The Study of Obtaining Composite Nickel Electroplatings with Detonation Nanodiamonds and Diamond Charge

V.Yu. Dolmatov [1]*, G.K. Burkat [2], I.V. Safronova [2], A. Vehanen [3],
V. Myllymäki [3], V.A. Marchukov [1], N.S. Almazova [1], Yu.V. Litovka [4], I.A. Dyakov [4]

[1] *Special Design and Technological Bureau "Technologist", 33-a, Sovetskiy pr., St. Petersburg, 192076, Russia;*
[2] *St. Petersburg State Technological Institute (Technical University), 26, Moskovsky pr., St. Petersburg, 190013, Russia;*
[3] *Carbodeon Ltd. Oy, 5, Pakkalankuja, Vantaa, 01510, Finland;*
[4] *Tambov State Technical University, 106, Sovetskaya st., Tambov, 392000, Russia*

* Corresponding author. Tel.: +7 812 700 23 10; +7 812 244 73 73. *E-mail*: diamondcentre@mail.ru

Abstract

The paper presents the results of studying the nickel electroplating process in the presence of nanodiamond additives. It shows that the use of detonation nanodiamonds (DND) and diamond explosive charge (DC) obtained by explosion of tetryl (N-methyl-2,4,6-trinitrophenylnitramine) can significantly improve the physicochemical properties of nickel platings: increase the microhardness up to 60 % (up to 448 kgf/mm^2 – 4393 MPa), obtain a non-porous nickel plaiting and reduce wear up to 28 times. The most effective was the use of non-expensive nanodiamonds, but cheap diamond charge obtained by the explosion of tetrile.

Introduction

Chromium and nickel electroplaitings are quite widespread in mechanical engineering. However, the widespread use of nickel plaiting is hindered by low wear and corrosion resistance.

The study [1] showed that to achieve high microhardness, wear and corrosion resistance, it is necessary to apply the plaiting from electrolytes containing additives of nanomaterials.

It is known that DND was used under the patent [2]. The disadvantages of this method include the high volume of labor costs for preparing the DND suspension in the electrolyte (up to 50 hours at a temperature of 55 °C); the need to introduce a suspension of nanomaterials into the electrolyte in equal small portions; low stability of nanodiamonds in the electrolyte; low quality indicators of composite nickel plaiting.

The composite nickel plaiting with a microhardness of 292–374 kgf/mm^2 (2864–3668 MPa) was obtained from an electrolyte [3] containing salts of

nickel sulfates and DND with a concentration of 2 to 42 g/L at a high current density of 15 A/dm^2. The disadvantages of this method include the high energy consumption, high consumption of nanodiamonds, as well as complex operations for the preparation of nanodiamonds (treatment of DND with acids, alkalis, and disintegrator) to the introduction into the electrolyte with a modest result.

In [4], when applying Ni-DND plaiting from the classical Watts electrolyte, the authors managed to increase the microhardness from 242 to 412 kgf/mm^2 (from 2373 to 4040 MPa), while the concentration of DND-TAN was 2 g/L, and the current density was 1 or 2 A/dm^2. The wear of such a plaiting dropped by 2–4 times. DND was obtained by the explosion of an alloy of TNT with hexogen in a 50/50 ratio.

In [5], the effect of a diamond charge, an intermediate product of DND synthesis, also obtained by the explosion of an alloy of TNT with hexogen, on the nickel plaiting deposition process and its results was studied. The classical Watts electrolyte was also used.

Even more significant results were obtained: at a DC content of 5 g/L and a current density, the microhardness increased from 280 to 520 kgf/mm^2 (from 2746 to 5100 MPa), the wear of the plaiting fell from ~ 23 % to ~ 1 %, i.e. the wear resistance increased by ~ 23 times, and the porosity of the Ni-AL plaiting decreased from ~ 17 % to 2.5 %.

The aim of this work is to obtain low-porosity and wear-resistant nickel platings by adding detonation nanodiamonds and diamond charge obtained by the explosion of tetryl (N-methyl-2,4,6-trinitro-phenylnitramine) to the electrolyte.

Experimental part

Obtaining nanodiamonds and electrolysis mode

A diamond charge was obtained by detonating charges from an individual explosive (tetril) in an Alfa-2M explosive chamber with a capacity of 2.14 m^3. Detonation nanodiamonds (DND) were obtained from DC by purifying it with a mixture of 10 % wt. HNO_3 with 10 % wt. NH_4NO_3 [6].

The object of the research was an electrolyte close in composition to Watts's electrolyte and contained:
  – heptahydrate nickel sulfate – 205–215 g/l;
  – sodium chloride – 11–16 g/l;
  – boric acid – 21–26 g/l;
  – pH – 4.1–4.4;
  – electrolysis temperature, average 19 °C;
  – current density – 0.6–2.1 A/dm^2.

The working electrode was a nickel-plated copper plate. The auxiliary electrodes were pure nickel plates. Polarization curves were recorded in potentiostatic mode. Each experiment was repeated 2 or 3 times.

Determination of corrosion currents

An IPC ProMF potentiostat was used to determine the corrosion currents. Corrosion curves were recorded in an aqueous 3 % NaCl solution in a potentiostatic mode (1 mV/s). Cathodic curves were obtained in the range of –1780 to 2110 mV and anodic curves were obtained in the range of –1780 to 1710 mV.

Procedure for determining corrosion resistance

A KKI 1 salt spray chamber was used.

For conducting the tests, a sodium chloride solution with a concentration of (50 ± 5) g/dm^3, pH 6.5–7.2 was used according to GOST 9.308–85.

While testing, the samples were placed in a KKI 1 chamber heated to a temperature of (35 ± 2) °C and exposed to salt fog. During the tests, the solution was sprayed continuously. The average filling rate of the solution in each collector for 24 h was 1–2 cm^3/h. At the end of the tests, the samples were removed from the chamber. The assessment of corrosion damage was carried out in accordance with GOST 9.311–87 and GOST 9.908–85.

Methods for determining microhardness

The microhardness tester PMT-3 was used.

The microhardness measurement was based on the method of static indentation of a diamond pyramid under a low load (20 g) into the plaiting under study. The measurements were carried out in accordance with GOST 9.450–76. The resulting rhombic imprint (on the thin section of the plaiting) was observed under a microscope. The average value of the imprint diagonal was taken from 9 to 13 measurements on each sample.

The microhardness value (MPa) was calculated by the formula:

$$H_\mu = \frac{1854P \cdot 9.8}{(0.3d)^2},\qquad(1)$$

where P is the load, g; d is average diagonal of the print, μm.

In order to measure the microhardness, plaitings with a thickness of 15 μm were applied to the steel base, which exceeds the minimum thickness of galvanic deposits in the case when the base is softer than the plaiting. The average microhardness value was obtained from five experiments. The measurement error was ± 6 %.

Procedure for determining porosity

The potentiostat IPC ProMF was used.

The porosity in this work was measured by the method of anodic polarization curves in a 0.1 N solution of potassium thiocyanate on a steel sample with a nickel plaiting. On the recorded polarization curves, we chose the potential at which the steel dissolves and the nickel plaiting was in a passive state. At this potential, current-time curves were recorded. The pore area in the plaiting was calculated using the formula:

$$S_{pore} = i_{st} + Ni/i_{st},\qquad(2)$$

where $i_{st} + Ni$ is constant anode current established at the selected potential on steel with nickel plating, mA/cm^2; i_{st} is constant anode current established at the selected potential on steel, mA/cm^2.

The thickness of the investigated plaiting was 5 μm. The average porosity value for each type of plaiting was obtained from 3 to 5 experiments. The measurement error was ± 5 %.

Discussion of the results

Micrographs of nickel plaiting

The addition of DND-TAN (T) and DC (T) to the nickel-plating electrolyte led to a change in the plaiting structure as compared to the structure of similar plaiting that did not contain nanodiamond additives.

Fig. 1 demonstrates that the surface of the nickel plaiting without nanodiamond additives is inhomogeneous and has a clearly pronounced layered structure. The microcracks are observed which increases the porosity of the plaiting. The nickel grain size is ~ 240 nm.

Adding only 1 g/l of DND-TAN (T) to the electrolyte causes a change in the plaiting structure (Fig. 2). The nickel plaiting becomes more uniform, but its layered structure is retained, microcracks are less pronounced, and the formation of aggregated DND-TAN (T) particles is visible on the surface. The nickel grain size dropped from 240 to 215 nm. It was previously shown that DND, especially DND-TAN (T), have surface-active properties and affect the structure of the plaiting.

An increase in the concentration of DND-TAN (T) in the electrolyte (Fig. 3) significantly affects the structure of the plaiting – the nickel deposit becomes much more uniform and the number of cracks decreases. The nickel grain size naturally drops to 145 nm, as a larger number of nanodiamond particles gives rise to a larger number of nickel crystallization centers.

As can be seen from Fig. 4 DC (T), has a more significant effect on the structure of the nickel plaiting than DND-TAN (T) of the same concentration in the electrolyte. The leveling of the nickel deposit surface and a significant decrease in the number of cracks are observed. Aggregates of various sizes are visible on the deposit surface. Faceted particles are noticeable at higher magnification. In this case, not only nanodiamond particles but also graphite-like carbon particles are introduced into the nickel plaiting. Nickel grains are ~ 185 nm in size.

With an increase in the concentration of DC (T) in the electrolyte to 5.0 g/l (Fig. 5), the nickel deposit surface is further leveled and fracturing decreases and, accordingly, the porosity decreases. Like DND-TAN (T), DC (T) has pronounced surfactant properties that affect the surface tension of the electrolyte. On the surface of the nickel deposit, both rather large and small aggregates are clearly visible, which shows a significant difference in the particle size in the DC (T). The average nickel grain size in the plaiting is ~ 170 nm.
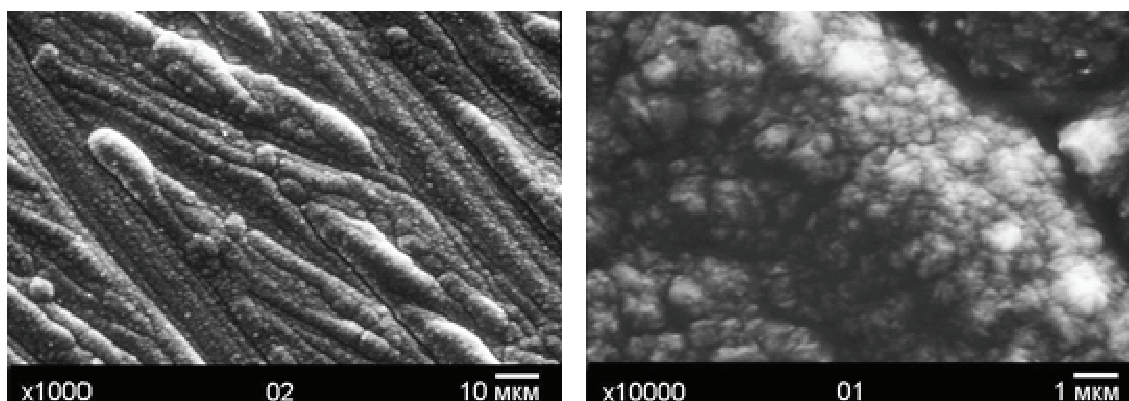

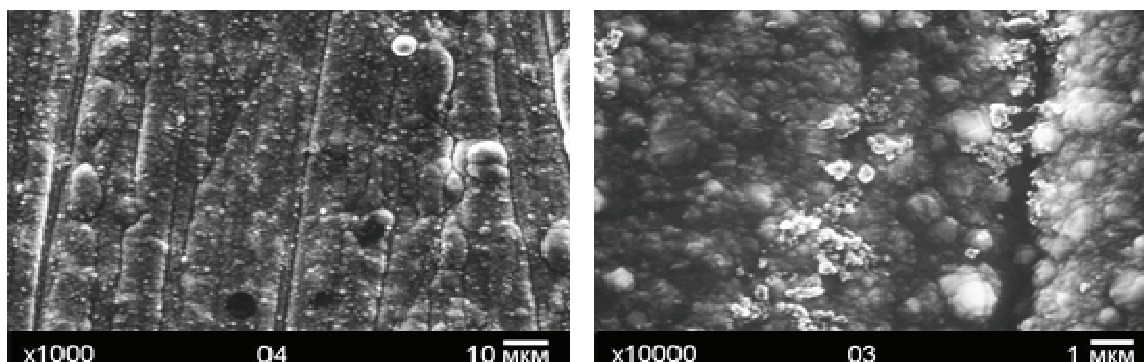**Fig. 1. Micrograph of nickel plaiting (without nanodiamond additives)**

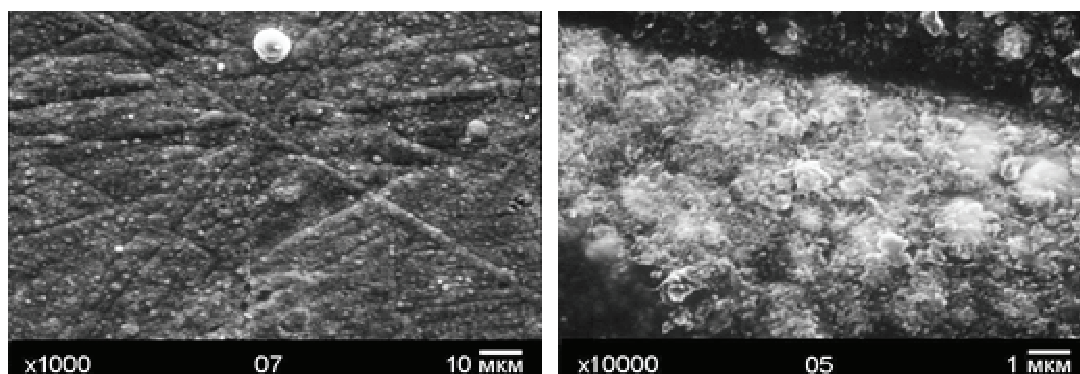**Fig. 2. Micrograph of the nickel plaiting (DND-TAN (T) 1.0 g/l)**

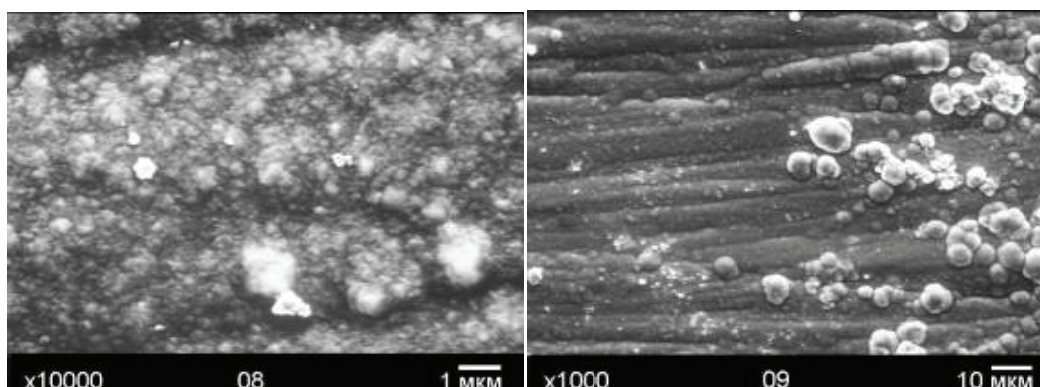**Fig. 3. Micrograph of the nickel plaiting (DND-TAN (T) 5.0 g/l)**

Fig. 4. Micrograph of the nickel plaiting (DC (T) 1.0 g/l)
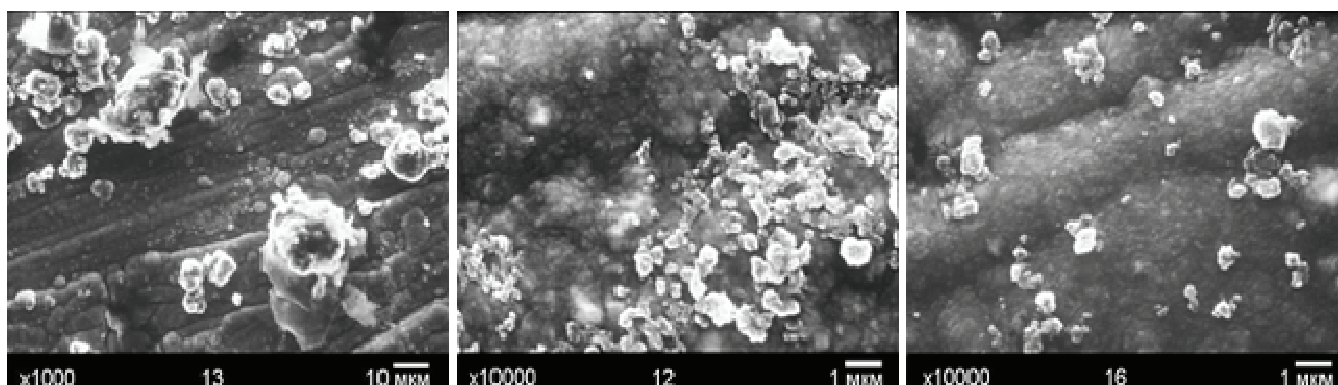

Fig. 5. Micrograph of the nickel plaiting (DC (T) 5.0 g/l)

The dissipative power of the electrolyte

To assess the scattering ability of the nickel-plating electrolyte (uniformity of plaiting) with DND-TAN (T) and DC (T), the electrical conductivity of electrolytes was studied at first (Table 1).

The addition of low-conductivity tetrile DND-TAN (T) leads to the insignificant increase in the electrical conductivity of the electrolyte, while the use of tetryl DC (T) significantly increases the electrical conductivity. This is due to the fact that the surface of tetryle DC (T) contains a noticeable amount of unsaturated carbon bonds, including carbonyl groups, as well as amine and amide groups. Due to this, as well as the graphite component of the DC (T), electronic transfer occurs between the particles of the DC (T) and the redox particles in the electrolyte or on the electrode.

The quality and properties of plaitings are largely determined by the uniformity of metal distribution over the layer thickness, i.e. scattering power, and the scattering power depends on the polarizability and electrical conductivity, which characterize the criterion of electrochemical similarity G. It is often used to determine the current dissipation of electrolytes.

Table 1

Influence of temperature on the electrical conductivity of electrolytes χ, (cm/cm^2)·10^2

Nanodiamond additive, g/l	Temperature of electrolyte, °C			
	50 ± 1	40 ± 1	30 ± 1	20 ± 1
–	8.13	7.21	6.06	4.82
DND-TAN (T), 1.0	8.23	7.50	6.20	5.07
DND-TAN (T), 2.0	8.62	7.85	6.61	5.19
DND-TAN (T), 5.0	8.58	7.93	6.66	5.62
DC (T), 1.0	11.47	9.97	8.88	7.50
DC (T), 2.0	11.39	10.03	8.92	7.40
DC (T), 5.0	11.88	10.33	9.09	7.80

The polarizability $\Delta E/\Delta i_k$ was determined from the corresponding polarization curves, and the electrical conductivity of the electrolyte χ was measured using a conductometer. The same electrolyte was chosen as the basic composition of the electrolyte, while the concentration of additives in the electrolyte was insignificant, therefore, most likely, it was the polarizability value that would have the greatest effect on the value of G. Initially, the electrical conductivity of the electrolyte with DND-TAN (T) and DC (T) was determined.

It is known that electrolytes for nickel plating have poor scattering ability, and the electrical conductivity of the electrolyte increases G. Table 2 shows that the presence of DC (T) increases the electrical conductivity by ~ 1.5 times, which is associated with the presence of graphite-like components in the DC (T). Therefore, DC (T) can have a significant effect not only on the G-factor, but also on the properties of the applied plaiting.

Table 3 provides an estimate of the G-factor for nickel electrolytes. The addition of DNA-TAN (T) at a concentration of 5 g/l increases the G-factor by ~1.4 times. However, the addition of DC (T) at only 2 g/l increases the G-factor by ~1.96 times.

Nickel current output

Nickel current efficiency is an important characteristic of nickel plating electrolyte (Table 4). Earlier it was shown that the use of DC (T) increases the overpotential of hydrogen evolution and thereby increases the nickel current efficiency as the concentration of DC (T) increases up to 97–99 %. However, the use of DND-TAN (T) does not allow increasing the current efficiency of nickel: it remains within 91–93 %, which agrees with the hydrogen curves for electrolytes both without this additive and with it.

Thus, when using DC (T), we can raise the nickel current output to 97–99 % (maximum value).

Table 2

**Influence of DND-TAN (T) and DC (T) concentration
on the electrolyte conductivity χ (cm/cm)·10^2 from concentration**

Nanodiamond additive	The amount of nanodiamond additives, g/l			
	–	1.1	2.1	5.2
DND-TAN (T)	4.882	5.056	5.181	5.618
DC (T)	4.882	7.304	7.497	7.798

Table 3

Criterion of electrochemical similarity for electrolyte with nanodiamond additives, Δi_k=0,01 A/cm^2

Additive content in nickel electrolyte, g/l	ΔE, B	Electrode polarizability $\Delta E/\Delta i_k$, Ohm·cm^2	Electrical conductivity of the solution χ, (cm/cm^2) · 10^2	Coefficient of electrochemical similarity $G = \chi \cdot \Delta E/\Delta i_k$, cm
–	0.051	4.882		24,0
DND-TAN (T) – 1.0	0.051	5.056	5.1	24.2
DND-TAN (T) – 2.0	0.049	5.181	4.9	25.2
DND-TAN (T) – 5.0	0.059	5.618	5.9	33.4
DC (T) – 1.0	0.056	7.497	5.6	42.1
DC (T) – 2.0	0.066	7.304	6.6	47.3
DC (T) – 5.0	0.062	7.798	6.2	48.2

Table 4

Nickel output (with DC and DND) by current

DC and DND-TAN (T) content, g/l	i_k, A/dm^2			
	1.1	1.3	1.6	1.8
DC				
–	93	94	92	92
1.1	95	96	96	96
1.6	93	92	95	95
2.1	99	94	95	93
5.2	97	100	95	91
DND-TAN				
–	93	94	92	92
1.1	92	91	93	91
2.1	93	91	91	92
5.2	91	92	92	91

Table 5

Microhardness of plaiting, MPa

Additive	Content of electrolyte additives, g/l	i_k, A/dm^2	
		1.1	2.1
–	–	2736	2324
DC (T)	1.1	4393	3119
	2.1	3472	3481
	5.2	3893	3226
DND-TAN (T)	1.1	3746	3344
	2.1	3746	3472
	5.2	3893	3472

The introduction of diamond additives increases the microhardness of the nickel plaiting in comparison with the nickel plaiting without nanodiamond additives. The difference between the effect on the microhardness of DND-TAN (T) and DC (T) is small: in the first case, the increase in microhardness is 40–48 %, and in the case of using a tetrile mixture it is 41–43 %. However, for nickel plating, the microhardness is only a preliminary approximate value for assessing the physicochemical properties. The wear resistance and corrosion resistance of the plaiting are of paramount importance.

Microhardness of nickel-diamond plaiting

During electrochemical deposition, DND-TAN (T) and DC (T) particles are embedded in the crystal structure of the plaiting forming dislocations in the deposit and changing the strength properties of nickel. In addition, DND-TAN (T) and DC (T) particles embedded in the plaiting are microbarriers when microcracks appear which also strengthens the nickel plaiting. In the previous studies it was shown that DND and DC have surface-active properties which contributes to the decrease in the grain of the nickel plaiting.

Table 5 shows that the use of DC (T) and DND-TAN (T) leads to the significant increase in the microhardness of the nickel plaiting.

Wear resistance of the nickel plating

Tribochemical processes are very complex and in this work we consider only the resultant abrasion of samples with pure nickel and nickel-diamond plating. The wear of the plating during abrasion was determined by weighing, and the results are shown in Figs. 1 and 2.
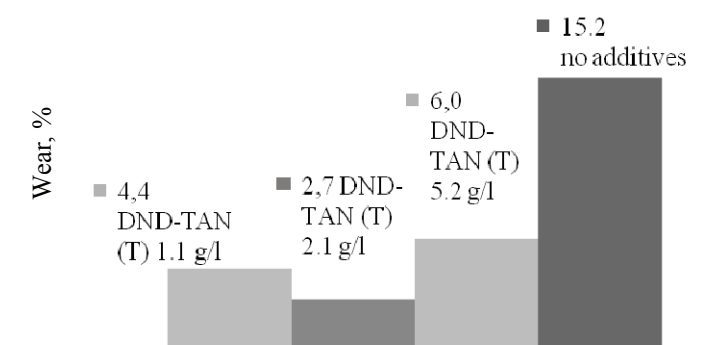
Fig. 6. Wear diagram of nickel electrolyte plating with DND-TAN (T), i_k additive 1,1 A/dm^2

Fig. 7. Wear diagram of the deposit samples of a nickel electrolyte with the DC addition, current density 1A/dm^2

Since the DC (T) contains a significant amount (62 % wt.) of diamond nanocrystals, and DND-TAN (T) consists almost entirely of DND, the latter are embedded in the nickel plating and create a composition that is sufficiently resistant to abrasion. At the same time, DC (T) contains 38 % wt. graphite-like structures. Thus, getting into the plating, nanographite significantly reduces the coefficient of friction and the combined action of DND and nanographite reduces wear by ~ 28 times, but the use of individual DND-TAN (T) leads to a decrease in wear only by ~ 6 times.

Porosity of the nickel-diamond plating

Obtaining a non-porous nickel plating is critical. As a rule, electrochemical nickel plating is almost always porous. At the same time it is a cathode plating and can protect the matrix from possible corrosion only in the absence of pores. Studies of the porosity of the platings were carried out by obtaining anodic polarization curves (current-time).

Porosity of Ni-DC (T) platings

The current-time curves for a plating obtained from a nickel electrolyte with different concentrations of DC (T) are located in the region of very low current loads, and in the presence of DC (T), the curves are located significantly lower than the curve obtained from an electrolyte without additives, which indicates a decrease in porosity.

Table 6 shows the calculation of the pore area for the deposition of nickel platings. Table 6 shows that the minimum porosity is available for the nickel plating at a current density of 1.1 A/dm^2 and DC (T) concentration in the electrolyte of 1.1–1.6 g/l. It is 515 times less than that of the plating without additives. At the same time, nickel platings obtained at DC (T) concentration in the electrolyte of 2.1 g/l and a current density of 1.1–1.6 A/dm^2 have quite acceptable porosity.
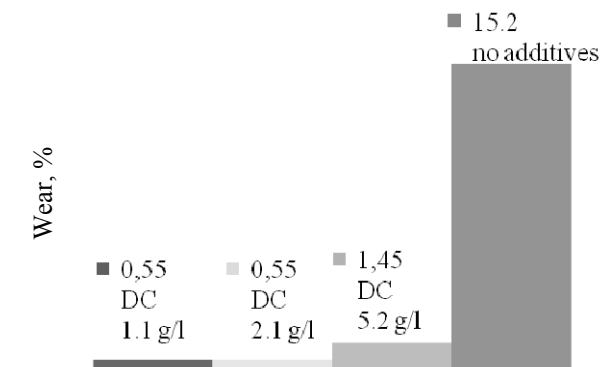
Table 6

**Pore area of nickel platings
(electrolyte with DC (T))**

Plating pore area with DC, %				
Content of DC (T) in electrolyte, g/l	i_k, A/dm^2 Plating thickness – 3 μm			
	1.1	1.3	1.6	1.8
Pure Ni	20.7	23.2	32.6	47.1
1.1	0.16	4.6	2.3	3.7
1.6	0.04	1.6	4.0	8.5
2.1	1.2	1.5	1.6	9.7
5.2	5.7	9.3	6.3	1.2

Porosity of Ni-DND-TAN (T) platings

The data obtained from the current-time curves for a nickel electrolyte plating with different concentrations of DND-TNA (T) are shown in Table 7.

Table 7

Pore area of nickel platings with DND-TAN (T)

Content of DND-TAN (T) in electrolyte, g/l	Pore area i_k, A/dm^2 Plating thickness – 3 μm			
	1.1	1.3	1.6	1.8
–	20.7	23.2	32.6	47.1
1.1	16.0	16.0	23.1	20.3
2.1	26.9	19.4	18.2	7.6
5.2	11.7	20.4	14.1	8.0

Table 8

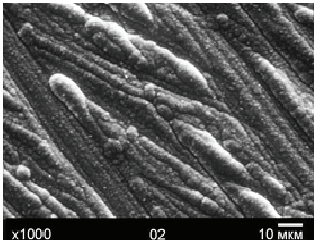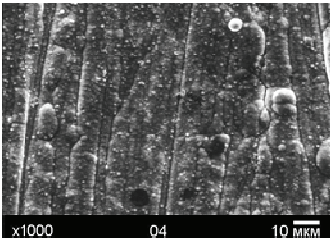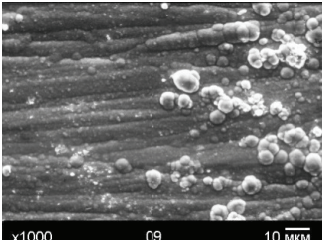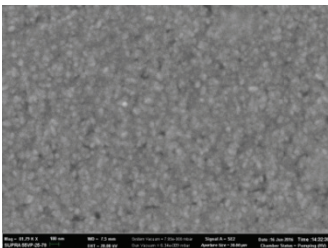**Physicochemical properties of the nickel plating including DND-TAN (T) and DC (T)**

Properties	Current density 1,1 A/dm^2		
	Electrolyte with out additives	Electrolyte with DND-TAN (T) 1,1 g/l	Electrolyte with DC (T) 1,1 g/l
Micrograph of the deposit surface			
Microsection structure			–
Microhardness, MPa	2628	3746	3217
Pore area, %	20.7	16.0	0
Wear, %	15.2	4.5	0.55

Table 7 shows that the lowest porosity is achieved when using DND-TAN (T) with a concentration of 2.1–5.2 g/l in nickel electrolyte at a current density of 1.8 A/dm^2 ($\sim$ 6 times less than that of the nickel plating without additives). However, the pore-free nickel plating obtained with the DC (T) introduced into the electrolyte is incomparable with the quality of the same plating when using DND-TAN (T), where the significant porosity is observed.

The obtained data on porosity are consistent with the results of determining the corrosion resistance in the salt spray chamber. The final data, including micrographs of the surface of thin sections of nickel platings, are given in Table 8.

Comparison of the data in Table 8 implies the absolute advantage of using DC (T) in the nickel co-deposition from the classic Watts electrolyte – the microhardness is entrained by 60 % (compared to nickel plating without additives); the pore area is reduced from 20.7 % (very high porosity) to practically zero, and the wear is reduced by 27.6 times.

Conclusion

1. Additives DND-TAN (T) and DC (T) have a strong effect on the microstructure of the nickel deposit during its electrochemical deposition, thickening the deposit and reducing the nickel grain size.

2. The microhardness of the plating increases up to 60% when using nanodiamond additives.

3. The wear resistance of the nickel plating when using DND-TAN (T) and DC (T) increases up to 28 times. The use of DND-TAN (T) turned out to be significantly less effective than the use of DC (T).

4. The use of DC (T) makes it possible to obtain practically pore-free nickel plating, while DND-TAN (T) allows to reduce the porosity by only 6 times at best.

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