Effect of doping atoms in the surface morphology of dense palladium-based diffusion membrane-filters

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Abstract. Atomic force microscopy (AFM) and high-precision scanning electron microscopy methods were used to study the morphology of the surface of diffusion filter-membranes Pd-Pb. Analysis of the AFM microscopy data and microelectronic photographs showed the individual features of the formation of the membrane alloy’s surface topology. The predisposition of the alloy to cavitation was revealed both in the technological process of manufacturing filter-membranes and under exposure to hydrogen.

1. Introduction
According to the contemporary understanding of hydrogenation processes, hydrogen molecules dissociate into atoms during chemisorption on the surface of metal alloys and hydrogen penetrates deep into the objects [1,2]. Due to the small size of atoms (0.47 Å), their introduction and diffusion by the internodes of the crystal lattice lead to interaction with the defects, generate new defects and create internal stresses in hydrogenated materials [3,4]. The consequences of the introduction of hydrogen into the crystal lattice of metals can be the formation of cracks and surface flecking [5,6]. This initiates destruction of hydrogenated objects.

The question of the stability of palladium-based membrane alloys is particularly important in the diffusion processes of high-purity hydrogen separation. Doping elements are introduced into palladium in order to improve the efficiency of diffusion filter-membranes [7,8]. Lead atoms show promising results in this respect [8, 9]. An analysis of X-ray data of the structure of the membrane alloy Pd95Pb5 and their changes in the hydrogenation processes is presented in paper [10]. However the morphology of the surface of the diffusion filter-membranes was not considered in that work. At the same time, it is known that the surface of filter-membranes has a strong influence in the stable operation of the system as a whole and the degree of purity of hydrogen [9].

This motivated the present study, which considers changes in the processes of reversible hydrogenation and the effect that doping elements, namely lead atoms, have on the morphology of the surfaces of palladium-based filter-membranes and their response to hydrogen exposure from the gas phase.

2. Samples and experiment
50 μm-thick Pd95Pb5 membranes were prepared by the research group of the Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences. Alloy films were prepared from high purity materials (≈ 99.9%) by electric arc melting and cold rolling of blanks on a four-roll rolling mill with intermediate vacuum annealing at a temperature of 900 °C for 3 hour [7,8].
In systems Pd-Pb the states of continuous solid solutions are limited to an alloying component content of up to 11.5 at. % at 300 °C [11]. Despite the face-centered crystal lattice of both components of the alloy, the 28% difference in their atomic sizes (1.75 Å and 1.37 Å for lead and palladium, respectively) excludes solid solutions of lead in palladium from the Hume-Rothery rule [12]. This allows the formation of intermetallic inclusions in the membranes and the associated deformation fields. The volume of the unit cell of lead exceeds the volume of the unit cell of palladium by 2 times. The values of electronegativity are 2.2 and 2.33 (for Pd and Pb, respectively, according to Pauling scale [13]). There is a significant difference in melting temperatures: 1554 °C and 600.6 °C for palladium and lead, respectively. All these characteristics of the elements connected in the membrane alloy determine the necessity and relevance of a comprehensive study of the surface in diffusion filter-membranes and their possible changes in the hydrogenation processes.

In this paper, we consider the state of the alloy surface before hydrogenation from the gas phase and after 240, 5860 and 14840 hours of relaxation of the alloy at external temperature and atmospheric pressure. Hydrogenation was performed at 300 °C and the hydrogen pressure of 16 atm in a Siverts-type equipment. The surface of the membrane filter was studied using a scanning microscope Supra_MSU and the AFM method on a scanning probe microscope «Smen-A».

The choice of the regime of the AFM measurements, contact or semi-contact, was determined by the degree of roughness of the membrane surface. Standard silicon cantilevers HA_NC ETALON with length 80-110 μm, with resonant frequencies 130-250 kHz and the radius of the rounded tip less than 10 nm were used. Measurements on the Supra_MSU scanning microscope were carried out at an accelerating potential difference of 10 kV. The obtained microelectronic photos were used to estimate the grain size by the secant method [14].

3. Experimental results and discussion

Figure 1 shows the surface of alloy Pd_{85}Pb_{15} for original state of membranes on an area 81 μm². The image in Figure 1(a) allows us to analyze the features of topography and defects of the investigated surface. The height of each point of it is matched with the color (see the color bar on the right).

One can see layers of substructure elements (the enlarged fragment on the insert in Figure 1(a) and the areas indicated by the solid arrows on it). The width of such layers is from 0.19 to 0.30 μm. They have the form of lamellae separated by interlayer boundaries. The maximum width of theirs is about 0.1 μm. More pronounced boundaries with recesses frame groups of such lamellae. The recesses diameters are from 0.2 to 0.5 μm (Figure 1(b)).

We see also the individual globular formations of size about 0.14 microns surrounded by deformation fields (see arrows).

According to our AFM data, the maximum surface roughness of alloy Pd_{85}Pb_{15} for original state is 100 nm (Figure 1(c)).

The image in Figure 1(d) is phase imaging of the surface. The data reflect the change in the rigidity coefficient of the material when the cantilever moves on the surface [15]. Light areas correspond to a decrease in rigidity.

Electron microscopic images of the initial surface under formed state (Figure 2 (a)) revealed surface ulceration in the form of craters in the body of individual alloy grains. Diameters of the most craters are 0.2 μm. The grain boundaries are clearly visible in Figure 2 (a). For palladium doped with other elements: Y, In and Ru, such detections were not typical and the grain boundaries were not so clearly observed [6,16].

The analysis of the grain sizes by the secant method [14] showed that theirs average size is 8.1 μm before hydrogenation. The minimum size is 2.7 μm, the maximum size is 33.4 μm.

After hydrogenation the Pd_{85}Pb_{15} membrane alloy showed a tendency to cavitation in the near-surface layers and deformation distortions (Figure 2(b)). After hydrogenation and relaxation for 240 hours, the minimum grain size is 3.9 μm, the maximum is 45.8 μm (Figure 2(b)). The average grain size is 9.1 μm for this state.
Figure 1. AFM images of the surface for the alloy Pd\(_95\)Pb\(_5\) before hydrogenation: (a)-topography image; (b)-surface topography by the cross-section plane; (c)-3D image of the surface; (d)-phase image in tapping mode.

After hydrogenation and relaxation for 5860 hours, the minimum grain size is 5.2 \(\mu m\), the maximum is 39.2 \(\mu m\) (Figure 2(c)). The average grain size is 16.2 \(\mu m\).

It can be seen that after hydrogenation the grain sizes are extremely inhomogeneous. We can see the secondary recrystallization-the system move to a more stable state. We can be reasoned that extremely inhomogeneous of grain sizes is a result of a single reversible doping with hydrogen.

Figure 2(d) shows the surface at an angle of 70º after hydrogenation and the relaxation for 5860 hours. One can see grain boundary and shear deformations along it. There are also recesses on the surface. Their diameters are from 0.2 \(\mu m\) to 0.5 \(\mu m\). The most common diameter is 0.2 \(\mu m\).

AFM images of the alloy surface after reversible doping with hydrogen from the gas phase (300ºC, 16 atm) and 14840 hours of relaxation showed (Figure 3) that the relief has changed dramatically.
Figure 2. Electron microscopic images of the surface of membranes: (a)-before hydrogenation; (b)-after hydrogenation and relaxation for 240 hours; (c)-after hydrogenation and relaxation for 5860 hours; (d)-the surface at an angle of 70° after hydrogenation and relaxation for 5860 hours.

The maximum surface roughness is 20 nm now. Globular formations are more numerous after hydrogen exposure (solid arrow) and their size varies from 0.1 to 0.17 μm. Deformation fields are more pronounced (see arrows).

As before the introduction of hydrogen into the structure, we see layers of substructure elements (in a frame of Figure 3(a)). Now the width of such layers is from 0.14 to 0.20 μm, which is less than before hydrogenation.

One can see that there are numerous vacancy funnels with a maximum diameter of 0.5 μm and a depth of up to 12 nm and flat hollows of irregular shape (Figure 3(a)-(b)) with a depth of up to 7 nm with the most common diameter of 2 μm (Figure 3(b)-(c)) in the surface. The form of these flat hollows resembles the appearance of flecking on the surface of the Pd₉₃Y₇ membrane alloy [6]. But there are no fracture surfaces in the Pd₉₅Pb₅ alloy: we do not detect decohesion along the grain boundaries and flecking of the surface layer of the grains themselves (Figure 2(d)).

Significant changes were received in the distribution of regions with differences in rigidity of the membrane after its operation in hydrogen. We see this by comparing the phase images of the surface in Fig. 1 (d)-before and in Fig. 3 (d)-after the hydrogenation.
Figure 3. AFM images of the surface for the alloy Pd₉₅Pb₅ after its hydrogenation and 14840 hours relaxation: (a)-topography image; (b)-surface topography by the cross-section plane; (c)-3D image of the surface; (d)-phase image in the contact mode.

4. Conclusion
As a result of this research, an insight into the surface morphology of the Pd₉₅Pb₅ membrane alloy was obtained.

This work reported about the observation of changes in the surface morphology of membrane filters of Pd₉₅Pb₅ alloy, when they are hydrogenated from a gas medium.

The predisposition of the alloy to cavitation during the manufacture of a membrane filter and its reversible doping with hydrogen is revealed and confirmed.

A decrease in the degree of surface roughness is established as a result of reversible hydrogen doping, which can affect the hydrogen permeability of diffusion filter membranes.

The practical significance of this study is the development of technologies for the diffusion separation of high-purity hydrogen.
Acknowledgment
We thank Dr. T I Lakoba for editing the English version of the manuscript also the research group of Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, and the research group of Laboratory of Energy Capacious and Catalytically Active Substances Lomonosov Moscow State University.

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