Electrodeposition of MWCNTs/silver composite coatings with enhanced mechanical characteristic

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Abstract. The paper describes the technology for producing silver electrochemical coatings containing multi-walled carbon nanotubes (MWCNTs). The MWCNT effect on the roughness, structure and tribological properties of silver coatings obtained with the addition of the nanotubes to an electrolyte in the low concentration range (0 to 80 mg/L). An increase in the microhardness and a decrease in the coefficient of friction were found for the modified coatings at the MWCNTs concentrations in the electrolyte of 40 and 60 mg/L, respectively.

1. Introduction
Silver has a low transition (contact) electrical resistance, high corrosion resistance, electrical and thermal conductivity, which ensures its wide application in coatings of movable contacts of electronic equipment. At the same time, silver is a soft metal and has great wear, which limits the resource of its functioning. Numerous methods for increasing wear resistance and reducing transition resistance based on the technologies of applying various kinds of coatings with a thickness of up to several micrometers, high microhardness, low friction coefficient and low surface roughness have been proposed. Among them, electroplating from electrolytes with the addition of carbon nanomaterials seems rather prospective [1-3]. The use of electrodeposition makes it possible to achieve homogeneous distribution and fix carbon nanomaterials in metal matrixes [4-6]. Nanocomposite-based electrochemical coatings possess high mechanical and technical characteristics, in particular, strength [7-12], hardness [7-9, 12], wear [13-16], and corrosion resistance [16, 17]. To obtain high mechanical and functional properties of nanocomposite coatings and considerably increase the cost of final products in large-scale manufacturing, carbon nanoparticle concentrations in electrolytes significantly higher than 0.1 g/L are used.

Considering the aforementioned, the main goal of the present work was to synthesize silver electroplating coatings with improved mechanical and operating characteristics based on an electrolyte, enriched with low concentrations of multi-walled carbon nanotubes (MWCNTs).
2. Materials and methods

2.1. Multi-walled carbon nanotubes (MWCNTs)
A Taunit carbon nanomaterial, representing MWCNTs with a diameter of 20-50 nm and a length of up to 10 µm, was used herein. The nanomaterial was synthesized by NanoTechCenter Ltd. (Tambov, Russia) through the method of catalytic pyrolysis of natural gas on a Ni/Mg catalyst at atmospheric pressure and a temperature of 620°C.

2.2. Electrochemical deposition of the coatings
The coating was applied to a copper billet with a pre-polished surface size of 2x2 cm. The preparation of blanks included: degreasing in an organic solvent and drying; assembling parts on copper hook and isolation; electrochemical degreasing at a cathode current density of 5 A/dm² and a temperature of 60°C for 2 min in an aqueous solution of the following composition: NaOH – 2%, NaHCO₃ – 4%, Na₃PO₄·12H₂O – 4%; rinsing under warm running water; rinsing in cold running water; chemically activating a 10% aqueous solution of H₂SO₄ at 25°C for 1 min; and, again, rinsing in cold running water.

Electrochemical silvering was carried out using a ready-for-use 07-SG electrolyte acquired from Ecomet (Moscow, Russia), which represents a colorless transparent aqueous solution with a density of 1.11±0.02 kg/m³ and includes a silver-containing compound. The pH value of this electrolyte was kept in the range of 8.6-10.0. The anode was made of platinum. The ratio of anode and cathode surfaces was 2:1. Electrochemical deposition of silver was carried out at a cathode current density of 0.2 A/dm² and a temperature of 55°C for 18 min. Under these conditions and deposition time, the estimated coating thickness was about 2-3 µm. The processing of the samples after applying the silver coating includes: capturing the electrolyte silvering in two baths; dismantling the hook; rinsing in cold running water; rinsing in hot running water; and drying.

The above described procedure additionally consisted in introducing the Taunit MWCNTs into the silver plating electrolyte at concentrations varying from 20 to 80 mg/L. The MWCNT-modified electrolyte was processed with an ultrasonic disperser at a frequency of 22 kHz, amplitude of 80 microns, and sound intensity of 786 W/cm² for 10 min. Ultrasonic treatment was performed immediately before the electrochemical deposition to minimize the aggregation of the nanotubes, increase their wettability, and achieve a uniform distribution in the electrolyte bulk. For each nanotubes concentration, a separate electrolyte was prepared, with which five coating samples (replicates) were obtained for all the studies presented in the work.

2.3. Characterization of the coatings
Morphology and microstructure of the silver coating surface, as well as single MWCNTs, was carried out using a Merlin scanning electron microscope (Carl Zeiss, Germany), and a JEM 2100F transmission electron microscope (JEOL, Japan).

To determine the crystalline size, internal strains and phase composition of the coatings, diffraction patterns were obtained using a D2 Phaser X-ray diffractometer (Bruker AXS, Germany). Diffraction patterns were recorded in the θ-2θ Bragg-Brentano reflection geometry within the angular range of 10-80 °2θ. The following crystallographic data were used for Ag when calculating peak positions and intensities: space group Fm-3m (225), and a = 4,085 Å. Values and errors for the data obtained for five samples at each MWCNT concentration were calculated using the Rietveld method.

An NT 9080 optical profilometer (Veeco, Город, USA) was used to study the surface topography of the samples. The roughness was measured in the central part of the samples in randomly selected three areas with a size of 460x615 µm. Each of them produced mapping of the surface and calculation of roughness parameter values – mean arithmetic deviation of profile Ra and the root mean square deviation of profile Rq.

Five coating samples were obtained for each MWCNT concentration in the electrolyte from the studied range to gather reliable information on the mechanical and tribological properties.
The tribological properties of the samples were studied by scratching (nanoindentation) of the surface layer using a G200 nanoindenter (MTS Nano Instruments, USA). Before mechanical testing, the coating surfaces were mechanically polished to reduce the influence of roughness on the accuracy of scratch width measurements. The scratch was applied to a Berkovich corner diamond indenter; its curvature radius is 20 nm, and a constant scratching speed was 10 mm/s.

The normal load on the indenter, $F_N = 15$ mN, was selected experimentally considering that the scratch depth is no more than 40% of the silver coating thickness. The scratch length $L$ was 500 µm. During the scratching, the tangential force $F_T$ was measured.

Similar to the conventional friction coefficient [18], the value $\mu$ was calculated based on $F_N$ and $F_T$:

$$\mu = \frac{F_T}{F_N}, \quad (1)$$

where, $\mu$ – friction coefficient, $F_T$ – tangential force (friction force), $F_N$ – normal load. The scratch cross-sectional area, multiplied by its length, is characteristic of volumetric and gravimetric wear (wear resistance).

If the scratch length was constant, then the scratch width was characteristic of wear resistance coatings, linearly depending on it. The scratch width was measured experimentally. The microhardness of the coating was calculated for pyramidal indenters according to the following equation:

$$H_s = \frac{4 F_N}{b^2}, \quad (2)$$

where, $H_s$ – microhardness, $F_N$ – normal load, $b$ – scratch width [18].

To study the tribological characteristics of friction and wear (determined by the scratch width), the nanomodified coating samples were additionally polished, since the parameter $R_q$ should to be less than 100 nm.

The porosity of the material affects its corrosion resistance and surface roughness and, accordingly, its wear resistance mainly during the second stage of wear (performance wear), which refers to the normal operation of the friction assembly and lasts for the longest time. The porosity was estimated based on the SEM images of the mechanically polished surfaces ($R_q < 100$ nm) of the silver coating samples. Only pores larger than 0.5 µm were considered.

3. Results and discussion

3.1. Morphology, roughness and structure of the nanomodified coatings

The SEM images of the coating samples obtained at different Taunit MWCNT concentrations ($C_{MWCNT}$) are presented in figure 1. A qualitative analysis of figures 1a, 1b and 1c shows a decrease in the roughness of the coatings when increasing the nanotubes concentration in the electrolyte from 0 to 40 %, which is quantitatively confirmed by the results presented in figure 2. The samples obtained at $C_{MWCNT} = 60$ mg/L (figure 1d) and $C_{MWCNT} = 80$ mg/L (figure 1e) have a more suitable morphology (close to the profile of the sliding surface) to ensure minimum wear during a long operational period.

The roughness effect on the wear resistance occurs due to the fact that the contact surfaces take place only at surface protrusions. The area of actual contact (especially, during the initial break-in period) is relatively small. On the contact pads, high local pressure may arise, under the influence of which elastic compression and plastic deformation take place. As a result, vertices of the irregularities of the contact areas are sheared off. Over the time, the height of the irregularities (roughness) decreases, the actual touch area increases, and the specific pressure on the contact pads decreases, thereby reducing the wear.
Figure 1. Surface morphology images of the coating samples obtained at different MWCNT concentrations: 0 (a), 20 (b), 40 (c), 60 (d), and 80 mg/L (e).

Figure 2 shows the dependence of the surface roughness on different MWCNT concentrations in the electrolyte. As can be seen, the error magnitude is large (10-20 %) and may be caused by the significant difference between the roughness values obtained for different samples with the same nanotube concentration. The Ra and Rq value scattering on different parts of the same sample was found to be considerably less and not to exceed 5 nm (figure 2).

Figure 2. Influence of MWCNT concentration in electrolyte on the surface roughness.

The surface studies of the samples showed that the addition of the nanotubes to the coating solution leads to a 15-20% decrease in the surface roughness (at 60 mg/L MWCNTs). The reduction of the surface roughness of the nanomodified coatings at > 60 mg/L MWCNTs indirectly confirms the uniform distribution of the nanotubes in the metallic matrix and leads to a decrease on wear and tear. The obtained result lies in good agreement with the experimental data presented elsewhere [11].
The dependence of the pore surface concentration $C_P$ on the MWCNT concentration is shown in figure 3. The presence of pores on the coating surface increases the surface roughness and reduces the corrosion resistance (figures 3a and 3b). The pores larger than 0.5 µm were not available in the coating samples obtained at $C_{MWCNT}$ of 40-80 mg/L. The addition of the MWCNTs at these concentrations to the electrolyte will contribute to an increase in the wear resistance and durability of the nanomodified coatings (figure 3c).

The results show that when introducing small nanotube into the electrolyte, there are no apparent changes in the crystalline size (figure 4). The relative deformation of the grains in all the coatings is small (hundredths of a percent) and virtually unchanged at varying MWCNT concentrations. Our experimental data differ significantly from the results of the works presented in [1,20], since in our case, the CNTs do not affect the crystallite size of the coating. This is probably due to the use of low CNTs concentrations in the electrolyte and the type of metal matrix.
In the paper [19], the authors describe the electrodeposition of nickel on the surface of MWCNTs. They demonstrate that with increasing current density the number of the nuclei of the crystal on the nanotube surface increases as a result of activation of larger number of surface defects, which could start the crystallization. Therefore, for large current density values (more than 0.5 A/dm²) nanotubes acted as additional crystallization sites, resulting in decreased grain sizes of the coating. This effect was also noted by the authors of the works [9,11,20]. In our case, probably, there was no change in the crystalline size and internal stresses for the reference (non-modified) and nanomodified coatings, since the electrodeposition was carried out at a low current density (0.2 A/dm²), which was not enough for activating the nanotubes.

3.2. Mechanical and tribological properties

The abrasion (wear) resistance (wear) and the transitional electric resistance of the moving contacts depend on many factors such as load, sliding speed, temperature, lubrication, media parameters, and properties of the rubbing materials. Under the conditions of our experiments, all the factors, except friction properties of the materials, remained unchanged, so their influence was neglected. The main characteristics and parameters affecting the wear resistance included surface roughness, microhardness, friction coefficient, and porosity.

It is known that the harder the friction material, the less the wear is [15]. Therefore, the microhardness is characteristic of coatings that indicates abrasion resistance. Due to constant shape of the indenter, and, consequently, the shape of the scratch profile, it was concluded that the scratches on various samples differ only by their width and depth, and the dependence of the scratch cross-sectional area is linear relative to its width. The scratch cross-sectional area, multiplied by its length, is characteristic of volumetric and mass wear (abrasion resistance).

Figure 5 demonstrates the dependences of the scratch width and microhardness/friction coefficient on the MWCNTs concentration in the electrolyte. The scratch width and amount of material removed from the friction surface decrease (figure 5a), which was confirmed experimentally and is consistent with the results obtained elsewhere [6,8,11-13,17]. This is the results of the fact that the lowest wear and the highest microhardness were reached in the samples obtained at $C_{\text{MWCNTS}} = 40$ mg/L, while the lowest friction coefficient value (0.46) was achieved at $C_{\text{MWCNTS}} = 60$ mg/L (figure 5b). Introducing the MWCNTs into the electrolyte hardens the coating and reduces its friction coefficient.
Figure 5. Effect of MWCNTs concentration in electrolyte on the scratch width (a) and microhardness and friction coefficient (b).

The microhardness $H_v$ of the modified coating is 40-50% higher than that of the reference coating (figure 5b). The analysis of electron microscopic images shows that the porosity of the modified and reference coatings is very different (figure 3). The additive contribution of the MWCNTs to the microhardness of the obtained coatings may be 25%, if the nanotube strength close to the theoretical value of $\sim 100$ GPa is assumed. However, due to their defects, the nanotubes used in the present work have strength well below 10 GPa. Accordingly, the additive contribution of the MWCNTs to the microhardness may not exceed 1...2%. The size of crystallites and internal stresses in the reference and nanomodified coating as well as in nanomodified coatings do not differ (figure 4). Consequently, the nanomodified coating is hardened due to the reduction in porosity.

4. Conclusion
The technology was developed to obtain silver electroplating coatings with improved quality indicators from the electrolyte with the addition of a nanomaterial. The differences from the conventional technology are as follows: 1) the MWCNTs were introduced into the electrolyte; 2) the electrolyte was treated using an ultrasonic disperser; 3) the MWCNT concentration in the electrolyte was kept within the specified limits. The technology made it possible to increase the wear resistance of the coatings. It was found that at the MWCNT concentrations of 40 and 60 mg/L, the best mechanical and tribological properties of the coatings and lower surface roughness were achieved. Thus, varying the concentration of MWCNT in electrolyte, one can selectively control the morphology, roughness and mechanical properties of nanomodified silver coatings.

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