Research Article

# Research of the Process of Electrochemical Deposition of Chromium in the Presence of a Composite Compound Based on Detonation Diamond-Containing Carbon

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**Abstract:** The purpose of the study is to develop a method for obtaining high-quality electrochemical chromium coating using a new type of diamond-containing additive that has significant advantages over traditionally used detonation nanodiamonds (DNA) in the form of aqueous suspensions. Detonation diamond-containing carbon (DDC) obtained by detonation of charges from tetryl was used as an additive. DDC contains 63,0 wt. % DNA and 4.4 wt. % non-combustible impurities. We used standard chromium electrolyte: $CrO_3$ - 250 g/l, $H_2SO_4$ – 2,5 g/l, DNA – from 0,2 to 5 g/l, traditional methodologies and algorithm of experimentation. The scope of the study is limited to the creation and application of a specific, easy to handle and prepare formulation with DDC. DDC can be added to the standard chromium electrolyte directly or in the form of freshly prepared aqueous suspension, it is environmentally safe.

The originality of the work lies in the application of a cheap diamond-containing product obtained directly after the explosion of an individual explosive (tetryl) and providing stability of DDC suspensions. An increase in microhardness of wear-resistant chrome coating by 1,5 times (up to 11 GPa) and hard chrome coating by 1,7 times (up to 13,3 GPa) was achieved. The wear resistance of the obtained coatings increased by 1,9 times. Concentration (per pure detonation nanodiamond (DNA)) from 0,63 to 3,15 g/l in the electrolyte (very low).

*Keywords*: chromium plating; detonation diamond-containing carbon; detonation nanodiamonds; tetryl; microhardness; wear resistance

## 1. Introduction

Chromium plating is the most important process of electrochemical deposition of functional coatings and finds wide application in various industrial fields, such as mechanical engineering, shipbuilding, machine tool building, and tool industry.

It has been previously shown that the inclusion of nanodiamond particles (DNA-TAN) modified with ammonia at high temperatures and pressure [1] and detonation diamond-containing carbon (DCC) in chromium coating [2–4] leads to a significant increase in microhardness, wear resistance, and corrosion resistance at high

concentration of additives in the electrolyte (more than 10 g/l). The nature of the effect of additives on the rate and mechanism of processes occurring during the deposition of chromium, as well as on the properties of coatings is ambiguous and is determined by several factors: concentration, type and modification of the additive, electrolysis parameters [3–7].

The known methods of DNA application have significant disadvantages – high cost of DNA and necessity to use aqueous suspensions with concentration of ~5% wt. The latter leads to the necessity to transport together with DNA ~95% wt. water, which is economically expensive; DNA suspension occupies considerable area during storage; suspension must be protected from freezing in cold season (when freezing DNA irreversibly coagulate). Besides, technologically it is more convenient to introduce dry powders of nanodiamonds precisely determined by weight into electroplating baths. The use of conventional dry purified DNA powders for electrochemical coatings is currently impossible due to their strong aggregation.

Previous developments on chrome plating technologies with DND are used in industrial practice by the Russian company "RAM Ltd" (Korolev, Moscow region, Russia), the Belarusian company "Sinta" (Minsk), the South Korean company "Samhung".

Modern technology and industry attach increasing importance to the physical and chemical properties of coatings, and conventional metal films and alloys cannot meet the increased requirements for wear resistance, corrosion resistance, coating uniformity, porosity, microhardness. Therefore, electrochemical composite coatings (ECC) are attracting more and more attention. They are created by incorporating foreign particles of another phase into the electrolytic precipitate. The strength of the coatings is significantly affected by microcracks, which are stress concentrators. The dispersed particles included in the coatings are microbarriers on the path of these microcracks, defects and dislocations, which leads to hardening of the material [8]. The decrease in porosity of coatings and, consequently, the increase in corrosion resistance occurs due to the interference created by the ECC particles to the movement of dislocations in the plane of their sliding [9]. It is also known that particles in the material prevent the growth of grains - the coating becomes fine crystalline. When the particle size decreases and their volume concentration remains unchanged, the distance between the particles decreases. This causes the formation of porous metal films [10].

Various disperse materials (borides, oxides, nitrides, silicides, etc.) are used in the creation of ECC, different electrolytes and methods of obtaining coatings are used.

There are three stages in the process of ECC formation: movement of dispersed phase particles and ions from the electrolyte volume into the near-electrode layer; transfer of ultradispersed particles and ions to the cathode from the near-electrode layer; overgrowth of particles on the matrix surface.

Composite coatings are metallic or non-metallic matrices with a given distribution of various hardeners in them. Powders, fibres, whiskers, etc. are used as hardeners. [11]. The substance used as a dispersed phase should not: interact with the deposited metal; dissolve in it up to its melting point; undergo phase transitions with volume change under the conditions of operation of such a coating.

Nanodiamond materials fulfil these conditions.

Purified solid DND is a clustered carbon nanomaterial consisting of aggregates of rounded or irregularly shaped particles with an average particle diameter of 5 nm [10]. DND particles have a complex structure: a classical diamond core, with a diameter of about 40, and a carbon X-ray amorphous shell with a thickness of 4-10 [12, 13]. The shell consists of $sp^2$-hybridised carbon atoms [14]. It is inhomogeneous on the surface and contains various inclusions, mainly oxygen-containing functional groups [15]. Moreover, these non-diamond components are organic components of DNDs [16, 17], which determine their specific properties.

**Table 1.** Content of impurity elements in DND, wt, %

| Element | Classic DND |
|---|---|
| Iron | 0,1 |
| Chromium | 0,5 |
| Silicon | 0,15 |
| Aluminium | 0,01 |
| Sodium | 0,05 |
| Potassium | 0,002 |
| Copper | 0,003 |
| Calcium | 0,01 |
| Magnesium | 0,005 |
| Manganese | 0,001 |
| Titanium | 0,002 |
| Lead | 0,001 |
| Non-combustible residue | 1,4 |

Electrolytes containing DND or DND in amounts recommended for each metal (nickel, chromium) have high stability due to the small size of nanodiamond particles, their chemical resistance and, especially, hydrophilic surface properties. When DND is introduced into electrochemical coatings, their microhardness, wear resistance, corrosion resistance, appearance is improved, porosity is reduced, the coefficient of friction is significantly reduced, and the dissipation capacity of electrolytes is increased [18]. The main reason for this is the reduction in the size of the coating domains, since the primary aggregates of DND particles are very small (10 - 40) nm, a sufficiently dense and uniform distribution of them in the coating is achieved at a very low DND content - tenths of per cent [19].

The aim of the work is to develop and prove the use of powdered diamond-containing composition (DCC is obtained by subversion of charges from tetryl), capable of replacing aqueous suspension of DNA in the process of electrochemical chromium plating while maintaining the achieved high quality parameters.

## 2. Literary part

The process of chromium deposition occurs under the conditions of three processes occurring together:
- incomplete reduction of hexavalent chromium to the trivalent state $Cr^{6+} + 3e \rightarrow Cr^{3+}$;
- release of hydrogen $H_3O^+ + e \rightarrow H_{ads.}$; $H_{ads.} + H_{ads.} \rightarrow H_2\uparrow$;
- release of metallic chromium $Cr^{6+} + 6e \rightarrow Cr^0$.

The totality of phenomena occurring at the cathode during the precipitation of chromium from chromic acid solutions makes it difficult to elucidate the mechanism of this process. Such phenomena may include chemical interaction of the cathode metal surface with chromium electrolyte, limiting current of one of the joint electrochemical reactions, mixing of the cathode layer by the released hydrogen and others.

Analysis of literature data and preliminary experiments showed that on different metals the reaction of incomplete reduction of chromium proceeds at different rates. It is also known that the electrodeposition of chromium is accompanied by the formation of a colloidal (gel-like) film on the cathode, which is formed only when the current is switched on and in the presence of an extraneous anion, the role of which is performed by $SO_4^{2-}$. When the current is switched off, this film is destroyed. In the absence of colloidal film, chromium is not deposited.

The reaction of incomplete reduction of chromium $Cr^{6+} \rightarrow Cr^{3+}$ on an electrode coated with galvanic chromium proceeds at a very low rate at 25°C, and at 50°C it practically does not proceed at all. On the steel electrode, this reaction proceeds at a considerable rate, and at 45°C at a higher rate than at lower temperatures. Such a difference in the reaction rate of incomplete reduction of chromium is due to the different state of the surface of the chromium and steel electrode. It can be assumed that there is a dense oxide film on the surface of the chromium electrode, which is a barrier preventing the incomplete reduction reaction from proceeding, while on the steel electrode the existing phase oxide film is fragile and does not prevent this reaction from proceeding.

Polarisation curves taken on a steel electrode showed that the introduction of DCC and DNA into the chromium electrolyte leads to an insignificant shift of the chromate ion reduction potential towards negative values, while with increasing concentration of DCC and DNA additives there is a decrease in the rate of reduction of $Cr^{6+} \rightarrow Cr^{3+}$. The value of the limiting current of the reaction of incomplete reduction of chromate ions decreases [20].

The greatest decrease is observed at the content of 5 g/l DND, further increase in the concentration of DND in the electrolyte up to 15 g/l leads even to a slight increase in the limiting current. While at the content of 1 and 10 g/l DCC the value of the limiting current of the reaction of incomplete reduction of chromium remains at the same level as for the solution without additives, and at the concentration of 2,5 g/l DCC the limiting current slightly increases. Such influence of additives on the process of incomplete reduction of chromate ions can be explained by very high chemical activity and high adsorption capacity of the studied additives, which slow down the reaction of incomplete reduction of chromium to the trivalent state. Processing of polarisation curves allows us to assume that at formation of the colloidal film at the electrode, particles of nanocarbon materials are included in its composition and influence its formation and densification, as well as in certain concentrations can act as surface active substances.

The introduction of DCC into the standard chromium electrolyte practically does not affect the cathodic polarisation, an insignificant shift to the electropositive side is observed relative to the curve taken in the standard chromium electrolyte without additives (the polarisation shift is up to 30 mV).

Hydrogen release curves taken in electrolytes with and without DCC are shifted to the electronegative side, as there is a hindered discharge of hydrogen ions on the electrode surface, on which adsorbed particles of DCC. The largest shift is observed with a lower concentration of DCC (2,5 g/l) and is 130 mV at a current density of

$0.4$ A/cm². Increase of DCC concentration up to 5 g/l leads to depolarisation of hydrogen release potential, most likely such influence of DCC is explained by desorption of the additive at its high concentration.

The addition of DCC does not affect the slopes of partial hydrogen release curves, and, therefore, the mechanism of hydroxonium ion discharge does not change (delayed stage of discharge followed by rapid removal of atomic hydrogen) [20].

In the articles [21, 22] it is shown that DNDs are the most environmentally friendly allotropy of nanocarbon (compared to fullerenes, graphenes, carbon nanotubes), LD >7,5 g/kg. Moreover, DNAs are proposed as the basis of drugs.

Indeed, due to the development of scientific and practical ideas about composite electrochemical coatings, which are electroplating coatings containing foreign microscopic particles in their structure, there is a possibility to significantly change the useful properties of coatings, such as microhardness, wear resistance, protective ability. This direction in the technology of electroplating coatings is becoming more and more widespread and is of great interest for research.

Since the deposition of thick chromium layers is a rather expensive process, in order to reduce the thickness and improve the physical and chemical properties of the chromium coating, the actual task is the development of the process of composite chromalmaz coatings using detonation nanodiamonds (DND).

DND (and DCC) was discovered in 1963 by a group of Russian scientists (V.V. Danilenko, K.V. Volkov, and V.I. Yelin). DND became widely known in 1984, when the world's first pilot production of DND with a capacity of up to 1 t/year was organised in the research and production association "Altai", Biysk, Russia. The first works on application of DND in electroplating and, first of all, on chrome-nanodiamond coatings were carried out by A.I. Shebalin [23]. The main buyer of DND at that time was Japan.

Due to the short duration of the detonation process (~0,1 μs), high temperatures (~3500 - 4000K) and pressures (~25 – 30 GPa), as well as the one-step occurrence of thousands of different reactions, the question of the mechanism of formation DND is still open, although, of course, there are works on this topic.

The process of nucleation and growth of DND particles, most likely, is exclusively chemical in nature. The formation of DND has a universal character regardless of the initial carbon-containing explosives used - hydrogen-containing (TNT, hexogen or hydrogen-free (benzotrifuroxane)), and the universal prastructure for DND formation is most likely a radical-like adamantane molecule. The process of nanodiamond crystallite growth occurs by diffusion mechanism due to the reaction of addition of the $C_2$ dimer present in the chemical reaction zone (between the shock wave and the Chapman-Jouguet plane) to the free bonds on the surface of diamond particles [24].

The cessation of DND growth occurs due to the accumulation of defects in the structure and the cessation of the transition of sp²-hybridised carbon to sp³-hybridised "diamond" carbon, as well as the depletion of carbon radicals due to their recombination [25].

The detonation transformation of explosives or mixtures such as $C_aH_bN_cO_d$ with negative oxygen balance (i.e., lower than stoichiometric oxygen content) in an unoxidised medium leads to the formation of a condensed carbon phase containing nanodiamonds. Such condensed carbon, called diamond charge (or DCC), can contain up to 75% nanodiamond particles. The complex process of refining DCC to DND significantly increases the cost of diamonds.

Particle growth occurs under conditions of interfacial turbulence, the occurrence of which is associated with unequal density of media, with the gradient of concentrations and temperatures, with the effect of flow inhibition on particles with a developed surface, with changes in surface tension. Turbulent flows contribute to the removal of crystallisation heat from the growing particle [26].

There is a qualitative incompatibility of strongly nonequilibrium conditions in the chemical reaction zone (CRZ) during detonation of explosives with the formation of a stable, in some cases, ideal crystalline phase of carbon. Therefore, most likely, we can speak not about crystallisation of nanosized diamond in the CRZ (due to the absence of heat removal from the formed nanocrystal and the short time of existence of the necessary P,T-conditions), but about the process of self-organisation of carbon into a condensed phase in accordance with the basic chemical properties of carbon atoms. Namely, the formation of different types of C-C bonds. Consequently, there is a probability of occurrence of fractal carbon grid with simultaneous fluctuations of carbon density in CRZ. In the "nodes" of this grid with the highest density, the carbon condensate has time to form a three-dimensional ordered core to a greater or lesser extent, while areas with a lower carbon density are repeatedly destroyed and recombined in the process of detonation product (DP) dispersal. In addition, known secondary processes - oxidation, graphitisation and amorphisation of dense carbon particles ("knots"), lead to a decrease in the DND fraction.

Thus, the prastructure of a DND particle may be a compacted carbon core, which beyond the Chapman-Jouguet plane becomes first liquid carbon, or the formed energetically favourable carbon framework of

cyclohexane, which beyond the Chapman-Jouguet plane, interacting with each other with even greater energy reduction, is rearranged into an adamantane radical molecule attacked by -C-C- radicals (diffusion mechanism of nanodiamond formation). It is possible that these two mechanisms of DND formation take place. Then there is crystallisation (amorphisation) of liquid carbon or cooling of DND crystallites obtained by diffusion from adamantane prastructure [27].

Fig. 1 presents small-angle X-ray scattering (SAXS) data, the processing of which makes it possible to estimate the nucleation and growth of the number of condensed carbon phase particles in the CRZ and the DP dispersion during the detonation of the investigated explosives [28, 29].
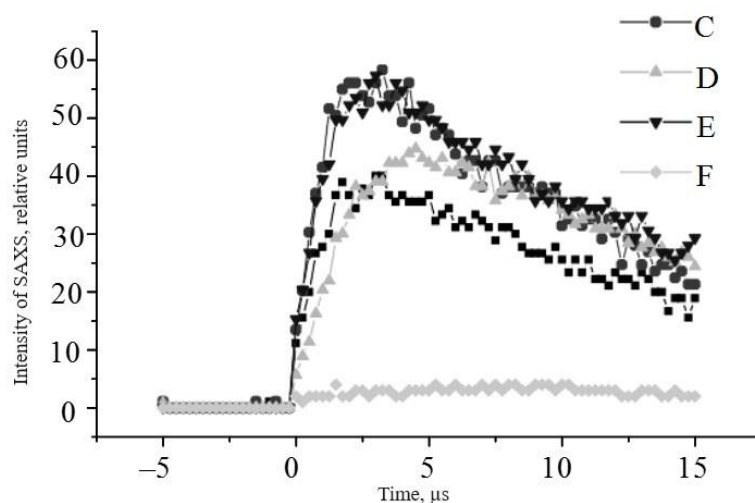


**Figure 1.** Small-angle X-ray scattering (SAXS) applied to the detonation process of condensed carbon-containing explosives, where B is TG 70/30 (■); C is TG 50/50 (-); D is TNT (▲); E is TG60/40 (▼); F is hexogen (♦) (authorised for use by E.R. Pruwell)

The technique of small-angle X-ray scattering, in our opinion, makes it possible to determine the parameters of forming particles in dynamics: the dependence of the size of particle number growth on the time of the detonation front appearance, the time output on the maximum particle size, the beginning of the size and number of particles drop.

Processing of a series of SAXS curves taken during detonation with an interval of 250 ns made it possible to obtain information on the dynamics of growth in the number of carbon nanoparticles. It was found that within 4 µs the average size of nanoparticles increased from 5 to 8 nm.

The connection of the SAXS data with the nanocarbon particle size, despite the designation of the maximum particle size of 7–8 nm in [28, 29], in our opinion, does not look convincing. Although the main number of DND crystallites obtained from various explosives falls within the range of 4-8 nm, a significant number of DND crystallites with sizes of tens of nanometres (20 – 35 nm), including those with well-defined facets, are also obtained. The MURR data presented in Fig. 1, most likely, indicate not the size of particles, but the growth of their number. Indeed, the curve of the time dependence of the scattering intensity during the detonation of a hexogen charge lies very low above the abscissa axis. According to our data, the yield of DAU from hexogen is very small (4,1 wt. %), and its DND content is quite high (21,5 wt. %). At the same time, the curve of the same dependence for TNT, on the contrary, lies very high above the abscissa axis, and the yield of DCC is abnormally high – ~20 wt%, but its DND content is very small – 4,7 wt%. Thus, the integral value between the obtained curves and the abscissa axis can characterise only the amount of obtained nanocarbon (DCC and DND) released after detonation synthesis, and not its size.

The SAXS signal detects condensed carbon (without distinguishing between the diamond and non-diamond phases) already in the chemical reaction zone (CRZ) for TNT and TNT-hexogen mixtures (70/30; 50/50; 60/40).

The results of [28, 29] show (Fig. 1) that the condensed carbon phase with increased density appears immediately behind the detonation wave front for TNT and TNT-hexogen charges. The rapid increase of the MURR signal lasts up to ~1,8 µs. Then there is a peculiar plateau - up to 4,4 µs, and then a slow decline to 15 µs and further.

The process of formation of the DND prastructure clearly begins in the CRZ, but is formalised in the form of a tightly bound diamond-non-diamond carbon structure (DND) far beyond the CRZ. Thus, in [28, 29] charges with diameters of 10 mm (TNT with hexogen, casting) and 12,5 mm (pressing, TNT and hexogen) were used. Having carried out the simplest calculations, taking into account the detonation velocity of TNT ~ 7000 m/s, TNT

with hexogen ~ 7500 m/s (for TG 70/30; 50/50; 60/40) and ~ 8500 m/s for hexogen, knowing the width of the CRZ and the reaction time in it, as well as the mass velocity of DP dispersal ~ 2000 m/s, it turns out that for 1.8 μs the distance travelled is ~4,4 mm, which is ~44% of the charge diameter, and for 4,4 μs ~ 9,5 mm (95% of the charge diameter). In fact, this is the DND formation zone as we already know it, i.e., the process of completion of DND crystallite formation occurs at a distance in the range of ~0,5 – 1,0 of the charge diameter from the detonation wave front (with a charge diameter of approximately 10 mm).

Then there is a sharp drop in pressure and temperature with attack on the formed nanocarbon, including DND crystallites of aggressive gases ($CO_2$ and $H_2O$), contributing not only to the reduction of DCC particle sizes, but also to graphitisation of DND crystallites.

# 3. Experimental part

The following electrolyte and modes of coating deposition were used: $CrO_3$ – 250 g/l; $H_2SO_4$ – 2,5 g/l; t = 45°C, i = 50 – 70 A/dm$^2$ (hard chrome plating mode); t=60°C, i=25 – 40 A/dm$^2$ (wear-resistant chrome plating mode). Each experiment is carried out 3 – 5 times to check the reproducibility. DCC additive was introduced into the chromium electrolyte in the following concentrations: 0,1; 0,2; 0,5; 1; 5 g/l. The tables and graphs show average values.

The choice of such an electrolyte is explained by the fact that it is stable in composition and at the same time has a better scattering and covering ability than a more concentrated electrolyte.

As a diamond-containing composition we used detonation diamond-containing carbon (DCC), obtained by explosion of tetryl (2,4,6-trinitro-N-methyl-N-nitroaniline), in the explosion chamber of «Alpha-2M» (St. Petersburg, Russia). Each charge had a mass of 0,5 kg and was detonated in a plastic bag with distilled water. The ratio of water:explosives = 8:1. The DCC contained 63% DNA; 4,4% noncombustible impurities and the rest was non-diamond carbon.

The following techniques were used to determine coating quality and electrolyte properties: microhardness determination, wear resistance measurement, taking polarization curves, determination of coating friction coefficient.

Microhardness testing was carried out by indentation using the reconstructed imprint method - an imprint was made on the test surface under the action of a static load applied to the diamond tip for a certain time. After removing the load and measuring the parameters of the resulting imprint, the number of microhardness was determined using formulas or tabulated values [30].

Wear resistance was measured using the method of registering the convergence of samples, which consists in moving the free surface of the fixed sample relative to the base of the movable sample [31].

The polarization curves were taken using a computer program and the methodology specified in [32].

The determination of the friction coefficient of coatings was calculated according to the method [33].

# 4. Discussion of the results

The data obtained in the process of work with chromium electrolyte with addition of DCC are summarized in Tables 2 and 3. In the tables for comparison the values obtained in pure electrolyte are given.

**Table 2.** Current yield for wear-resistant chromium with DCC additive, %

| Current density, i, A/dm$^2$    c (DCC), g/l | 0 | 0,1 | 0,2 | 0,5 | 1 | 5 |
|---|---|---|---|---|---|---|
| 25 | 13 | 13 | 10 | 10 | 12 | 15 |
| 35 | 15 | 16 | 11 | 13 | 14 | 17 |
| 40 | 15 | 17 | 12 | 16 | 14 | 18 |

**Table 3.** Current yield for solid chromium with DCC additive, %

| c (DCC), g/l Current density, i, A/dm² | 0 | 0,1 | 0,2 | 0,5 | 1 | 5 |
|---|---|---|---|---|---|---|
| 50 | 17 | 17 | 18 | 19 | 19 | 19 |
| 60 | 19 | 17 | 20 | 20 | 20 | 20 |

According to the results obtained, it can be concluded that the introduction of DCC additive slightly increases the current yield both in the case of wear-resistant and in the case of hard deposition mode of chromium coatings. In addition, there is an increase in the current yield with increasing current density, which is characteristic of pure chromium electrolyte.

To study the kinetics of chromium extraction, cathodic polarization curves were taken on an IPC-PRO potentiostat. The cathodic polarization curves were taken in pure electrolyte and in electrolytes with the addition of DCC (c=0,2; 1; 5 g/l) at temperatures of 50°C (hard chromium plating) and 60°C (wear-resistant chromium plating). The obtained data were summarized in graphs, which are presented in Figures 2 and 3.
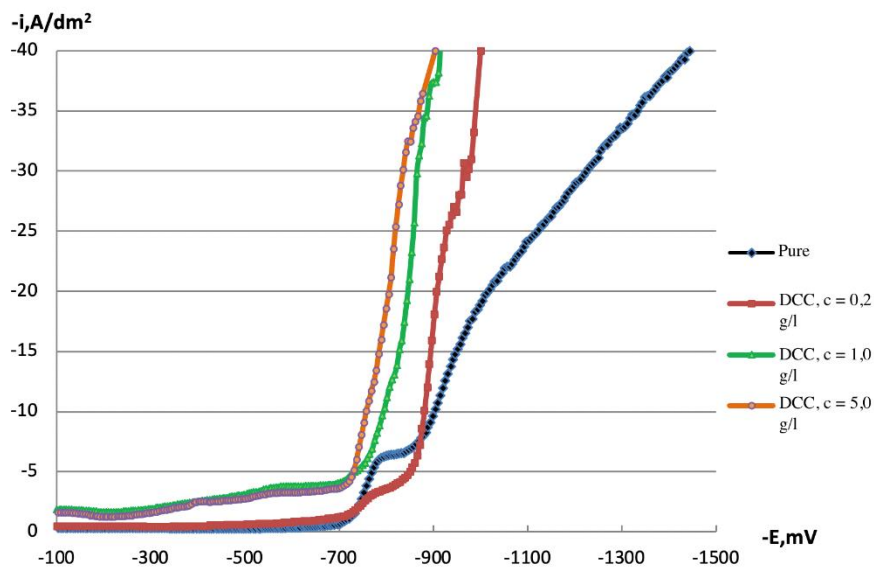


**Figure 2.** Cathodic polarization curves for chromium electrolyte when DCC is introduced at 60°C
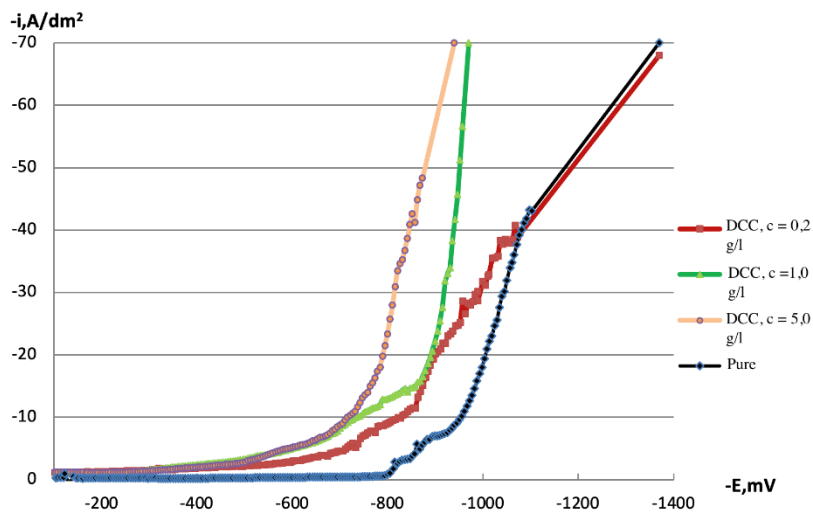


**Figure 3.** Cathodic polarization curves for chromium electrolyte when DCC is introduced at 50°C

As can be seen from Figure 2, under the conditions of deposition of wear-resistant chromium (T=60°C, i=25 – 40 A/dm$^2$) there is a shift of the potential (about 200 mV) in the region of positive values relative to the value obtained in pure electrolyte (without additive). Thus, the overvoltage of chromium release decreases, probably due to adsorption of the DCC additive on the sample surface. With increasing the concentration of the additive from 0,2 g/l to 5 g/l, the same tendency of shifting the potential to the region of positive values (about 120 mV) is also observed.

As can be seen from Figure 3, under conditions of solid chromium deposition (T=50°C, i=50 – 70 A/dm$^2$) there is a shift of the potential (about 300 mV) in the region of positive values relative to the value obtained in pure electrolyte (without additive). Thus, the overvoltage of chromium release decreases, probably due to adsorption of the DCC additive on the sample surface. At introduction of the lowest concentration of nanocarbon additive (0,2 g/l), there is no change during the chromium release curve. With further increase in the concentration of the additive from 0,2 g/l to 5 g/l, there is a tendency of shifting the potential to the region of positive values, which indicates the facilitation of the process of chromium extraction.

The effect of DCC on the electrical conductivity of chromium electrolyte was investigated. Measurements were performed on a Metler Toledo Seven Compact conductometer at room temperature, 6 measurements were made in each electrolyte, from which the average was selected. The experimental results are summarized in Table 4. The dependence of the electrical conductivity on the introduced nanodiamond additives passes through an extremum, which agrees with the theoretical data.

**Table 4.** Current yield for wear-resistant chromium with DCC additive, %

| Concentration of additive, g/l | | Electrical conductivity, mS/cm |
|---|---|---|
| Pure | | 512 |
| DCC, g/l | 0,2 | 515 |
| | 1 | 518 |
| | 5 | 509 |

To compare the structure of chromium coatings, surface micrographs were taken at a magnification of 1000x. Samples coated with pure chromium (1), with DCC additives with concentration of c=1 g/l were investigated. The results are shown in Figures 4, 5 and Table 5.

**Table 5.** Mass percentage of carbon in chrome coatings

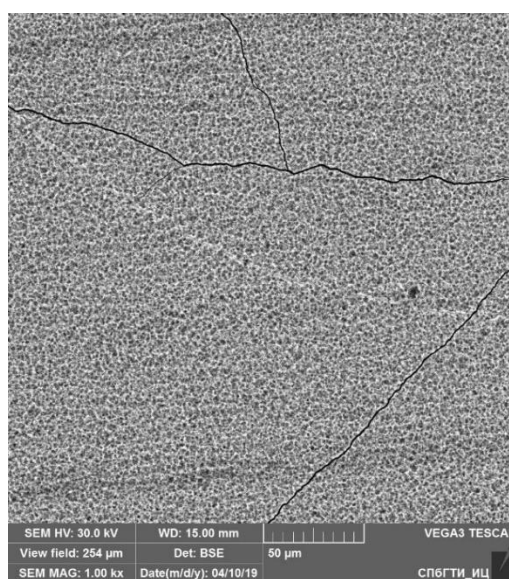| Investigated coating | Mass percentage of C content in the coating, wt % |
|---|---|
| (1) Pure Cr | 0 |
| (2) + DCC | 0,8 |



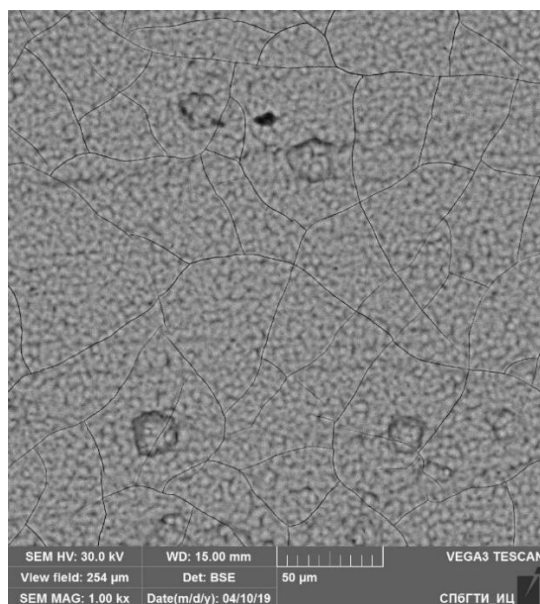**Figure 4.** Electrolyte surface without chromium plating

**Figure 5.** Chromium plating surface with DCC addition

As can be seen from the results obtained with the introduction of DCC, the coating becomes more uniform and homogeneous, which is consistent with the obtained polarization curves of chromium release. But at the same time the number of microcracks increases, which indicates high internal stresses of coatings.

The effect of DCC on microhardness of chromium coatings was investigated, the obtained experimental data were summarized in Tables 6 and 7 and in the graphs shown in Figures 6 and 7.

**Table 6.** Microhardness for wear-resistant chrome with DCC additive, GPa

| Current density, i, A/dm$^2$ \ c(DCC), g/l | 0 | 0,1 | 0,2 | 0,5 | 1 | 5 |
|---|---|---|---|---|---|---|
| 25 | 6,2 | 6,8 | 7,5 | 8,1 | 9,0 | 9,7 |
| 35 | 7,0 | 7,9 | 8,4 | 9,0 | 9,9 | 10,4 |
| 40 | 7,1 | 8,2 | 9,0 | 9,5 | 10,3 | 11,1 |

**Table 7.** Microhardness for hard chromium with DCC additive, GPa

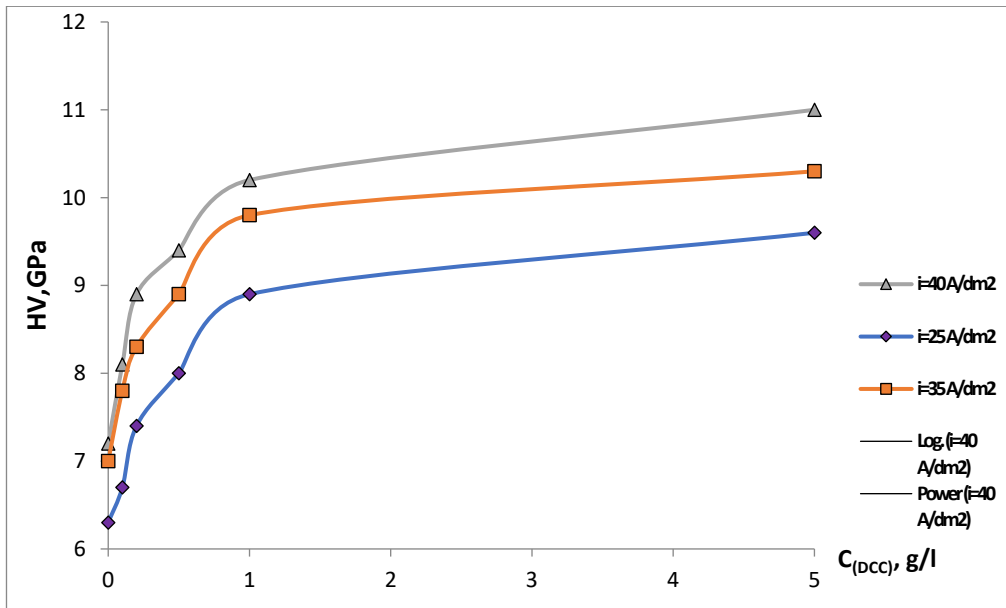| Current density, i, A/dm$^2$ \ c(DCC), g/l | 0 | 0,1 | 0,2 | 0,5 | 1 | 5 |
|---|---|---|---|---|---|---|
| 50 | 7,6 | 9,0 | 9,9 | 11,0 | 11,4 | 12,5 |
| 60 | 8,0 | 9,3 | 10,6 | 11,8 | 12,6 | 13,4 |

**Figure 6.** Dependence of microhardness on DCC additive concentration at different current densities for wear-resistant chromium
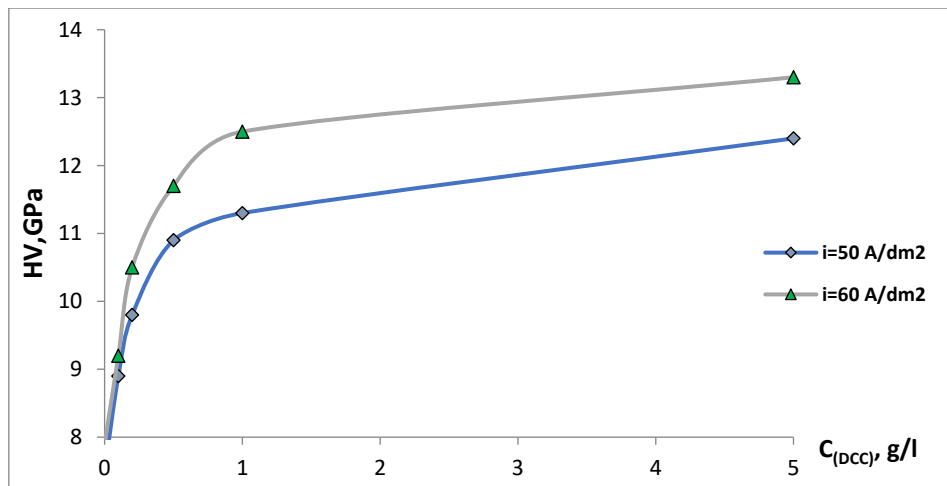


**Figure 7.** Dependence of microhardness on DCC additive concentration at different current densities for hard chromium

When the current density increases, the microhardness of coatings increases, the same happens when the concentration of DCC additive increases. The microhardness of coatings increases about 1,5 times with the introduction of DCC (c=5 g/l) and reaches a plateau.

The data on wear resistance of chrome coatings are summarized in Table 8 and histograms shown in Figures 8 and 9.

**Table 8.** Abrasion resistance with DCC additive, % of abraded coating weight in 20 hours

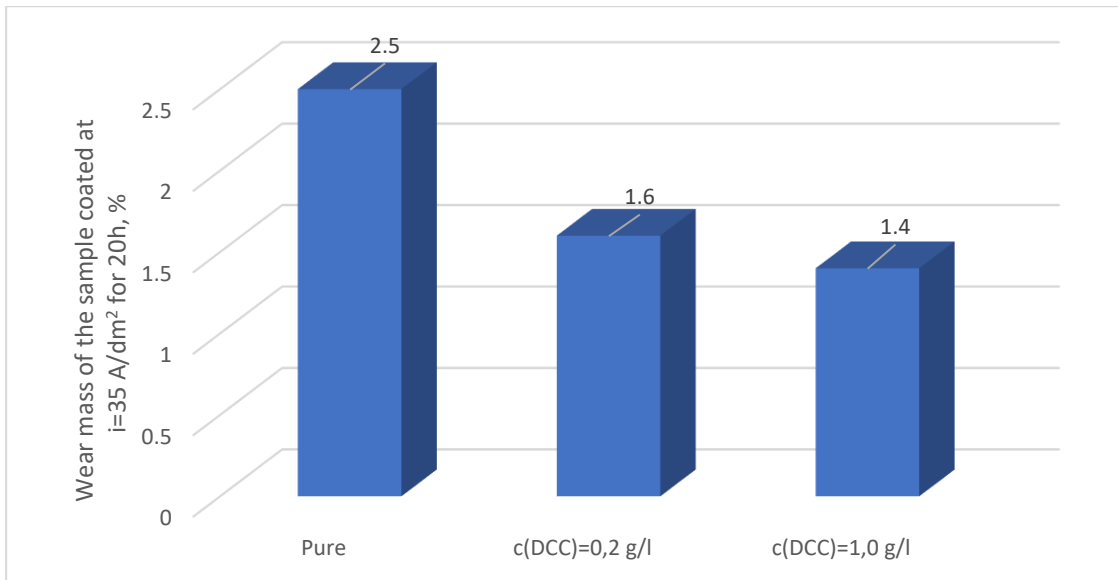| Current density, i, A/dm² \\ c(DCC), g/l | 0 | 0,2 | 1 |
|---|---|---|---|
| 35 | 2,5 | 1,6 | 1,4 |
| 40 | 1,6 | 1,4 | 0,7 |

**Figure 8.** Histogram of coating wear expressed in mass of frayed sample coated at i=35 A/dm$^2$ and T=60 °C



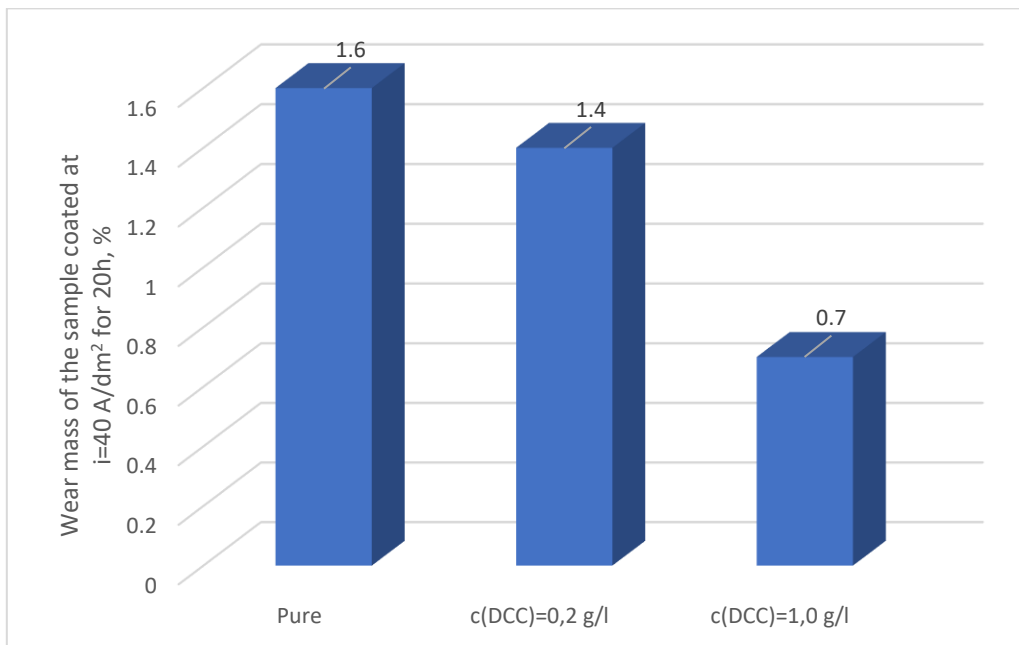**Figure 9.** Histogram of coating wear expressed in mass of frayed sample coated at i=40 A/dm$^2$ and T=60°C

Wear resistance was measured only for chromium coatings (with DCC) obtained in the wear-resistant chromium plating mode. It sharply increases (1,8 – 2,3 times) in comparison with wear resistance of coatings obtained from pure chromium electrolyte. It is noticeable that the increase in wear resistance occurs both due to the increase in current density and due to the increase in DCC concentration.

# 5. Conclusions

1. To obtain functional chromium coatings with enhanced physical and mechanical properties, a standard chromium electrolyte was selected and the nanodiamond additive DCC was investigated.
2. Polarization curves were obtained in pure electrolyte as well as with the introduction of DCC. It is shown that the introduction of DCC significantly shifts the potential to the positive region, and hence the discharge of chromium is facilitated. The largest potential shift was of the order of 300 mV.

3. With the introduction of DCC, the electrical conductivity and dissipation capacity of the electrolyte are practically unchanged.
4. It is shown that with the introduction of DAU into the electrolyte, the microhardness of the coating increases by a factor of 1.5. The highest values of microhardness of chromium coatings (13,4 GPa) are observed in the electrolyte at concentration c=5 g/l, i=60 A/dm$^2$, T=50°C. In previous works [33], microhardness values of 11 GPa are achieved under the same conditions and using TNT-hexogen-type DCC. The wear resistance of chromium coatings increases up to 2,3 times with the introduction of DCC.
5. As a result of research can be recommended for use standard electrolyte chromium plating composition: SrO$_3$ - 250 g/l, H$_2$SO$_4$ – 2,5 g/l. To obtain coatings with increased microhardness of about 13,4 GPa it is necessary to introduce DCC with a concentration of 5 g/l, temperature 50°C and current density i=60 A/dm$^2$.

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