

The Effect of Combinations of Carbon Nanomaterials on the Microhardness of the Chromium Galvanic Coating

M. Nasraoui^{1*}, Yu.V. Litovka¹, V.Yu. Dolmatov²

¹ Tambov State Technical University, 106 Sovetskaya, Tambov, 392000, Russia;

² "Tekhnolog" Special Design Engineering Bureau (Federal State Unitary Enterprise) 33-a, Sovetsky prospect, Ust-Slavyanka, St. Petersburg, 192076, Russia

*Corresponding author. Tel: +7 926 674 90 56. E-mail: nasraoui.mariem@gmail.com

Abstract

A method to increase the microhardness of the chromium galvanic coating by adding a mixture of carbon nanomaterials (nanodiamonds, single-walled and multi-walled nanotubes, graphene oxide) into a standard chromium galvanic coating electrolyte was proposed. The increase in the microhardness of the chromium galvanic coating was revealed and explained. This is due to 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 method of obtaining parts with a higher service life when using traditional chromium galvanic coating, as well as when using multi-walled carbon nanotubes, single-walled carbon nanotubes, nanodiamonds, and graphene oxide separately, was demonstrated. The best result was obtained using a mixture of nanodiamonds and multi-walled carbon nanotubes. The microhardness of the nanomodified chromium galvanic coating was measured, and it was found to increase by 27 %.

Keywords

Chromium galvanic coating; microhardness; multi-walled carbon nanotubes; nanodiamonds; single-walled carbon nanotubes; graphene oxide.

© M. Nasraoui, Yu.V. Litovka, V. Yu. Dolmatov, 2020

Introduction

Carbon nanotubes (CNTs), nanodiamonds and graphene oxide belong to the family of carbon nanomaterials. They have attracted much attention in science, technology and industry due to their unusual physical, chemical, optical, mechanical and thermal properties – high strength, good electrical and thermal conductivity, high elastic deformation values, chemical and thermal stability.

Chromium galvanic coatings are widely used in mechanical engineering to impart protective, decorative and special properties to parts. Among the special properties stands out the wear resistance associated to the high hardness of chromium. If the hardness of steel St20 is 167 kg/mm², then the microhardness of a traditional chromium galvanic coating is 750–900 kg/mm². The application of a hard chromium coating with a thickness of 30–100 microns on the surface of a black steel part allows to increase its service life during friction operation by 2 to 3 times.

In such an increasingly competitive environment, machine-building enterprises are striving to improve the quality of their products. The demands on the wear resistance of chromium-plated parts are increasing, especially for parts operating in extreme conditions (for example, piston rings of automobile engines). Accordingly, new technologies are being developed, and existing technologies are being improved.

One of the directions of increasing the microhardness of chromium coatings is the use of various additives in electrolytes. Recently, positive results have been obtained by adding nanoadditives to electrolytes – oxides, carbides, nitrides, carbon nanomaterials. At the same time, from the point of view of economic indicators, it is preferable to use carbon nanomaterials, since their productions are affordable and their prices are decreasing; TAUNIT multi-walled carbon nanotubes (MWCNTs) (NanoTechCenter LLC, Tambov, Russia), TUBALL single-walled carbon nanotubes (SWCNTs) (OCSiAl LLC, Novosibirsk, Russia), nanodiamonds (SKTB Technolog FSUE,

St. Petersburg, Russia), graphene oxide (GO) (NanoTechCenter LLC), and others.

The study aims to investigate ways of increasing the microhardness of chromium galvanic coatings by electrochemical deposition from a standard electrolyte containing combinations of carbon nanomaterials (single- and multi-walled carbon nanotubes, nanodiamonds and graphene oxide).

Methods and Materials

The experiments were carried out using a laboratory installation for obtaining a chromium coating, including a galvanic bath with a volume of 1.5 liters; bath temperature stabilization system; rectifier Flex Kraft.

The experimental research plan included the following stages.

a) applying a chromium plating from a standard electrolyte without additives;

b) applying a coating with carbon nanoadditives (separately nanodiamonds, single- and multi-walled carbon nanotubes, graphene oxide) with various concentrations of every additive;

c) identifying the concentration of nanoadditives at which the highest microhardness of the chromiumgalvanic coating were observed;

d) applying a coating with combinations of nano-additives, with concentrations of nano-additives providing the maximum microhardness identified in step (c).

The first nanoadditive is an aqueous suspension of a diamond charge containing 62 wt. %, as well as detonation nanodiamonds (Fig. 1) obtained by detonating charges TG 50/50 (an alloy of TNT and RDX). The suspension is prepared by processing a diamond batch in an aqueous medium using a cavitation disintegrator.

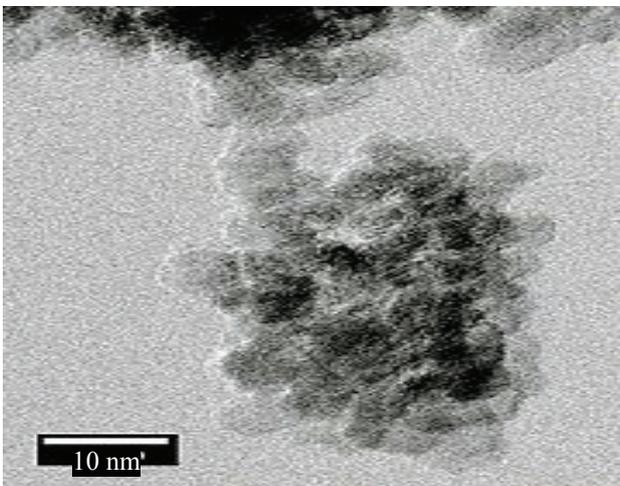


Fig. 1. Detonation nanodiamond

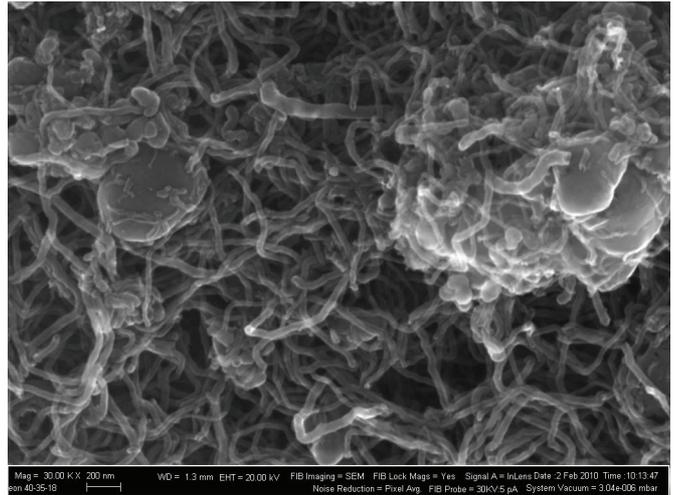


Fig. 2. TAUNIT multi-walled carbon nanotubes (MWCNTs)

Before being introduced into the electrolyte, the suspension was treated with ultrasound on an IL 100-6/4 device, frequency 22 kHz, sound intensity 786 W/cm^2 , processing time – 30 min.

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

The second nanoadditive was presented by MWCNTs, a nanocarbon material registered under the TAUNIT trademark [1]. They represent long hollow fibers, consisting of graphene layers (no more than 30), 10–60 nm in diameter, up to 1 μm long (Fig. 2).

To distribute TAUNIT MWCNTs in the volume of electrolyte and to obtain a stable colloidal solution, the technology of using soluble effervescent tablets was used [2]. The MWCNTs were mixed with the following components: surfactant (surfactant) – polyvinylpyrrolidone, NaHCO_3 (sodium bicarbonate) and citric acid, after which it was pressed into tablets with a pressure of 32 kg/mm^2 .

The MWCNTs-based tablets were added to the electrolyte. The dispersion of agglomerates of nanotubes was carried out by the action of carbon dioxide released during the dissolution of sodium bicarbonate. The state of a highly dispersed metastable colloid was achieved through the use of a surfactant.

The concentration of the TAUNIT MWCNTs in the electrolyte was varied from 10 to 125 mg/l.

The third nanoadditive was presented by SWCNTs registered under the TUBALL trademark. They are extremely thin graphene fibers rolled into a cylinder; diameter 1.6 nm; length over 5 μm (Fig. 3). The distribution of the SWCNTs in the electrolyte was carried out using effervescent soluble tablets, similar to the process for the MWCNTs.

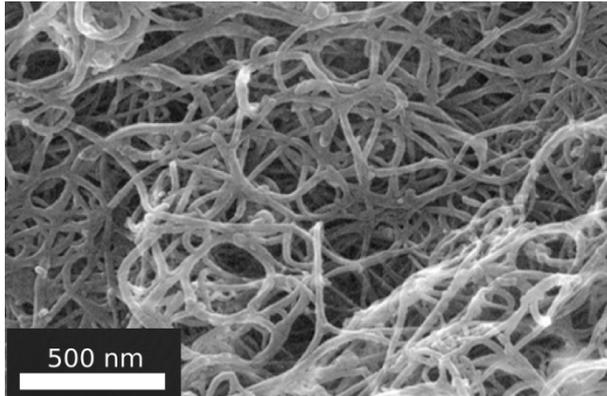


Fig. 3. MWCNT “Taunit”

The SWCNT concentration in the electrolyte was varied from 10 to 90 mg/l.

The *fourth nanoadditive* was graphene oxide produced by NanoTechCenter LLC (Fig. 4). The technology for producing graphene oxide is based on the improved Hammer-Offeman’s method, which consists in the oxidation of natural graphite with potassium permanganate in concentrated sulfuric acid and diluting the reaction mixture with water. After that, the reaction mixture is treated with a second oxidizing agent (hydrogen peroxide) and the obtained carbon-containing oxidation product is washed with an acid solution, then with water [3]. After washing from acids and manganese salts, the product is an aqueous dispersion with a dry matter (graphene oxide) concentration of 1 %. NanoTechCenter LLC produces two types of graphene oxide – standard graphene oxide and deep oxidation graphene oxide. Deep oxidized graphene oxide is characterized by a smaller lateral size of flakes (on the order of 1–5 microns) and improved colloidal stability in aqueous solutions. We used deep oxidized graphene oxide.

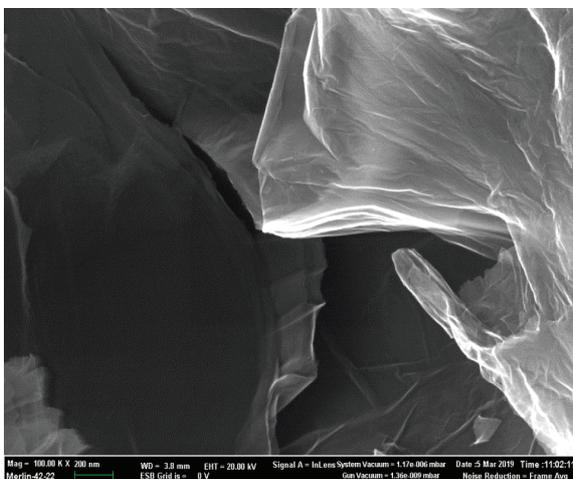


Fig. 4. Graphene oxide

Before being introduced into the working electrolyte, an aqueous dispersion of deep oxidized graphene oxide was sonicated to reduce particle aggregation. The processing was carried out on an IL 100-6 / 4 setup, with the frequency of 22 kHz, sound intensity of 786 W/cm^2 , and processing time – 3 min.

The concentration of graphene oxide in the electrolyte was varied from 7 to 52 mg/l.

Obtaining a chromium galvanic coating was carried out using the standard sulfate chromium galvanic coating electrolyte, which is most widespread in the industry, of the following composition: chromic anhydride CrO_3 – 250 g/l and sulfuric acid H_2SO_4 – 2.5 g/l.

In our study, we used square plates made of St3 steel with an area of 0.1 dm^2 ($30 \times 30 \text{ mm}$) as a cathode. The side facing the anode was covered, while the reverse side was isolated. A lead plate of the composition – 10 % tin and 90 % lead – was used as the anode. The anode-cathode area ratio was 1 : 1.

When applying chromium galvanic, the electrolyte temperature was automatically maintained at $55 \text{ }^\circ\text{C}$.

The current mode of variation of the cathode current density i_k with time τ is shown in Fig. 5.

The microhardness H_μ of the obtained coating was measured using a PMT-3M device. The PMT-3M microhardness tester is designed to measure the microhardness of materials by indenting a Vickers diamond tip with a square base of a tetrahedral pyramid into the material being tested, which provides geometric and mechanical similarity of indentations as the indenter deepens under load. The measurement of the diagonals of the prints is carried out using a photoelectric eyepiece micrometer FOM-1-16 with automatic processing of the measurement results. The measurement error was 2 %.

On each sample, the microhardness was measured at 5 points, at which the imprints were obtained symmetric, after which the result was averaged. Further, the averaging was carried out over all samples of each experiment.

To identify the presence of nanoadditives in chromium galvanic coating, the following technique was used. The sample was broken mechanically and electronic images of the fracture were taken on an NT MDT Integra Spectra atomic force microscope.

Experimental results and discussion

The *first series of experiments* was devoted to studying the effect of each additive separately [7]. The research results are shown in Figs. 6 – 9.

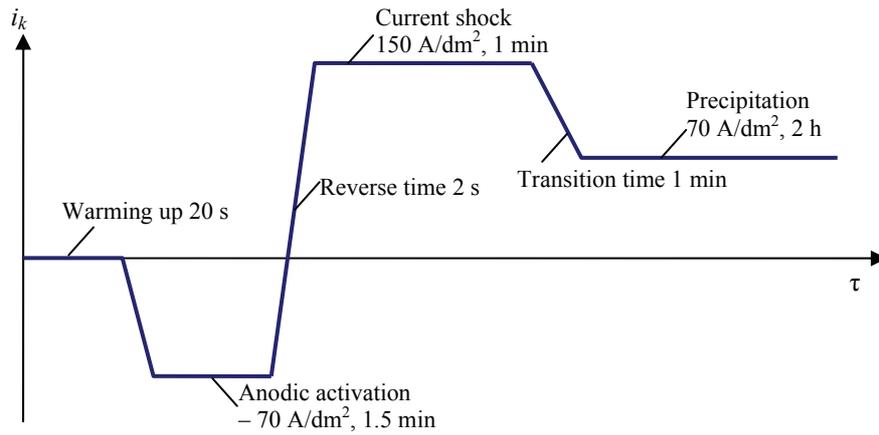


Fig. 5. Change in current density during chromium galvanic coating

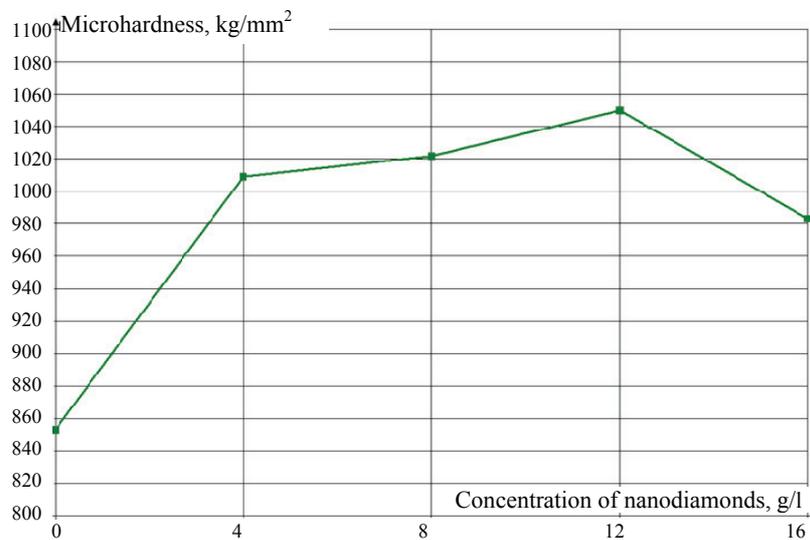


Fig. 6. Dependence of the microhardness of the chromium coating on the concentration of nanodiamonds

The highest value of the microhardness of the chromium coating was obtained at a nanodiamond concentration of 12 g/l.

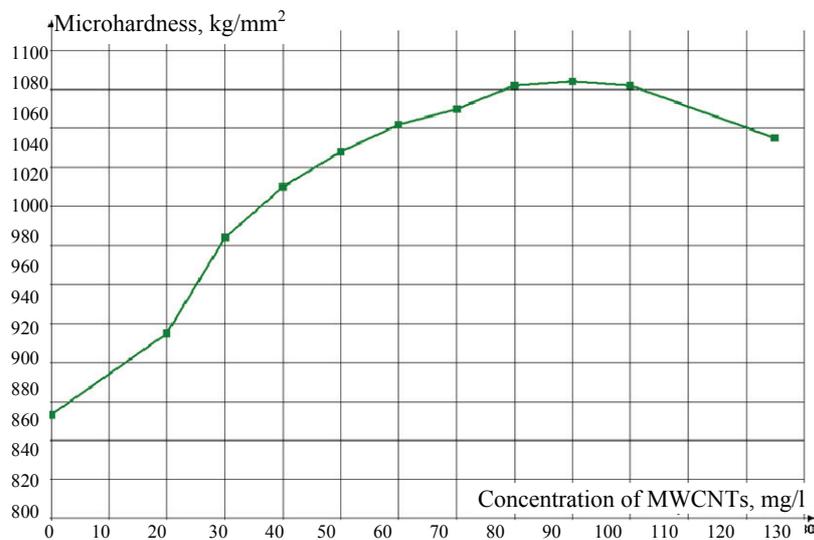


Fig. 7. Dependence of the microhardness of the chromium coating on the concentration of MWCNTs

The highest value of the microhardness of the chromium coating was obtained at a MWCNT concentration of 80 mg/l.

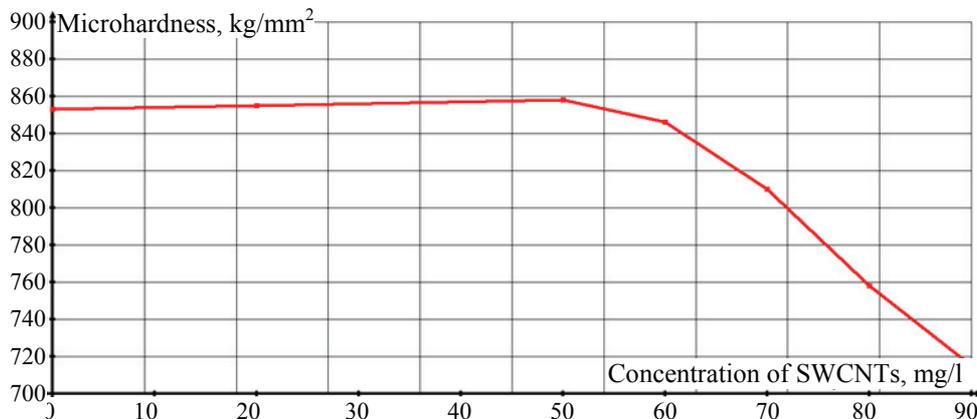


Fig. 8. Dependence of the microhardness of the chromium coating on the SWCNT concentration

The highest value of the microhardness of the chromium coating was obtained at a SWCNT concentration of 50 mg/l [4].

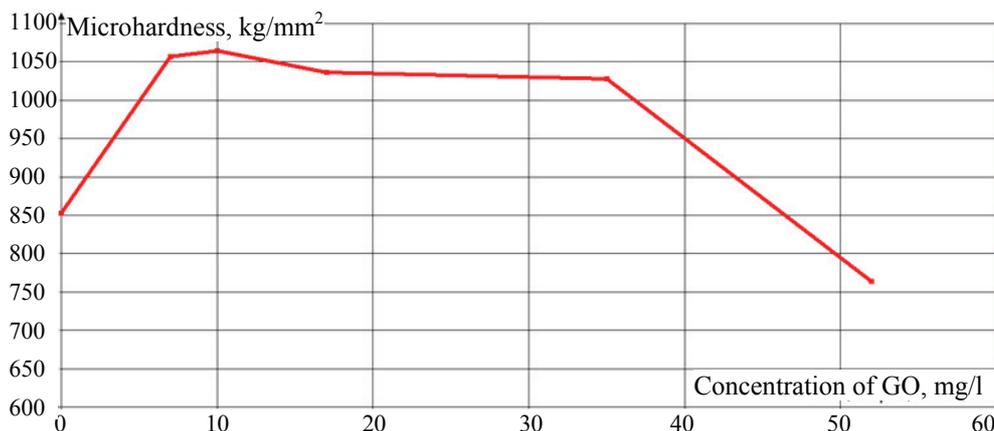


Fig. 9. Dependence of the microhardness of the chromium coating on the concentration of graphene oxide

The highest value of the microhardness of the chromium coating was obtained at a graphene oxide concentration of 10 mg/l [5].

The second series of experiments was carried out with the addition of mixtures of carbon nanomaterials, with values of concentrations of nano-additives used are those in which the highest microhardness in the first series of experiments was obtained.

Adding a mixture of nanodiamonds (12 g/l) and TAUNIT MWCNTs (80 mg/l) to the chromium galvanic electrolyte. The microhardness of the chromium coating increased to 1084 kg/mm². The increase in microhardness is 27 % compared to a chromium galvanic coating obtained from a standard chromium coating electrolyte without additives. Fig. 10 shows an example of microindentation [6, 7].

Adding a mixture of TUBALL SWCNTs (50 mg/l) and TAUNIT MWCNTs (80 mg/l) to the chromium

galvanic coating electrolyte. The microhardness of the chromium galvanic coating increased to 1043 kg/mm² (compared to the chromium galvanic coating obtained from a standard chromium galvanic coating electrolyte without additives, the increase in microhardness is 22 %).

Adding a mixture of graphene oxide (10 mg/l) and TAUNIT MWCNTs (80 mg/l) to the chromium galvanic coating electrolyte. The microhardness of the chromium galvanic coating increased to 1068 kg/mm². The increase in microhardness is 25 % compared to the chromium galvanic coating obtained from a standard chromium galvanic coating electrolyte without additives.

Adding of a mixture of graphene oxide (10 mg/l), TAUNIT MWCNTs (80 mg/l) and nanodiamonds (12 g/l) to the chromium galvanic coating electrolyte.

The microhardness of the chromium coating increased to 1063 kg/mm². The increase in microhardness is 24 % compared to the chromium galvanic coating obtained from a standard chromium galvanic coating electrolyte without additives.

Fig. 11 shows a comparison of the results of experiments of determining the microhardness of the chromium galvanic coating modified with various nanoadditives [7].

Experiments on obtaining chromium galvanic coatings from an electrolyte with various carbon nanomaterials have shown an improvement in the microhardness of the coating.

The analysis of the experimental results showed that the highest value of the microhardness of the chromium galvanic coating when using combinations of nanomaterials is 1084 kg/mm². This value was obtained using a mixture of nanodiamonds at a concentration of 12 g/l and TAUNIT MWCNTs at a concentration of 80 mg/l. Compared to a chromium galvanic coating obtained from a standard chromium plating electrolyte without additives, the increase in microhardness is 27 %.

The experimentally revealed phenomenon of an increase in the microhardness of a chromium galvanic coating when using an electrolyte with additives of carbon nanomaterials required an explanation of the mechanism of this phenomenon. It was suggested that carbon nanomaterials, getting into the coating during its deposition, change their properties. The basis for this

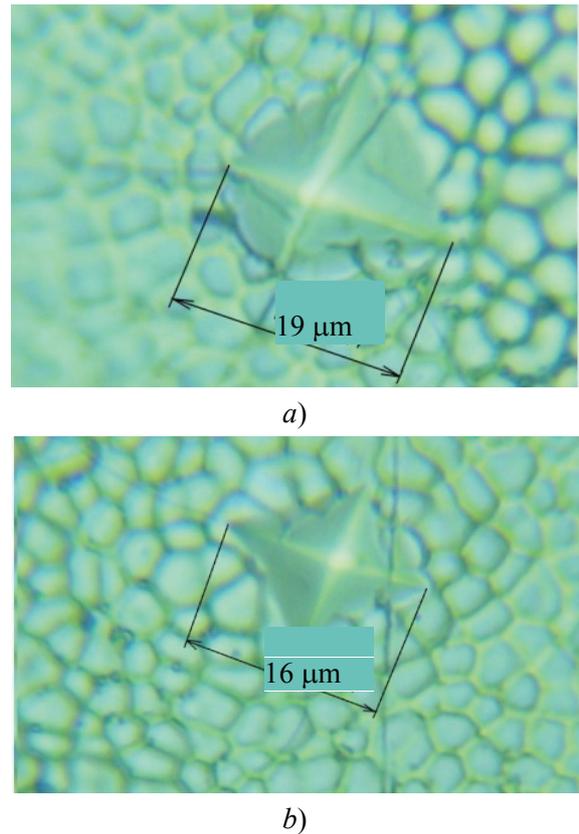


Fig. 10. Examples of microindentation.
Chromium galvanic coating:

a – no additives; *b* – with a mixture of nanodiamonds (12 g/l) and TAUNIT MWCNTs (80 mg/l)

assumption was the data on the change in the properties of nanomodified chromium galvanic coatings when carbon nanomaterials are incorporated into them.

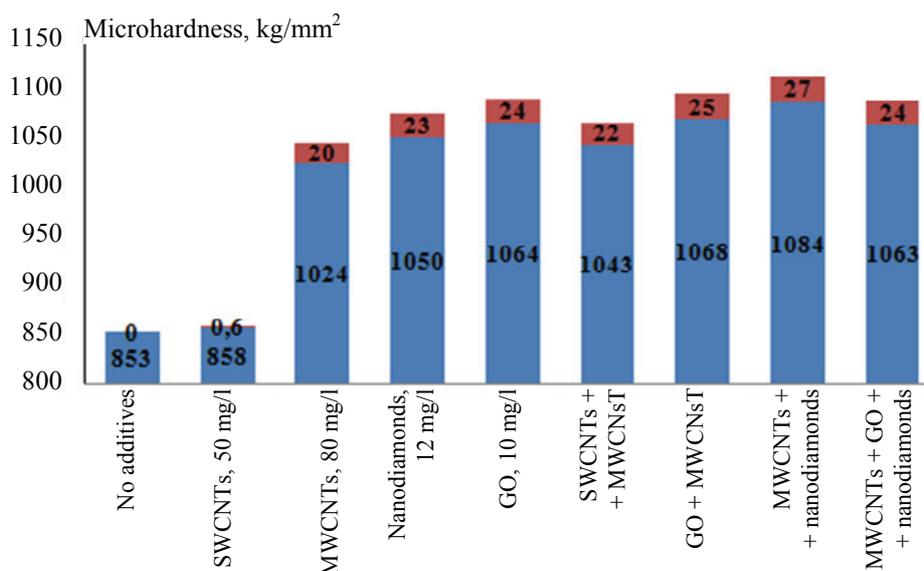


Fig. 11. Dependence of the microhardness of the chromium galvanic coating on various nanoadditives in the electrolyte
(Nano-additives: ■ – microhardness of the chromium galvanic coating; ■ – relative increasing value, %)

Ultradispersed detonation synthesis diamonds with an average size of 4–6 nm and possessing unique properties are a material for filling and hardening a metal matrix in composite electrochemical coatings. Dispersed particles included in the coating represent microbarriers in the path of microcracks, defects and dislocations in the coatings, leading to the strengthening of the material. Electroplated chromium-diamond coatings have increased the microhardness. The presence in the coating of extremely developed in area and strong chemical bonds of boundary layers “metal-diamond” provides not only wear resistance, but also increased their microhardness.

The mechanism of the effect of multi-walled carbon nanotubes, single-walled carbon nanotubes, and graphene oxide on the microhardness is the appearance of additional crystallization centers on defects in carbon nanoadditives. As a result, the size of the crystals decreases. Because of this, the microhardness increases [7].

Figs. 12 and 13 show electronic images of chromium galvanic coating fracture specimens taken with an atomic force microscope NT MDT IntegraSpectra. Fig. 12 shows multi-walled carbon nanotubes embedded in the chromium coating; in Fig. 13 a graphene oxide plate is visible.

To reveal the fact of the decrease in the size of the crystals of chromium galvanic coatings, the diffraction patterns of the chromium galvanic coating were taken on a D8 DISCOVER X-ray diffractometer – without additives (Fig. 14) and with the addition of a mixture of nanodiamonds and multi-walled carbon nanotubes to the electrolyte (Fig. 15).

There are few peaks due to the peculiarities of the chromium crystal lattice. The grain size measured from a more intense peak (approximately 82°) is (11 ± 1) nm for a sample without additives and (10.5 ± 1) nm for a sample with a mixture of nanodiamonds and multi-walled carbon nanotubes added to the electrolyte. Thus, it was revealed that the size of the crystals decreases slightly.

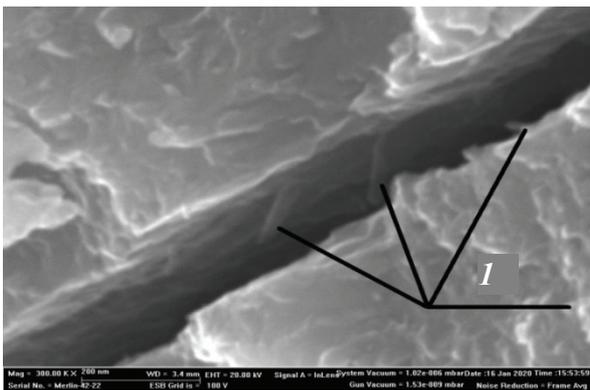


Fig. 12. Electronic image of the fracture of chromium galvanic coating fracture specimens (1 – MWCNTs)

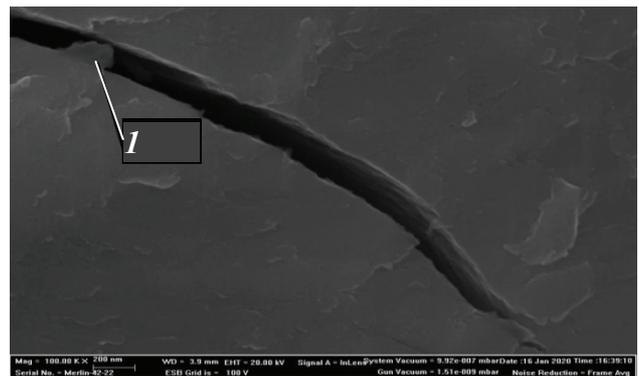


Fig. 13. Electronic image of a fracture of chromium galvanic coating fracture specimens (1 – GO)

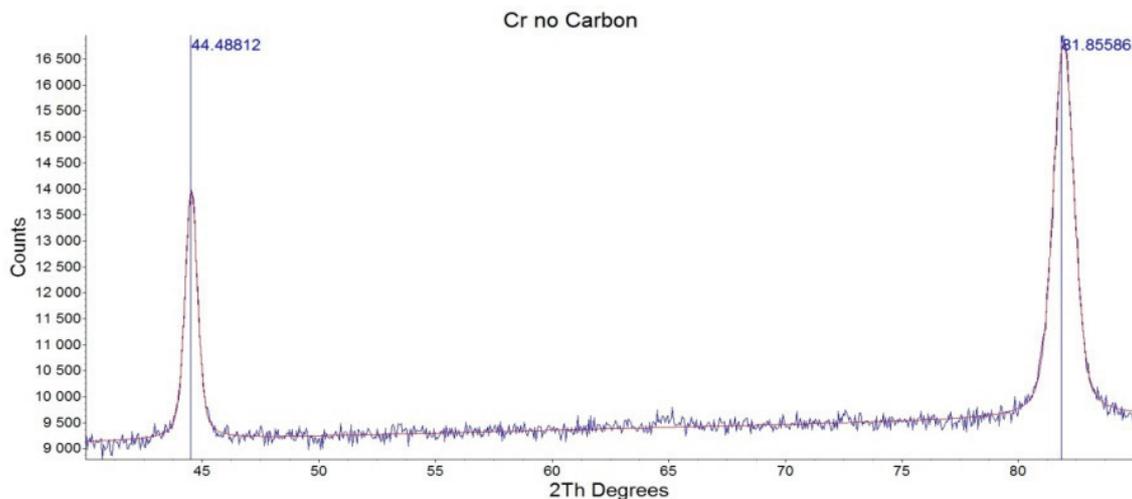


Fig. 14. Diffraction pattern of chromium coating obtained from electrolyte without additives

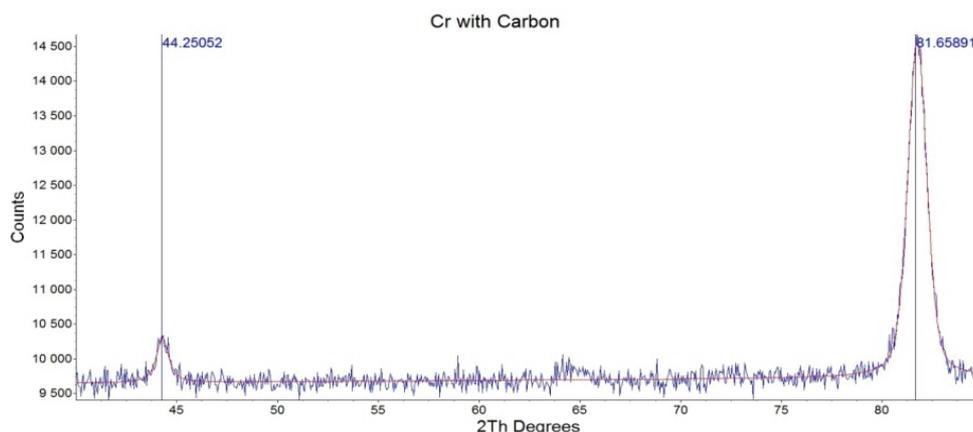


Fig. 15. Diffraction pattern of a chromium coating obtained from an electrolyte with the addition of a mixture of nanodiamonds and multi-walled carbon nanotubes

We noted that in the sample obtained from an electrolyte with the addition of a mixture of nanodiamonds and multi-walled carbon nanotubes, the intensities of the peaks at 45° and at 82° strongly differ. This can be caused by the preferred orientation of the crystallites in the material.

Conclusion

The study revealed a tendency to increase the microhardness of the chromium galvanic coating by adding a mixture of carbon nanomaterials (nanodiamonds, single-walled and multi-walled nanotubes, graphene oxide) into a standard chromium galvanic coating electrolyte.

The applied significance of the developed technologies for machine-building enterprises is as follows:

- if the products with nano-modified chromium plating are the final products of the enterprise, they have a competitive advantage over similar products due to increased wear resistance;

- if a plant uses nano-modified chromium-plated products in a manufacturing process, production costs are reduced. So, at the enterprises “TPZ-Instrument” and “Tulamash”, Tula, due to an increase in wear resistance by 20 % of self-made tools covered with nano-modified chromium coating, the number of tools used decreased by 20 % per year.

The developed technologies become more and more relevant as the cost of carbon nanomaterials produced in the Russian Federation decreases.

The increase in the microhardness of the chromium galvanic coating is due to 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 service life of the parts obtained is significantly higher than when using traditional chromium galvanic coating, as well as when using multi-walled carbon nanotubes, single-walled carbon

nanotubes, nanodiamonds, and graphene oxide separately.

The best result was obtained using a mixture of nanodiamonds and multi-walled carbon nanotubes. The microhardness of the nano-modified the chromium galvanic coating increased by 27 %.

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

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

References

1. Mishchenko S.V., Tkachev A.G. *Uglerodnyye nanomaterialy. Proizvodstvo, svoystva, primeneniye*. [Carbon nanomaterials. Production, properties, application]. Moscow, Mechanical Engineering, 2008. 320 p. (Rus)
2. Patent RF No. 2477341 IPC C25D15/00, B82B1/00. *Sposob prigotovleniya elektrolita dlya polucheniya kompozitsionnykh pokrytiy na osnove metallov*. [Method of electrolyte preparation for obtaining composite coatings based on metals]. Litovka Yu.V., Tkachev A.G., Pasko A.A., Dyakov I.A., Kuznetsova O.A., Tkachev M.A. BI No. 7, 2013. (Rus)
3. Patent RF No. 2709594, IPC C01B 32/198, B82B 3/00, B82Y 40/00. *Sposob polucheniya oksida grafena*. [Method for producing graphene oxide]. A.G. Tkachev, A.V. Melezhhik, A.A. Osipov, M.A. Tkachev / Applicant and patentee of NanoTechCentre LLC (RU). No. 2018134006; declared 09/26/18; publ. 12/18/19, Bul. No. 35.
4. Litovka Yu.V., Nasraoui M., Kuznetsova O.A., Maistrenko N.V. Chromium galvanic coatings modified by single-layer carbon nanotubes. *Strengthening technologies and coatings*, 2018, 14 (10), 463-465.
5. Litovka Yu.V., Nasraoui M. Chromium electroplated coating modified with graphene oxide. *Nanoindustry*, 2020, 13, 1 (94), 34-38. doi: 10.22184/1993-8578.2020.13.1.34.38.
6. Litovka Yu., Nasraoui M., Dolmatov V. Improved microhardness of chrome galvanic coatings with combining nanodiamonds and nanotubes. *IOP Conf. Series: Materials Science and Engineering*, 2019, 693. doi:10.1088/1757-899X/693/1/012012.
7. Litovka Yu.V., Nasraoui M. *Modifitsirovannyye kombinatsiyey uglerodnykh nanomaterialov*. [Chromium galvanic coatings modified with a combination of carbon nanomaterials]. LAP LAMBERT Academic Publishing, 2020, 42 p. (Rus)