Synthesis and gas-transmission parameters of Pd-Ag membranes with modified surface

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Abstract. Methods to modify the surface of Pd-23% Ag alloy films were developed in order to increase the velocity of hydrogen transmission; we obtained palladium coating of “nanoparticles” and “nanopores” type. Modification of Pd-Ag films surface, obtained by nanoporous palladium coating with a predominant distribution of particles from 0 to 50 nm, makes it possible to achieve a hydrogen flow density of 0.48 mmol / (s*m2), which is 1.4 times greater in comparison with modification by “nanoparticles” coating under low temperature (<90 °C) and pressure (<0.6 MPa) conditions. Experimental evidence is obtained that velocity of hydrogen transmission, under the given conditions, is limited by dissociative-associative processes at the boundaries, and it can be significantly increased (up to order of magnitude) due to acceleration of the limiting stage of process with the help of palladium nanostructured coating formation on the surface.

1. Introduction
The dramatic development of hydrogen energy leads to increase in demand for high-purity hydrogen. The most common method to obtain it is reforming of organic raw materials with gas mixture formation and subsequent release of high-purity hydrogen, with the help of various types of metal membrane filters. As a basis for creation of these membrane filters palladium and its alloys are used as they have unique properties in relation to the hydrogen transmission.

Despite of large number of publications [1-7] and patents [8-11] the problem of creating high-performance devices of hydrogen diffusion purification is still far from its solutions. The reason for this is relatively low productivity of palladium alloys and the complexity of production of thin yet robust membranes on its base. In particular this applies to membranes operated within the temperature range from 20 to 200° C, which membranes technologies are currently in the least developed field of researches since the balance between molecular hydrogen in gas phase and atomic hydrogen absorbed in the palladium phase at temperatures below 200 °C is achieved very slowly and with great difficulty mainly because of inactive or contaminated surface [12]. This condition can be partially overcome by modifying the working surface of the membrane with powdered hydrogen-chemisorbing substances (for example, Fe, Co, Ni, Cu, platinum metals) which being in contact with compact Pd samples can significantly accelerate the dissolution of hydrogen at room temperature or make this dissolution possible at all [13]. This modification may be effective in case of limiting the process of hydrogen transfer through the membrane by dissociative-associative absorption-elimination processes at the boundaries.

The formation of nanostructured palladium layer capable for chemisorbing of hydrogen on the surface of membrane increases the actual operating surface, which leads to increase of chemisorption centers quantity, which role is most often played by crystallites angles and facets. Moreover in case of sufficiently small Pd crystal size the majority of octahedral interstices belong to the surface [14], that facilitates the transmission of hydrogen and reduces the probability of hydrogen atom capture by various kinds of surface defects.
Since the 30’s of the last century the question of limit value of hydrogen flow density through a metal membrane has been discussed from point of view of its possible limitations both by dissociative-associative absorption-elimination processes at the boundaries and volume diffusion under conditions of undiluted hydrogen solution in metal [15]. For today the experimental achievement of the highest values of hydrogen flow density through palladium-containing membranes makes interest both for understanding the mechanisms of hydrogen transmission by metals and, from practical point of view, for development of high-efficiency membrane filters, hydrogen electrodes and electrochemical systems for hydrogen isotopes separation [16].

In the present work an attempt is made to create a thin palladium-silver membrane and its modification by creating a nanostructured layer on its surface, which accelerates the chemisorption and dissociative processes of hydrogen transmission. The developed membrane can become the base not only for low-temperature diffusion purification of hydrogen and creation of hydrogen electrode for oxygen-hydrogen fuel element [17], but also for processes of hydrogen isotopes separation, for example, membrane production of water with modified isotopes composition widely known for its biological effects [18, 19]. Also, these membranes are integrated into methanol steam reforming plants, which allows to make compact membrane reformers effective for producing hydrogen in situ.[20, 21].

2. Methods and materials
To obtain thin palladium-silver films the magnetron spattering method was used. Plates of silver and palladium with different ratio of its areas were used as a target for the magnetron [22-24]. Magnetron spattering was performed on the Quorum Q150TS / E / ES device. The chemical composition of the obtained films was studied by method of micro-X-ray spectral analysis on INCA (Oxford) semiconductor energy dispersive add-on device with JEOL JSM-7500F scanning electron microscope. To obtain a film with silver content of 23%, which is optimal for hydrogen permeability and mechanical properties [25], a target with an areas ratio S (Ag) / S (Pd) = 20.8 / 79.2 was used. Two methods were used to modify the surface of the films: “nanoparticles” method and “nanopore” method. In the first method the “nanoparticles” — Pd-23% Ag alloy film – were fixed in a holder, washed by 96% ethanol, defatted by boiling for 30 min. in concentrated 6 M NaOH solution, and then transferred for mordanting to 60% HNO3 solution for 30 sec., then immediately put into a vessel with flowing distilled water for 10 minutes. Then the film on inert holder was transferred to electrolytic cell for coating, as a current feeder of the cathode we used the mass of the holder, made of silver with 99.99% purity. Contact was made by silver wire. The palladium-silver alloy film was then transferred to a cell with 0.1 M HCl and anodically polarized at a current density of 10-20 mA / cm2 using a potentiostat-galvanostat P-250I, washed, cathodically polarized at 0.05 M H2SO4 at current density of 10-20 mA / cm2, then filled with 2% H2PdCl4 solution. The black precipitation was carried out at current density of 2-6 mA / cm2 for 1.5 hours, after that it was washed with bidistillate and cathodically polarized in 0.05 M H2SO4.

In the second method of “nanopores” the modification of surface of Pd-23% Ag alloy foil was produced by magnetron spattering of alloy films followed by diffusion annealing and etching. For spattering zinc was used as an active component of Raney palladium alloy, because Zn has spattering current rate of 50 A close to the spattering current rate of Pd – 30 A. To modify the surface of the palladium-silver alloy composition with 50% Zn was chosen. The next stage of the method was diffusion annealing in 99.99%. inert argon medium. The volumetric flow rate is 2 l/min in order to firmly adhesion of Raney alloy to the support material in order to maximally fix the highly dispersed grains of platinoids after etching of the highly active component (zinc). The last phase of the method is leaching of the soluble component (Zn) in 6 M solution of NaOH.

To estimate volumes of the obtained nanoparticles and formed nanopores, electron microscopy was conducted by scanning electron microscope JEOL JSM-7500F. Measurement of hydrogen permeability in the obtained film samples was conducted with the help of the device developed by us (Fig. 1) on the basis of a microgasvolumetric method, which is a diffusion cell 1 intended for fixing
and reliable sealing of the test sample, fixed in a bath of a liquid thermostat 2 TZh-TS-01 / 100 (accuracy of temperature maintaining is 0.1 °C, temperature range 20-200 °C), helium balloon cylinder 3 (99.999 vol.%), and argon balloon cylinder 4 (99.999 vol.%).

Inert gases were used to purge and check the system for leaks. Hydrogen for measurements with the content of the main substance 99.9999 vol. % came from the hydrogen generator “Spectrum” 5, equipped with automatic manometric valve which allows maintaining the output pressure from 0 to 0.6 MPa with 0.05 Mpa increments. The gas circulation circuits in gas lines of the measuring plant were equipped with six gas valves 6-11. The tap 7 allows connecting (disconnecting) the differential mercury U-shaped manometer 12 which indicates excess pressure on input side of membrane with accuracy of 0.5 mm. Hg, and also allows to connect the pre-membrane purge circuit with atmosphere or block the gas line of the input circuit of the membrane. To analyze and measure the volume of diffusate hydrogen the plant was equipped with a gas analyzer 13 and a measuring capillary of constant cross section 14 respectively.

3. Results and discussion
The microphotographs of the films surface obtained by JEOL JSM-7500F scanning electron microscope are shown in Fig. 2. When analyzing the electron microscopy data of the obtained nanocoatings we can note the following: when obtaining the nanoparticle-type coating, about 70% of the nanoparticles have an average size of 0-50 nm, 20% of the particles have an average size of 50-100 nm (Fig. 2a, b) the size distribution does not principally change. When obtaining a nano-pore coating about 70% of nanopores has an average size of 0-30 nm, 20% of the particles have an average size of 30-50 nm (Fig. 2c, d), after a month the size distribution does not principally change.

Fig. 3 shows the data on the measurement of hydrogen permeability for a palladium-silver alloy modified by coating of “nanoparticles” type (a) and coating of “nanopores” type (b). From the obtained results it can be concluded that at ambient temperatures the hydrogen permeability of palladium-silver membrane modified by “nanopores” type of coating is 1.3 times that of a “nanoparticles” type of coating. This can be explained, that during superficial diffusion inside the pores of the modifying coating on the film surface the potential energy of the hydrogen atom and its mobility are changed. The activation energy of surface diffusion, as the distance between the pore walls approaches to the value of the constant lattice, gradually approaches to the activation energy of diffusion in solid grains. On the contrary, the activation energy for transition through the pore walls decreases. When the pore narrows to the normal distance between the lattice planes, it becomes equal to activation energy of diffusion.
Figure 2. Microphotographs of palladium-silver films surface with modified surface, obtained by the method of “nanoparticles” (a, b), and by the method of “nanopores” (c, d).

The thickness of the modifying coating layer obtained by the method of “nanoparticle” was 2.094 μm (Fig. 2a). The thickness of the modifying coating layer obtained by the method of “nanopore” was 2.687 μm (Fig. 2b).

Figure 3. Microphotographs of palladium-silver films sections modified by the method “nanoparticles” (a) and the method of “nanopores” (b).
Figure 4. Dependence of the rate of fluence (the ratio of hydrogen flow to the area of a sample) on the excess pressure of hydrogen on the outer face of the membrane for the method “nanoparticles” (a) and the method of “nanopores” (b).

When the metal surface which chemisorbs hydrogen approaches to the surface of the hydrogen dissolving metal, and the distance between them goes to distance comparable to the distances between the lattice planes, the activation energy of the hydrogen transition through the surface of this metal tends to zero [13]. From fig. 4 it is obvious that the dependence of the flow density on hydrogen overpressure on the input side of the membrane with modified surface is well approximated by a line of the 1st order, which indicates according to [26, 27] that hydrogen penetration velocity is limited by dissociation of hydrogen on the surface.

4. Conclusion

Thus it has been experimentally confirmed that the velocity of hydrogen transmission under conditions of low temperature (<90 °C) and pressure (<0.6 MPa) through sufficiently thin palladium membranes (<10 μm), is limited by dissociative-associative processes at the boundaries, and can be significantly increased (up to order of magnitude) due to acceleration of the limiting stage by applying a superficial modifying palladium coating. Modification of membranes with “nanopores” type of coating allows achieving hydrogen flow density up to 0.48 mmol / (s*m²) that is 1.4 times greater than with modified by “nanoparticles” type of coating.

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5. References

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