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The Effect of Low Temperature Nonequilibrium Plasma on Copper and Chromium Electrodeposited Coatings

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Abstract: *The influence of the cold plasma on a copper coating was found to cause fragmentation of the initial crystallites, the change in the structure and aligning of the residual stresses in the coating and substrate. Clarifying of the chromium coatings, a decrease in microhardness by 1-1.5 GPa, the change in the structure, and an increase in wear resistance were observed.*

Keywords: *low temperature nonequilibrium air plasma, morphology, structure, wear*

In order to transform the structure and properties of materials pulse effects can be successfully used. It can be physico-thermal, magnetic, laser, or ultrasonic effects [1-4]. Of special interst are the studies of a low temperature plasma, which makes it possible to vary the properties of the materials at a large depth from the surface, excluding the thermal influence and at the same time enhancing durability of the treated articles [1, 5]. It has been found that the effect of the low temperature nonequilibrium air plasma on metal copper causes the change in the copper microstructure to 10 mm after contacts with plasma, the structure dispersiveness increases and microhardness becomes more uniform [6]. Under the above effect, steel 45 is found to initiate the formation of martensitic structure with a microhardness increase by 2.5-3 times, which can be attributed to a possible influence of high thermodynamic stresses on the surface perlite of the sample [5]. Analyzing the transformation of the structure of materials after being affected by plasma, it was assumed that the change in position of ions in the lattice, distrotion of its symmetry and the the change in the density of dislocations resulted from the plasma influence [7].

Taking into account that in the process of the electrolysis there exist limitations in the increase of physical and mechanical properties involved by the use of specific types of power sources, the electrolyte compositions and the modes of deposition, the application of the pulse methods of affecting the properties of coatings after their deposition is of high priority. This is supported by the studies of the magnetic pulsed treatment of electroplated coatings which showed that the structure and wear resistance of chromium coatings changed significantly [8].

1. Experimental Methods

The investigations were carried out using the copper coatings deposited from a sulfate electrolyte ($CuSO_4 \cdot 5H_2O$ - 200 g/l, H_2SO_4 - 50 g/l, t_{el} – 20°C, i_k – 0,2-0,4 kA/m^2), and chromium coatings from a standard solution (CrO_3 – 250 g/l, H_2SO_4 – 2,5 g/l, t_{el} – 55°C, i_k – 5,5 kA/m^2). A 60W 3-phase power source and an inductance-capacitance device (ICD) which included inductance (L) and capacitance (C) connected in parallel were used. The latter were connected in series to the galvanic circuit [9]. To develop the coatings with identical thickness which were produced at the current densities of 0.2 and 0.4 kA/m^2,the deposition time selected was 5 and 2.5 h, relatively. The cylindrical Steel 3 and copper samples (D – 20 mm, h – 10 mm), whose preliminarily polished flat surfaces were plated, were used for the experiments.

To produce the plasma effect, we used the experimental equipment based on a high frequency generator (f = 5,28MH$_z$), which made it possible to treat the samples with the nonequilibrium cold plasma with a capacitive discharge (NCEP) at low pressures (P ~ 1 Torr) energized in air medium (Fig. 1). The device was equipped by the apparatuses (6, 8. 9, 10) to control the operating modes: the current values I = 1.5 – 9 A, the discharge energy J = 0.4 - 3.5 kw, the high frequency voltage from inductor (5) of a VCI-62-5-1G-101 experimental facility (1) via tuning capacitor (7) and induction coil (5') was connected to the main electrode (3). The operating mode of VCER was set up by a VDG-1 pressure detector, a Rogowcki-type detector (8) and a C1-90 voltmeter (6). The samples were placed on the electrode that was connected to earth and cooled with flowing water. In aur experiments we used discharge energy 1 w/cm^2, the electrodes wear situated at the distance of 20 mm and the time of treatment of the samples after the preliminary examinations was 20 min.

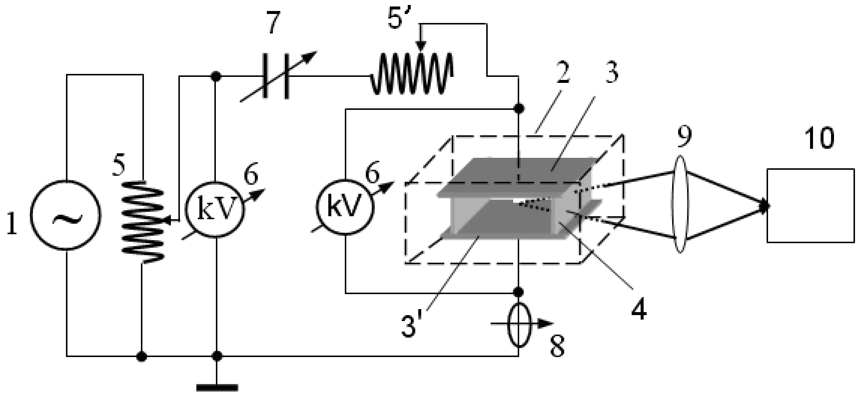


Fig1. *VCER experimental device: 1 – the generator: 2 – the discharge chamber; 3, 3' – the electrodes of high frequency and ground adapter receptacle; 4 – the quartz window; 5, 5' – the induction windings; 6 – the kilovoltmeter; 7 – the capacitor; 8 – Rogowski-type detector; 9 – the objective; 10 – the spectrometer.*

The spectral-energenic characteristics of plasma were checked using an SL100 (10) spectrometer which was equipped with a two-dimensional matrix with the sizes of 256x 256 pixels.

At the chosen modes, the limits of measuring errors of temperature at various distances from the electrodes does not differ and was $T_g = 300^oK$. Therefore, one may state that the samples placed on the bottom electrode were not exposed to heating.

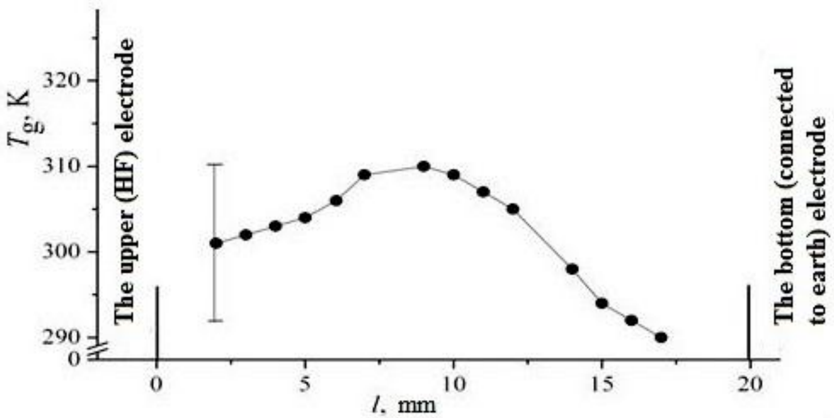


Fig2. *Distribution of temperature between the electrodes*

The morphology of the coatings was studied using the microscopes optica; NEOPHOT and MICRO200 with a video camera and a computer, and the electron TESLA and TESCAN. The X-ray analyses were carried out using a DRON-3 facility, according to the known methods [10]. The remaining stresses were calculated according to the following formula:

$$G = \frac{E}{\mu} ctg\theta\Delta Q ,$$

Where E is the modulus of elasticity, – μ is the Poisson constant (reference data),

θ is the maximal position of the etalon line, ΔQ is the shift of the maximal position of the sample line with respect to the maximal position of the etalon line.

During the calculations of the sizes of the blocks the line widening was taken into account. The microhardness of the coatings was evaluated using a PMT-3 apparatus.

The conditions of the tribological studies were chosen taking into account the recommendations of [11, 12]. The experiments were performed dry, using the experimental friction machine with a see-saw motion at a rate of 180 double strokes/min and a load of 2 kg. Temperature in the friction zone and the friction coefficient were registered using the computer. The coatings were deposited on the plate with a surface of 50 x 10 mm^2. The thickness of the coating after poloshing (R_z> 0,32μm) was 0,15 μm. The counterbody was made of cast iron (Sc 15-32) with the sizes of 1,5x 10 mm^2. The length of the travel distance of the sample was 40 mm. An analytical balance within the accuracy of 0.1 mg was used to determine the wear value.

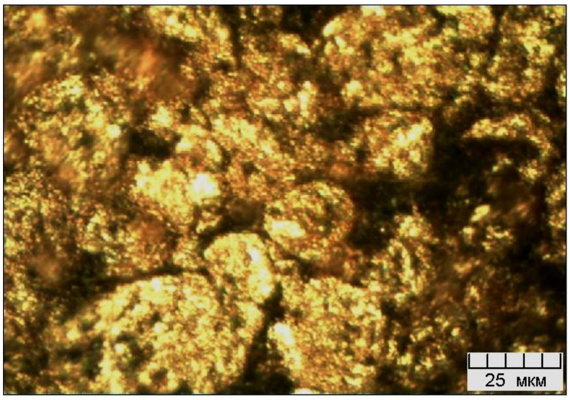
2. Results and Discussions

The conditions of deposition of copper coatings are listed in Table 1.

Table1. *The conditions of deposition of copper coatings*

№ of sample.	Current density i_kkA/m^2	Time of deposition, h	ICD	
			L, G_n	C, μ F
a	0,2	5	-	-
b	0,2	5	10	17600
c	0,2	5	2,5	17600
d	0,4	2,5	2,5	17600
e	0,4	2,5	-	-

Plasma treatment affects substantially the morphology of the sediments (Fig. 3): the coating surface is observed to becomes markedly smoother and its morphology more uniform after being treated using the ICD. With an increase in the current density (i_k = 0,4 кA/m^2), the coatings that were deposited without the ICD treatment are found to have fragmentation of the initial aggregates after being exposed to plasma (Fig. 3, samples a, e).



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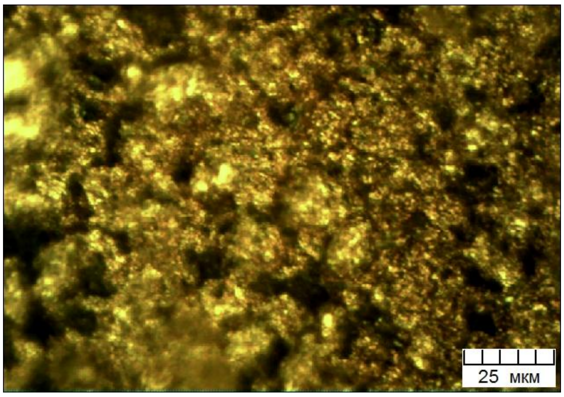

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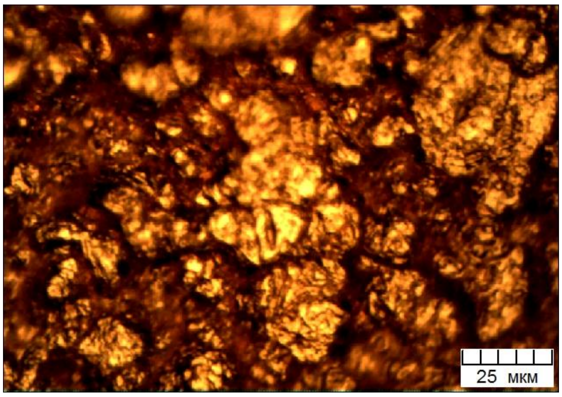

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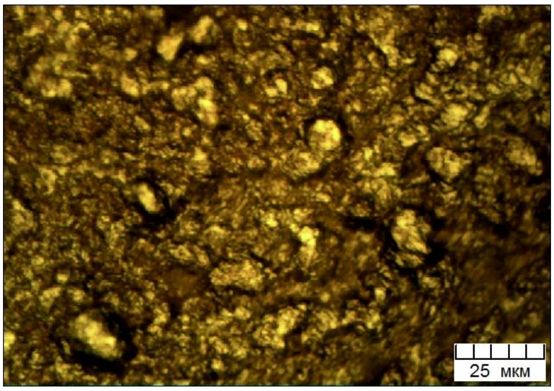

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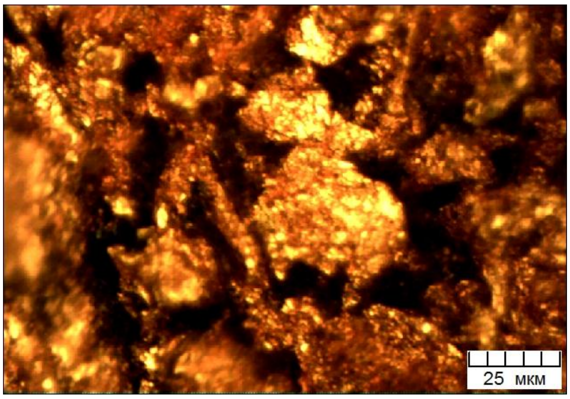

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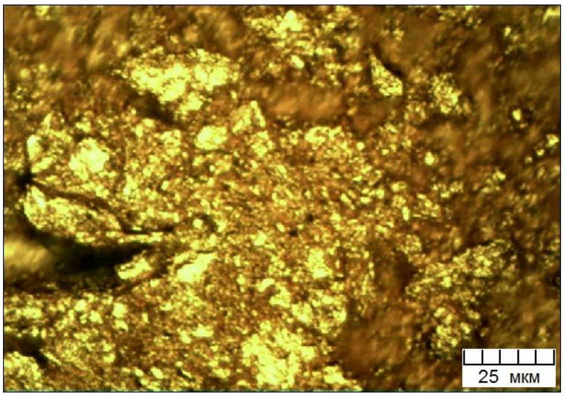

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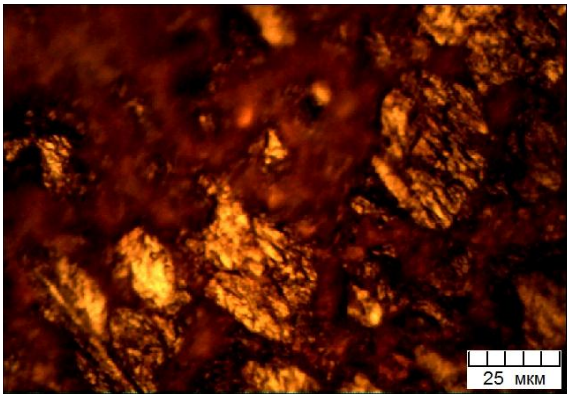

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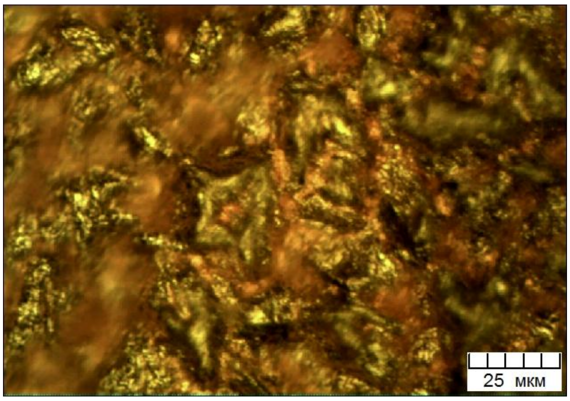

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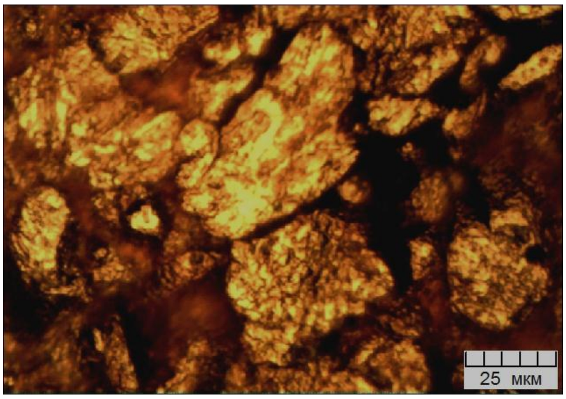

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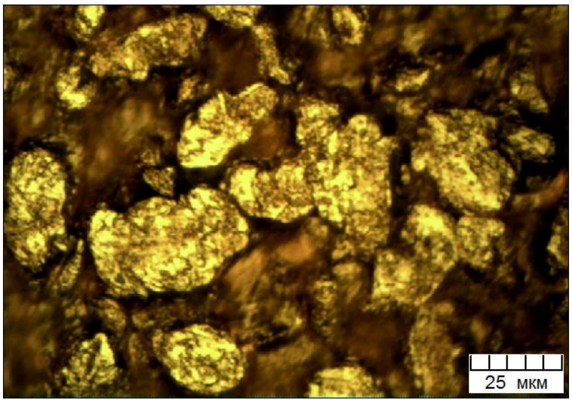


10

e

Fig3. *The morphology of copper coatings (Table 1): 1, 3, 5, 7, 9 – the initial morphology; 2, 4, 6, 8, 10 – the morphology after plasma effect.*

The X-ray analyses of the copper coating (sample a) showed (Table 2) that after plasma effect the intensity of all lines changed with regard to line (III) that was taken as 100%.

Table2. *Intensity of copper line and sizes of blocks*

State of the sample	(200), %	(220), %	(3II), %	$D{\cdot}10^{-6}$cm
Initial coating	34,9	297	23,5	7,64
After the treatment	37	216,9	26,5	10,9
Initial substrate	113,4	62,4	38,1	8,05
After the treatment	146	200	59,4	9,6
Table values	46	20	17	

Great changes in the substrate structure occur after the treatment, which can probably be attributed to its plastic deformation during the operation of rolling (Table 2).

The intensity of lines (200) and (311) of the initial coatings after and prior to the treatment differed insignificantly, whereas the intensity of line (220) both of the coating and of the substrate differed greatly.

The sizes of blocks in the coatings and substrate after the treatment will increase, but unlike the earlier results, they changed more in the coatings (Table 2).

The treatment of the samples affects the remaining stresses of the coatings, and in the substrate, they decrease and align with the stresses in the sediment (Fig. 4).

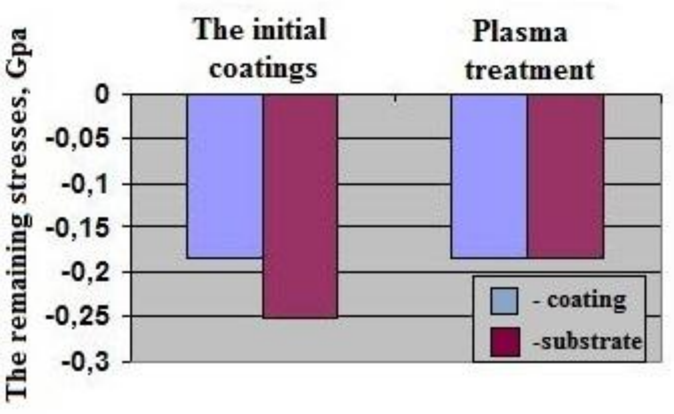
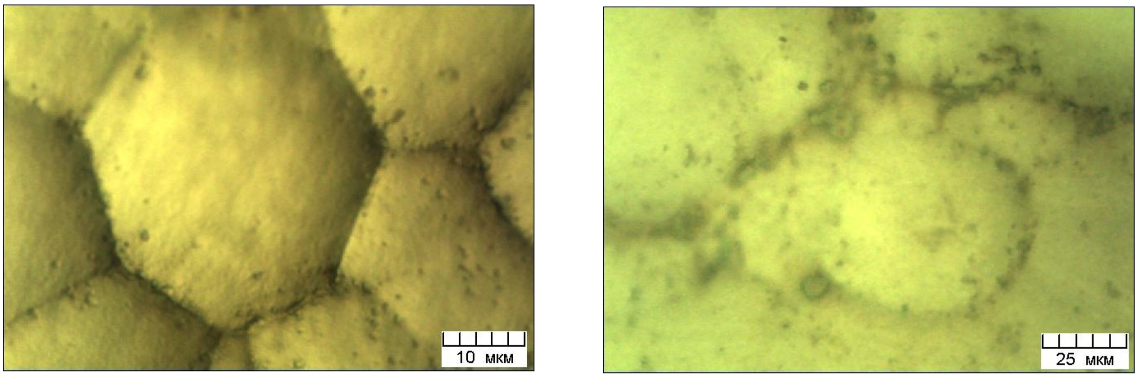


Fig4. *The change in the remaining stresses*

These changes in the remaining stresses after the treatment can affect positevily the cyclic strength of the coatings of the samples, since the coating initiates the plastic deformation of the substrate in the interfacial zone [13].



a b

Fig5. *The surface morphology of chromium coatings: a – initial, b – after the plasma treatment.*

The study of the surfaces of the coatings showed that after the deposition the chromium aggregates' form is bulging (Fig. 5a). After the plasma effect, the surface is smoothed and clarified; at the boundaries the impurity inclusions can be detected that were likely to be formed in the process of the deposition of the sediments (Fig. 5 b). In addition, the interfacial boundaries of the aggregates loose their distinct lines, they don't look like accurate polygons, more resembling grain structures of metal alloys.

Table3. *Intensity of lines in chromium coating*

State of sample	(200),%	(210),%	(211),%	(220),%	(310),%	(320),%
Initial				47	50	
After treatment		12		42	50	
Coating deposited using ICD:L = 6·3 Gn, C = 17600 μF	50			260	50	
After treatment			30	200	50	30
Table values	60	100	80	10	50	40

The X-ray studies of chromium coatings showed that the intensity of the lines (with respect to (310) that was taken as 50%) is esentially influenced by the conditions of the deposition of coatings, namely, in the coatings that were deposited being exposed to the ICD treatment, the intensity of line (220) differs significantly and, in addition, line (200) is revealed, which is absent in the standard coating (Table 3). The phase analysis showed the presence of β Cr in the coatings in small amounts, as well as possibly of amorphous films, which can affect the intensity of the lines of the coatings under study. These coatings differ too by the sizes of the lattice parameters, i.e., the lattice parameter of the initial coatings is 4.663 and after the ICD it is 4.654 Å.

After the effect of plasma, the X-ray patterns and intensity of the lines differed greatly: new line (210) appeared in the initial coatings and lines (210), (320) originated in the coatings that were deposited using the ICD, line (200) was absent, which obviously resulted from the microplastic deformations of the sediment, redistribution of the remaining stresses and structural imperfections (Table 3). The lattice parameters changed more in the coatings that were deposited with the use of the ICD (4,676 Å), than those in the initial ones (4,652 Å). The remaining stresses decreased in the initial sediments and increased in the coatings that were deposited using the ICD. Microhardness of the initial coatings was 10 GPa with the use of the ICD – 11.26 GPa, and after plasma effect it was 9 and 9.7, relatively. Taking into account that microhardness of the coatings after the plasma effect decreases by 1-1.5 GPa one can assume that as a result of the plasma effect the main changes in the structure of the coatings ensure the decrease in the coatings' brittleness.

The above chromium sediments were tested for wear also in the coatings from the standard electrolyte without the ICD with a magnetic pulse treatment using a VCI-62-5-1G-101 high frequency generator, which creates the electromagnetic field of high intensity at a frequency of 5.28 MHz. The process was performed in air medium [8].

The investigations showed that the plasma treatment of the samples in electromagnetic field ensures an degrease of wear by 3 and 1.7 times, correspondingly, compared to the untreated initial coatings (Fig. 6).

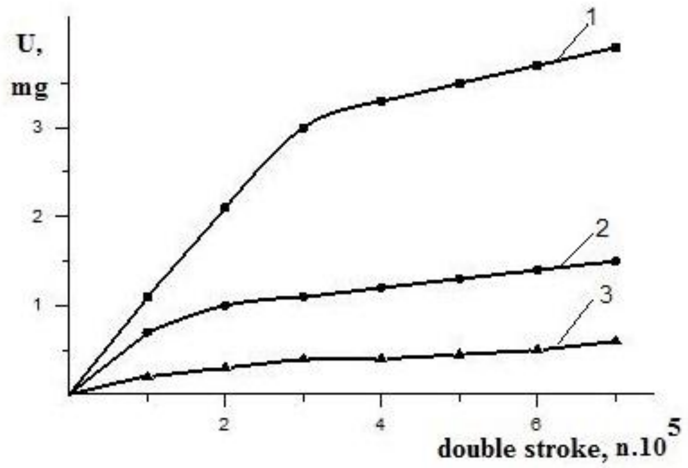
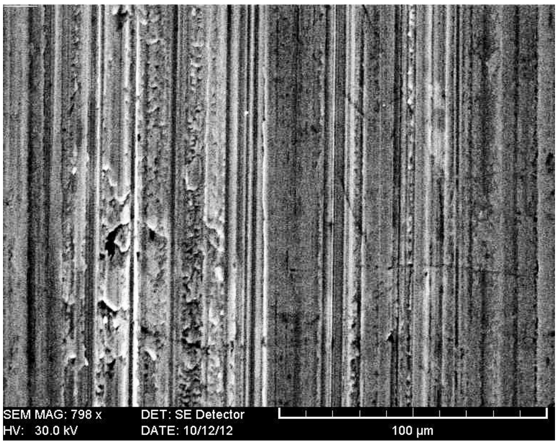


Fig6. *The wear of standard chromium coatings: 1 – before the treatment; 2 – and after the magnetic pulse effect; 3 – after the plasma effect*

The wear degree of the coatings that were deposited using the ICD after the plasma effect and in the magnetic pulse field does not differ from that of the treated initial coatings, which is obviously connected with a similar mechanism of structure formation in the process of the coating deposition and after the treatment, since the earlier studies of those coatings without the treatment showed that they wear by 2 times less in comparison to the initial ones [12]. The weight loss of the counterbody correlates with the coating degree of wear. The examination of friction surface showed that the defects accumilated on it cause its destruction (Fig. 7). On the friction surface of the standard coatings the cracks were found, which tear out the particles of the coating (Fig. 6a). The contact of the rest of the coatings was more plastic, which affected the aging process and the settled down wear of the sediments (Fig. 6).



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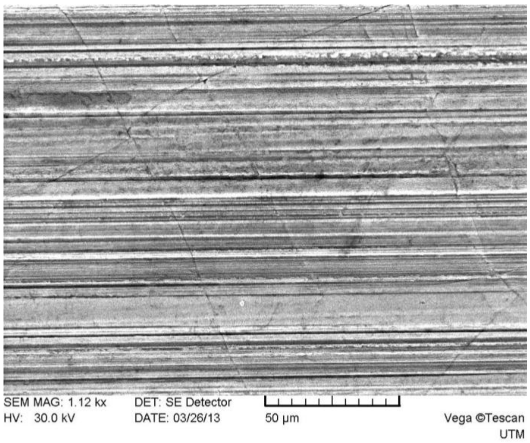

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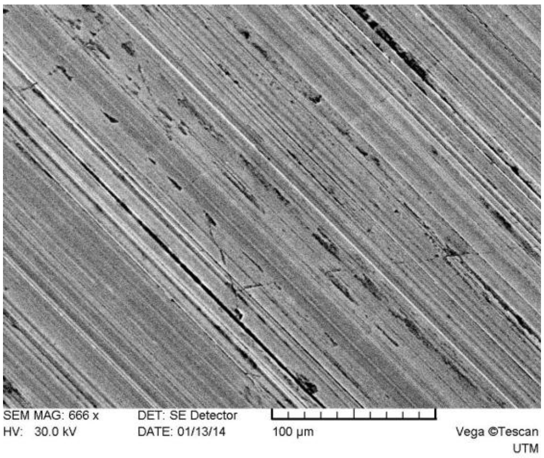

c

Fig7. *The worn-out surface of the standard chromium coatings: a – before the treatment; в – after the magnetic pulse effect; c – the same coatings after the plasma effect.*

Thus, the aforementioned studies showed that the treatment of the galvanic coatings using the low temperature plasma in air affect positively their structure and the properties.

3. CONCLUSIONS

As a result of the performed investigations it was found that the effect of the low temperature nonequilibrium air plasma changes the morphology of the surface of Cu galvanic coatings and decreases microhardness of Cr coatings by 1-1.5 GPa, aligning the remaining stresses of the coating and substrate. The treatment with plasma of Cr coatings increased their wear resistance compared to the initial coatings owning to the decrease in brittleness with the sediments. The degree of plasma effect on the properties of the coatings depends on the conditions of the deposition of sediments.

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