrate of nickel. The mesh pressed TM to the substrate very closely by a constant magnet in the form of a plate. After nickel growth in the pores, the polymer of a track template was removed by means of dissolution in the water solution NaOH with addition of 2% methyl alcohol. The sample surface with the grown columnar submicron structures of nickel was investigated using scanning electron microscope, SEM.

Figures 1–2 present micropictures of submicron columnar structures, on a nickel substrate, which were grown via a track template with pore diameter of 75–120 nm.

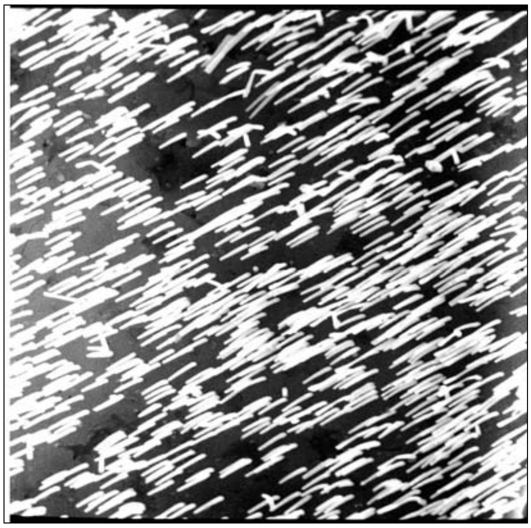


Fig. 1. Micropicture of columnar submicron structure of Ni on a massive substrate of Ni, $K = 6000$

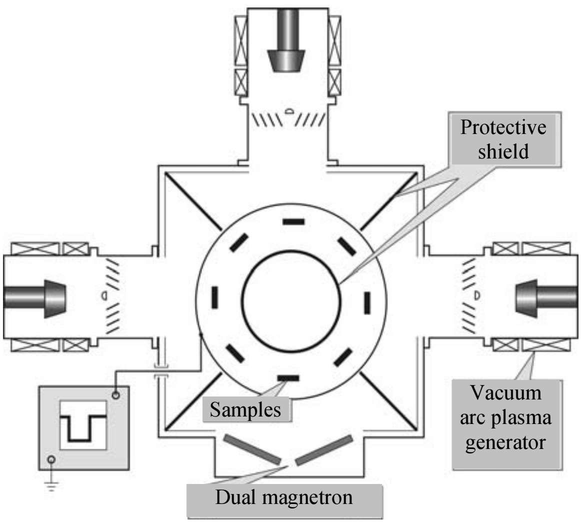
Fig. 2. Nickel release from pores of a track template on the surface of TM, $K = 10000$

Then, the multilayer thin film coatings will also be applied on the substrate with columnar structures for the creation of a hydrogen-selective membrane.

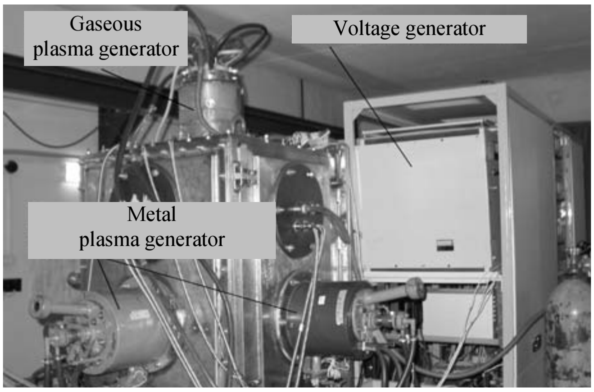
4. Equipment for the coating formation

Formation of multilayer nanostructure coatings was realized on the installation of ion-beam and plasma material treatment (Figure 3).

In the base kitting-up, the installation is equipped with six vacuum-arc evaporators (VAE) with the devices for metal plasma microparticles filtering (MPF), high frequency dual magnetron, gaseous plasma generator with a heated cathode, source of ion beams and plasma of conductive materials based on vacuum-arc discharge (VAD), high voltage pulsed generator for realization of regime of high-frequency short-pulse plasma-immersion ion implantation and (or) coating deposition [7–10].



a



b

Fig. 3. New generation installation of ion-beam and plasma material treatment: *a* – scheme; *b* – external view

5. Regimes of multilayer coating deposition

On the first stage of treatment using high frequency bias voltage generator, the surface etching by Ar ions have been realized with the purpose of a substrate surface cleaning and creation of a surface layer with large amount of active centers of sorption.

The bias voltage amplitude to 4 kV in combination with pulse repetition rate to 440 kHz enables to efficiently realize the surface heating including an efficient sputtering of thin films being formed between the voltage pulses. When the bias voltage pulse repetition rate and amplitude decrease, the plasma flow on the target exceeds the flow of atoms, sputtered from the target surface.

It provides conditions for ion mixing of a border between the base and coating with a formation of a transition layer. The sample temperature during treatment was maintained on the level of 400–450 °C. The coating formation was realized at U_c = (–300–2500) V.

According to experimental results, in case of a constant bias potential application, the voltage of the initial stage of coating deposition does not exceed as a rule 150–200 V and is limited by explosion-emission processes on the sample surface. The microarcs occurrence on the surface of the coating and substrate is accompanied with crater formation and coating destruction.

The deposition parameters have been chosen experimentally when working out the regimes. It was found that at arc currents for nickel cathode 90 A, niobium cathode 100 A, titanium cathode 90 A the formed coating approaches by its chemical composition to the optimal one – $Nb_{56}Ti_{23}Ni_{21}$ (Fig. 4).

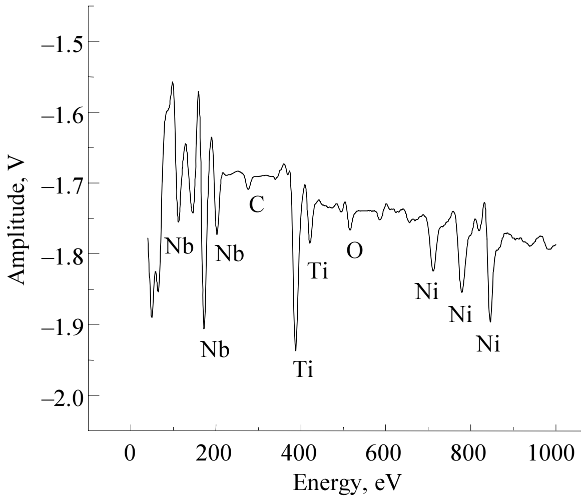


Fig. 4. Auger-spectrum from the $Nb_{56}Ti_{23}Ni_{21}$ coating

During formation of multilayer coating on the basis of NbTi and TiNi system, the vacuum chamber was separated into sections using protective shields. It prevented plasma mixing from different arc evaporators. Opposite each of the samples, the additional heating elements were installed in order to maintain the set temperature regime. The multilayer coating formation was realized during the movement of a holder with a sample from one VAE to another one. The thickness of separate layers was set by the rate of sample movement. The formation of the necessary phases was provided due to partial overlap of plasma flows from separate arc evaporators as well as due to ion mixing of section borders of separate layers at the expense of amplitude change of high-frequency, short-pulse, negative bias potential on the target.

After coating deposition, the level of residual tensions in them has been analyzed. The estimation of the residual tensions was carried out by the values of Young modulus and results of a scratch test on adhesion strength of a coating.

The formed structurally-gradient coatings had considerable compressive stresses which can prevent from development of hydrogen embrittlement and at the same time retain high selectivity and hydrogen permeation.

As Nb, Ti and Ni coatings had practically no difference in their colors, when working out the regimes of multilayer alternating coatings deposition in one of the experiments, the nitrogen was supplied into the vacuum chamber with the purpose of revealing the multilayer structure.

The image of spherical section of a multilayer coating is presented in Fig. 5.

Fig. 5. Spherical section of a multilayer, gradient-structure coating

As is seen from the presented data, the formed coating presents a periodic structure of the sequence of light and dark rings – the light ones (yellow) – TiN.

6. Discussion

The investigations of multilayer coatings, which base consists of alternating in properties, nanosize (from 2 to 100 nm) and nanostructure layers of various composition showed that alternation of nanosize layers prevents from phase growing and their size is limited by the thickness of the layer being formed.

Such multilayer coatings formed on the surface of porous substrates of stainless steel and substrates with submicron columnar structures enable to create highly efficient hydrogen-selective membranes, which price will be sufficiently cheaper than that of the familiar membranes of palladium.

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