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The effect of annealing at 450°C on the microstructure of a deformed Cu-1.5Pd-3Ag (at.%)

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Experiments were performed in order to study the surface and microstructure of the Cu-1.5Pd-3Ag alloy after deformation and annealing at a temperature of 450°C for 48 hours with air cooling. It is shown that, after this treatment, silver is segregated on the alloy surface in the form of droplet-like particles that are well identified by atomic force microscopy and scanning electron microscopy. The particles lateral sizes are $0.1-0.5\,\mu$m, in some cases up to $1\,\mu$m. Experiment on X-ray photoelectron spectroscopy indicates that an oxide film with a thickness of no more than 10 nm is formed on the Cu-1.5Pd-3Ag alloy surface, which protects the sample from further oxidation over the its entire volume. According to X-ray diffraction analysis, it was found that, during annealing of the Cu-1.5Pd-3Ag alloy, fractions of two phases with different silver enrichment degrees are segregated: practically pure Ag and a compound close to Ag-31 at.% Pd.

Keywords: copper-palladium-silver alloys, microstructure, X-ray diffraction analysis, X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy.

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1. Introduction

Copper-based alloys have low electrical resistance and are therefore used in electrical engineering [1]. Alloys with two or more alloying elements are currently used to achieve high functional properties, and their strong plastic deformation is also used as well. This approach allows combining different hardening mechanisms [2–4]. In addition, additional corrosion resistance requirements have recently been imposed on conductors. Copper conductors, for example, are coated with a thin layer of palladium to solve this problem [5]. However, palladium diffuses rather quickly during the operation of such wires, forming a set of ordered phases at the interface.

We found in [6] that lean alloying of copper with palladium (1.5 at.%) and silver (3 at.%) makes it possible to increase strength properties by combining solid-solution hardening and decomposition; it is shown that the aging of the alloy Cu-1.5Pd-3Ag in the temperature range below 450°C results in the release of silver-based phase particles in the Cu matrix. It is of interest to study the structure of the triple alloy Cu-Pd-Ag and the morphology of silver-based phase particles in more detail using various techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical properties of the surface and near-surface layers are supposed to be studied by X-ray photoelectron spectroscopy (XPS).

Cu-Ag alloys are aged as a rule, at a temperature of 375−450°C for 12−20 h [7–9]. Silver particles are released during such annealing. The annealing time of the Cu-1.5Pd-3Ag alloy was 48 h at a temperature of 450°C in this study. This holding time was chosen to ensure the completion of all thermal diffusion processes, as well as to ensure the equilibrium state of the alloy. Previously, we found [6] that the electrical resistance of the alloy Cu-1.5Pd-3Ag practically does not change with an increase of the holding time from 12 to 48 h ($\sim 3.2 \cdot 10^{-8}\,\Omega \cdot \mathrm{m}$), which indicates that an equilibrium state has been reached; microhardness decreases from 1000 to 870 MPa in this case due to the return/recrystallization processes.

The purpose of this work is to study the microstructure and surface of the deformed alloy Cu-1.5Pd-3Ag (at.%) after annealing for 48 h at a temperature of 450°C and to study the composition and morphology of the silver-based phase.

2. Material and methodology

Cu-1.5Pd-3Ag (at.%) alloy was smelted from copper, palladium, and silver with purity of 99.98, 99.99, and 99.99%, respectively. The smelting was carried out in a vacuum with a residual gas pressure of less than 10^{-2} Pa and poured into a graphite crucible. SEM in the phase analysis mode showed the following chemical composition of the alloy: Cu-2.4Pd-5.2Ag (mass.%)/Cu-1.5Pd-3Ag (at.%). All heat treatments were performed in evacuated glass or quartz ampoules.

∅5 mm ingot was homogenized at a temperature of 800°C for 3 h. The ingot was subjected to a mechano-thermal transformation by successive operations, including 1 h exposure at a temperature of 700°C with quenching in water and further 90% deformation. Thus, plates with a thickness of 0.3 mm were obtained from the ingot.

The processes of restructuring the structure and the evolution of properties were studied by annealing at a temperature of 450°C for 48 hours followed by cooling in air. The samples were studied after annealing and cooling, as well as after additional polishing using a diamond paste.

XRD was performed using a PANalytical Empyrean Series 2 diffractometer in CuK_α-radiation.

Since the composition and structure of the surface layers of various metals determine their corrosion-electrochemical properties [10,11], the surface and near-surface layers of the alloy Cu-1.5Pd-3Ag were also studied by the XPS method. The XPS measurements were performed using PHI 5000 VersaProbe X-ray photoelectron spectrometer (UrFU, Yekaterinburg). The spectra were processed in the PHIMultiPak spectrometer software package.

Tescan MIRA LMS SEM was used to study the microstructure of the surface. SolverNext atomic force microscope (IMP UB RAS, Yekaterinburg) was used to study the alloy surface by imaging with high spatial resolution. Measurements using the scanning spreading resistance microscopy were carried out in contact mode using a CG30/Pt conductive probe with a conductive platinum coating. An offset voltage was applied to the probe, and measurements of the resulting current through the sample were carried out, depending on the position of the probe, simultaneously with obtaining relief data using the constant force method. Assuming constant resistance of „probe–surface" contact at a given offset voltage, the value of the measured current is proportional to the local resistance of the studied sample. A detailed description of the AFM method can be found in Ref. [12].

3. Experimental results and their discussion

The XRD study of Cu-1.5Pd-3Ag alloy in its initial deformed state revealed the presence of two sets of peaks: intense reflections correspond to a solid solution of palladium in copper with a face-centered cubic (FCC) lattice (diffraction pattern *1* in Figure 1). The parameter *a* of the palladium crystal lattice is greater than that of copper. Therefore, the introduction of Pd leads to an increase of the lattice parameter of Cu-Pd solid solution to $a = 0.3644$ nm. In addition, several low-intensity peaks are observed, which are probably reflections from the silver-based phase.

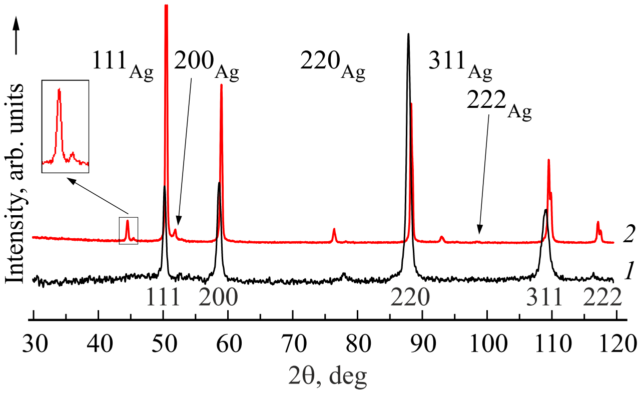

Figure 1. Diffraction patterns of alloy samples Cu-1.5Pd-3Ag: curve *1* — after deformation by 90%, *2* — after annealing of the initially deformed alloy at 450°C, 48 h, air cooling.

Annealing at 450°C for 48 h results in a decrease of the crystal lattice parameter of Cu-Pd matrix to 0.3622 nm (which is close to the value specified in Ref. [13] for the alloy Cu-3 at.% Pd: $a = 0.3626$ nm): the main peaks shift to the right, and in addition, reflections from new phases are observed (diffraction pattern *2* in Figure 1). It can be concluded that a supersaturated solid solution decomposes during annealing, resulting in the appearance of particles of the segregation phases in the matrix of the studied alloy. Lower intensity peaks from the silver-enriched FCC phase are also observed in addition to intense reflections from the matrix phase. In addition, a bifurcation of these peaks is observed (see the insert in Figure 1). This may indicate the formation of areas with varying degrees of silver enrichment during annealing. The lattice parameter of one segregation phase (for peaks on the left, with higher intensity) is 0.4080 nm, which is close to the lattice parameter of pure silver (0.4086 nm). The lattice parameter of the second phase (for peaks on the right, low intensity) is 0.4007 nm, which roughly corresponds to the composition of Ag-31 at.% Pd [14]. The assumption that particles of this composition can form is supported by the fact that the atomic masses and atomic radii of silver and palladium are close, so the lattice stresses in the Ag-Pd alloy are lower than in the Cu-Pd alloy; in addition, the ratio of the number of atoms of palladium and silver is 1 : 2 in the initial alloy, which roughly corresponds to the composition of Ag-31 at.% Pd compound.

Thus, it follows from the XRD data that two phases are separated in Cu-1.5Pd-3Ag alloy as a result of annealing, one of which consists of particles of almost pure silver, the second phase is a solid solution of Ag-Pd. The separation of a silver-based phase has been repeatedly observed previously in Cu-Pd-Ag alloys with a high content of palladium and silver. For example, the formation of Pd-Ag particles in an atomically ordered matrix Cu-Pd [15] was observed by field ion microscopy in Cu-50Pd-20Ag (at.%) alloy.

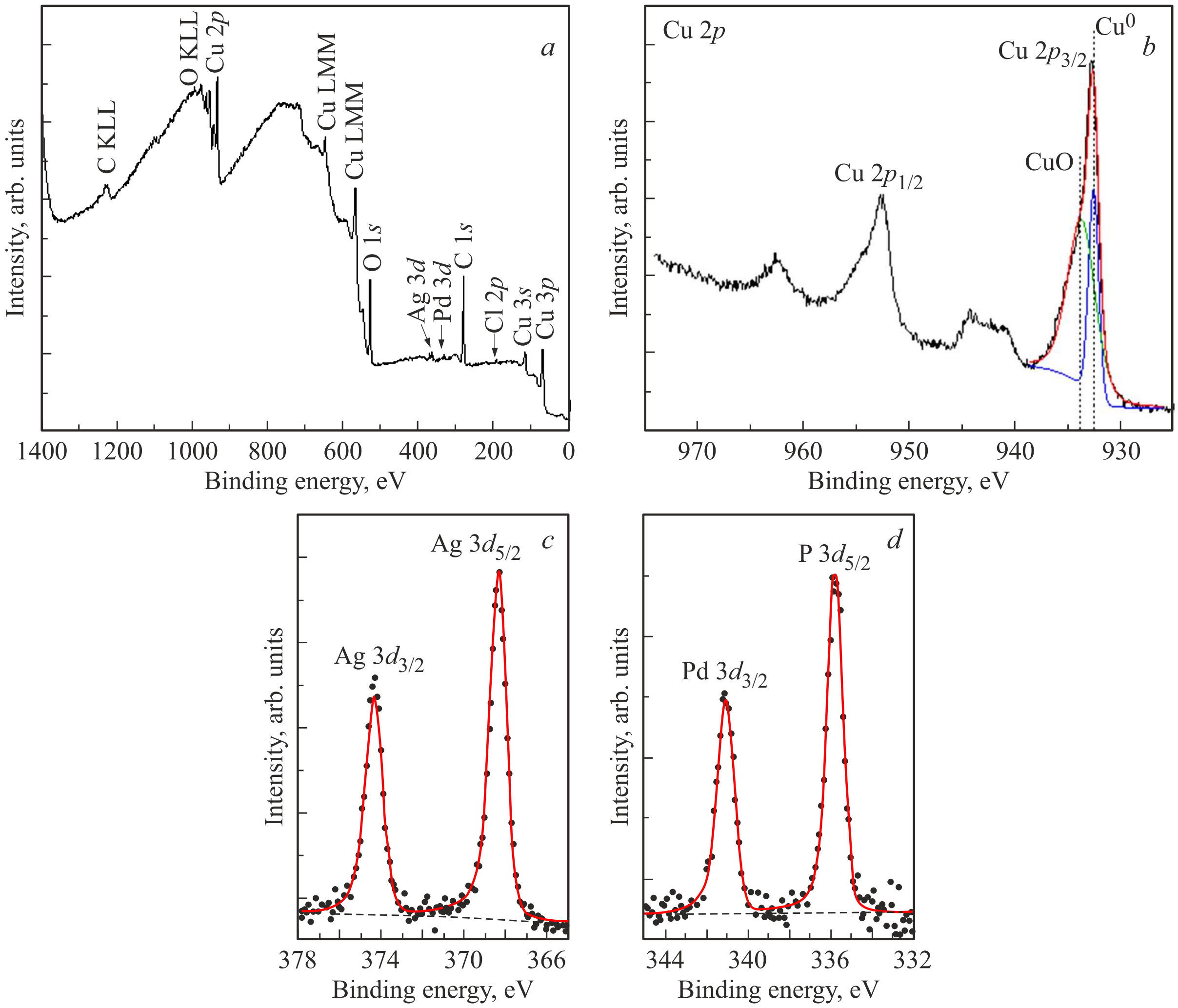

Figure 2. *a* — survey X-ray photoelectron spectrum of Cu-1.5Pd-3Ag sample; *b* — high-resolution X-ray photoelectron spectrum of Cu2p; high-resolution X-ray photoelectron spectrum of Ag3d (*c*) and Pd3d (*d*).

Table 1. Chemical composition of the surface of Cu-1.5Pd-3Ag (at.%) sample

C	O	Cu	Cl	Ag	Pd
58.6	26.8	12.7	1.1	0.5	0.3

It is necessary to clarify the sample surface state after prolonged exposure to atmospheric air to test the possibility of using the alloy under consideration as a material for creating corrosion-resistant conductors of weak electrical signals. For this purpose, studies were conducted using the XPS method. Figure 2, *a* shows the X-ray photoelectron spectrum of Cu-1.5Pd-3Ag alloy after annealing at 450°C. Table 1 shows the chemical composition of the sample surface determined from this spectrum.

The surface is naturally polluted with carbon and oxygen compounds adsorbed from the atmosphere. Traces of chlorine were also found, which probably appeared after washing the samples in chlorinated tap water. If the contribution of these adsorbed atoms is not taken into account, then only Cu, Ag, and Pd atoms are present in the chemical composition of the sample surface. Approximate chemical composition of the surface according to the XPS data, excluding the contribution of pollutants: 94 at.% Cu; 2.2 at.% Pd; 3.7 at.% Ag. The depth of the analysis is determined by the free path length of the photoelectrons and is about 10 nm. The discrepancy with the results of the SEM chemical analysis (see below) is explained by the greater depth of the secondary characteristic X-ray radiation output from the sample and, as a result, the larger area of analysis over which the chemical composition data is averaged. In addition, the natural heterogeneity of the distribution of chemical elements on the sample surface is also affected.

Figure 2, *b* shows the core spectrum (i. e., the spectrum in a narrow energy range of photoelectrons from the inner shell of a particular atom) of Cu2p, in which, a satellite structure is observed, characteristic of CuO compound in

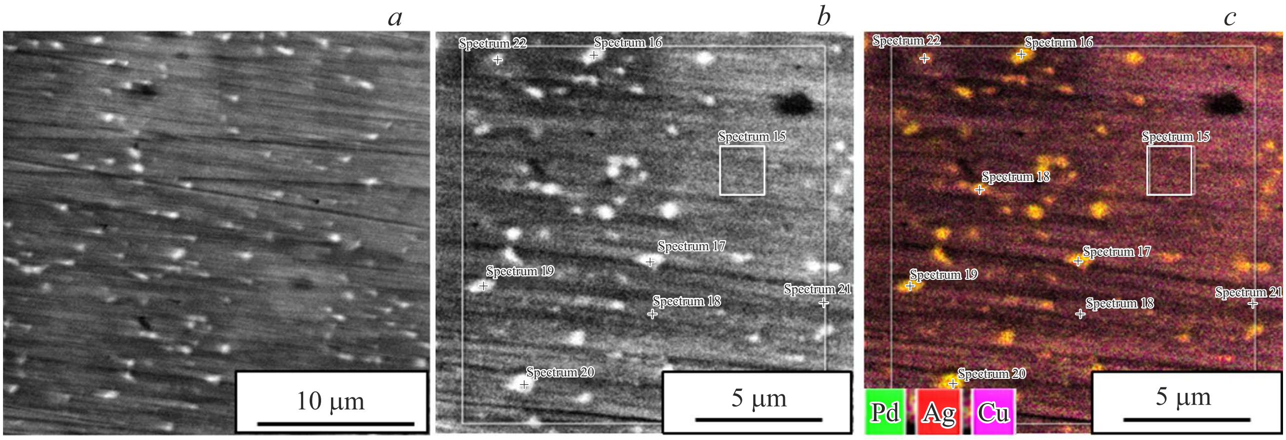

Figure 3. Microstructure of the alloy Cu-1.5Pd-3Ag after 90% deformation and subsequent annealing at a temperature of 450°C for 48 h with air cooling: *a* — typical type of microstructure, *b* the site from which the map (*c*) of the chemical element distribution was obtained.

addition to Cu2p$_{1/2}$ and Cu2p$_{3/2}$ doublet. The position of Cu2p$_{3/2}$ maximum at 932.9 eV does not coincide with the literature data [16]. However, two components can be identified at 932.6 and 933.7 eV in case of decomposition of Cu2p$_{3/2}$ peak in Figure 2, *b*, corresponding to Cu-Cu bonds in metallic copper and Cu-O in CuO compound.

A doublet with maxima of 368.35 and 374.35 eV and a half-height line width of 0.9 eV is observed in the Ag3d spectrum (Figure 2, *c*). Obviously, silver is also in the oxidized state in this sample (since narrower bands are observed in the spectrum of metallic Ag, and Ag3d$_{5/2}$ maximum is observed at 368.2 eV). A doublet with maxima at 335.8 and 341.0 eV and a half-height line width at 0.9 eV is observed in the Pd3d spectrum (Figure 2, *d*). Similarly, it is possible to conclude that palladium is also oxidized in this sample by comparing the experimental data with the spectrum of metallic Pd3d, in which Pd3d$_{5/2}$ maximum is observed at 335 eV.

So, it is shown that all metals — Cu, Pd, Ag — are in an oxidized state on the surface of the sample, there are bonds of „metal-oxygen" type. The thickness of this oxide film can be determined semi-quantitatively, based on the consideration that the depth of the XPS analysis is no more than 10 nm — this is the maximum depth of the photoelectronic output. But Cu-Cu metal bonds already occur in this layer, i. e. not all copper is oxidized. This indicates that oxygen penetrates to a depth of no more than 10 nm. No special measures were taken to protect the sample from oxidation, therefore, the oxide layer formed on the surface is dense enough to successfully prevent further oxygen penetration into the sample. At the same time, the small thickness of the film does not affect the functional properties, for example, electrical conductivity. Pd and Ag metal bonds were not detected in the spectra due to the very low content of these metals in the sample. In addition, almost all metal atoms on the surface are already contained by oxide compounds, which further reduces the number of metal bonds. The chemical composition of the alloy is close to the nominal one. No impurities were found in the composition, except for the natural contamination of the surface.

Table 2. Chemical composition according to SEM data in phase analysis mode

Structure	Cu, mass.%	Ag, mass.%	Pd, mass.%
Matrix 1	93.1	4.6	2.3
Matrix 2	93.5	4.2	2.3
Spot 1	45.2	53.9	0.9
Spot 2	54.8	44	1.2
From the whole image	92.4	5.2	2.4

Figure 3 shows a SEM image of the microstructure of the initially deformed alloy Cu-1.5Pd-3Ag after annealing at a temperature of 450°C for 48 h. Light spots are observed in a darker matrix. A similar microstructure was observed after the aging of Cu-6 mass.% Ag alloy [17]. The chemical composition of Cu-1.5Pd-3Ag alloy is provided in Table 2.

The spots represent a phase significantly enriched in silver. It is most likely that these are pure silver particles. The high copper content in them is explained by the electrons reflected from the Cu matrix hitting the detector. These particles have a rounded shape, and their sizes range from ~ 0.4 to $\sim 1\,\mu$m. The silver-based phase particles look „smeared", since the image was obtained after sample preparation by polishing on a diamond paste.

It can be concluded from a comparison of the results of chemical analysis by two different methods (XPS and SEM) that silver is not concentrated on the surface in the detected particles, but is present in the sample volume. Both methods give a close value of the amount of silver both in the near-surface layers (XPS, depth of analysis is ~ 10 nm) and in the sample volume (SEM, depth of analysis is $1-2\,\mu$m), and it is close to the nominal value. This indicates that there was no silver stratification, it is evenly distributed both on the

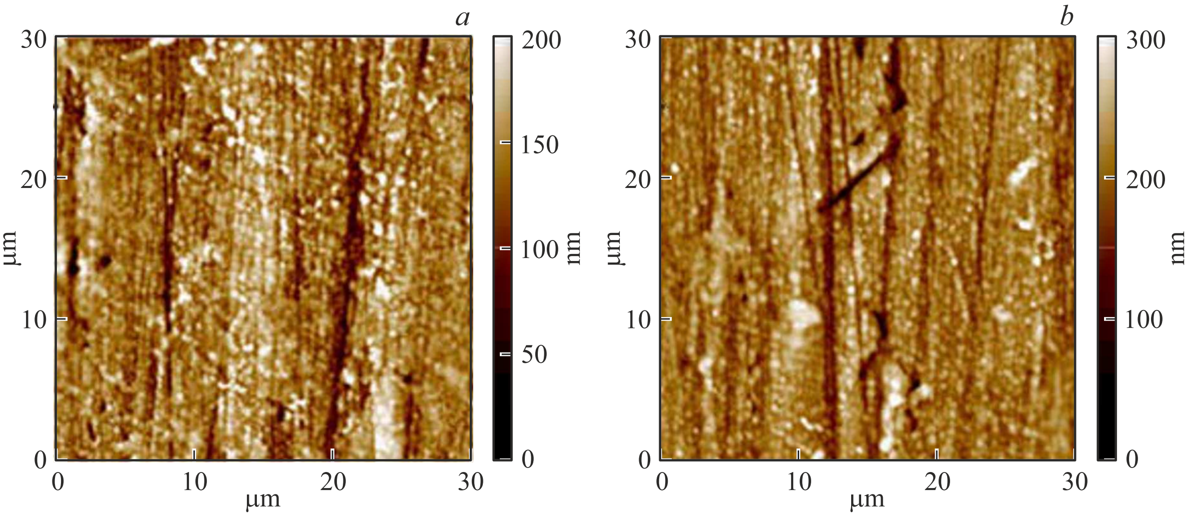

Figure 4. Examples of the surface topography of a sample of Cu-1.5Pd-3Ag alloy at various points *a* and *b*.

surface and in the volume of the alloy. Otherwise, the SEM would have shown a very small amount of silver in volume, whereas the XPS result would have significantly exceeded the nominal value.

Figure 4 shows the results of the AFM sample study after deformation and annealing (before polishing). Topographic images clearly show particles that rise 50–100 nm above the overall surface of the matrix (brighter, i.e. higher). Most of the particles have a rounded shape. The elongated or irregular shape of individual formations is apparently caused by the fusion of closely spaced particles. The transverse particle sizes are $\sim 1\,\mu$m.

Figure 5, *a* shows the profile of the surface section along a straight line intersecting such a formation. It can be seen that its height exceeds 200 nm. It is possible to estimate the shape of the cluster by redrawing the axes of the graph to the same scale (Figure 5, *b*). The particle's asymmetry is most likely related to the relief of the initial surface.

The assumption that the particles represent a silver-rich phase is supported by comparing the topographic image with a picture of the same surface area taken using the phase contrast method. The essence of this method is as follows. The probe of the microscope oscillates during scanning. When the probe needle interacts with the sample surface in a semi-contact mode during the oscillation process, it experiences not only repulsive, but also adhesive, capillary, and a number of other forces. The competitive action of these forces on the probe results in a shift not only in the frequency, but also in the phase of the oscillations relative to the exciting oscillations of the piezoelectric vibrator. If the surface of the sample is heterogeneous in its properties, even if it is perfectly flat topographically, a change of these forces will lead to a change of the phase shift. Then areas with different properties will be visible in the image using the phase contrast method, even if they do not differ in height and are not visible in the topographic image. The phase contrast is affected by changes of properties such as chemical composition, density, electrical conductivity, etc.

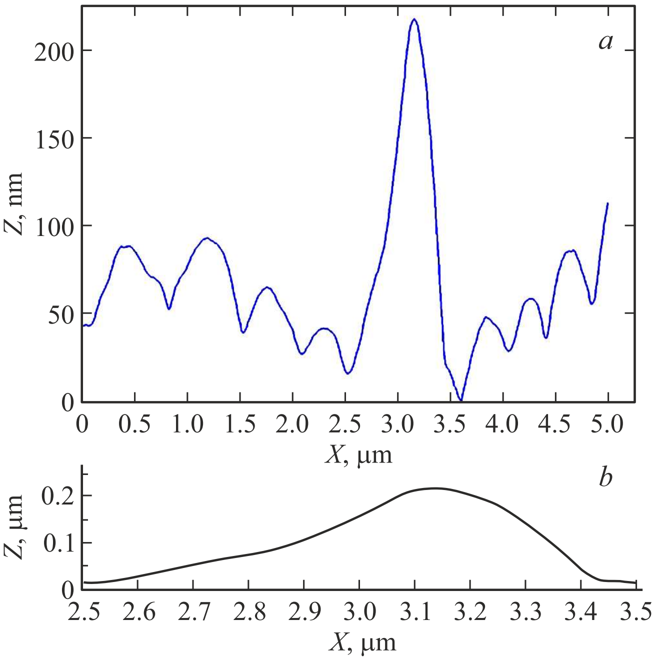

Figure 5. Example of *a* — a cross-section profile of a surface and *b* — a particle profile on an equal scale along axes.

The lightest spots in topographic images (Figure 6, *a*) usually correspond to dark spots (or groups of them) in phase contrast images (Figure 6, *b*). This confirms that „droplets" are particles with different properties than the surrounding matrix. The difference of chemical composition has already been verified by the SEM method. One of these different properties of the matrix and the particle should be electrical conductivity, which is checked by the scanning spreading resistance microscopy.

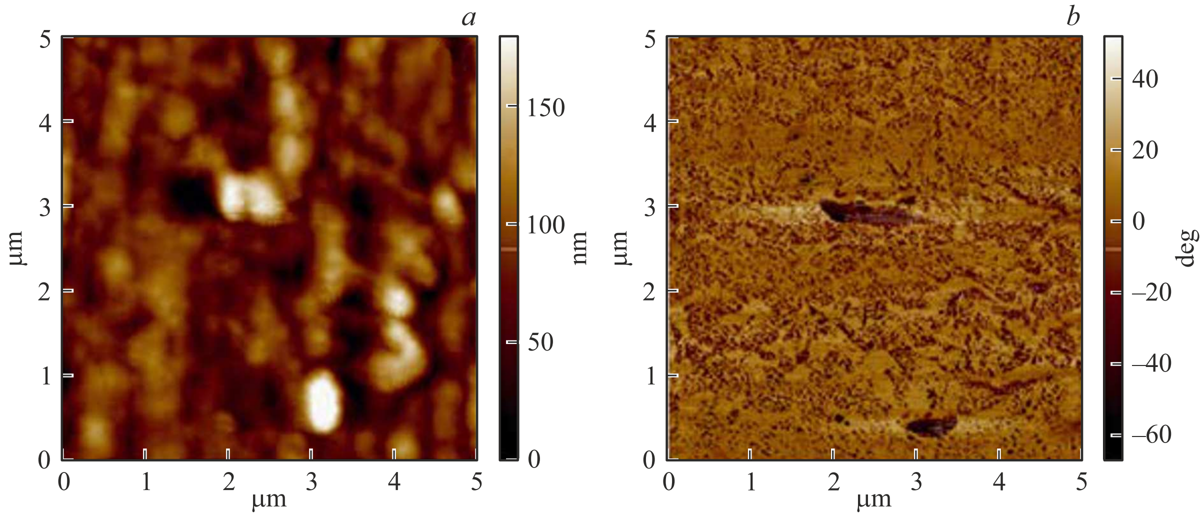

Figure 6. AFM sample analysis results: topography (*a*), phase contrast (*b*).

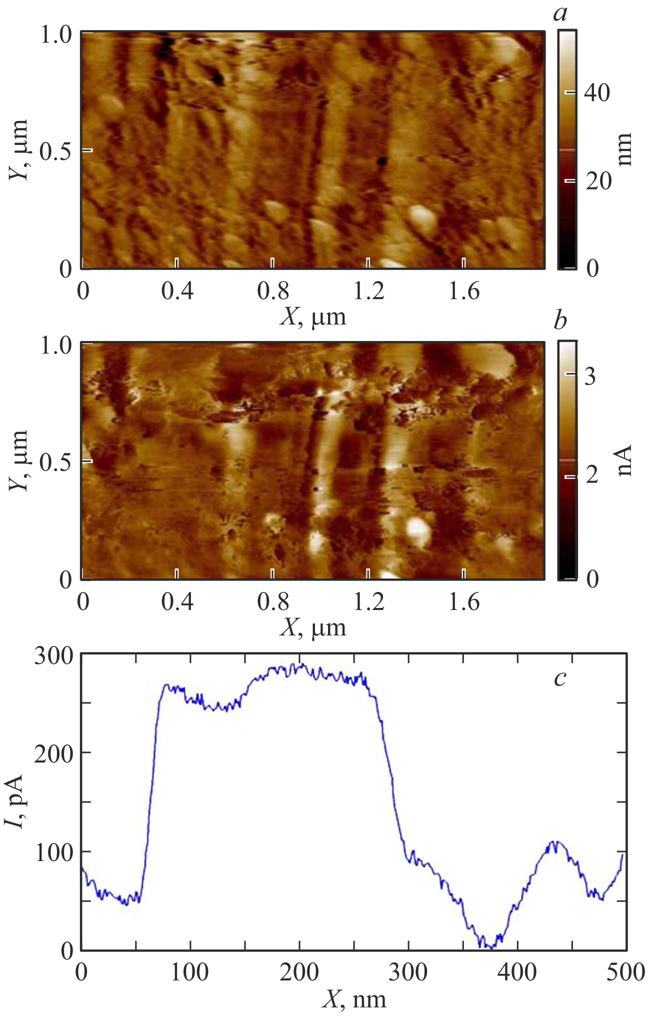

Figure 7. AFM sample scanning results after diamond paste polishing: *a* — topography, *b* — spreading current (applied voltage 8 V), *c* — cross-section profile of spreading current distribution over the sample surface.

Measurements by this method were also carried out on a sample pre-polished with diamond paste. The topographic images (Figure 7, *a*) show that the light droplets (silver particles) were „smeared" and stretched along the grooves formed during polishing. But they still have a higher height than the surrounding surface (on average by 20–30 nm). The spreading current map plotted for the same surface area (Figure 7, *b*) shows that these elongated formations have a higher conductivity (lighter) than the matrix. This also confirms that they are at least enriched with silver. Figure 7, *c* shows the cross-section profile of the spreading current map along a straight line intersecting a silver particle. It can be seen that the current curve in its area has a noticeable jump.

4. Conclusions

1. A matrix of almost pure copper is formed as a result of annealing in the initially deformed Cu-1.5Pd-3Ag alloy, in which particles of two phases based on silver are detected.

2. AFM and SEM experiments confirm the formation of silver-based phases on a surface on which particles with a high silver content are clearly identified.

3. The XPS results indicate the formation of a thin (no more than 10 nm) oxide film on the surface of the sample, which prevents oxygen from penetrating into the depth of the sample and can provide the alloy with high corrosion resistance.

4. It can be concluded taking into account the results of the study in Ref. [6] that varying of the duration of annealing of the initially deformed Cu-1.5Pd-3Ag alloy makes it possible to control the particle sizes of the silver-based separation phases and obtain the necessary strength values in combination with high electrical conductivity and corrosion resistance.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] O.E. Osintsev, V.N. Fedorov. Med' i mednye splavy. Otechestvennye i zarubezhnye marki: spravochnik. 2-e izd., pererab. i dop. Innovacionnoe mashinostroenie, M. (2016). 359 p. (in Russian).

[2] S. Gorsee, B. Ouvrard, M. Gouné, A. Poulon-Quintin. J. Alloys. Compounds **633**, 42 (2015).

[3] B. An, R. Niu, Y. Xin, W.L. Starch, Z. Xiang, Y. Su, R.E. Goddard, J. Lu, T.M. Siegrist, E. Wang, K. Han. J. Mater. Sci. Technol. **135**, 80 (2023).

[4] C. Iwamoto, N. Adachi, F. Watanabe, R. Koitabashi. Metallurg. Mater. Trans. A **49**, *10*, 4947 (2018).

[5] H. Xu, I. Qin, H. Clauberg, B. Chylak, V.L. Acoff. Acta Materialia **61**, *1*, 79 (2013).

[6] O.S. Novikova, Yu.A. Salamatov, A.E. Kostina, A.Yu. Volkov. Izvestiya. Non-Ferrous Metallurgy **30**, *4*, 66 (2024).

[7] I. Shakhova, Y. Sakai, A. Belyakov, R. Kaibyshev. Mater. Sci. Forum **667**, 493 (2011).

[8] L. Tang, W. Xie, X. Xiao, H. Chen, H. Wang, B. Yang. Mater. Res. Express **7**, *12*, 126517 (2020).

[9] H. Cho, B.S. Lee, J.H. Ha, H.H. Jo. Adv. Mater. Res. **47–50**, 1047 (2008).

[10] N.D. Tomashov, G.P. Chernova. Teoriya korrozii i korrozionnostojkie konstrukcionnye splavy. Metallurgiya, M. (1993). 413 p. (in Russian).

[11] I.V. Semenova, G.M. Florianovich, A.V. Khoroshilov. Korroziya i zashchita ot korrozii. Fizmatlit, M. (2002). 336 p. (in Russian).

[12] N.V. Andreeva, A.V. Filimonov, A.I. Rudskoi, G.S. Burkhanov, I.S. Tereshina, G.A. Politova, I.A. Pelevin. Phys. Solid State **58**, *9*, 1862 (2016).

[13] P.R. Subramanian, D.E. Laughlin. J. Phase Equilibria **12**, *2*, 231 (1991).

[14] I. Karakaya, W.T. Thompson. Bull. Alloy Phase Diagrams **9**, *3*, 237 (1988).

[15] N.N. Syutkin, V.A. Ivchenko, A.B. Telegin, A.Yu. Volkov. FMM **62**, *5*, 965 (1986). (in Russian).

[16] I.S. Zhidkov, A.I. Kukharenko, M.A. Milyaev, E.A. Kravtsov, M.V. Makarova, V.V. Gapontsev, S.V. Streltsov, S.O. Cholakh, E.Z. Kurmaev. Coatings **13**, 926 (2023).

[17] Z. Zhang, Y. Ru, T. Zuo, J. Xue, Y. Wu, Z. Gao, Y. Liu, L. Xiao. Mater. **16**, *10*, 3632 (2023).

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