Electroplating of Chromium Incorporating High-Dispersion Black Carbon Particles

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Abstract. Electrochemical composite coatings allow successfully solving many practical problems of surface-hardening of structural parts and their tooling components, as well as renewing their fast-wearing components. Electrochemical chromium-matrix composite coatings are used to enhance the thermal and wear resistance of steel articles and parts operating in friction conditions and under increased temperatures, but under low shock loads.

This paper presents the results obtained from studying how fine black carbon particles affect the properties of composite coatings. Optimal conditions are found for producing high-quality coatings, such as the suspended electrolyte mixing rate and graphite concentration in electrolyte. We have also studied how heat treatment affects the microhardness and surface morphology of coatings. High-dispersed black graphite can be used to produce chromium-matrix composite coatings having increased microhardness and wear resistance.

1 Introduction

Current technology is in desperate need for materials that can withstand continuous mechanical and thermal loads and efficiently offset the impacts of wear, aggressive media, and loads.

Currently, a great attention is given to composites and composite coatings.

Composite coatings combine the high values of electro- and heat conductivity, plasticity, weldability, and other properties of metals, such as Ni, Cu, Cr, etc., and simultaneously high-temperature strength, chemical inertia, high hardness, or other characteristics of disperse phase, i.e., borides, oxides, other binary compounds, and simple substances.

One of the ways to produce composite coatings is electroplating, i.e., depositing the electrochemical composite coatings (ECC) from suspended electrolytes by refilling the galvanic deposit of particles and microfibers dispersed in the electrolyte [1].

Suspended electrolytes are prepared from a “pure” electrolyte modified by a certain amount of the dispersed phase (DPh) substance (of any nature or state, but resistive in electrolyte or weakly reacting with it). ECC formation depends on some factors. These are the nature of electrolyte, i.e., its ionic content, *pH*, etc., electrolysis conditions, and nature of the metal. One of the factors affecting the structure and properties of composite coatings

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is the characteristic of DPh particles, i.e., their nature, concentration, dispersiveness, electric conductivity, density, dissolubility, and wettability [2].

Along with the “classical” DPh substances, i.e., powders of aluminum or titanium oxides, as well as carbon, particles of SiC, WC, Al₂O₃, TiO₂, etc. are used.

Chromium-based electrochemical composite coatings are most promising in the conditions of abrasive wearing and aggressive media. Many mechanical engineering parts and products, in which electrochemical chromium coatings are used, are operated at increased temperatures and in the conditions of cyclic heat loads.

Currently, both in Russia and abroad, active studies are performed regarding composite coatings modified nanosized particles of different nature. This trend is related to the emergence of new materials, such as nano diamonds, fullerenes, carbon nanotubes, graphene, etc. Coatings developed have new functional properties. For example, introducing graphite particles into the chroming electrolyte, electrodeposited coatings have a lower friction coefficient, which allows using them in products operating in the dry friction conditions. Currently, composite coatings are being actively studied, which are modified by nanosized carbon particles. Introducing carbon nanotubes into a coating results in the noticeable improvement of the operation properties of the coatings, i.e., hardness, wear resistance, and corrosion resistance. Diamonds and diamond-like additives added to the electrolyte based on chromic acid allow obtaining coatings having a low friction coefficient and high wear resistance. Microhardness of coatings increases with increasing graphite contents. It is shown that carbon does not change the crystallographic structure of deposited chromium, but provides significant effects on the coating quality [3].

Authors of [4] developed a method to obtain composite chromium coatings for metal goods, which can be used in metallurgy and mechanical engineering to obtain corrosion-resistant hard chromium coatings. Electrolyte composition: 250 g/l of CrO₃, 20 g/l of calcium sulfate CaSO₄, and 10-20 g/l of disperse graphite produced from carbon-containing aluminum-production solid wastes as carbon skim floatation tailings.

A considerable number of publications deals with the joint depositing of chromium with nanodiamond particles. It is also suggested that nanodiamond particles are good for the structure of coatings due to changing the kinetics of depositing, but they are included into electrolytic chromium residues, although in small amounts (up to 1.0 % wt.) [5].

In [6], studies are described that were performed on the wearing resistance of Cr-ECC with ultradisperse diamond (UDD) inclusions on flat and cylindric samples. Joint UDD-chromium depositing enhances manifold the wearing resistance of surfaces operating in the conditions of the increased friction of parts, significantly surpassing hard chromium in wearing resistance. Being uniformly distributed within the chromium volume, diamond particles block the growth of crystals, atomize them, and increase the density and hardness of the coating being formed.

We have studied the structural state, microhardness, and thermal stability of chromium coatings modified by the nanosized additives of carbon-containing particles of different types in the conditions of cyclic heat loads and annealing within the temperature range of 770-870 K. It is found that modifying chromium coatings with carbon-containing nanoadditives ensures increasing the microhardness and thermal stability of coatings. The highest thermal stability at the temperatures of up to 820 K was in chromium coatings modified by the particles of the partly refined diamond-graphite furnace charge and nanodiamond particles. At high thermal cycling temperatures, chromium coatings modified by nanodiamond particles are characterized by increased thermal stability [7].

The study was aimed at investigating how high-dispersion black carbon particles can affect the properties of Cr-ECC.

2 Objects and Methods

To study applying the chromium-matrix-containing ECC, we used the standard chroming electrolyte composed as follows (g/dm^3): CrO_3 – 250 (2.5 M) and H_2SO_4 – 2.5 (0.025 M).

Coatings were applied onto steel samples sized 2 x 3 cm. Fine graphite was used as the second-phase particles: $C_{\text{gen}} = 99.9\%$, $S_{\text{sp}} = 110 \text{ m}^2/\text{g}$, $\rho = 3.51 \text{ g/cm}^3$. Powder concentrations: 10 and 20 g/l . Electrolysis mode: $t = 50 \pm 5^\circ \text{C}$; cathodic current density = 30 A/dm^2 , and electrolysis duration = 1 h. Lead plates were used as anodes, while electrolysis was performed at permanently mixing with a magnetic mixer at 40 and 50 rpm. Current efficiency (CE) of metal was computed by Faraday law. Coating thicknesses were measured gravimetrically in accordance with the Russian standard GOST 9.302-88. Chemical compositions of layers within the Fe-Cr system and the coating thicknesses were identified using the X-ray fluorescent (XRD) analyzer of coatings (X-STRATA 980). Microhardness of coatings was identified using the microhardness tester PMT-3M in accordance with GOST 9.450-76. Surface morphology was studied using microscope ALTAMI MET-15. Structures of control coatings were investigated using the electronic microscope REM-100U with energy-dispersive analyzer EDAR. Electronic microscope was intended for imaging the object surface with high (up to 0.4 nanometers) spatial resolution, including information on the compositions, structures, and some other properties of near-surface layers.

3 Experiment Outcomes and Discussion

Considering potential interaction between graphite and the electrolyte components, we performed tests thereof in the relevant media: In 2.5 M of H_2SO_4 to identify the DPH behavior regarding the H^+ ion as oxidizer, with a concentration that is approximately relevant to its concentration in the chroming electrolyte; in the chroming electrolyte – assuming that oxidizers are Cr(VI) represented as CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and other ions, and H^+ ions; and in the HCl solution (1:1) used to dissolve the coatings and extract DPH from them.

Graphite manifested high resistivity in the media under research. Mass loss is lower than 1 %. At the same time, the powder has an extremely low wettability with acids and the chroming electrolyte.

We performed preliminary experiments aiming at finding the optimal graphite concentration in electrolyte. Concentration of DP particles in electrolyte is the most important parameter determining the properties of the ECC obtained. At the graphite concentration of 50 g/dm^3 , we only managed to obtain from a portion of electrolyte the samples with an extremely unsatisfactory appearance (only edges of the sample were coated, and there were many graphite inclusions). Graphite concentration was reduced to 20 g/dm^3 . That resulted in uniform gray surfaces obtained. Increasing the current density up to 60 A/dm^2 results in glossy surfaces. For our further studies, we chose the graphite concentrations in electrolyte of 10 and 20 g/dm^3 .

To identify the optimal parameters of obtaining composite coatings, we investigated how the concentrations of high-dispersion black carbon particles and the suspended electrolyte mixing rates affected the properties of Cr-ECC.

Table 1 shows the results of finding the thicknesses and depositing rates of coatings, as well as the current efficiency of chromium, depending on the graphite concentration in electrolyte and one the mixing rate.

Table 1. Properties of chromium coatings, depending on particles concentration in electrolyte and on mixing.

Mixing, rpm	40			50		
Particles concentration in electrolyte, g/l	0	10	20	0	10	20
Coating thickness, μm	18.1	18.3	17.1	17.9	19.6	17.1
Deposition rate, $\mu\text{m/s}$	0.3	0.305	0.28	0.298	0.33	0.28
Current efficiency (CE) of metal, %	12.06	12.18	11.42	12.87	13.09	11.02

Coating obtaining lasted 1 hour. We selected it to study how the concentration of particles affects the deposition rate and thickness of the composite coating produced. It is found that, with increasing the mixing rate of the suspended electrolyte from 40 to 50 rpm, coating thickness increases up to 19.6 μm at the concentration of 10 g/l. Number of graphite particles contained in coating a_m was found using mass method, by dissolving the samples in hydrochloric acid, followed by centrifuging the solution. Analyses showed an insignificant content of particles in the coating: 0.3 % at the particles concentration of 10g/l of a_m and 0.9 % at the concentration of 20 g/l of a_m .

The higher the depositing rate, the higher the current efficiency of metal. It is known that chroming is characterized by an extremely low current efficiency of metal, which makes about 13 % in the standard chroming electrolyte and only may reach 18-20 % in same electrolytes, including those containing organic additives and/or disperse phase particles. In rare cases, particles can be found in Cr-ECC in the amounts exceeding 2% of volume. This is explained by the low current efficiency of chromium, hydrogen effervescing that obstructs the penetration of particles into the coating, levelling power of the chroming electrolyte, and its high superficial tension.

Based on the data obtained, it is found that the highest current efficiency of chromium is achieved at the carbon concentration of 10 g/l. At the mixing rate of 50 rpm, this value is 13.09%.

It was found that the particles of high-dispersion black carbon affect the quality of coatings obtained. Results of identifying the microhardness are shown in Table 2.

Table 2. Microhardness of chromium coatings, depending on the particles concentration in electrolyte and on mixing.

Mixing, rpm	40			50		
Particles concentration in electrolyte, g/l	0	10	20	0	10	20
Microhardness, hPa	9.6	9.1	9.4	10.0	9.1	7.6

It follows from Table 2 that graphite particles reduce the microhardness of chromium coatings, regardless of the electrolyte mixing rate. At increasing the mixing rate, a considerable reduction of the microhardness of coatings down to 7.6 hPa is observed, as compared to the control coating, in which it is 10 hPa. Reducing the hardness of a composite coating can be explained by the low density of graphite. At the time of contacting the cathode, these particles, in most cases, do not have an impulse force sufficient for creating a close contactand, in some cases, penetrate the coating as agglomerated groups that increase the porosity of the coating [8].

It is known that chromium coatings contain CrH, which, as we have already noted, is explained by the low current efficiency of chromium and high hydrogen release. Hydrogen content in a coating can be reduced by using annealing at the temperature of 200-300° C, the main mass of hydrogen being released at the temperature close to 200° C.

At heat treatment, the dispersed-phase substances can be either partly removed from the superficial layer or modified and, therewith, affect the coating structure.

Annealing was performed at the temperature of 300° C. At the same time, the mass of coatings decreased by thousandths of a gram.

For annealed coatings, microhardness was identified (Table 3).

Table 3. Microhardness of annealed coatings, depending on the particles concentration in electrolyte and on mixing.

Mixing, Rpm	40			50		
Particles concentration in electrolyte, g/l	0	10	20	0	10	20
Microhardness, hPa	10.9	11.4	11.5	12.0	9.9	8.4

In Table 3, we see that the graphite nanoparticles in the annealing conditions increase the microhardness of chromium coatings. Enhancing the hardness of the control coating and ECC is determined by changing the matrix structure, i.e., grain refinement, increasing the resistance against shifting the components of the system with the existing particles, and finally, the presence of the second-phase substances [2].

This is confirmed by changing the surface morphology of the samples obtained. Morphology of chromium coatings and ECC based on it, depending on the dispersed-phase content in the coatings, is shown below (Figures 1-4).

Fig. 1. Morphology of control sample

Fig. 2. Morphology of annealed control coating

Fig. 3. Coating morphology; particles concentration in electrolyte is 10 g/l

Fig. 4. Coating morphology; concentration 20 g/l

It can be seen in microphotographs that chromium coatings have different structures. Where a chromium coating without DPh passes to ECC, the microstructure of the surface changes markedly. The surface is better developed and has a noticeable gloss; it also has darker sections that may be relevant to possible inclusions of graphite particles in the

matrix. Morphology of annealed control surface is smooth and even, while, as noticed above, the microhardness of such surfaces is higher than that of non-annealed samples. Figures 5 and 6 show the structure of control coatings.

Fig. 5. Structure of the control coating, hundredfold magnification

Fig. 6. Structure of the control coating, thousandfold magnification

It can be seen from Figures 5 and 6 that the structure of pure chromium has large and deep cracks. It is visible clearly that the surface is very uneven, the presence of dendrites is observed as a well-formed globule. Dense globules 30–50 μm in diameter, consisting of needle-like elements. Oxygen content: 4.67 %, chromium content: 95.36 %.

It is known that different thicknesses of the applicable metal (conicity) is typical of for chromium coatings. This may affect identifying the operating properties of coatings. One of the reasons for that is the low throwing and covering powers of electrolytes. Therefore, various techniques are used to enhance the uniformity of coatings.

To identify the thickness and chemical composition of coatings, we used X-ray diffraction (XRD) analysis. We have already used this method to identify the concentrations of basic components and the thicknesses of coatings with different metal matrices. Our findings are described in articles [9, 10].

Points to measure the coating thickness were selected as the “upper part,” “middle part,” and “lower part” of the sample. The findings are presented in Table 4.

Table 4. Effects provided by the particles on the thickness of coatings, depending on the particles concentration in the electrolyte and mixing.

Mixing, Rpm	40			50		
Concentration of particles in electrolyte, g/l	0	10	20	0	10	20
“Upper part”	0.3	1.5	1.6	1.5	0	0
“Middle part”	9.6	13.7	13.5	8.5	20.1	12.1
“Lower part”	26.5	22.9	25.9	19.8	18.9	31.2

The table above shows that, with increasing the concentration of graphite particles, the thickness of coatings grows, especially in the lower parts of the samples. Optimal mixing condition is the rate of 50 rpm. Data shown in Table 4 differ from the findings shown in Table 1. In Table 1, gravimetric method was used to identify the results, which consists in

finding the coating mass by weighing the samples with analytical scale before and after applying the coating.

Chemical composition in the Fe-Cr system was identified, as well (Table 5).

Table 5. Chemical composition in the Fe-Cr system depending on the concentration of particles in the electrolyte and mixing. Coating thickness is $\sim 18 \mu\text{m}$.

Mixing, rpm		40			50		
Concentration of particles in electrolyte, g/l		0	10	20	0	10	20
“Upper part”	Cr	62.03	67.22	64.23	71.8	66.64	43.55
	Fe	13.23	10.09	10.80	5.5	10.76	37.82
“Middle part”	Cr	77.34	79.89	81.62	79.5	85.29	80.01
	Fe	2.71	1.51	1.58	1.4	0.66	2.83
“Lower part”	Cr	90.88	90.75	89.91	87.8	94.84	86.61
	Fe	0.1	0.37	0.27	0.2	0.14	0.32

It follows from Tables 4 and 5 that DP affects the distribution of coating composition thicknesses.

Changes in the coating thicknesses are especially visible in the upper and middle parts of samples. At the mixing rate of 40 rpm and particles concentration of 10 g/l, the coating thickness at all measurement points increases from $1.5 \mu\text{m}$ to $22.9 \mu\text{m}$. The same regularity is observed at the concentration of 20 g/l.

A more noticeable change in the chromium thickness over the sample surface is observed at the mixing rate of 50 rpm. At the particles concentrations of 10 and 20 g/l, a considerable increase in the thickness is observed in the middle parts of the samples. In these samples, the thicknesses are 20.1 and $12.1 \mu\text{m}$. In the upper parts of the samples, the decrease in the coating thickness down to 0 is observed due to the fact that in electrolysis, there is non-electrolyte-wetted graphite on the electrolyte surface and this part of the sample contacts with particles, not with electrolytes. Therefore, chromium does not deposit in the upper part of the sample.

Table 5 confirms the findings shown in Table 4 above. Since the system under study is a single-layer one, it is natural that the larger the coating thickness is, the higher the chromium content is.

For wearing tests, bases of cylindric samples were coated by chromium at the thickness of $20 \mu\text{m}$ from suspended electrolytes at the mixing rate of 40 rpm. Results are shown in Table 6.

Table 6. Mean wear of coatings depending on the graphite concentration in the electrolyte.

Electrolyte composition	Mean wear
Standard electrolyte	0.0114
Standard electrolyte +10 g/l	0.0094
Standard electrolyte +20 g/l	0.0115

Table 6 shows that the lowest wear is found in coatings obtained from a suspended electrolyte with the particle concentration of 10 g/l.

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