ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2024.26/12223

Mechanical properties and catalytic activity of the Cu-36Pd (at. %) alloy foil surface after cleaning

N. B. Morozova[1,2], A. I. Dontsov[1,2]✉, T. N. Khmelevskaya[1]

[1]Baykova Institute of Metallurgy and Materials Science of the Russian Academy of Sciences, 49 Leninsky pr., Moscow 119991, Russian Federation

[2]Voronezh State University, 1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The purpose of the study was to evaluate the effect of mechanical treatment and ion sputtering on hydrogen sorption and the mechanical properties of the surface of the membrane foil of the Pd-Cu solid solution system obtained by rolling.

The efficiency of mechanical and ion beam treatment in cleaning of the surface of membrane foil of the Pd-Cu solid solution system obtained by rolling was assessed using cyclic voltammetry, Auger electron spectroscopy and atomic force microscopy.

It was established that ion beam treatment (Ar^+) and mechanical treatment reproduce the elemental composition of the surface, corresponding to the original composition of the solid solution, and forms a developed relief. The change in the asymmetry of the relief roughness after ion-beam treatment indicates the formation of microcracks on the foil surface, which reduce hardness and plasticity. Ion-beam surface treatment also contributes to the cleaning of the surface from rolling artefacts, which leads to a twofold increase in the ionization rate of atomic hydrogen, compared to a sample subjected to mechanical treatment.

Keywords: Cu-36Pd (at. %) solid solution, thin foil, surface cleaning, voltammetry, atomic force microscopy, nanoindentation

Funding: The study was supported by the Russian Science Foundation grant No. 2 3-19-00767 (https://rscf.ru/project/23-19-007671/)

For citation: Morozova N. B., Dontsov A. I., Khmelevskaya T. N. Mechanical properties and catalytic activity of the Cu-36Pd (at. %) alloy foil surface after cleaning. *Condensed Matter and Interphases*. 2024;26(3): 483–489. https://doi.org/10.17308/kcmf.2024.26/12223

Для цитирования: Морозова Н. Б., Донцов А. И., Хмелевская Т. Н. Механические свойства и каталитическая активность поверхности фольги сплава Cu-36Pd (ат. %) после очистки. *Конденсированные среды и межфазные границы*. 2024;26(3): 483–489. https://doi.org/10.17308/kcmf.2024.26/12223

✉ Alexey I. Dontsov, e-mail: DontAlex@mail.ru

1. Introduction

Solid solutions of the Pd-Cu system in a wide range of concentrations may form an ordering with the formation of a CsCl-type structure (β-phase) [1]. Interest in these solid solutions has been ongoing for several decades due to the limited information on the mechanism of ordering processes (α(FCC) → β) and disordering (β → α), on the substructure of the β-phase, including possible manifestations of deviations from the equiatomic composition, including in its properties. In terms of practical application the interest is due to the peculiarity of the properties: multiple changes in electrical conductivity during α ↔ β transformations [2]; the high mechanical characteristics of foil with the β-phase structure [3, 4], its advantage in hydrogen permeability in comparison with the α-phase, with pure and doped palladium (the activation energy of hydrogen diffusion in the β-phase is significantly lower) [5]. Therefore, the ordered solid solution foil is promising in the production of effective membranes for deep hydrogen purification, since it provides possibility of a multiple increase in productivity without the reduction with hydrogen, typical for samples made of pure and doped palladium. The low activation energy of hydrogen diffusion in an ordered structure allows the operation of the membrane at a temperature before the start of disordering.

Due to the stage-by-stage nature of the overall mass transfer process, along with the elemental composition, structure and substructure of the foil, it is necessary to take into account the state of the surface (elemental composition, morphology), which may be due to the manufacturing process (rolling, variants of ion sputtering of a target of the corresponding composition [6], galvanizing [7]). Thus, the cleaning of these membrane foil surfaces is an urgent task.

The aim of the study was to evaluate the influence of mechanical treatment and ion sputtering on hydrogen sorption and the mechanical properties of the surface of the membrane foil of the Pd-Cu solid solution system obtained by rolling.

2. Experimental

The rolling process was carried out according to the scheme described in [8], rolling from 2 mm was carried out sequentially up to a thickness of 100 μm. An ingot of Cu-36Pd (at. %), corresponding to the maximum temperature of the existence of the β-phase (about 550 °C), which ensured the formation of a single-phase structure was produced for rolling.

The original foil had a two-phase nanocrystalline structure (α- and β-phases [9]). For the ordering of the atomic structure (b-phase) the original foil was heated to 800 °C in a vacuum followed by rapid cooling to room temperature. The diffraction pattern in Fig.1 shows the structure of the foil, heat-treated to 800 °C and cooled to room temperature. As can be seen, the β-phase with an average size of the coherent scattering region of more than 1 μm was restored.

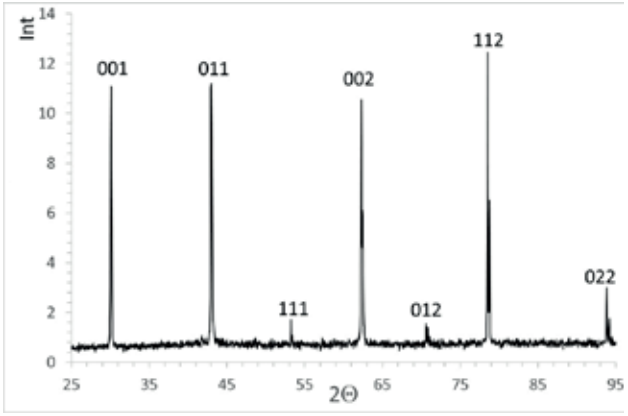

Fig. 1. X-ray diffraction pattern of the foil sample after heating at 800 °C and cooling to room temperature

The phase composition was controlled using X-ray diffractometry*. (RD, ARL X`TRA). The elemental composition of the sample surface was assessed using Auger electron spectroscopy (DESA-100 analyser), and quantitative analysis was performed using yield coefficients [10]. The surface morphology of the original foil and after its surface treatment was studied using atomic force microscopy (AFM, Solver Pro EC). The results of the following cleaning options were compared: 1 – mechanical treatment (MT) of the surface by successive use of sandpaper (grain size 2500), aqueous suspension of MgO and ethanol; 2 – ion beam treatment (IBT) for 180 min in an Ar environment (10^{-1} Pa) with an energy of about 50 eV, the initial vacuum is 10^{-3} Pa, to ensure uniform etching, the substrate with the foil was rotated at a speed of 1 rad/s.

* VSU Centre for the Collective Use of Scientific Equipment.

The mechanical properties of the foil surface were studied using the nanoindentation method on a Nano Hardness Tester (maximum load 20 mN, loading and unloading rate 20 mN/min).

The efficiency of foil treatment was assessed using cyclic voltammetry [11, 12] based on the degree of sensitivity to potential cycling, manifested as a local increase in current in the range of 0.1–0.5 V (at a potential scanning rate of 5 mV/s), corresponding to hydrogen ionization [13], and the complex sorption parameter (K_D, mol/cm^2 s$^{1/2}$) [14]. Since the samples had the thickness higher than 10 μm, atomic hydrogen did not pass through the foil during the experiment. It was not possible to determine the diffusion coefficient (D) of atomic hydrogen for the used model.

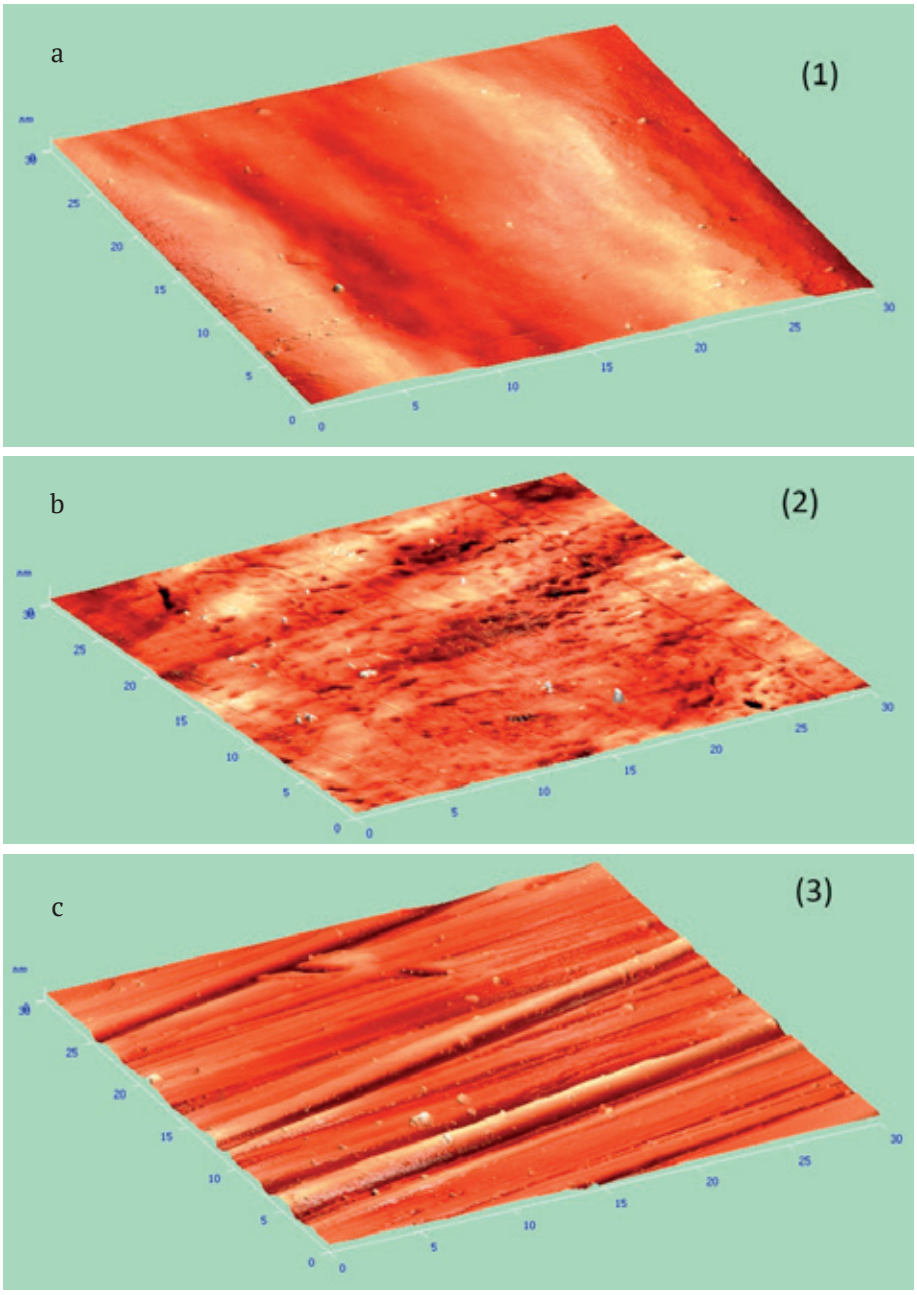

Fig. 2. AFM image of the surface areas of annealed foil (a), after ILD (b) and after mechanical treatment (c)

3. Results and discussion

AFM images of the surface of an annealed sample (a), after ion beam treatment (b) and after mechanical treatment are shown in Fig. 2. The results of image processing are presented in Table 1. After IBT, the height of the surface relief increased by 1.5 times. The type of surface roughness changes with hills (*S*sk > 0) on the depressions (*S*sk < 0) [15], which may indicate selective etching of the foil surface and the formation of pores and microcracks.

The surface relief (Fig. 2c) reflects traces of deformation as a result of the process of mechanical treatment of the surface with abrasive materials: the relief height and roughness increased by 2 times, the type of surface roughness did not change.

Figure 3 shows the distribution profile of elements along the depth of the surface layer, constructed using Auger electron spectroscopy data. Elemental composition of the unclean surface: sulphur - 17 at. %, carbon - 44 at. %, nitrogen - 8 at. %, oxygen – 11 at. %, palladium - 20 at. %. Transitions corresponding to copper atoms were not detected, which can be explained by the presence of rolling artefacts on the foil surface and a low electron yield coefficient of copper in comparison with the detected elements. At a depth of 300–500 nm, rolling artefacts almost completely disappeared, and the elemental composition corresponded to the original composition of the alloy.

The elemental composition of the foil surface after IBT and mechanical treatment is shown in Fig. 3(2) and 3(3), respectively. At the initial stage of etching, the concentration atoms was ~ 45 at. %, which was comparable to the concentration for an unclean surface. At a depth of more than 50 nm, the impurity concentration was ~ 5 at. %. This finding indicates that impurity elements were sorbed in the surface layer of the foil from the atmosphere, and not as a result of the rolling process.

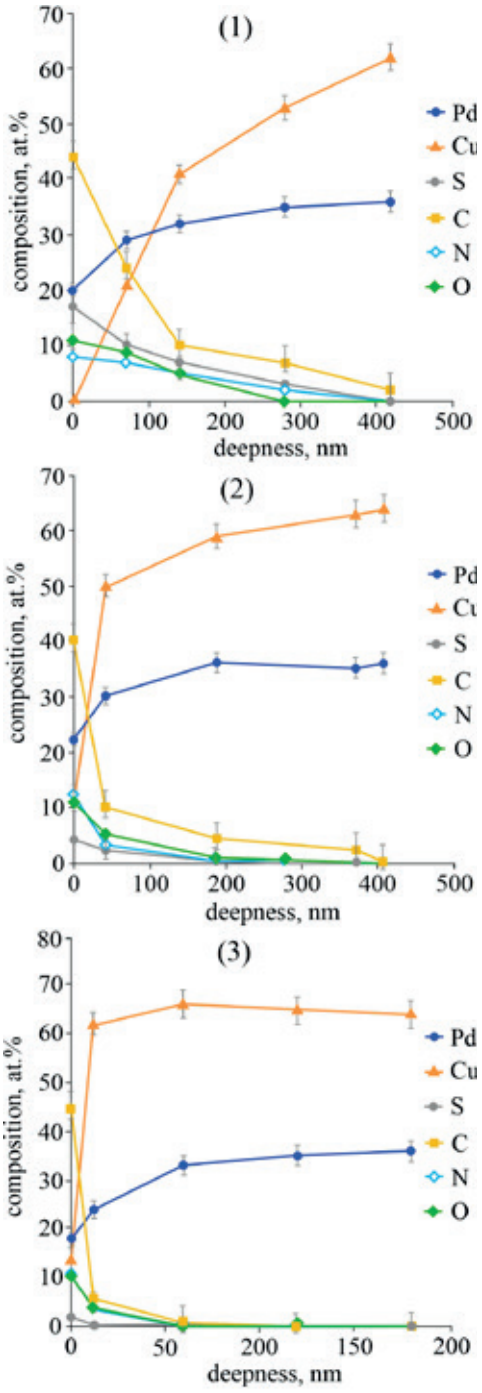

Fig. 3. Profiles of element distribution by depth of the near-surface layer (1) of annealed foil, (2) after ILD and (3) after mechanical treatment

Table 1. Surface roughness parameters

Sample	Параметры шероховатости поверхности			
	Maximum height, Sy (nm)	Average height, Sz (nm)	Roughness, Sa (nm)	Roughness asymmetry, Ssk
Without treatment	294	161	26	0.17
After treatment <1>	458	227	10	–0.67
After treatment <2>	583	290	41	0.27

An assessment of the hardness and plasticity of the surface of the uncleaned foil (1), after IBT (2) and MT (3) was performed based on *P-h* diagrams (Fig. 4): *Hv* = 325±10 MPa and *h* = 54±1%, *Hv* = 240±10 and *h* = 44±1%, *Hv* = 268±10 MPa, *h* =44±1% respectively. The presence of bends on the loading and unloading branches of curve (*2*) indicated a high concentration of microcracks caused by the selective etching of the foil surface with argon ions, which is confirmed by AFM data (see Table 1).

The decrease in hardness and plasticity is explained by the increase in the number of defects on the surface of the cleaned foil compared to the annealed one.

The voltammograms of an annealed sample (1) and the sample after mechanical treatment (2) are shown in Fig. 5. The untreated surface was virtually insensitive to potential cycling, as evidenced by the height (about 0.2 mA/cm^2) of the local maximum in the potential range of 0.3–0.5 V, characterizing the ionization process of atomic hydrogen. Hydrogen sorption constant (K_D) was equal to 2.44·10^{-9} mol cm^{-2}·s$^{-1/2}$.

The effect of mechanical surface treatment was expressed through an increase in the ionization peak, the height of which exceeded 0.7 mA/cm^2 (Fig. 2). This indicates an increase in the hydrogen ionization rate by 3.5 times compared to the untreated sample and an increase in K_D to 5.48·10^{-9} mol cm^{-2}·s$^{-1/2}$.

Ion beam surface treatment also helped to clean the surface from rolling artefacts (Fig. 6),

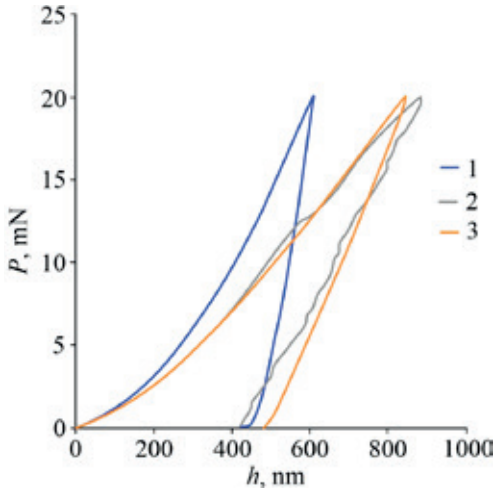

Fig. 4. Load diagram (P) - nanoindenter penetration depth (h) for 100 μm thick foil samples after rolling and annealing (1), after IBT (2), after MT (3)

which led to an increase in the ionization peak to 1.4 mA/cm^2, i.e. to a twofold increase in speed, compared to a sample subjected to mechanical treatment (K_D to 7.14·10^{-9} mol cm^{-2}·s$^{-1/2}$.) This was not only due to the unblocking of sorption centres during the IBT process, but also due to an increase in surface area caused by the formation of microcracks.

A quantitative assessment of hydrogen permeability was carried out using a mathematical model of images of semi-infinite thickness, describing injection ($\vec{k}$) and extraction ($\overleftarrow{k}$) of atomic hydrogen.

The extraction rate constant increased by 2 times when using ion beam treatment and was ~ 8.0·10^{-4} cm/s, which can be explained by

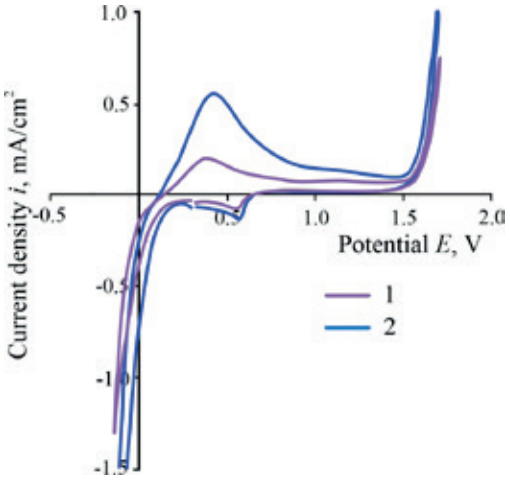

Fig. 5. Cyclic voltammograms obtained on an annealed sample (1) and a sample after mechanical treatment (2). (4 cycles of voltammograms are shown)

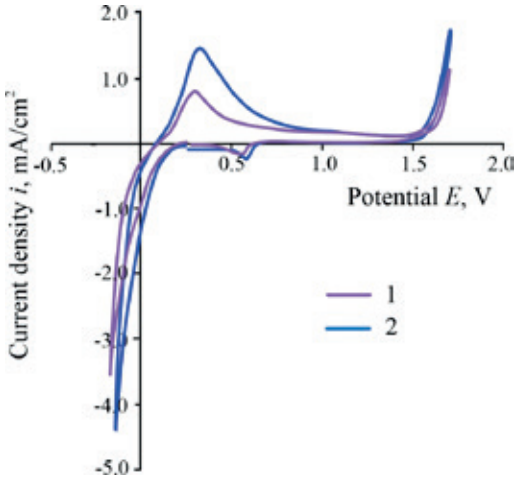

Fig. 6. Cyclic voltammograms obtained on a sample after mechanical treatment (1) and after ILD (2). (4 cycles of voltammograms are shown)

significant changes in the surface structure of the foil after the treatment.

Thus, as a result of IBT, the surface was completely freed from rolling artefacts, relief was developed, microcracks were formed and, accordingly, the effective surface area was increased.

Out of the two studied options for cleaning the surface of foil obtained by rolling, both options were effective. However, such treatment leads to the formation of microcracks on the surface of the foil, which significantly reduced its hardness and plasticity.

4. Conclusions

1. Ion beam treatment (Ar^+) and mechanical treatment reproduce the elemental composition of the surface corresponding to the original composition of the solid solution and form a developed relief.

2. The change in the asymmetry of the relief roughness after IBT indicates the formation of microcracks on the foil surface, which reduce hardness and plasticity.

3. Ion-beam surface treatment also helps to clean the surface from rolling artefacts, leading to a twofold increase in the ionization rate of atomic hydrogen compared to a sample subjected to mechanical treatment.

Contribution of the authors

The authors contributed equally to this article.

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. Subramanian P. R., Laughlin D. E. Cu-Pd (Copper-Palladium). *Journal of Phase Equilibria* 1991;12: 231–243. https://doi.org/10.1007/bf02645723

2. Senchenko A. A., Zelenin L. P., Sachkov I. N., Bashkatov A. N., Kotov A. P., Geld P. V. Measurement of temperature phase state on electrical resistive alloys Pd, Cu and Pd, Cu, In*. *Fizika metallov i metallovedenie*. 1989;67(V.1): 122–128. (In Russ.)

3. Telegin A. B., Syutkin N. N., Shashkov O. D. Structure and mechanical properties of ordered copper-palladium alloy*. *Fizika metallov i metallovedenie*. 1981;52(V.Z): 627–633. (In Russ.)

4. Golikova N. N., Laptevskij A. S., Syutkina V. I. Electrical and mechanical properties of ordered alloys based on palladium - copper with a B2 superstructure. *Fizika metallov i metallovedeniya*. 1996;82(3): 150–160. (In Russ.). Available at: https://www.elibrary.ru/item.asp?id=14934742

5. *Hydrogen in metals*. (Topics in applied physics; v. 28–29). Includes bibliographical references and indexes. Contents: v. 1. Basic properties.v. 2. Application-oriented properties. 1. Metals-Hydrogen content. 1. Alefeld G., 1933, I1. Ve1kl, J., 1936-TH690.H97. https://doi.org/10.1002/bbpc.19800840221

6. Ievlev V. M., Dontsov A. I., Novikov V. I., ... Burkhanov G. S. Composite membranes based on Pd-Cu and Pd-Pb solid solutions. *Russian Metallurgy (Metally)*. 2018;9: 854–858. https://doi.org/10.1134/S0036029518090070

7. Alique D., Imperatore M., Sanz R., Calles J. A., Baschetti M. G. Hydrogen permeation in composite Pd-membranes prepared by conventional electroless plating and electroless pore-plating alternatives over ceramic and metallic supports. *International Journal of. Hydrogen. Energy*. 2016;41: 19430–19438. https://doi.org/10.1016/j.ijhydene.2016.06.128

8. Mironova E. Y., Yaroslavtsev A. B., Dontsov A. I., Morozova N. B., Gorbunov S. V., Ievlev V. M. Lamp processing of the surface of PdCu membrane foil: hydrogen permeability and membrane catalysis. *Inorganic Materials*. 2021;57(8): 781–789. https://doi.org/10.1134/S0020168521080057

9. Phase diagrams of binary metal systems. A Handbook, in 3 volumes: Vol. 2. Lyakishev N. P. (ed.). Moscow: Mashinostroenie Publ.; 1997. 1024 p. (In Russ)

10. Davis L. E., MacDonald N. C., Palmberg P. W., Rich G. E., Weber R. E. (eds.), *Handbook of Auger Electron Spectroscopy*. Physical Electronics Industries, Inc., 1976.

11. Uluc A.V., Moa J. M. C., Terryn H., Böttger A. J. Hydrogen sorption and desorption related properties of Pd-alloys determined by cyclic voltammetry. *Journal of Electroanalytical Chemistry*. 2014;734(1): 53–60. https://doi.org/10.1016/j.jelechem.2014.09.021

12. Iwaoka H., Ide T., Arita M., Horita Z. Mechanical property and hydrogen permeability of ultrafine-grained Pd–Ag alloy processed by high-pressure torsion. *International Journal of Hydrogen Energy*. 2017;42(38): 24176–24182. https://doi.org/10.1016/j.ijhydene.2017.07.235

13. Fedoseeva A. I., Morozova N. B., Dontsov A. I., Kozaderova O. A., and Vvedensky A. V. Cold-rolled binary palladium alloys with copper and ruthenium: injection and extraction of atomic hydrogen. *Russian Journal of Electrochemistry*. 2022;58(9): 812–822. https://doi.org/10.1134/S1023193522090051

14. Morozova N. B., Vvedensky A. V., Beredina I. P. The phase-boundary exchange and the non-steady-state diffusion of atomic hydrogen in Cu-Pd and Ag-Pd alloys. I. Model analysis. *Protection of Metals and Physical Chemistry of Surfaces*. 2014;50(6): 699–704. https://doi.org/10.1134/S2070205114060136

15. Kurth S., Kenan C., Daniel M., Lars W., Seume J. R. Systematic roughness variation to model the influence of skewness on wall bounded flows. *Journal of the Global Power and Propulsion Society*. 2023;7: 177–187. https://doi.org/10.33737/jgpps/163089

** Translated by author of the article*

Information about the authors

Natalia B. Morozova, Cand. Sci. (Chem.), Associate Professor, Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation); Senior Researcher, A. A. Baikov Institute of Metallurgy and Materials Science Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0003-4011-6510

mnb@chem.vsu.ru

Alexey I. Dontsov, Cand. Sci. (Phys.–Math.), Associate Professor, Department of Materials Science and Industry of Nanosystems, Voronezh State University (Voronezh, Russian Federation); Senior Researcher, A. A. Baikov Institute of Metallurgy and Materials Science Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-3645-1626

dontalex@mail.ru

Tatyana N. Khmelevskaya, Cand. Sci. (Chem.), Researcher, A. Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences (Moscow, Russian Federation).

tatiana_ilinova@mail.ru

Received 08.09.2023; approved after reviewing 28.09.2023; accepted for publication 20.11.2023; published online 01.10.2024.

Translated by Valentina Mittova