Improved microhardness of chrome galvanic coatings with combining nanodiamonds and nanotubes

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Abstract. The method is developed for obtaining nanomodified galvanic coatings by adding a mixture of nanomaterials to the electrolyte. An experimental study of the microhardness of the precipitate of the technological process of obtaining nanomodified by a combination of nanodiamonds and multilayer carbon nanotubes; by a combination of single-layer carbon nanotubes and multilayer carbon nanotubes of chromium galvanic coating from a standard electrolyte was carried out. When nanodiamonds 12 g/l and multilayer carbon nanotubes "Taunit" 80 mg/l are added to the electrolyte, the microhardness of the chromium coating increases by 27% compared to the chromium coating obtained from the standard chromium plating electrolyte without additives. When single-layer carbon nanotubes 50 mg/l and multilayer carbon nanotubes "Taunit" 80 mg/l are added to the electrolyte, the microhardness of the chromium coating increases by 22% compared to the chromium coating obtained from the standard chromium plating electrolyte without additives. The service life of the parts, the chrome coating on which is obtained from the electrolyte with a mixture of nanodiamonds and multilayer carbon nanotubes "Taunit", single-layer carbon nanotubes and multilayer carbon nanotubes is significantly higher than when using a traditional chrome coating, as well as using multilayer carbon nanotubes, single-layer carbon nanotubes or nanodiamonds separately.

1. Introduction

Chrome galvanic coatings are used to give products special properties. Microhardness and, as a consequence, the wear resistance of the chrome coating are important characteristics in the case working of coated parts in friction mode [1]. Modern industry places ever higher demands on the quality of galvanic coatings. In this regard, the task of increasing the microhardness (an important qualitative indicator of galvanic coating) is relevant.

To increase the microhardness, various methods are used: changing the current modes; using additives in electrolytes. In recent years, due to the development of nano industry and a significant reduction in the cost of nanomaterials, have developed the methods of increasing microhardness is the use of nano-additives in chromium plating electrolytes. Good results were obtained using nanodiamonds [2-4] as an additive. Depending on the brand of nanodiamonds, the value of microhardness reached 1100 – 1300 kg/mm². Good results were obtained with multilayer carbon nanotubes (MCNT) [5] (microhardness by a concentration of 0.06 g/l exceeded 1100 kg/mm²) and single-layer carbon nanotubes (SCNT) [6] (microhardness by a concentration of 0.05 g/l exceeded 850 kg/mm²).
The effect of additives in electrolytes on the microhardness of galvanic coatings of nanodiamonds, SCNT and MCNT has different mechanisms. Due to the introduction of nanodiamonds in the crystal lattice of metals, a composite electrochemical coating is obtained, which has improved characteristics compared to the original metals. The presence in the coating of extremely developed in area and strong chemical bonds boundary layers "metal-diamond" provides not only wear resistance, but also increased microhardness [7]. The mechanism of influence of MCNT and SCNT on microhardness consists in emergence of the additional centers of crystallization on defects of carbon nanotubes. As a result, the size of crystals decreases [5]. Because of that, the microhardness increases.

In this regard, we suggest that the combined use of nanodiamonds and MCNT, SCNT and MCNT can give an effect that exceeds the sum of the effects of each additive.

The aim of the work is to study the effect of additives in the electrolyte in the form of a combination of nanodiamonds and MCNT, combination of SCNT and MCNT on the microhardness of the chromium coating.

2. Experimental part
The plan of experimental studies included the following stages.

a) application of chrome plating from a standard electrolyte without additives;

b) coating with additive nanodiamonds of different additive concentrations;

c) identification of the nanodiamonds concentration at which the highest microhardness of the chromium coating is observed;

d) coating with the addition of MCNT with different concentrations of the additive;

e) identification of the MCNT concentration at which the highest microhardness of the chromium coating is observed;

f) coating with nanodiamonds and MCNT with concentrations providing the maximum microhardness detected in stages (c) and (e).

g) coating with the addition of SCNT with different concentrations of the additive;

h) identification of the SCNT concentration at which the highest microhardness of the chromium coating is observed;

i) coating with SCNT and MCNT with concentrations providing the maximum microhardness detected in stages (e) and (h).

At each stage, at each concentration of the additive, a coating must be applied to at least 5 details.

2.1 Methods and materials
Getting a galvanic chrome coating was performed using the most common in industry of standard sulfate electrolyte chromium of the following composition: chromic anhydride CrO$_3$ 250 g/l; sulfuric acid H$_2$SO$_4$ 2.5 g/l.

The first nano-additive is an aqueous suspension of diamond charge containing 62 wt. %, and detonation nanodiamonds obtained by detonating charges TG 50/50 (alloy of TNT and hexogen). The contents of detonation nanodiamond in the diamond material is 71.0 wt. %. The suspensions were obtained by treatment of diamond charge in an aqueous medium using a cavitation disintegrator. Before the introduction of the suspension into the electrolyte was treated with ultrasound on the installation of IL 100-6 / 4, frequency 22 kHz, sound intensity 786 W/cm$^2$; processing time - 30 min.

The concentration of nanodiamonds in the electrolyte varied from 4 g/l to 16 g/l.

The second nano-additive is fullerene-like multilayer carbon nanotubes (MCNT) - a nanocarbon material registered under the brand name "Taunit" [8]. It is a long hollow fiber consisting of graphene layers (no more than 30), 10-60 nm in diameter, up to 1 μm in length. For the distribution of MCNT "Taunit" in the volume of the electrolyte and to obtain a stable colloidal solution, the technology of soluble effervescent tablets was used [9]. MCNT "Taunit" was mixed with the following components: surface – active agent, soda and citric acid, and then pressed into tablets. Pressing force of 10 tons. Pressure 32 kg/mm$^2$. 


Tablets with MCNT "Taunit" were added to the electrolyte. Division of agglomerates of nanotubes was carried out by the action of carbon dioxide released during dissolution of soda. The state of a highly dispersed metastable colloid was achieved by using a surfactant.

The concentration of MCNT "Taunit" in the electrolyte varied from 10 to 125 mg/l.

Square plates made of St3 steel with an area of 0.1 dm² (30x30 mm) were used as the cathode. Only the side facing the anode was covered; the reverse side was insulated. As an anode, a plate with a size of 30x30 mm of the following composition was used: 10% tin and 90% lead. Anode-cathode area ratio 1:1.

When applying the chrome coating, the electrolyte temperature was automatically maintained at 55°C.

Change in time of cathode electric current density $i_k$ is shown in figure 1.

The microhardness of the Hµ coating was measured using the PMT-3M device. Microhardometer PMT-3M is designed to measure the microhardness of materials by pressing into the test material of the diamond tip of Vickers with a square base of a four-sided pyramid, which provides geometric and mechanical similarity of the prints as the indenter deepens under load. The measurement of the diagonals of the prints produced by a photoelectric ocular micrometer FOM-1-16 with the automatic processing of the measurement results. Measurement error 2%.

On each sample, the microhardness was measured at 5 points, in which the prints were symmetrical, after which the result was averaged. Then averaging of all samples of each experiment was carried out.

![Figure 1](image-url)  
Figure 1. The change in cathode current density in the chrome plating process.

3. Results and discussion

The results of the studies dependence determine the microhardness of chromium coating with the addition of nanodiamonds are presented in figure 2.

The highest value of the microhardness of the chromium coating was obtained at a concentration of nanodiamonds 12 g/l. The result is in good agreement with the previously published experimental data [4,10]. In these studies, the maximum microhardness is also achieved at a concentration of 12 g/l nanodiamonds.

The results of the studies dependence determine the microhardness of chromium coating with the addition of MCNT are presented figure 3.

The highest value of the microhardness of the chromium coating was obtained at a concentration of MCNT 80 mg/l. The result is in good agreement with the previously published experimental data [5]. In this work also the maximum microhardness is achieved at a concentration of MCNT 60-80 mg/l.
Figure 2. Dependence determine the microhardness of chromium coating with the addition of nanodiamonds.

Figure 3. Dependence determine the microhardness of chromium coating with the addition of MCNT.

The analysis of the experimental results shows that the highest value of the microhardness of the chromium coating was obtained at a concentration of nanodiamonds 12 g/l and at a concentration of MCNT 80 mg/l. The next series of experiments was carried out with the addition of a mixture of
nanodiamonds (with a concentration of 12 g/l) and MCNT (with a concentration of 80 mg/l). The results are summarized in Table 1.

**Table 1.** Results of experiments to determine the microhardness of chromium coating with various additives.

| No | Additives                          | Microhardness, kg/mm² | Microhardness (relative significance), % |
|----|-----------------------------------|------------------------|------------------------------------------|
| 1  | 0                                  | 853                    | 100                                      |
| 2  | Nanodiamonds, 12 g/l              | 1050                   | 123                                      |
| 3  | MCNT "Taunit" 80 mg/l             | 1024                   | 120                                      |
| 4  | Mixture nanodiamonds (12 g/l)     | 1084                   | 127                                      |
|    | + MCNT "Taunit" (80 mg/l)         |                        |                                          |

When adding a mixture of nanodiamonds 12 g/l and MCNT "Taunit" 80 mg/l, the microhardness of the chrome coating increases to 1084 kg/mm² (compared with the chrome coating obtained from the standard electrolyte chromium plating without additives, the increase in microhardness is 27%). Thus, the addition of a mixture of nanodiamonds and MCNT allow to obtain a microhardness value exceeding on 4-7% the values of this qualitative indicator when using nanodiamonds and MCNT separately [1,5].

The results of the studies dependence determine the microhardness of chromium coating with the addition of SCNT are presented in figure 4.

The highest value of the microhardness of the chromium coating was obtained at a concentration of SCNT 50 mg/l. The result is in good agreement with the previously published experimental data [6]. In this work, the maximum microhardness is also achieved at a concentration of SCNT 50 mg/l.

The analysis of the experimental results shows that the highest value of the microhardness of the chromium coating was obtained at a concentration of SCNT 50 mg/l and at a concentration of MCNT 80 mg/l. The next series of experiments was carried out with the addition of a mixture of SCNT (with a concentration of 50 mg/l) and MCNT (with a concentration of 80 mg/l). The results are summarized in Table 2.

When adding a mixture of SCNT 50 mg/l and MCNT "Taunit" 80 mg/l, the microhardness of the chrome coating increases to 1043 kg/mm² (compared with the chrome coating obtained from the standard electrolyte chromium plating without additives, the increase in microhardness is 22%). Thus, the addition of a mixture of SCNT and MCNT allow to obtain a microhardness value exceeding on 2 – 20% the values of this qualitative indicator when using SCNT and MCNT separately [5,6].

![Figure 4. Dependence determine the microhardness of chromium coating with the addition of SCNT.](image-url)
Table 2. Results of experiments to determine the microhardness of chromium coating with various additives.

| No | Additives                              | Microhardness, kg/mm² | Microhardness (relative significance), % |
|----|---------------------------------------|-----------------------|------------------------------------------|
| 1  | 0                                     | 853                   | 100                                      |
| 2  | SCNT, 50 mg/l                         | 858                   | 100.6                                    |
| 3  | MCNT "Taunit" 80 mg/l                 | 1024                  | 120                                      |
| 4  | Mixture SCNT (50 mg/ l) + MCNT "Taunit" (80 mg/l) | 1043 | 122                                      |

4. Conclusion
As a result of the study, the tendency is revealed to increase the microhardness of the chrome coating by adding a mixture of carbon nanomaterials (nanodiamonds, single- and multi-layer nanotubes) to the electrolyte. The applied significance of the developed technologies for machine-building enterprises is as follows. If products with nanomodified chrome coating are the final products of the enterprise, they have a competitive advantage over similar products due to increased wear resistance. If products with nanomodified chrome coating are used in technological processes within the enterprise, production costs are reduced. So, at enterprise «TPZ-Tool», Tula, due to increase in wear resistance of the tool covered with the nanomodified chrome covering, the number of the tool decreased by 20% a year. The developed technologies are becoming more relevant as the cost of carbon nanomaterials produced in the Russian Federation decreases.

The increase in the microhardness of the chromium coating is caused by a combination of two mechanisms: the introduction of nanodiamonds into the crystal lattice of the coating metal and the appearance of additional crystallization centers on defects in carbon nanotubes.

The operation life of the obtained parts is significantly higher than when using a traditional chrome coating, as well as when using multilayer carbon nanotubes, simple-layer carbon nanotubes or nanodiamonds separately.

The obtained value of the microhardness of the chromium galvanic coating exceeds this figure obtained by known technologies.

The developed method opens up prospects for the joint use of various nano-additives in galvanic electrolytes to improve the quality of coatings.

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