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Pd–Pb nanoscale films as surface modifiers of Pd,Cu alloy membranes used for hydrogen ultrapurification

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Abstract

The purpose of the article is to reveal the role of the thickness of the layer of the lead-palladium alloy deposited on a copper-palladium membrane in the processes of cathodic injection and the anodic extraction of atomic hydrogen.

The objects of the study were ~ 4 μm thick copper-palladium film electrodes obtained by magnetron sputtering of a target with a composition of 56 at. % Cu and 44 at. % Pd. The studies were carried out by cyclic voltammetry and double step anodic-cathodic chronoamperometry in a deaerated 0.1 M H₂SO₄ aqueous solution. The calculation of the parameters of hydrogen permeability for samples of finite thickness was carried out by mathematical modelling.

Cathodic injection and anodic extraction of atomic hydrogen were used to study the effect of the surface modification of the foil membrane of a Pd-Cu solid solution on the diffusion and kinetic parameters of hydrogen permeability.

It was found that even a small addition of Pd-Pb (a 2 nm thick film) leads to a decrease in the concentration of atomic hydrogen and the diffusion coefficient in the foil. With an increase in the thickness of the coating there is an increase in the diffusion parameters of the hydrogen injection and extraction processes. However, the hydrogen permeability does not reach the level of the unmodified alloy. The main kinetic parameter, the hydrogen extraction rate constant, changes nonlinearly with an increase in the thickness of the coating.

Keywords: Pd-Cu and Pd-Pb solid solutions, Film electrodes, Cathodic injection and anodic extraction of atomic hydrogen, Hydrogen permeability

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1. Introduction

Currently, there is increasing demand for high-purity hydrogen (~ 99.999 wt%), which is used, for example, in low-temperature fuel cells with a polymer membrane electrolyte [1]. The most promising materials for hydrogen purification are metal membranes made of palladium or palladium-based binary alloys, which are characterised by a higher selectivity as compared to polymers [2]. In addition, palladium alloys have a rather rare combination of properties such as strength and ductility, high specific hydrogen permeability, low hydrogen dilatation, and increased corrosion resistance in corrosive gas media [3].

The disadvantages of pure palladium include, first of all, hydrogen embrittlement, the presence of the α -Pd–H \leftrightarrow β -Pd–H phase transition, and a susceptibility to catalytic poisoning [4]. To eliminate these disadvantages, pure palladium is alloyed with other metals. Homogeneous Pd–Cu alloys are of particular interest, since they reduce the cost of the membrane material due to the reduced Pd content. Moreover, the palladium-enriched fcc phase of the solid solution increases the resistance of Pd–Cu alloys to the H₂S surface poisoning [1].

One of the most acceptable methods of obtaining membranes for hydrogen purification is magnetron sputtering of the target of the corresponding composition [5–7]. In particular, the mechanical strength of an ordered Pd–Cu solid solution obtained by magnetron sputtering is noticeably higher than the mechanical strength of palladium. Therefore, such alloy can be recommended to be used in the form of a thin foil to manufacture membranes for hydrogen ultrapurification.

It is also important that, according to various research data, the catalytic efficiency of palladium in electrooxidation processes can be significantly improved by lead doping [8, 9].

High strength and ductility is a necessary combination of properties for foils of membrane elements for hydrogen ultrapurification [5]. A Pd–Pb solid solution (5 at% Pb) obtained by magnetron sputtering is formed by discrete generation with a further growth of islands and their coalescence. An average thickness of the coating of ~10 nm allows achieving the labyrinthine morphology of the surface.

Reports of studies conducted using Pd,Pb-alloys in the hydrogen evolution reaction are extremely limited. Most of them are devoted to the study of the catalytic properties of the alloys of this system in the reactions of electrooxidation [10–12], organic synthesis [13], and in quantum-chemical studies [14]. Increasing the selectivity of catalysts used in industrial processes is also important in terms of improving the production technologies.

The purpose of this work is to identify the role of the thickness of the lead-palladium alloy layer sprayed on the copper-palladium membrane in the processes of cathodic injection and anodic extraction of atomic hydrogen.

2. Experimental

The studies were carried out using copper-palladium film electrodes with a thickness of ~ 4 μ m obtained by magnetron sputtering of the target with a composition of 56 at% Cu and 44 at% Pd. A coating with a thickness of 2 to 10 nm was applied to the surface of the electrodes by magnetron spraying of the target with a composition of 95 at% Pd and 5 at% Pb. The sputtering was carried out in the Ar (10⁻¹ Pa) medium, the initial vacuum was 10⁻³ Pa. The growth rate was 4 nm/s. The power of the magnetron in the growth process of the foil of the Pd–Cu solid solution was 750–790 W, whereas for the coating of the Pd–Pb solid solution it was 630–650 W. To assess the coating structure of the Pd–Pb solid solution, the coating was simultaneously applied to the surface of the foil and to the surface of the synthetic mica. The structure was investigated by transmission electron microscopy (TEM) (Carl Zeiss Libra 120, Germany*).

Electrochemical measurements were conducted in a three-electrode glass cell with a help of an IPC-Compact potentiostat using the methods of cyclic voltammetry and double step anodic-cathodic chronoamperometry in a deaerated aqueous solution of 0.1 M H₂SO₄ [15]. The potentials were recalculated relative to the standard hydrogen electrode.

The working electrode was made of spectrally pure graphite. The samples of films were applied to its surface with the help of conductive graphite adhesive.

* The study was carried out using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University.

To remove the traces of surface oxides which form on alloys even in deaerated solutions, prior to obtaining voltammograms, the electrode was kept for 500 s at a constant potential of $E_{pp} = 0.40$ V, at which the electrode drew a weak cathodic current (at a level of $-1 \div -5$ μ A). The values of E_{pp} were chosen so that $E_{pp} < E(0)$ and the duration of pretreatment was determined by the transition of the cathodic current to a steady state value.

The forward and reverse potentiodynamic $i, E(t)$ -curves were obtained at the potential scan rate of $dE/dt = 5$ mV/s. Cyclic voltammetric curves were limited by potentials corresponding to the evolution of hydrogen ($E_c = -0.15$) and oxygen ($E_a = 1.55$ V). Cyclic voltammograms for all electrodes were obtained starting with the potential E_{pp} in the cathodic region till the appearance of a noticeable cathodic current of hydrogen reduction. Then the direction of the potential scanning was changed and the potential returned to the value E_{pp} .

Before receiving each double step anodic-cathodic i, t -curve, a prepolarisation potential of $E_{pp} = 0.40$ V was applied to the working electrode for 500 s. The curve corresponding to the cathode current transient was obtained at the cathode hydrogenation potential of $E_c = -0.15$ V, which was the same for all tested samples. The hydrogenation time t_c varied within the range of 1–10 s. After that, the ionisation potential of atomic hydrogen E_p^a was applied to the electrode. E_p^a was preliminarily found from the anodic peaks on the cyclic voltammogram corresponding to each sample to take into

account the inhomogeneity of the surfaces of the samples after their modifications. The current transient was recorded until it reached a constant value, which usually occurred within ~ 500 s. After that, without turning off the cell and without removing the electrode from it, the prepolarisation potential E_{pp} was again applied to it and the procedure was repeated with a sequential increase in the hydrogenation time.

It is important that at a hydrogenation time of less than 10 s, no palladium hydrides were formed, and the hydrogen concentration in the alloy (Pd/H) calculated from experimental data for a hydrogenation period of 10 s did not exceed 0.02 and remained at the level of the α -phase of the Pd-H solid solution.

It should be noted that the results were only processed using the data for cathode current transient corresponding to $t_c = 10$ s. The hydrogen permeability parameters for the samples of finite thickness were calculated using the method of mathematical modelling [17].

3. Results and discussion

Fig. 1 shows TEM images of a Pd-Pb alloy coating with a thickness of 5 (a) and 10 nm (b).

The 5 nm thick coating consists of individual Pd–Pb island fragments. An increase in the coating thickness to 10 nm leads to the fusion of nanoscale islands and the formation of a labyrinthine morphology.

Typical cyclic voltammograms obtained for a thin PdCu electrode without its modification and with a Pd–Pb coating of various thicknesses are shown in Fig. 2.

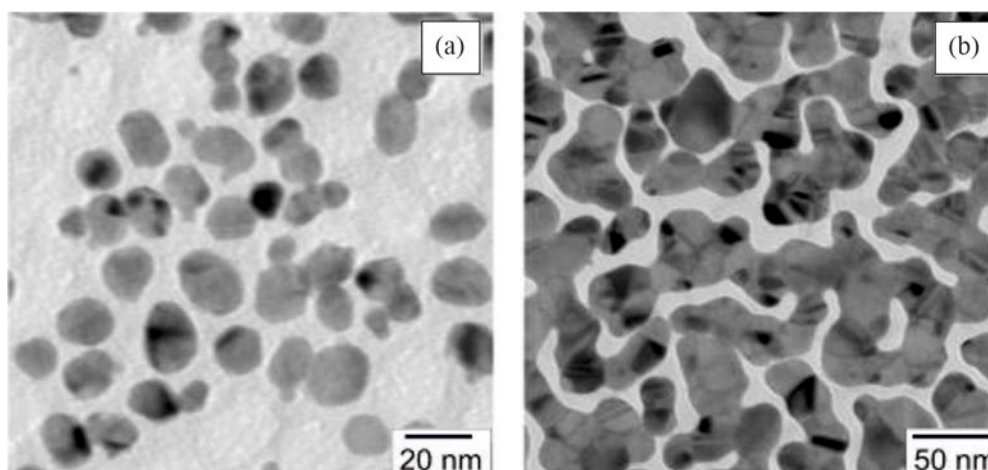


Fig. 1. TEM images of Pd-Pb alloy films (5 at. % Pb) with a thickness of 5 nm (a) and 10 nm (b) [5]

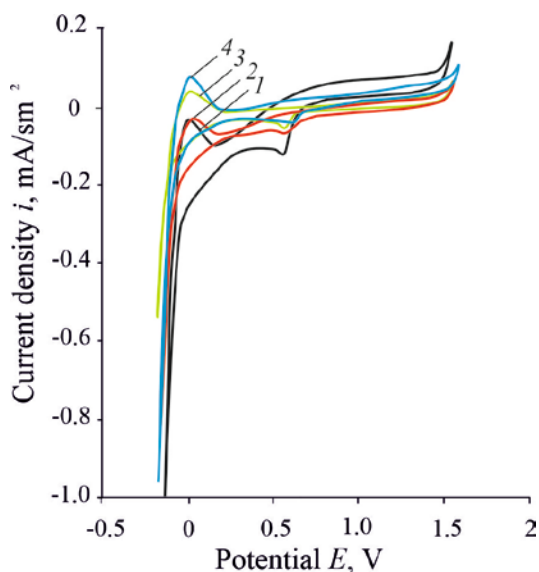


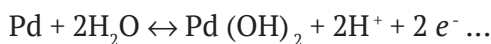
Fig. 2. Cyclic voltammogrammes for the initial foil samples of the Pd–Cu solid solution (1) and after applying a Pd–Pb coatings of various thicknesses L : 2 (2); 5 (3); 10 nm (4)

At the potential of $E \approx 0.00$ V, an ionisation peak of atomic hydrogen appears on the anodic branch of the curve. In case of unmodified PdCu electrode, the ionisation peak is located within the region of negative currents. However, the appearance of even a thin (~ 2 nm) coating of the Pd–Pb solid solution has a noticeable effect on the ionisation of atomic hydrogen, which is expressed in a slight decrease and broadening of the anodic peak.

For the unmodified foil sample within the potential range of 0.75–1.25 V, there is a small indistinct peak, which can be associated with the oxidation of palladium according to the equation



or



The equilibrium potential for both reactions is $E_{\text{eq}} = 0.825$ V [16]. Surface oxides of neither copper nor lead form in the studied solution ($\text{pH} \sim 1.2$). For other samples, such a peak is not typical, which can be attributed to the fact that the surface is blocked by island nanoscale Pd–Pb fragments. At a potential of ~ 0.60 V, the cathodic branch of the curve shows a clear peak of the reduction of oxidised palladium.

The stepped anodic–cathodic chronoamperogrammes obtained for all studied samples

are shown in Fig. 3. With an increase in the hydrogenation time t_c there is a gradual increase in the rate of hydrogen ionisation. The character of the current transient in both anodic and cathodic chronoamperogrammes for all samples remains unchanged, which indicates that the mechanism of the hydrogen injection and extraction processes is still present. It should be noted that for all studied samples, the main anodic current transient occurs within 20 seconds.

With an increase in the thickness of the nanoscale coating, there is an increase in the ionisation and injection rate of atomic hydrogen. Moreover, a sample with a coating thickness of $L = 10$ nm is characterised by the maximum rate of the process at $t_c = 10$ s.

Thus, a Pd–Pb coating even 2 nm thick has a noticeable effect on the kinetics of the process. This is reflected in an increase in the injection and extraction rate of atomic hydrogen with an increase of the thickness of the coating.

As follows from the modelling data of the hydrogenation of film samples [17], the cathode current transient at potentiostatic polarisation of the electrode is described by the equation:

$$i_c(t; \eta_c) = i_c^\infty(\eta_c) + \frac{F\bar{k} [c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e]}{\left(1 + \frac{\bar{k}L}{2D}\right)} \cdot \exp\left[-\frac{\bar{k}t}{\left(1 + \frac{\bar{k}L}{2D}\right)L}\right]. \quad (1)$$

Here, i_c^∞ is the maximum cathodic current, D is the coefficient of solid-phase diffusion of atomic hydrogen, L is the thickness of the film sample, \bar{k} is the rate constant for the atomic hydrogen extraction, $\Delta c_{\bar{H}} = [c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e]$ is a change in the concentration of atomic hydrogen \bar{H} located in the subsurface region of the alloy, $c_{\bar{H}}^s$ is the molar concentration \bar{H} in the near-surface layer of the membrane, and $c_{\bar{H}}^e$ is the equilibrium concentration of atomic hydrogen in a metal sample.

After a series of transformations, equation (1) for the case of $\frac{\bar{k}L}{2D} \ll 1$, when the process of atomic hydrogen introduction into the film is significantly inhibited, has a simpler form:

$$\ln[i_c(t; \eta_c) - i_c^\infty(\eta_c)] = \ln[F\bar{k}[c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e] - \frac{\bar{k}t}{L}]. \quad (2)$$

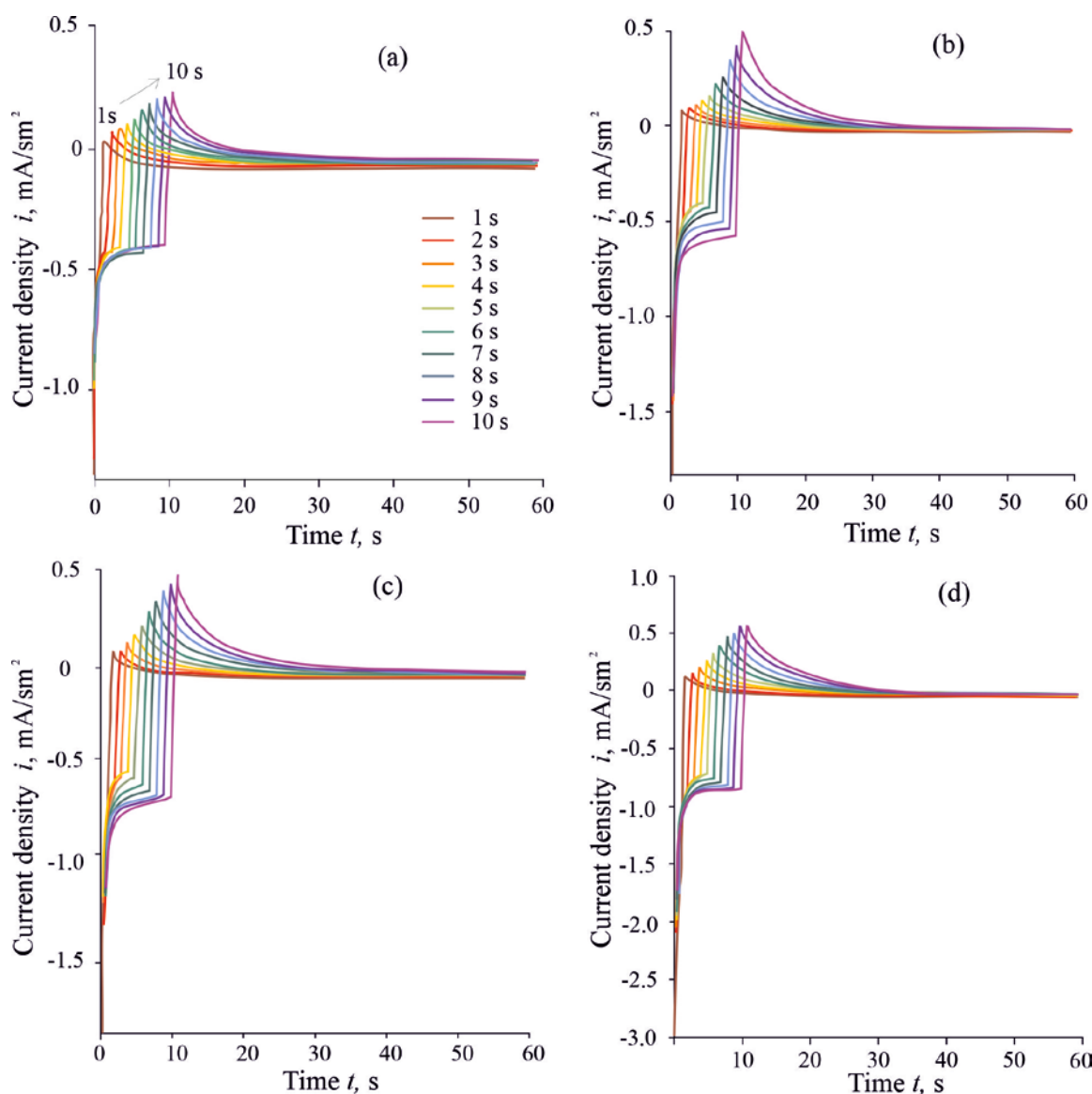


Fig. 3. Cathodic-anodic chronoamperograms for foil samples of the Pd-Cu solid solution: uncoated (a), with a Pd-Pb coating with a thickness of: 2(b), 5(c) 10 nm (d)

This equation corresponds to a rather short, up to 4 s, duration of the current transient and corresponds to the regime of mixed diffusion-phase-boundary kinetics. For the case when $\frac{\bar{k}L}{2D} \gg 1$, as well as in the case of diffusion kinetics of the atomic hydrogen injection, equation (2) is transformed:

$$\ln[i_c(t; \eta_c) - i_c^\infty(\eta_c)] = \ln\left[\frac{2FD}{L}[c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e]\right] - \frac{2Dt}{L^2} \quad (3)$$

According to (2) and (3), it is possible to straighten the cathodic chronoamperogramme in the criteria coordinates $\ln[i_c(t; \eta_c) - i_c^\infty(\eta_c)] - t$.

The linearised chronoamperogrammes were used to calculate the main parameters of the hydrogen permeability of the modified Pd-Cu samples, which are shown in Fig. 4. Since the studied samples were only used once in the experiment, the relief of the foil surface slightly differed from experiment to experiment, which resulted in rather high values of the confidence intervals for the obtained parameters.

Fig. 4c shows the hydrogen permeability coefficients K_D for all studied samples which were calculated by the formula:

$$K_D = D^{1/2} \Delta c_{\bar{H}}. \quad (4)$$

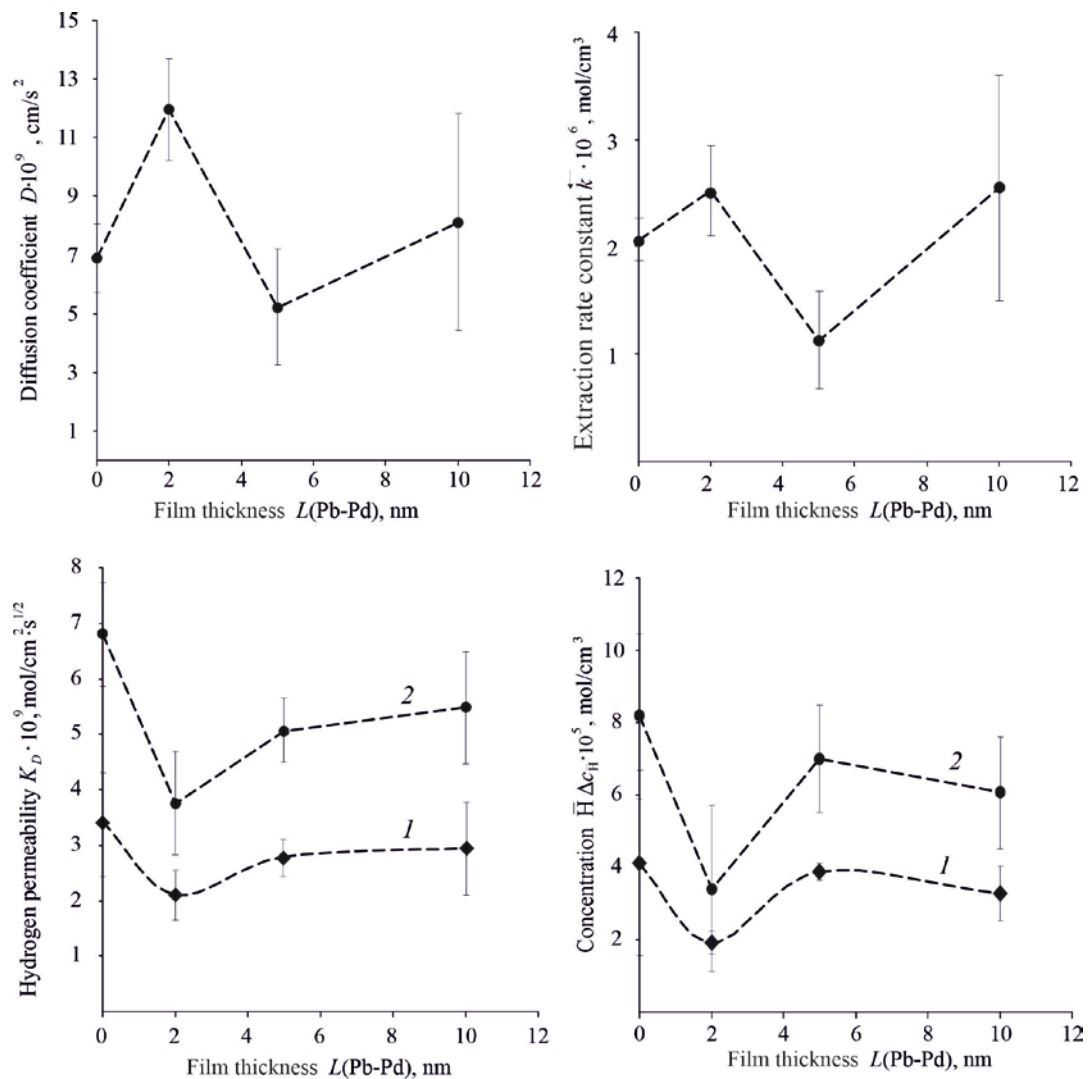


Fig. 4. Dependences of the diffusion and kinetic characteristics of the hydrogenation process on the thickness of the Pd–Pb alloy coating obtained under the modes of diffusion (1) and mixed (2) polarisation

It is convenient to use this coefficient when it is impossible to find the diffusion coefficients separately, as well as for comparison with the values of hydrogen permeability found by other methods.

The analysis of the obtained data revealed that there is an ambiguous effect of the coating thickness on the parameters of hydrogen permeability. Even with a coating thickness of ~ 2 nm, there is a significant increase in the diffusion coefficient D compared to the unmodified alloy. A further increase in the thickness of nanoscale coatings L was accompanied by a decrease in D . However, an increase in the soundness of coatings at a thickness of 10 nm demonstrated a slight increase in the diffusion coefficient. The nature

of the dependence of the rate constant for the extraction \bar{k} on L is similar to the dependence of the diffusion coefficient.

The opposite effect is observed for the dependence of the change in the concentration of atomic hydrogen $\Delta c_{\bar{H}}$ on the coating thickness. It should be noted that these values were calculated taking into account different kinetic regimes of the process of atomic hydrogen injection. It is logical to assume that the quantities $\Delta c_{\bar{H}}$ corresponding to the initial time are rather small, whereas with an increase in the injection time, an increasing amount of H can penetrate into the metal membrane.

Of considerable interest is the dependence of the hydrogen permeability coefficient on L

(Fig. 4c). According to (4), the largest contribution to the K_D value is made by the value $\Delta c_{\bar{H}}$. It can be concluded that, regardless of the implemented mode of atomic hydrogen injection into the foil, the modification of the foil surface with a Pd–Pb solid solution generally reduces its hydrogen permeability. At the same time, with an increase in the thickness of the coatings, the hydrogen permeability increases, although it does not reach the value for the unmodified sample. It is assumed that the Pd–Pb coating blocks the active centres of hydrogen sorption on the surface of the Pd–Cu substrate without creating new catalytically active centres if the coating thickness is 2 nm.

According to [17], the complete anodic current transient is described by the equation

$$i_a(t) = i_a^\infty + \frac{2FD}{L} [c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e] \times \left(\exp\left(-\frac{\pi^2 D(t-t_c)}{4L^2}\right) - \exp\left(-\frac{\pi^2 D(2t-t_c)}{4L^2}\right) \right), \quad (5)$$

which is linearised at sufficiently noticeable values of t comparable with t_c :

$$\ln\left(\frac{i_a(t) - i_a^\infty}{i_a(t_c) - i_a^\infty}\right) \approx -\frac{\pi^2 D(t-t_c)}{4L^2}, \quad (6)$$

which allows using graphical processing to calculate D . Further, using the obtained value for D the graphical linearisation of the complete equation (5) presented in a logarithmic form is carried out:

$$\ln[i_a(t) - i_a^\infty] = \ln\left(\frac{2FD}{L} [c_{\bar{H}}^s(\eta_c) - c_{\bar{H}}^e]\right) + \ln\left(\exp\left(-\frac{\pi^2 D(t-t_c)}{4L^2}\right) - \exp\left(-\frac{\pi^2 D(2t-t_c)}{4L^2}\right)\right). \quad (7)$$

It should be noted that equation (7) is valid within the framework of a very general model of mixed solid-phase diffusion kinetics which occurs at sufficiently long (> 20 s) times of the process.

Table 1. Characteristics of anodic extraction of hydrogen into film samples of the Pd-Cu solid solution with different thicknesses (L) of the modifying Pd–Pb layer

L , nm	$D \times 10^9$, cm ² /s	$\Delta c_{\bar{H}} \times 10^5$, mol/cm ³	$K_D \times 10^9$, mol/cm ² s ^{1/2}
0	4.83 ± 1.89	8.13 ± 3.79	5.65
2	3.90 ± 0.41	4.95 ± 1.25	3.10
5	2.31 ± 1.04	3.29 ± 2.26	1.58
10	0.85 ± 0.43	17.54 ± 10.59	5.11

The analysis of the parameter values calculated by the anodic current transients (Table 1) allows us to conclude that with an increase in the film thickness there is a decrease in both the diffusion coefficients and the concentration of atomic hydrogen in the alloy.

Nevertheless, the hydrogen concentration and the hydrogen permeability coefficient for the sample with a coating thickness of 10 nm is higher as compared to other samples. It can be assumed that an increase in the surface area of the substrate has a definite effect on the hydrogen permeability. In particular, the parameters calculated by the anodic current transients D turned out to be somewhat lower than those found by cathodic chronoamperogrammes. The latter can be explained by the dilatation effect of the crystal lattice of Pd alloys [18], as well as by the irreversible sorption of atomic hydrogen by the bulk of the solid phase [19].

4. Conclusions

Surface modification of the Pd,Cu-alloy (56 at% Cu and 44 at% Pd) with nanoscale island films of the Pd–Pb alloy has a rather noticeable effect on the parameters of hydrogen permeability. In particular, with an increase in the average thickness of the Pd,Pb film, there is an increase both in the injection and ionisation rate of atomic hydrogen.

Even a small addition of Pd–Pb (2 nm thick film) leads to a decrease in both the concentration of atomic hydrogen in the Cu–Pd alloy and the diffusion coefficient K_D .

As the thickness of the Pd,Pb film increases on the surface of the Pd–Cu alloy substrate, there is an increase in the diffusion parameters of the H injection and extraction processes. However, the hydrogen permeability does not reach the level of the unmodified alloy. The main kinetic parameter, the hydrogen extraction rate constant, changes nonlinearly with an increase in the thickness of the coating.

More reliable data about the kinetics of the hydrogenation process can be obtained by processing cathodic chronoamperogrammes that are not complicated by the phenomena of dilatation and irreversible sorption of hydrogen.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Al-Mufachi N. A., Steinberger-Wilckens R. Influence of temperature and pressure on surface modified Pd-Cu alloy foils for hydrogen purification applications. *Thin Solid Films*. 2018;646: 83–91. <https://doi.org/10.1016/j.tsf.2017.11.032>
2. Akamatsu T., Kume Y., Komiya K., Yukawa H., Morinaga M., Yamaguchi S. Electrochemical method for measuring hydrogen permeability through metals. *Journal of Alloys and Compounds*. 2005;393: 302–306. <https://doi.org/10.1016/j.jallcom.2004.10.007>
3. Gorbunov S. V., Kannykin S. V., Penkina T. N., Roshan N. R., Chustov E. M., Burkhanov G. S. Palladium-lead alloys for the purification of hydrogen-containing gas mixtures and the separation of hydrogen from them. *Russian Metallurgy (Metally)*. 2017;2017(1): 54–59. <https://doi.org/10.1134/S0036029517010050>
4. Endo N., Furukawa Y., Goshome K., Yaegashi S., Mashiko K., Tetsuhiko M. Characterization of mechanical strength and hydrogen permeability of a Pd-Cu alloy film prepared by one-step electroplating for hydrogen separation and membrane reactors. *International Journal of Hydrogen Energy*. 2019;44(16): 8290–8297. <https://doi.org/10.1016/j.ijhydene.2019.01.089>
5. Gorbunov S. V., Dontsov A. I., Sinetskaya D. A. Structure and orientation changes in the growth process of solid solution films Pd-5 (at%)Pb. *Materials Science*. 2019;5: 10–13. <https://doi.org/10.31044/1684-579x-2019-0-5-10-13>
6. Ievlev V. M., Solntsev K. A., Dontsov A. I., Maksimenko A. A., Kannykin S. V. Hydrogen permeability of thin condensed Pd–Cu foil: Dependence on temperature and phase composition. *Technical Physics*. 2016;61(3): 467–469. <https://doi.org/10.1134/s1063784216030105>
7. Ievlev V. M., Maksimenko A. A., Kannykin S. V., Belonogov E. K., Volodina M. S., Roshan N. R. Structure and mechanical properties of the condensed foil of Pd–Cu solid solution. *Kondensirovannyye sredy i mezhfaznyye granitsy = Condensed Matter and Interphases*. 2016;18(4): 521–529. Available at: <https://elibrary.ru/item.asp?id=27474855> (In Russ., abstract in Eng.)
8. Wang Y., Nguyen T. S., Liu X. W., Wang X. Novel palladium–lead (Pd–Pb/C) bimetallic catalysts for electrooxidation of ethanol in alkaline media. *Journal of Power Sources*. 2010;195(9): 2619–2622. <https://doi.org/10.1016/j.jpowsour.2009.11.072>
9. Diao Y. Y., Yan R. Y., Zhang S. J., Yang P., Li Z. X., Wang L., Dong H. F. Effects of Pb and Mg doping in Al₂O₃-supported Pd catalyst on direct oxidative esterification of aldehydes with alcohols to esters. *Journal of Molecular Catalysis A: Chemical*. 2009;303: 35–42. <https://doi.org/10.1016/j.molcata.2008.12.023>
10. Anderson J. A., Richard J. M., Wells P. K. Pd catalysed hexyne hydrogenation modified by Bi and by Pb. *Journal of Catalysis*. 2009;261(2): 208–216. <https://doi.org/10.1016/j.jcat.2008.11.023>
11. Xingwen Y., Peter G.P. Novel Pd–Pb/C bimetallic catalysts for direct formic acid fuel cells. *Journal of Power Sources*. 2009;192(2): 279–284. <https://doi.org/10.1016/j.jpowsour.2009.03.036>
12. Faroppa M. L., Muscia J. J., Chiossoab M. E., Caggianoa C. G., Bideberripecb H. P., Garacia Fierro J. L., Siri G. J., Casella M. L. Oxidation of glycerol with H₂O₂ on Pb-promoted Pd/Γ–Al₂O₃ catalysts. *Chinese Journal of Catalysis*. 2016;37(11): 1982–1990. [https://doi.org/10.1016/S1872-2067\(16\)62531-7](https://doi.org/10.1016/S1872-2067(16)62531-7)
13. Khawar A., Aslam Z., Zahir A., Akbar I., Abbas A. Synthesis of Femur extracted hydroxyapatite reinforced nanocomposite and its application for Pb (II) ions abatement from aqueous phase. *International Journal Biological Macromolecules*. 2019;122: 667–676. <https://doi.org/10.1016/j.ijbiomac.2018.10.223>
14. Wei L., Yao X., Tian X., Cao M., Chen W., She Y., Zhang, S. DFT investigation of the effects of doped Pb atoms on Pd_n clusters (13 ≤ n ≤ 116). *Computational and Theoretical Chemistry*. 2011;966(1-3): 375–382. <https://doi.org/10.1016/j.comptc.2011.03.041>
15. Morozova N. B., Vvedenskii A. V., Beredina I. P. Katodic injection, anodic extraction and hydrogen diffusion in metallurgic Cu, Pd and Ag, Pd-alloys. I. Theoretical model. *Kondensirovannyye sredy i mezhfaznyye granitsy = Condensed Matter and Interphases*. 2014;16(2): 178–188. Available at: <https://elibrary.ru/item.asp?id=21785796> (In Russ., abstract in Eng.)
16. Abiyev R. Sh., et al. *Novyy spravochnik khimika i tekhnologa. Elektrodneye protsessy. Khimicheskaya kinetika i diffuziya. Kolloidnaya khimiya* [A new reference book of a chemist and technologist. Electrode processes. Chemical kinetics and diffusion.

Colloidal chemistry]. St. Petersburg: Mir i Semia Publ.; 2004. 837 p. (In Russ.)

17. Morozova N. B., Vvedenskii A. V., Maksimenko A. A., Dontsov A. I. Thin layer multicycle cathodic-anodic chronoamperometry of atomic hydrogen injection-extraction into metals with regard to the stage of phase boundary exchange. *Russian Journal of Electrochemistry*. 2018;54(4): 344–354. <https://doi.org/10.1134/s1023193518040067>

18. Barlag H., Opara L., Züchner H. Hydrogen diffusion in palladium based f.c.c. alloys. *Journal of Alloys and Compounds*. 2002;330-332: 434–437. [https://doi.org/10.1016/S0925-8388\(01\)01459-1](https://doi.org/10.1016/S0925-8388(01)01459-1)

19. Morozova N. B., Vvedenskii A. V. Cathodic injection, anodic extraction and hydrogen diffusion in metallurgical Cu, Pd- and Ag, Pd-alloys. III. Accounting irreversible hydrogen sorption. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2016;18(1): 81–90. Available at: <https://elibrary.ru/item.asp?id=25946624> (In Russ., abstract in Eng.)

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