Universal Journal of Carbon Research
https://ojs.wiserpub.com/index.php/UJCR/

Research Article

Influence of Doped Detonation Nanodiamonds on the Physical and Chemical Properties of Electrochemical Chromium Coatings

V.Yu. Dolmatov [1*], G.K. Burkat[1], Kiselev M.N.[2]

[1]FSUE «SCTB "Technolog"» 192076, Sovietsky pr., 33-a, St. Petersburg, Russia
[2]JSC "Selmash" 610035, Kirov, st. Shchorsa, 66, Russia
E-mail: diamondcentre@mail.ru

Received: 23 March 2023; **Revised:** 1 June 2023; **Accepted:** 31 July 2023

Abstract: Chromium deposition process regularities are analyzed in the standard chromium plating electrolytes, with and without detonation nanodiamonds additives modified with boron, phosphorus (DND-boron, phosphorus-DND) at a temperature of 50º to 55ºC while stirring the solution and without. It was studied by method of recording the partial polarization curves the concentration effect of additives DND-boron (in the range of 2,5 ÷ 10 g/l) on the kinetics of the chromate ion partial and full reducing. It has been shown that increasing the concentration of DND-boron leads to inhibition of the reaction Cr (VI) → Cr (III) and Cr polarization curves shift reaction (VI) → Cr (0) to a negative potential on the magnitude of 40-70 mV. While stirring the electrolyte chromium deposition occurs at more positive potentials than in quiescent electrolyte. Dependence of the electrode potential on the current density logarithm in all cases are linear with a slope close to 120 mV, indicating a limiting step of attaching the first electron. Mechanism of deposition of chrome in the presence of boron-DND does not change. Shiny, smooth, uniform coatings are deposited in electrolytes with DND-boron additives. Increased polarization in the chromium precipitation of electrolytes with DND-boron causes a change in precipitation structure, and as a consequence an increase in microhardness of chrome coatings from 955 kgf/mm^2 for pure chromium to 1430 kgf/mm^2 for chromium with embedded DND-boron nanodiamond particles. Wear resistance is increased: using DND-TAN - 2-3 times compared to standard chrome plating, using DND-phosphorus - in 3 times in comparison with DND-TAN, and using DCS (Si), doped silicon, wear is not detected (under the test conditions).

***Keywords*:** detonation nanodiamonds; DND; chromium plating; additive; wear resistance; microhardness; deposition; modified; reduction reaction

Abbreviations

CE	current efficiency
CPC	cathodic polarization curves
DCS	diamond-containing stock
DND	detonation nanodiamond
LTI	Leningrad Technological Institute
PCPC	partial cathodic polarization curves
TAN	modified with ammonia at high temperature and pressure
TNT	trinitrotoluene

DOI: https://doi.org/10.37256/ujcr.1220232731

1. Introduction

In recent years, more and more attention of researchers attracted to the possibility of the detonation nanodiamonds (DNDs) use to obtain chromium coatings with improved physical and mechanical characteristics. Previously shown that the embedment of nanodiamond particles DND-TAN (modified with ammonia at high temperature and pressure [1]) and diamond-containing stock (DCS) in the chrome plating [2–4] leads to a significant increase in micro-hardness, wear resistance, corrosion resistance. The nature of the additives influence on the rate and mechanism of the processes occurring in the chromium deposition, as well as on the properties of the coatings is ambiguous and depends on several factors: concentration, additive type and its modification, electrolysis parameters [3–6]. Detonation synthesis of new modified DND is carried out with the purpose of their use in electrochemical processes and ensure progress in achieved physical and mechanical properties of the coatings with DND. Of interest is study the effect of the modified additives introducing into electrolyte on the properties of coatings and on the kinetics of electrode processes. Despite numerous studies in the field of chromium electroplating coatings, it is still remains unclear the mechanism of occurring electrode processes.

The dominant factor, in the opinion of many authors [7–9], in the reduction reaction of the chromate ions to the metal is forming on the surface of solid colloidal film. In general, the process limited by the electrochemical act flowing phasically. However, it remains unclear which the electrochemical step is the limiting one. In is It is assumed in papers [10–12], based on the determination the kinetic parameters of the electrode process in chromium electrolyte, the participation of different anions in the reduction reactions Cr (VI) → Cr (0), and Cr (VI) → Cr (III). Thus, the first reaction proceeds under electrochemical control, where the Limiting step is the first electron attachment, the second parallel reaction proceeds according to the mechanism of mixed kinetics is controlled by diffusion and electrochemical act. The presence of analogues investigated supplements - DND-TAN and diamond charge [2] in the standard chromium plating electrolyte leads to a slight increase in polarization in the reduction of chromate ions to the metal and concomitant hydrogen evolution reaction, reduces the rate of reduction of hexavalent chromium to trivalent state.

The aim of this work was to study the kinetics of recovery Cr (VI) → Cr (0) of standard chromium plating electrolyte in the presence of DND-boron modified additives (undermining charge TNT-hexogen (50/50) in H_3BO_3 aqueous solution) by recording partial polarization curves and studying its effect on some physical and chemical properties of the coatings. The difference between the proposed additive of DND-boron and DND-phosphorus (undermining charge TNT-hexogen in $NH_4H_2PO_4$ aqueous solution) from the DND-TAN is in nanodiamonds modifying by doping with boron and phosphorus, boron and phosphorus content of the DND-boron and DND-phosphorus is 0.08% – 0.1% by weight.

The paper also studied the effect of diamond-containing stock additives (synthesis intermediate of DND) obtained by modification of the charges TNT-hexogen (50/50) with silicon containing polymer (DCS (of Si)) and DCS obtained by TNT and hexogen charge undermining 50/50 in urotropine aqueous solution [13].

2. Experimental Part

The synthesis of detonation nanodiamonds (DND) was carried out in the Alfa-2M storage chamber, with a capacity of 2.14 m^3, manufactured by Sibenergomash, Barnaul, Russia. An explosive charge (an alloy of TNT and RDX, 50/50, weighing 0.7 kg) was placed in the center of the storage chamber in a plastic bag with distilled water or H_3BO_3 solution (or $NH_4H_2PO_4$ solution) and blasted. The gaseous medium in the chamber was the gaseous products of previous explosions. The intermediate product obtained after the explosion - the diamond charge (DCS) contains from 40 to 60% wt. contained from 40 to 60 wt.% DND.

DCS was purified with 10% nitric acid mixed with 10% ammonium nitrate solution at a temperature of 230°C and a pressure of up to 100 atm. in continuous mode. The resulting suspension of purified DNDs was washed with distilled water to pH~6.

Next, an aqueous suspension of DND (without drying) or an aqueous suspension of native AS was added to the galvanic bath. Doping of DND with phosphorus, boron or silicon was carried out during the explosion of charges placed in an aqueous solution of sodium biacid phosphate, H_3BO_3 or an explosive charge with a silicon-containing polymer in an amount of 3% wt.

DND-TAN was obtained by treating a suspension of DND (post-chemical purification) with an aqueous ammonia solution at a temperature of 220°C and a pressure of 40–45 atm [1].

The content of phosphorus in DND (doped with phosphorus) is 0.3% wt., the content of boron in DND (doped with boron) is 0.96% wt.

Experiments were carried out in an electrolyte composition, g/L: CrO_3 - 250, H_2SO_4 - 2,5 under constant and periodic electrolyte stirring to maintain additives in suspension at temperature of 50º-55ºC (a hard chromium

plating mode). Cathodic polarization curves (CPC) have been recorded by potentiostatic method in a wide potential range (+ 300 ÷ -1100 mV). CPC measuring inaccuracy in the potential was ± 20 mV. The partial cathodic polarization curves (PCPC) of chromate ions reduction to metal is calculated from the galvanostatic curves taken at different current densities, when fixing the amount of electricity passed, potential changes over time and to determine the amount of deposited chromium. Polarization curves (PC) have been recorded on IPC-Pro MF potentiostat in a temperature-controlled (± 0.50) cell without separating the electrode spaces. The reference electrode used is a saturated silver chloride electrode. (Potential values specified in the work are given with respect to the saturated silver chloride electrode). The test electrode, which is made of steel 20 (ST 20, Russia) (S = 1,04 cm^2), was mechanically polished, degreased and activated in 10% H_2SO_4 solution before recording the curves. DND-boron and DND-phosphorus have been introduced as an aqueous suspension in quantities of 2.5; 5.0; 10 g/L. The next physico-chemical properties are studied: microhardness on PMT-3 microhardness tester (Russia), wear on the device with the back-and-forth motions (LTI method, Russia).

3. Results and Discussion

Total potentiostatic curves (CPC), taken over a wide potential range (Figure 1) reflect the rates of several reactions: reduction of hexavalent chromium to trivalent $Cr^{6+} + 3e \rightarrow Cr^{3+}$ in the range of E −300 ÷ −700 mV; reduction of chromate ions to metal $Cr^{6+} + 6e \rightarrow Cr^0$, runs parallel with the hydrogen evolution reaction $2H_3O + + 2e \rightarrow H_2 + 2H_2O$ and formation of trivalent chromium $Cr^{6+} + 3e \rightarrow Cr^{3+}$ in the potential range −800 ÷ −1100 mV. As can be seen from Figure 1 DND-boron additive has an inhibiting effect on the process of Cr (VI) → Cr (III) (E = −300 ÷ −600 mV), growing with concentration increasing, as evidenced by a decrease in maxima reaction current and shift curves to more negative potentials. However, the effect of additive concentration on the current maximums ambiguous. The greatest effect is at high and low DND-boron concentrations. The beginning of the current rising potential shift in the region of negative values is 100–150 mV. According to [14], the reaction rate greatly influences the structure and composition of the primary film formed at the moment of immersion of the electrode into a solution and consisting of chromium oxide (Cr (VI) and Cr (III)). The reaction takes place in the mixed mode of the kinetics and the current drop caused by the diffusion-limiting surface blocking with film forming by reaction products [15].

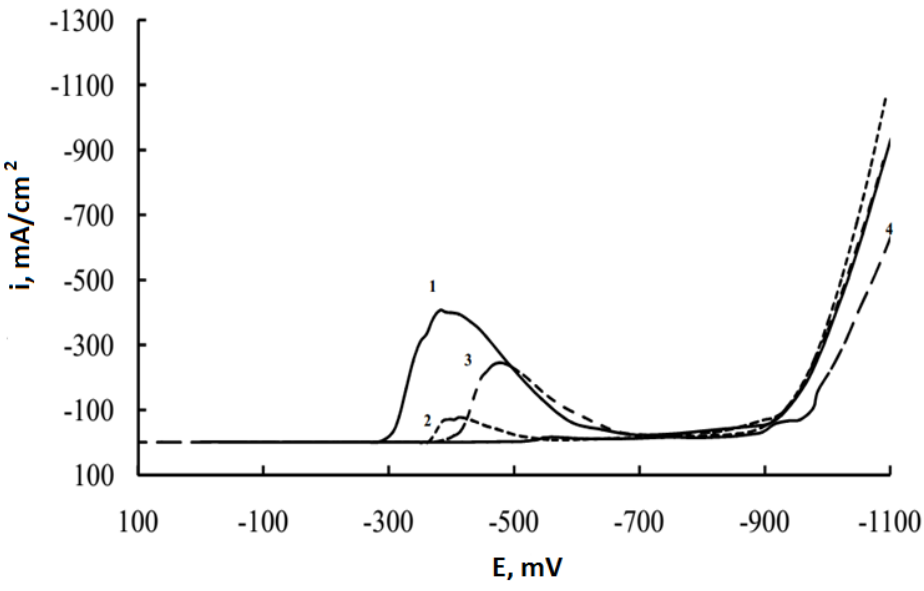

Figure 1. Cathodic potentiostatic curves taken in a chromium electrolyte in the presence of DND-boron with stirring. DND-boron concentration, g/L: 1–0; 2–2.5; 3–5.0; 4 – 10 (E – potential, mV; i – current density, mA/cm^2)

When recording curves it was observing that in the presence of a DND-boron in the solution currentless potential shift values to positive values at 200 ÷ 300 mV were higher than that of the additive-free solution, indicating some changes in the properties of primary film forming. The observed decrease in reaction rate at a concentration of additive 2.5 g/L is probably explained by adsorption of nanosized particulate fraction. It is known that the nanodiamonds high absorption capacity is possible due to particles present on the surface of oxygen-

containing functional groups of DND, such as: - COOH, - OH, - CHO, = CO [2]. With increasing concentration of the additive, due to agglomeration increasing the share of larger particles and thus amplifies the blocking effect of the particles penetrating into the film-forming Cr (III) compounds. It should be noted a possible additives mechanical effect on the surface of the electrode as the abrasive material. There is some increase in the viscosity of the solution with increasing concentration of the additive and, therefore, delivery and discharge of the reaction products are difficult. According to [2] the introduction of DND in the solution with concentration of 5 g/L leads to an increase in kinematic viscosity (at room temperature by 13% (from $1.244 \cdot 10^{-6}$ to $1{,}403 \cdot 10^{-6}$ m^2/s). During the deposition of metal particles suspended DND interact with the growing surface coating by electrostatic, adsorption and molecular forces.

Comparison of the reaction rate, occurring in solutions with DND-boron, was carried out with rates in a pure electrolyte and the electrolyte containing TAN-DND. The selected concentration of additives was 5 g/L, as indicated in these conditions the most significant change in the physico-mechanical properties of chromium coatings.

To calculate the partial chromium reduction rates, current efficiencies were determined depending on the current density in solutions with and without additives (Figure 2). Noted some differences in the nature of the influence of additives. At high current densities (500–700 mA/cm^2), both chromium additives reduce current efficiency (CE) at 1.0–1.5%, compared with pure solution. At low current density (25 A/dm^2) DND-TAN additive introducing causes an increase in the current efficiency by 4% as compared to pure electrolyte, while the DND-boron has almost no effect on current efficiency (Figure 2). Maximum CE of chromium electrolytes containing additives up to 20% at i = 70 A/dm^2. The main part of the current process is to release hydrogen. Gassing in the electrode layer increases the electrolyte resistance and makes greater the contribution in the resistive component of the measured value potential.

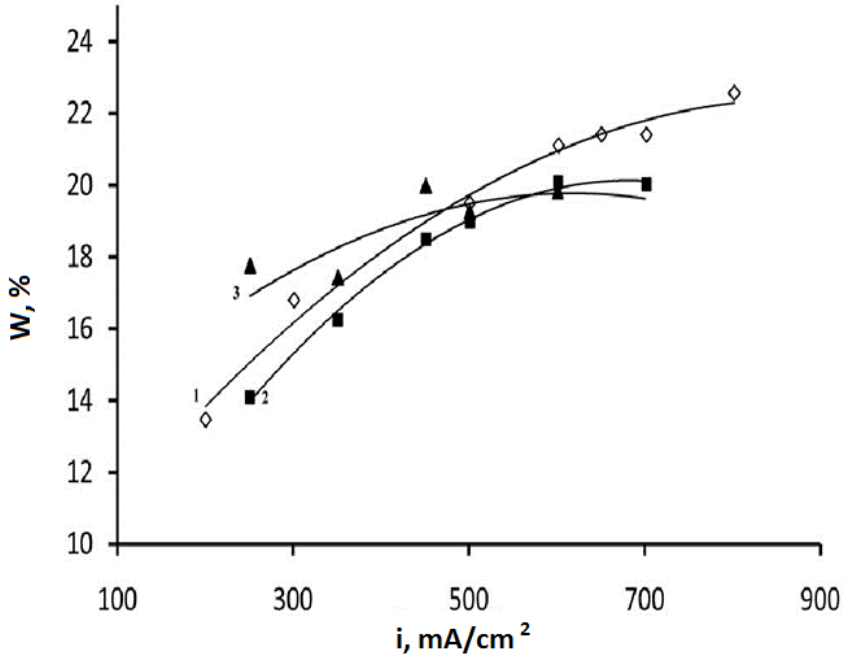

Figure 2. Dependence of the current efficiency of chromium on the current density in electrolytes: 1 - without additives, 2 - DND-boron, 3 - DND-TAN (i - current density, mA/cm^2, W - current efficiency, %)

The resulting dependence studies of the kinetics of deposition of chromium are linear, indicating that the reaction takes place under electrochemical control, in which the limiting step is the migration of the electron. The slopes of «b» E-lgi dependency in solution without additives and with DND-boron (132 and 125 mV, respectively) are close to 120 mV, indicating a limiting stage of the first electron attachment (α = 0,5). The solution with the addition of DND-boron straight line E-Lgi is shifting to more negative potentials the order of 35 mV, indicating the difficulty of the process is probably due to the embedding supplements into the film and the inclusion of additives in the growing sediment.

In [10–12] on the basis of the definition of basic kinetic parameters (transfer rate and reaction order for CrO_3 and H_2SO_4) has been suggested that film emerging in the chromium deposition is not a determining factor of the reaction kinetics. The data obtained by the authors with the chromium-based electrode at 200ºC was interpreting

due to the mechanism scheme proposed in [16]. According to [16] in the main process is assumed the anion part comprising three chromium ion $HCr_3O_{10}^-$. Of these, only one is electroactive chromium ion, the other two do not accept electrons. Limiting step in the whole process, it is the stage $HCr_3O_{10}^- + e \rightarrow HCr_3O_{10}^{2-}$.

The results presented here demonstrate that the presence of additives in the DND-boron and DND-TAN in the electrolyte reaction of chromium reduction proceeds with a large overvoltage compared with pure solution. It is known that electrochemical crystallization of metal greatly determined by the kinetic characteristics of the process (current exchange reaction, overvoltage and reaction mechanism), causing the structure and thus the physical and chemical properties of the deposited metal. Increasing the reaction overvoltage promotes deposition of a finely crystalline precipitation [17]. This fact for chromium coatings produced by deposition in electrolytes with DND-boron confirms with surface research results of DND-boron coatings conducted by scanning electron microscopy on the microscope SUPPA-55VP-25-78 (Zeiss) (Figure 3).

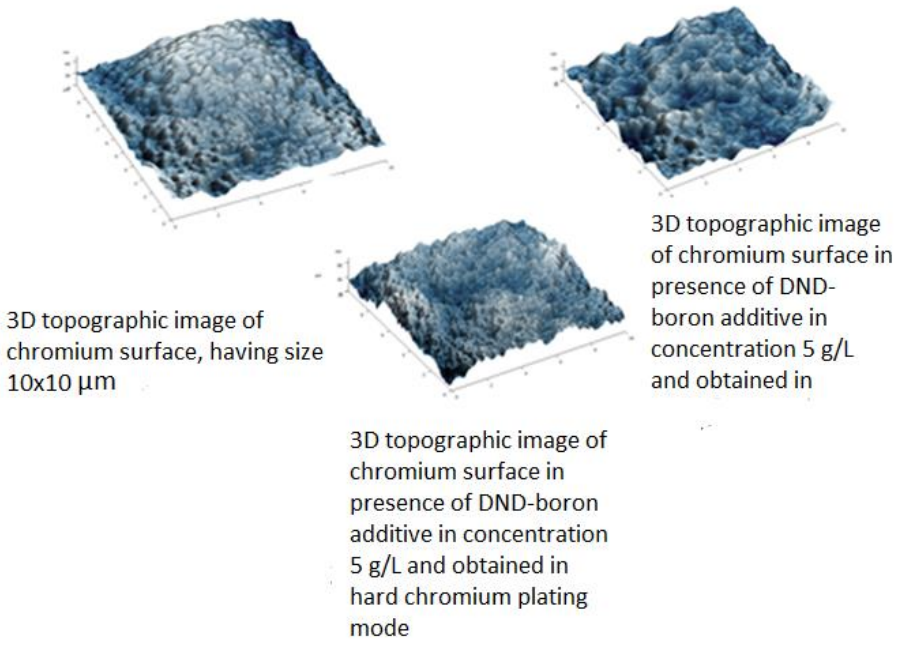

Figure 3. SEM - image of the surface of chromium coatings deposited in electrolytes without additives (a) and with DND-boron [2.5 g/L] (b). (Magnification 6000 times)

In the presence of additives precipitate a shiny, smooth, uniform coating on burning on the electrode edges disappears, especially typical for high current densities in pure solutions. Changing precipitation structure affects the microhardness and wear resistance of chromium coatings. Data on the effect of additives on the DND-boron microhardness chromium at 50°C and 55°C (hard and decorative chromium plating mode) is showing in Fig. 4 and 5. The microhardness increase at increase of concentration of the additive passes through curves with a maximum, in which in hard chrome plating mode is on the concentration 5 g/L, as is discussed in Section kinetic laws. Comparative data microhardness of chromium in the presence of DND of various modifications summarized in Table 1.

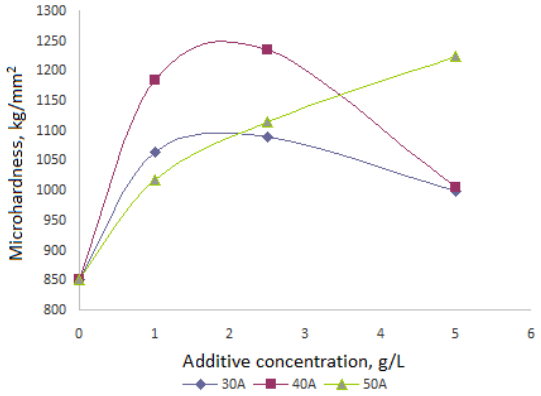

Figure 4. Microhardness [kg/mm^2] of chromium coatings depending on the concentration [g/L] of DND-boron additives, decorative chromium plating mode, t - 50ºC

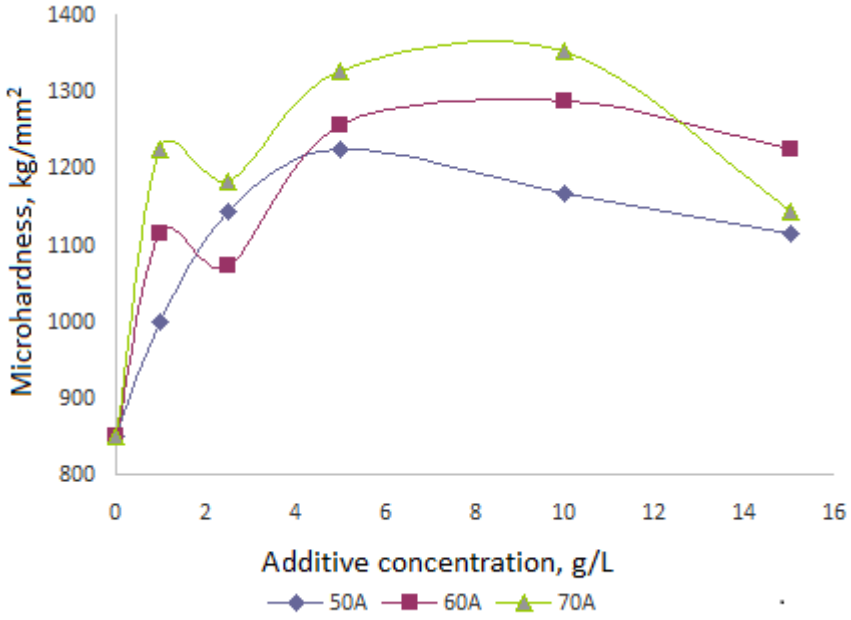

Figure 5. Microhardness [kg/mm^2] of chromium coatings depending on the concentration [g/L] of DND-boron additives, decorative chromium plating mode, t - 55ºC

Table 1. Chromium coatings microhardness, which are prepared in the presence of optimal minimally amounts of various DND modifications (5 g/L)

The concentration of additive	0		DND-TAN 5 g/L		DND-boron 5 g/L, boron modified		DND-phosphorus 5g/L, phosphorus modified	
t, ºC / Current density A/dm^2	55ºC	60ºC	55ºC	60ºC	55ºC	60ºC	55ºC	60ºC
50	940	-	1050	-	1427	-	932	-
70	955	-	1150	-	1430	-	1017	-
35	-	925	-	950	-	1280	-	1017
45	-	930	-	1050	-	1160	-	1017

Comparison of the DND-TAN additive and modified with boron and phosphorus at the same concentration (5 g/L) have shown that the greatest impact on micro-hardness has an additive modified with boron in the hard chrome plating mode, reaching a value of 1430 kg/mm^2, which is 50% more than microhardness of pure chromium. All additives DND in both modes increase the microhardness of chromium coatings. Apparently, boron compounds included in DND contribute to the embedment of the particle to a greater extent than pure DND-phosphorus and DND-TAN, thus there is a strong grain refinement, as shown in Fig. 3 dedicated to chromium in 3D microstructure modification. Comparative results of the wear resistance of chromium coatings produced from electrolytes with modified additives shown in Table 2.

Table 2. Comparative coating wear resistance values obtained from electrolytes with new DND-modified additives

The concentration of additive, g/L	Temperature 55-60ºC		Temperature 50-55ºC	
	25 A/dm^2	35 A/dm^2	60 A/dm^2	70 A/dm^2
without additive	-	4,8	6,2	4,3
DND-TAN, 5	-	2,0	-	2,80
	-	2,2	3,3	-
DND-boron, 5	2,8	1,42	3,4	1,8
	2,85	0	1,7	0,9
DND-phosphorus, 5	-	0,4	-	0,5
	-	2,5	-	0,5
DCS (silicon modif.), 5	-	0	-	0
DCS (reducing agent), 2,5	-	2,4	1,9	2,0

It should be noted that all tested coatings produced from electrolytes with nanodiamond additives, showed better results than chromium coating obtained from standard electrolyte. Coatings produced with DND-TAN additives to the electrolytes 2-3 times better in wear resistance than pure chromium. Coatings obtained with the addition of electrolyte DCS (Si) (silica-modified) in the modes of wear and hard chromium were virtually no wear (weight loss of 0%). DND-phosphorus and boron modified additives in chromium plating electrolytes have also shown good results in both electrodeposition modes. Best results are shown coatings obtained with the electrolyte addition of DND-phosphorus (compared to coatings obtained from electrolytes with DND-TAN and DND-boron). The wear resistance of the coating produced from the electrolyte with DND-phosphorus is 3–4 times higher than the wear resistance of the coating prepared from electrolyte-containing DND-boron additives. These data suggest that all the additives investigated in consideration of the entire set of properties can be used for a variety of coatings uses.

Corrosion tests were conducted for the samples with various additives shown that the samples with the addition of DND-boron (at a concentration of - 5 and 10 g/l) in the wear chromium mode gives the best results, that can be associated with significantly lower chromium coatings fracture obtained in wear resistant chromium mode, and all the presented additives created conditions for a strong grain refining, as indicated by the research results of the microstructure.

4. Conclusions

1. Studies of coating microstructure (lattice parameters) showed that for the samples obtained from electrolytes containing TAN-DND and DND-boron lattice distortion is more pronounced than for the coatings obtained from the standard chromium plating electrolyte. It can be concluded the inclusion of additives in the coating.

Submicroscopical study of the surface structure of the chromium precipitations have shown that DND-TAN and modified additives influence on the microstructure of chromium coatings. The addition of DND-TAN

contributes to obtaining coatings with a minimum number of microcracks. With the introduction of DND-TAN precipitation in the electrolyte, structure is a uniform and dense.

2. Of the atomic force microscopy data of coating obtained with the modified additives (DND-boron), have a finer grain structure than DND-TAN. The peaks (3D representation of the topography of the sample surface) for coatings produced in hard chrome mode of electrolyte with the addition of DND-boron are 2–3 smaller size (5–6 nm) and are denser, not having boundaries between the crystallites.

With the introduction of DND-TAN and DND-modified additives to the electrolyte the microhardness of chromium coatings increases.

3. Increased microhardness of chromium coatings in the presence of DND-TAN, DND- boron and DND-phosphorus can be associated with the embedment of particles of nanodiamond materials in chrome plating and grinding grain coating. This once again confirms surface-active properties of nanodiamond additives.

4. A study of microhardness of the coatings obtained from the electrolyte with DND-TAN and DND-boron has shown that the dependence of microhardness has two maxima (in the field of small concentrations of additives 1, 0 g/l, and at high values 5–10 g/l). Moreover, the highest values of (1430–1440 kgf/mm^2) are obtained in 5.0 g/l DND-boron additives (boron). Boron-modified DND in the hard chromium plating mode, besides its effect as a surfactant, apparently can produce embedment of boron in the coating. This can dramatically change the structure of the coating (creating intermetallic compounds) and distort the lattice parameters.

5. The wear resistance of chromium coatings is increased by 2–3 times with the introduction of DND-TAN in the standard chromium plating electrolyte. Increased wear resistance of chromium coatings obtained from electrolytes containing nanodiamond materials are obviously due to the lower gas dissolving in precipitations, which should reduce internal stresses in the coatings, as well as the favorable effect of additives on the changes in the structure.

6. Modified additives added to the electrolyte chromium plating, showed significantly better results to improve the wear resistance of coatings than the addition of DND-TAN. The best results were obtained with an additive in the electrolyte DCS-Si (silicon-modified). Coatings obtained from electrolyte in its presence hardly worn out, and the coating obtained from an electrolyte in the presence of DND-phosphorus additives is 3 times higher wear resistance than coatings prepared from electrolyte with additive DND-TAN. This may indicate that the modifier elements reduce the gas absorption, particularly hydrogen, as shown in theoretical studies and improving the current efficiency by 6–8% compared to coatings prepared from the standard electrolyte. Additionally, boron, phosphorus, silicon can distort the structure, compressing it, the boundaries between crystallites decrease, as shown by studies of the microstructure of atomic force. Carried out corrosion tests in a salt spray chamber showed that the samples obtained from the electrolyte with the addition of DND-boron in both solid and wear-resistant chromium plating mode protect from corrosion are 2–3 times better than a chromium coating formed from standard electrolyte. The thickness of the coating for all the samples was 20 microns.

7. This work was carried out under the Agreement on the provision of subsidies from the June 5, 2014 №14.579.21.0001 between FSUE "SCTB" Technolog" (Russia) and the Ministry of Education and Science of the Russian Federation, the federal program.

References

[1] Method for obtaining a stable suspension of detonation nanodiamonds [Text] : Pat. 2384524 Ros. Federation: 29.04.2008
[2] Dolmatov V.Yu. The detonation nanodiamonds. Preparation, properties and applications. Saint-Petersburg: NPO "Professional", 2011, P. 536
[3] Burkat G.K., Dolmatov V.Yu., Osawa E., Orlova E.A. Superhard materials. 2010. №2. P. 43
[4] Vashchenko SV Solovyova ZA Electroplating and Surface Treatment. 1992. Vol. 1. №5-6. P. 45
[5] Burkat G.K., Dolmatov V.Yu., Orlova E.A. Powder Metallurgy - Kiev. 2003. № 42. P. 587
[6] Tikhonov K.I., Burkat G.K., Dolmatov V.Yu., Orlova E.A. ZHPH. 2007. Vol. №7. P. 1112
[7] Vahramyan A.T., Usachev D.N. Izv. USSR Academy of Sciences - Vilnius. Gospolitnauchizdat. 1959. № 7. P. 194
[8] Shluger M.A., Kazakov V.A. ZHPH. 1960. T.33. №. 3. P. 644
[9] Vahramyan A.T., Solovyova Z.A. Results of science and technology. VINITI. Ser. Electrochemistry. 1966. № 1. P. 166
[10] Efimov E. Electroplating and Surface Treatment. 1992. Vol.1. №1-2. P.14
[11] Efimov E. Electrochemistry. 1996. Vol.32. № 6. P.776
[12] Efimov E., Current LD Electrochemistry. 1991. Vol. 27. № 1. P.111

[13] Pat. of Russian Federation №2359902 «Diamond-carbon material and its production method», priority of 30.12.2005, Registered. 27.06.2009, BI № 18 (application PCT RU 2005/000685 (30.12.2005), publ. PCT WO 2007/078209 (12.07.2007)
[14] Kudryavtsev Yu. D., Simchenko D.P., Pylypenko A.G. et al. Electrochemistry. 1974. Vol.10. № 3. P.395
[15] Efimov E.A., Tverdynina T.B. Current LD Electrochemistry. 1989 Vol. 25., №10. P.1398
[16] Houre J.P. J. Electrochem. Soc. 1979. V.126. P.190
[17] Hamburg Yu.D. Electrochemical crystallization of metals and alloys. Moscow: Janus-K, 1997. P. 384