Japan Bilingual Publishing Co.

New Environmentally-Friendly Materials

https://ojs.bilpub.com/index.php/nefm

ARTICLE

Electrochemical Deposition of Iron with Detonation Nanodiamonds

Valery Yu. Dolmatov [1*]**,** ***Kristina V. Lotnikova*** [1,2]

[1]*Federal State Unitary Enterprise "Special Design and Technological Bureau 'Tekhnolog'", 33a Sovetsky Ave., Saint Petersburg 192076, Russian Federation*

[2]*Saint Petersburg State Technological Institute (Technical University), 24-26/49 Moskovsky Ave., Building A, Saint Petersburg 190013, Russian Federation*

ABSTRACT

This work describes the iron plating of metal (copper) surfaces in the presence of detonation nanodiamonds (DNDs). A literature and patent review on methods for obtaining iron and iron-carbon electrochemical coatings is given, indicating the disadvantages of such coatings, and a detailed description of the modes, materials, and methods used in this work. A detailed description of the properties and behavior of ferruginous diamond-containing additives in electrolytes and their difference from known additives is given. Modes of conducting the ferruginization process and their results depending on the type of nanodiamond additive are discussed. The study was conducted using a simple and environmentally friendly sulfuric acid-based iron plating electrolyte, operating at room temperature. The objective of the study is to improve the key technical characteristics of the coating process and the iron coating itself: iron yield per current, microhardness and wear resistance. The new method resulted in a 30% increase in iron current efficiency, a multiple increase in microhardness (up to 750 kg/mm²), and wear resistance (up to 4.6 times) of the iron–diamond coating. Application: restoration of worn parts of cars, heavy machinery, equipment; hardening of working surfaces of low-carbon steel parts; application of wear-resistant coatings to products with low surface hardness.

Keywords: Electrochemical Iron Plating; Detonation Nanodiamonds; Detonation Diamond-Containing Carbon; Electrolyte Composition; Microhardness; Wear Resistance

*CORRESPONDING AUTHOR:

Valery Yu. Dolmatov, Federal State Unitary Enterprise "Special Design and Technological Bureau 'Tekhnolog'", 33a Sovetsky Ave., Saint Petersburg 192076, Russian Federation; Email: diamondcentre@mail.ru; dolmatov@sktb-technolog.ru

ARTICLE INFO

Received: 16 April 2025 | Revised: 29 April 2025| Accepted: 4 May 2025 | Published Online: 11 May 2025

DOI: https://doi.org/10.55121/nefm.v4i1.391

CITATION

Dolmatov, V.Y.; Lotnikova, K.V., 2025. Electrochemical deposition of iron with detonation nanodiamonds. New Environmentally-Friendly Materials. 4(1): 35–47. DOI: https://doi.org/10.55121/nefm.v4i1.391

1. Introduction

It is well known that electroplated iron coatings approach the hardness of steel and can be used to increase surface hardness and wear resistance in mechanical engineering (for restoring worn machine parts), and in the printing industry for reinforcing printing plates [1,2]. The increased hardness is believed to result from hydrogen dissolution in iron during deposition, leading to the formation of solid solutions and distortion of the crystal lattice that strengthens the coating. Composite electrochemical coatings (CEC) consist of a metallic matrix – in this case, iron – that contains a dispersed phase, particularly hard and superhard particles [3]. Such coatings usually exhibit enhanced physical and mechanical properties and wear resistance. In some cases, porosity decreases and corrosion resistance improves. According to Sokolovskaya [4], the physical-chemical, mechanical, and corrosion properties of various composite coatings reach their maximum values at a dispersed phase content of 5–10% (vol.) and a particle size below 0.5 µm. Composite coatings with dispersed particles are typically produced by electrodeposition from electrolytes containing both a metal salt and a dispersed phase [5]. The electrolyte composition and the properties of the dispersed phase — including size, nature, and resistance to sedimentation and coagulation – determine the quality of the resulting coating. A key requirement for dispersed particles is also their chemical stability in the electrolyte. For iron plating electrolytes, which tend to be aggressive, diamond particles are among the most suitable options due to their high chemical resistance [6]. Detonation nanodiamonds (DND) (4–6 nm), discovered back in 1963 [7], are produced by the explosion of powerful explosives. Every year, the number of works aimed at studying the properties and applications of DND increases [8–13], including electrochemical coatings with metals with nanodiamonds.

A known method for producing composite electrochemical coatings based on DNDs and metals (such as chromium, cobalt, zinc, nickel, cadmium, silver, gold, copper, palladium) is described in previous works [14,15]. In this method, DNDs are introduced into the electrolyte at concentrations of 2–20 g/L as an aqueous suspension with a DND concentration of 8–10%, containing no more than 2% impurities and a specific surface area of 400–500 m²/g. This approach led to increases in microhardness and wear resistance. Disadvantages of this method: the microhardness of the Cr-UDA coating increased by only 1–3%, which is within the margin of error of the experimental determination; wear resistance increased by 12–31%; the microhardness of the Ag-UDA coating increased by 10–38%, and wear resistance by 10–25%. According to Nikitin et al. [14], only 3 examples are given (Cr, Zn, Ag).

Another study describes the use of an electrolyte for depositing iron in the form of composite electrochemical coatings (CEC) with the following composition (g/L): iron chloride – 300; boric acid – 40; amorphous boron – 10–40 [16]; ultradispersed carbon condensate – 2–140; the ultradispersed carbon condensate contains the following components (wt.%): carbyne – 2–5, graphite – 1–15, non-crystalline carbon – 3–50, and diamond – remainder. The process of electrochemical metal deposition was conducted with constant agitation using compressed air. An essential stage in the process after applying the iron coating was heat treatment at 200–1050°C for 0.5 to 6.0 hours. The authors claim that the main advantage of their proposed method over known alternatives (only one of which without iron is described earlier) is a significantly lower heat treatment temperature. Wear resistance of heat-treated iron-, nickel-, and cobalt-based CECs increases by a factor of 3.8–7.0. However, no specific data are given for iron-based coatings. The disadvantages of this method are: the technological complexity; the requirement for heat treatment of the obtained coating; the need for continuous agitation of the electrolyte using compressed air; the use of only one type of diamond-containing additive, which limits the flexibility of the iron coating process, and the composition of the additive is not specified.

The objective of this work is to develop a method for obtaining an iron composite coating with high wear resistance and microhardness by electrochemical deposition from an iron-containing electrolyte containing a carbon-containing additive, in which purified detonation nanodiamond (DNA), detonation diamond-containing carbon (DDC) and oxidised DDC (ODDC) in an amount of 0.1–10.0 g/l. DDC is obtained by detonating powerful carbon-containing explosives [17]. The objective has been achieved.

2. Materials and Methods

The properties of iron coatings depend on many parameters, with the main ones being the composition of the electrolyte, temperature, and current density [3]. The microhardness of the coating decreases with increasing temperature and electrolyte pH, and conversely increases with higher current density. Copper samples were used as the substrate for iron deposition. The combination of properties of the coatings obtained by the proposed method, along with the simplicity of the process, makes this method competitive with any known technique for applying composite iron coatings. The main research was conducted using three different classes of electrolytes within the composition ranges listed in **Table 1**.

Table 1. Composition of Iron-Plating Electrolytes (g/L).

Electrolyte Name	$FeSO_4$ x 7 H_2O	$FeCl_2$ x 4 H_2O	NaCl	K_3BF_4	H_3BO_3	Glycine	Ascorbic acid
Sulfate-based	45	–	15	–	–	5	–
Acidic chloride-based	–	600	100	–	–	–	0.4
Fluoroborate-borate	200	–	–	100	10	–	–

The main process development was performed using the sulfate-based electrolyte (**Table 1**), due to its low cost, ease of preparation, and room-temperature operation (20°C). The optimal electrolyte acidity (pH) was determined by the combined influence on the iron deposition process and hydrogen evolution, and was maintained at pH 1.9 or 2.1, as the most commonly used in ironing with sulphuric acid electrolyte. As the dispersed phase, the study used (for comparison): purified detonation nanodiamonds (DNDs) with a particle size of 4–6 nm [17], standard detonation diamond-containing carbon (DDC), oxidized DDC (ODDC), all in aqueous suspension form. X-ray diffraction patterns of DDC showed, along with the three lines corresponding to the diamond carbon phase, a broad peak at d=0.42 nm, which corresponds to the X-ray amorphous carbon phase [18,19]. This peak is especially prominent in the oxidized DDC (ODDC), obtained by boiling standard DDC in 57–98% nitric acid for 3 hours. Within these processing conditions (57–98% HNO_3, 1–3 hours), the ODDC properties remain consistent. The particle size distribution of DDC was determined by small-angle scattering [18]. The distribution has a single peak between 40 and 60 Å, indicating that the carbon phases are not separated by particle size. Our study of DDC samples heated in air showed a broad exothermic effect on the DTA curve, peaking at 703–793K, indicating high material homogeneity. It was not possible to separate the material into diamond and non-diamond carbon without destroying the non-diamond phase.

To maintain a constant pH, a buffer additive – glycine – was introduced into the electrolyte. The optimal glycine concentration is 5 g/L. At this concentration, in addition to pH stabilization, the maximum current efficiency of iron (60%) was achieved (without diamond-containing additives). Glycine also prevents iron hydroxide formation by forming soluble complexes with iron ions. NaCl was added to prevent passivation of iron anodes.

The following is an example of an embodiment of iron-nanodiamond coating from a sulfate electrolyte on a copper sample. To prepare 1 liter of electrolyte with the following composition: $FeSO_4 \cdot 7H_2O$ – 45 g/L; Glycine (aminoacetic acid) – 5 g/L; NaCl – 15 g/L; ODDC – 5 g/L; pH – 1.9.

A 1.5-liter heat-resistant glass beaker is filled with 500 mL of distilled water, heated to 30–40°C. While stirring, 45 g of iron(II) sulfate is gradually added and dissolved completely. The solution is then filtered to remove any insoluble residue and adjusted to pH=1.9 using diluted (5–10%) sulfuric acid. Separately, 5 g of glycine is dissolved in 100 mL of distilled water, and 15 g of NaCl in another 150 mL of distilled water. While stirring, the glycine solution is added first to the iron sulfate solution, followed by the NaCl solution, and finally, a suspension containing 5 g of ODDC is introduced (for example, if the ODDC content in the original aqueous suspension is 9.3 wt.%, 53.8 mL of this suspension must be added). The total volume is then brought up to 1 liter with distilled water. The prepared electrolyte is poured into a plating bath with the temperature maintained at 20±2°C. Two iron anodes are placed in the bath opposite each other and connected to a power source. The copper workpiece is thoroughly cleaned and degreased using standard chemical and/or electrochemical methods, then rinsed. A standard DC power supply with adjustable voltage and current is used. The sample (copper substrate) is placed between the two iron anodes and connected to the power source. The cathode-to-anode surface area ratio is 1:2. The applied current density is 5 A/dm². The deposition rate is 0.9 µm/min. Iron–diamond coating deposition is completed after 30 minutes. The power is then turned off, the sample is removed from the bath, rinsed first with hot and then with cold running water, and dried. The microhardness of the coating, measured by pressing a natural diamond pyramid (with a 108.9° apex angle), reached 715 kg/mm². The wear of the coating, measured using the LTI method after 10 hours of abrasion, was 14.1%. Detonation diamond-containing carbon is a mixture of detonation nanodiamond and X-ray amorphous carbon phase with the following ratio, wt. %: detonation nanodiamond – 20–80; X-ray amorphous carbon phase – the rest; the content of X-ray amorphous phase in purified DHA is less than 1.5 wt. %. (The particle size and phase ratio were determined by X-ray line broadening on an X-ray meter of Rigaku, Japan).

3. Results and Discussion

3.1. Properties of the Diamond-Containing Additive in the Iron-Plating Electrolyte

The detonation (cluster) nanodiamonds (DNDs) used in this method (also referred to as ultradispersed diamonds, UDDs), whether in their pure form or as an intermediate product of detonation synthesis (a composite with X-ray amorphous carbon – DDC), are nearly spherical or oval in shape, with no sharp edges (non-abrasive). Their particle size, determined by production technology, ranges from 3 to 12 nm [17]. DNDs and DDCs form sedimentation- and coagulation-stable systems in electrolytes both at working and concentrated levels. Currently, DNDs (in a mixture with X-ray amorphous carbon) are synthesized by detonating specially prepared TNT-RDX explosive compositions in blast chambers filled with an inert gas medium [17,19]. The resulting DDC is then chemically purified. Morphologically, DNDs are a powder with a specific surface area of 150–450 m²/g and pore volume of 0.3–1.5 cm³/g (in dry form) [20]. In suspension, DND aggregates can reach up to 50 nm in size (0.05 µm) with special processing. The average size of individual diamond crystallites is 4–6 nm, generally ranging from 1 to 12 nm [21,22]. DNDs have a classical cubic (diamond) crystal lattice with numerous surface defects, which results in high surface energy. This excess surface energy is compensated by the formation of numerous functional surface groups, forming a chemically bonded shell ("fringe") around the crystal. These groups include hydroxyl, carbonyl, carboxyl, nitrile, quinonoid, and other combinations of carbon with elements from the explosive – oxygen, nitrogen, and hydrogen [23]. Without this shell, nanodiamond crystallites cannot exist under normal conditions – it is an integral part of cluster nanodiamonds and largely determines their properties. Thus, DNDs combine paradoxical characteristics – one of the hardest and most inert substances in nature (the diamond core) and a chemically active shell of various functional groups. This distinguishes them from both natural and synthetic diamonds of static and dynamic synthesis. In addition, even after some compensation of unpaired electrons via surface groups, DNDs still have significant unpaired electron density on their surface, making each crystallite effectively a multiple radical. Importantly, in this context, DDC is not a separate phase or set of particles and is not crystallographically identified as graphite or micrographite. The two carbon forms – diamond and non-diamond – are differentiated by their electronic state and chemical reactivity toward liquid-phase oxidizers [24]. The role of peripheral non-diamond structures is to enable maximum interaction of the particle with the matrix – iron – during electrocrystallization at the cathode. While the tetrahedral sp^3 diamond carbon is chemically and sorption-inactive, non-diamond configurations (sp^2 and sp) are much more labile and, with oxygen and hydrogen heteroatoms, form an adsorption-active shell bound to the diamond core via stable chemical bonds. During electroplating, suspended diamond particles in the electrolyte interact with the growing metal deposit through hydrodynamic, molecular, and electrostatic forces. This complex interaction results in the formation of a composite electrochemical coating.

During electrochemical deposition of iron, cluster diamonds act as nucleation centers due to their high physicochemical activity, initiating metal crystallization [17]. The involvement of a large number of particles leads to massive, multi-nucleation crystallization. The resulting coating consists of small structural fragments. The combination of almost inertialess mass transfer of DND particles and widespread crystallization ensures uniform coating across equipotential surfaces. Unlike other fine powders, DNDs act not only as fillers or a second phase but also as specific structure-forming agents in the electrocrystallization process of iron. Due to the small particle size and their low concentration in the coating (0.2–1.0%), the significant increase in microhardness and wear resistance of the Fe–DND coating cannot be attributed solely to the hardness of diamond. At the core of the favorable improvement in the performance properties of Fe–DND coatings lies a series of positive structural transformations in the iron–diamond deposit. The presence of highly developed interfacial layers between diamond and iron, with strong chemical bonding, provides increased microhardness. Calculations show that in a composite iron coating containing 1 wt.% DND with a specific surface area of approximately 300 m²/g, the area of interfacial boundaries reaches 20–25 m² per 1 cm³ of coating. The high chemical and adsorption activity of the DND surface ensures a higher strengthening effect than that provided by any other known nanosized particles lacking this unique combination of properties [17,19]. Thus, DNDs form a specific phase interface in the iron matrix where the particle-iron boundary acts not as a weak link (as is typically the case), but rather as a reinforcing and strengthening element of the composite coating structure. During the electrochemical deposition of iron, DND particles are embedded into the deposit and significantly influence its structure and properties. Strengthening occurs as the particles hinder dislocation movement along slip planes. It is known that pores and particles impede grain growth [25]. With decreasing particle size and constant volume fraction, the inter-particle spacing also decreases, leading to the formation of thin metal films with greater strength than bulk material. The use of diamond crystallites for producing electrochemical composite iron coatings leads to a shift in the coating formation mechanism and a significant improvement in properties: DNDs and DDCs form stable dispersions in iron-plating electrolytes; he small mass (and thus low inertia) of diamond nanoparticles ensures efficient mass transfer to the coated surface; due to their high physicochemical activity, nanodiamonds promote extensive iron crystallization, resulting in a fine-grained, pore-free coating structure with improved corrosion resistance and microhardness; the small size of DNDs and iron crystallites allows precise replication of the microrelief of the surface, increasing the total contact area and thus the ultimate load before coating delamination from the substrate; high coating quality is achieved at a low DND content (0.2–1.0 wt.%), making the process economical.

Furthermore, DNDs form high-quality coatings whether introduced in pure form or as part of DDC. DDC can be regarded as a modified form of DNDs, where the non-diamond carbon phase isolates the DND particles from each other, aiding their incorporation into the iron deposit as individual particles rather than as aggregates (as can occur with pure DNDs). This leads to further improvement in key practical properties such as microhardness and wear resistance of the iron–diamond coating. The concentration of DNDs and DDCs in the iron-plating electrolytes ranges from 0.1 to 10 g/L (calculated based on pure DND content). Increasing the DND content above 10 g/L leads to significant thickening and structuring of the electrolyte, which hinders convection and current flow. Reducing the content below 0.1 g/L significantly decreases coating quality. The electrolyte temperature and composition are maintained within the standard limits for the specific electroplating process; the addition of DND or DDC does not alter these parameters. The cathodic current density is selected from the typical working range for the given electrolyte composition. The set of properties achieved by this method and the simplicity of the process make it competitive with any known method for applying composite iron coatings. DDC produced by detonation synthesis consists of nanoparticles composed of two phases: a diamond core surrounded by a loose X-ray amorphous carbon shell. The diamond content in DDC ranges from 20 to 80 wt.%, with the remainder being amorphous carbon. The distribution of carbon forms in DDC was determined using X-ray photoelectron spectroscopy. In the cathodic polarization curves for the joint discharge of iron and hydrogen in the presence of DND, DDC, and ODDC, a shift of the potential to more positive values was observed – by about 70 mV for DND, 150 mV for DDC, and 100 mV for ODDC. The diamond-containing component in the electrolyte acts as a cation-active additive and inhibits hydrogen evolution due to adsorption on the cathode. This leads to an increase in iron current efficiency by approximately 30–40% for all types of diamond-containing additives. The effect of ODDC concentration on various parameters is presented in **Figure 1** and **Table 2**. **Figures 2–4** and **Table 2** show the influence of DND, DDC, and ODDC on the microhardness of iron deposits at various concentrations in the electrolyte. **Table 2** shows the decisive influence of the concentration of nano-diamond additives on the iron yield per current, microhardness and appearance of coatings. Nano-diamond additives, at a concentration of more than 10 g/L, easily agglomerate in strong electrolytes (any electrolytes, including those for ironing), together with iron, it is no longer individual nano-diamond particles or primary aggregates (from 10 to 20 nm) that are deposited, but aggregates from 50 to 300 nm [17]. This leads to a decrease in the quality (microhardness, wear resistance and appearance) of the coating. The data in **Table 2** and **Figures 2–4** show that the optimal concentration of nanodiamonds is 4–5 g/L. It is at this concentration that the highest values of microhardness and wear resistance are achieved (**Table 3**, **Figure 5**).

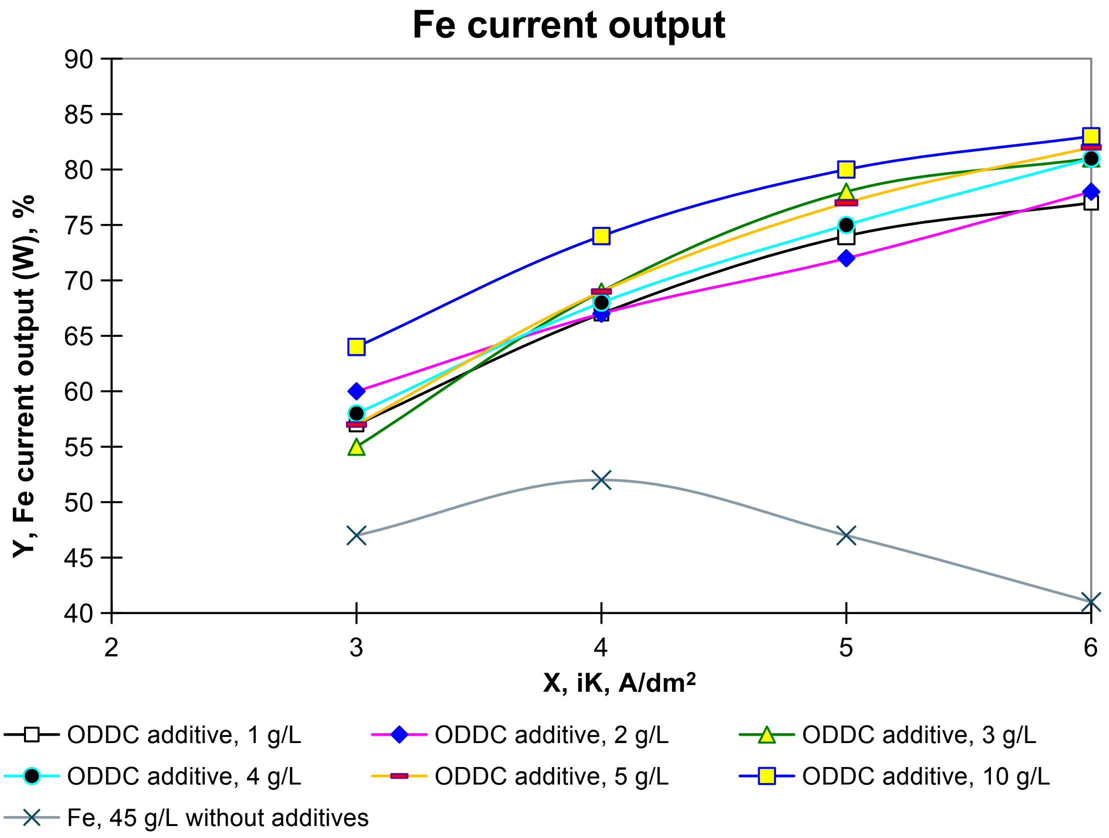

Figure 1. Effect of Current Density and ODDC Concentration on Iron Current Yield.

Table 2. Iron Coating Microhardness, Iron Current Yield and Coating Appearance (Sulphuric Acid Electrolyte).

Electrolyte composition		i, A/dm²	Iron current output, %	Microhard-ness, kg/mm^2	Appearance of the coating
1		2	3	4	5
$FeSO_4 \times 7H_2O$	45 g/L	3	47	150	Light grey precipitate
NaCl	15 g/L	4	52	310	Appearance of fracturing
Glycine	5 g/L				
pH	1,9	5	45	285	Dendrite formation at the edges
t°C	20	6	41	260	Same

Table 2. *Cont.*

Electrolyte composition	i, A/dm^2	Iron current output, %	Microhard-ness, kg/mm^2	Appearance of the coating
In the presence of: DND 1 g/L	3	16	342	Dark grey sediment without pitting or cracks
	4	34	375	Shiny light grey sludge without pitting
	5	47	461	Same
	6	54	503	Same
DND 2 g/L	3	40	287	Shiny light grey precipitate without pitting or cracks
	4	53	393	Semi-glossy light grey sludge
	5	55	407	Same
	6	59	422	Same
DND 3 g/L	3	56	192	Semi-glossy light grey sediment without cracks.
	4	61	403	Same
	5	57	485	Same
	6	55	499	Same
DND 4 g/L	3	51	337	Semi-glossy light grey sediment without cracks
	4	66	405	Same
	5	55	459	Same
	6	56	494	Same
DND 5 g/L	3	64	350	Semi-glossy light grey precipitate
	4	71	402	Mild pitting
	5	73	424	Same
	6	76	451	Same
DND 10 g/L	3	62	295	Light grey coating without pitting
	4	77	403	Semi-glossy light grey precipitate
	5	69	583	Same
	6	72	627	Same
DDC 1 g/L	3	34	473	Dark grey precipitate without pitting or cracks.
	4	43	515	Same
	5	55	610	Light grey sludge
	6	61	627	Same
DDC 2 g/L	3	31	495	Dark grey precipitate without pitting and without cracks
	4	47	548	Light grey sludge
	5	57	646	Matte grey sludge
	6	59	666	Same

Table 2. *Cont.*

Electrolyte composition	i, A/dm²	Iron current output, %	Microhard-ness, kg/mm^2	Appearance of the coating
DDC 3 g/L	3	32	510	Dark grey rough coating
	4	49	565	Matte finish without pitting
	5	58	655	Same
	6	62	692	Same
DDC 4 g/L	3	33	515	Matte finish without pitting or cracks
	4	51	625	Same
	5	64	700	Same
	6	67	731	Same
DDC 5 g/L	3	32	525	Matte finish without pitting or cracks
	4	54	650	Same
	5	68	732	Same
	6	71	752	Same
DDC 10 g/L	3	32	505	Matte finish without pitting or cracks
	4	56	628	Same
	5	67	718	Same
	6	75	749	Same
ODDC 1 g/L	3	57	490	Light grey shiny precipitate without pitting
	4	67	671	Same
	5	74	743	Same
	6	77	788	Same
ODDC 2 g/L	3	60	470	Light grey precipitate without pitting or cracks
	4	67	686	Appearance of roughness
	5	72	743	Light grey sludge without pitting and cracks
	6	78	798	Same
ODDC 3 g/L	3	55	504	Light grey sediment without pitting or cracks.
	4	69	698	Appearance of roughness
	5	78	751	Same
	6	81	790	Same
ODDC 4 g/L	3	58	482	Light grey sediment without pitting or cracks.
	4	68	682	Appearance of roughness
	5	75	767	Same
	6	81	824	Same
ODDC 5 g/L	3	57	498	Dark grey precipitate without pitting
	4	69	678	Roughness
	5	77	730	Same
	6	82	832	Same

Table 2. *Cont.*

Electrolyte composition	i, A/dm²	Iron current output, %	Microhard-ness, kg/mm^2	Appearance of the coating
	3	64	468	Dark grey precipitate without pitting
ODDC 10 g/L	4	74	587	Same
	5	80	613	Same
	6	83	633	Same

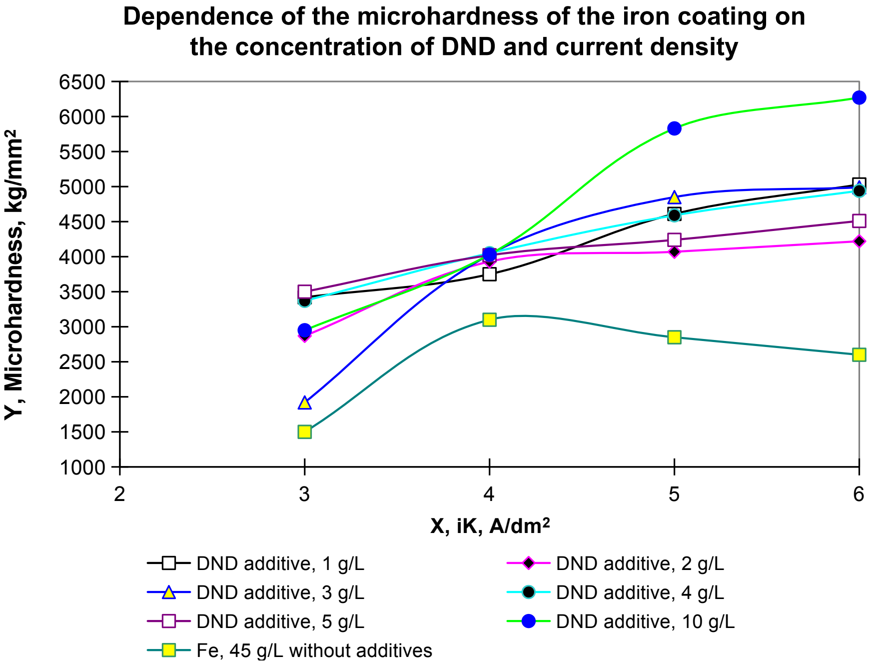

Figure 2. Effect of DND on the Microhardness of Iron Precipitate (pH of Electrolyte 1.9).

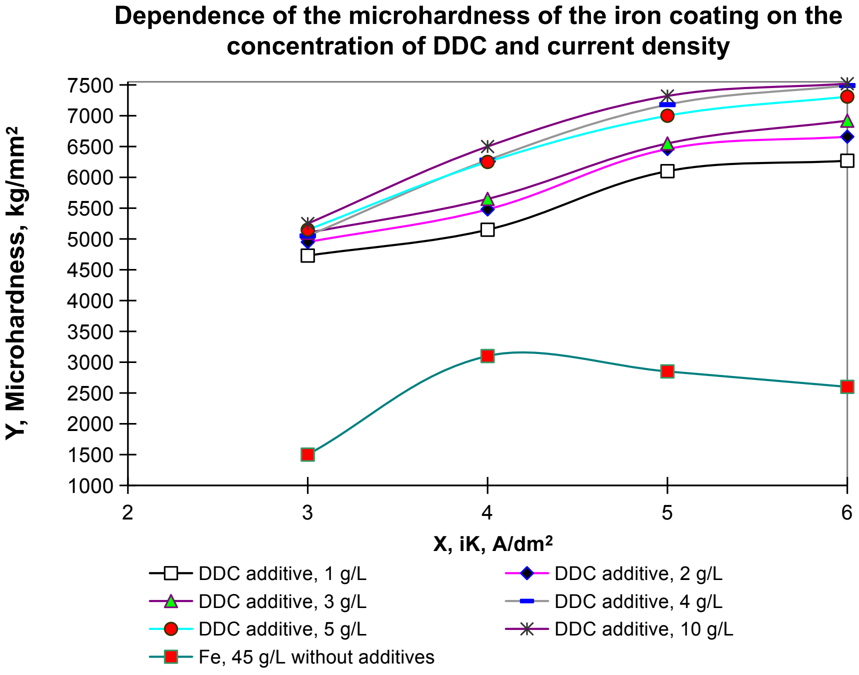

Figure 3. Effect of DDC on the Microhardness of Iron Precipitate (pH of Electrolyte 1.9).

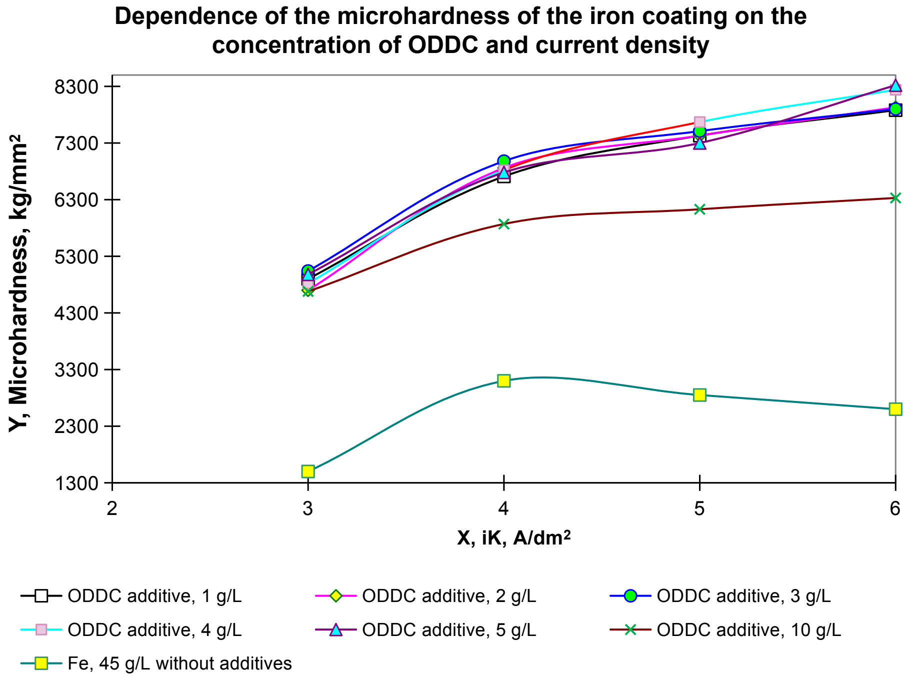

Figure 4. Effect of ODDC on the Microhardness of Iron Sludge (pH of Electrolyte 2.1).

Table 3. Wear Test Results of Iron-Nanodiamond Coatings.

Abrasion time (hours)	Weight Loss, wt.%			
	No Additive	DND	DDC	ODDC
1	4.3	2.2 (~2x less)	2.8 (~1.5x less)	1.4 (~3.0x less)
2	4.3	3.1 (~1.4x less)	2.6 (~1.7x less)	1.8 (~2.4x less)
3	6	3.2 (~1.9x less)	2.9 (~2.1x less)	1.8 (~3.3x less)
4	6.4	3.3 (~1.9x less)	3.1 (~2.1x less)	1.4 (~4.6x less)
5	5.1	3.3 (~1.5x less)	2.9 (~1.8x less)	1.4 (~3.6x less)
6	6.9	3.6 (~1.9x less)	2.8 (~2.5x less)	1.4 (~4.9x less)
7	8.5	3.6 (~2.3x less)	2.8 (~3.0x less)	1.4 (~6.1x less)
8	10.2	3.7 (~2.8x less)	2.8 (~3.6x less)	1.4 (~7.3x less)
9	11.1	3.8 (~2.9x less)	2.8 (~4.0less)	2.0 (~5.6x less)
10	11	5.3 (~2.1x less)	2.1 (~2.7x less)	1.9 (~5.8x less)
Total Wear	73.8	35.1 (~2.1x less)	27.6	15.9 (~4.6x less)
Relative increase in wear resistance	1	2.1	2.7	4.6

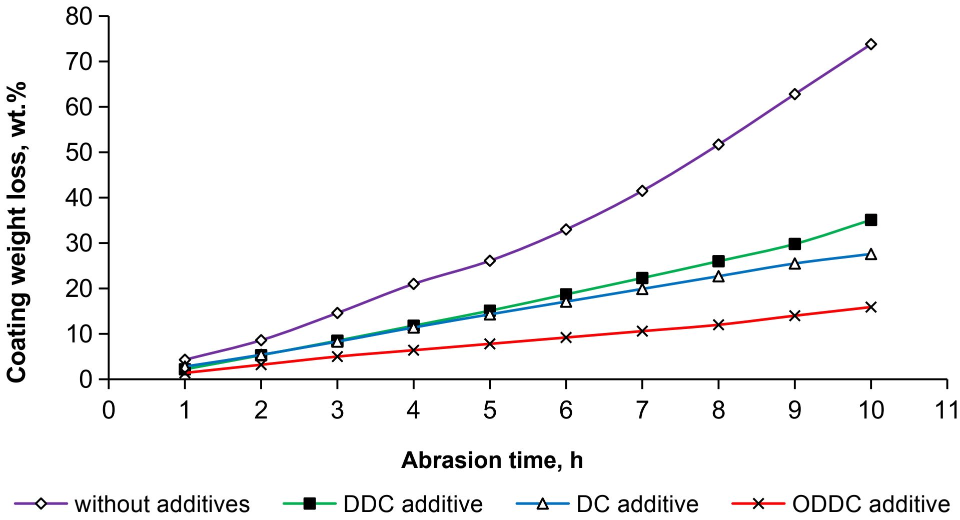

Figure 5. Effect of the Type of Diamond-Containing Additives on the Wear Resistance of Iron Coating (Concentration of Any Additive in the Electrolyte 5 g/L, ik =4 A/dm^2).

A specific sulphuric acid ironing electrolyte was chosen as the most commonly used due to its simplicity of manufacture, cost-effectiveness and ability to operate at room temperature, i.e. convenient in every respect [3]. The pH level (1.9 and 2.1) was also chosen as it has been well tested over many years in widespread industrial practice. The current density is also taken into account, with 4 A/dm^2 being used as a rule. How these factors interact is shown in **Figures 1–5** and **Tables 1–3**. The obtained dependencies are not complex and obey the previously known dependencies of electrochemical deposition of other metals (Cr, Ni, Sn, Ag, Au) [17,23,25].

The use of diamond-containing additives always increases the microhardness of the iron coating. When introduced into the coating, they harden it by changing its structure, preventing the formation of dislocations and microcracks. The effect of ODDC compared to DND and DDC is significantly stronger in this respect. As the current density increases from 3 to 5 A/dm^2, the microhardness of CEC increases due to the increase in polarisation and changes in the crystal structure of the coating. It was found that the optimum acidity of the electrolyte when using DND corresponds to pH=2.1, and when using DDC and ODDC pH=1.9. Data on the wear resistance of iron coatings obtained from electrolytes containing 5 g/L of DND, DDC, and ODDC (at a current density of 4 A/dm^2 and abrasion time of 10 hours) are presented in **Table 3** and **Figure 5**. The introduction of a diamond-containing additive into the electrolyte (and therefore into the iron coating) significantly increases abrasion resistance. The most effective results were achieved with ODDC, which is explained by a reduction in the friction coefficient due to the incorporation of stable, X-ray amorphous, non-abrasive carbon into the deposited iron. In contrast, DDC, in addition to diamond and oxidation-resistant amorphous carbon, also contains various easily oxidizable organic compounds, which negatively affect the coating structure. ODDC, having undergone oxidation, is free of these compounds and contains only DND and stable amorphous non-abrasive carbon.

3.2. Dependence of Iron Coating Wear on the Type of Nanodiamonds

The method is approved in pilot production, has simple technological solutions (there is no need for: heat treatment of deposited coatings, constant mixing of electrolyte, use of expensive and poisonous boron), and has a wide base of electrolytes and additives.

4. Conclusions

The use of nanodiamond-containing additives in the most environmentally friendly, simple, and cost-effective sulfate iron-plating electrolyte made it possible to significantly improve the main characteristics of the coating:

−Increase in iron current efficiency by ~30% – up to 77% with DND and ODDC, and up to 68% with DDC;

−Increase in coating microhardness by ~2 times – up to 580 kg/mm^2 with DND, up to 720 kg/mm^2 with DDC, and up to 750 kg/mm^2 with ODDC;

−Improved abrasion resistance: 2.1× with DND; 2.7× with DDC; 4.6× with ODDC.

The choice of additive depends on the intended application of the coated product.

Author Contributions

Conceptualization, V.Y.D.; methodology, V.Y.D.; investigation, V.Y.D. and K.V.L.; writing—review & editing, K.V.L. All authors have read and agreed to the published version of the manuscript.

Funding

This work received no external funding.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

The data presented in Tables of this article are based on experimental results obtained during the study. Although no separate datasets have been archived, the data are reliable and reflect the authors' long-standing research experience. The corresponding author has more than 400 publications in peer-reviewed journals and 6 scientific monographs.

Acknowledgments

The authors would like to express their deep gratitude to the electrochemistry expert Burkat Galina.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Busko, V.I., Zhulikov, V.V., 2021. Electrodeposition of iron and its alloys [in Russian]. Corrosion Protection Practice. 26(1), 48–61. DOI: https://doi.org/10.31615/j.corros.prot.2021.99.1-5

[2] Shluger, M.A., Tok, L.D., 1985. Electroplating in Mechanical Engineering: A Handbook [in Russian]. Mechanical Engineering: Moscow, Russia.

[3] Saifullin, R.S., 1972. Combined electrochemical coatings and materials. Khimiya Publishing House: Moscow, Russia.

[4] Sokolovskaya, E.M., 1976. Physical chemistry of composite materials. Moscow State University Publishing House: Moscow, Russia.

[5] Dolmatov, V.Yu., 2003. Ultrafine detonation synthesized diamonds: production, properties, application: monograph. Publishing House of SPbGPU: St. Petersburg, Russia.

[6] Bogatyreva, G.P., Voloshin, M.N., 1998. Characterization and some properties of shock-wave diamond powders. Sverkhtverdye Materialy (Russia). 4, 82–87.

[7] Volkov, K.V., Danilenko, V.V., Elin, V.Y., 1990. Synthesis of diamond from carbon in the detonation products of explosives. Combustion, Explosion and Shock Waves. 26(3), 366–368. DOI: https://doi.org/10.1007/BF00751383

[8] Liu, Q., Duan, Y., Ma, H., et al., 2020. Review on the exploration of condensed carbon formation mechanism in detonation products. AIP Advances. 10(5), 050701. DOI: https://doi.org/10.1063/1.5142521

[9] Thalassinos, G., Stacey, A., Dontschuk, N., et al., 2020. C — Journal of Carbon Research. 6(1), 7. DOI: https://doi.org/10.3390/c6010007

[10] Mochalin, V., Shenderova, O., Ho, D., et al., 2012. The properties and applications of nanodiamonds. Nature Nanotechnology. 7(1), 11–23. DOI: https://doi.org/10.1038/nnano.2011.209

[11] Ducrozet, F., Girard, H., Leroy, J., et al., 2021. New Insights into the Reactivity of Detonation Nanodiamonds during the First Stages of Graphitization. Nanomaterials. 11(10), 2671. DOI: https://doi.org/10.3390/nano11102671

[12] Batsanov, S.S., Gavrilkin, S.M., Dankin, D.A., et al., 2023. Transparent Colloids of Detonation Nanodiamond: Physical, Chemical and Biological Properties. Materials. 16(18), 6227. DOI: https://doi.org/10.3390/ma16186227

[13] Arnault, J.-C., 2017. Nanodiamonds: Advanced Material Analysis, Properties and Applications. Elsevier: Amsterdam, Netherlands.

[14] Nikitin, E.V., Polyakov, L.A., Kalugin, N.A. (inventors), 2000. Method for obtaining composite metal-diamond coatings. Russian Federation Patent. 2156838. 2000 September 27. https://patentscope.wipo.int/search/ru/detail.jsf?docId=RU29363523&_cid=P11-MCYOXT-97272-1

[15] Korytnikov, A.V., Nikitin, E.V., Zaitseva, T.N., et al. (inventors). Method for electrochemical application of chrome-diamond coatings. Russian Federation Patent. 2096535. 1997 November 20. https://patentscope.wipo.int/search/ru/detail.jsf?docId=RU29305126&_cid=P11-MCYP4R-07494-1

[16] Guslienko, Yu.A., Savvakin, G.I., Luchka, M.V., et al. (inventors), 1995. Composition for obtaining composite electrochemical coatings based on iron group metals (iron, nickel, cobalt). Russian Federation Patent. 2026892. 1995 January 20. https://patentscope.wipo.int/search/ru/detail.jsf?docId=RU29501597&_cid=P11-MCYPEW-20606-1

[17] Dolmatov, V.Yu., 2011. Detonation nanodiamonds. Production, properties, application. [in Russian] NPO Professional: Saint Petersburg, Russia.pp. 17–36

[18] Danilenko, V.V., 2003. Synthesis and sintering of explosion-grown diamond. [in Russian] Energoatom: Moscow, Russia. pp. 21–28

[19] Shenderova, O., Gruen, D., 2006. Ultrananocrystalline diamond, synthesis, properties, and application. William Andrew Pub: Norwich, UK.

[20] Dolmatov, V.Yu., 1998. Experience in and prospects for non-traditional use of explosion-synthesized ultradispersed diamonds [in Russian]. Superhard Materials [in Russian]. 4, 77–81.

[21] Dolmatov, V.Yu. (inventor), 2011. Nanodiamond and a method for the production thereof. United States Patent. 7867467. 2011 January 11. https://patentscope.wipo.int/search/ru/detail.jsf?docId=US43184374&_cid=P11-MCYRUT-23129-1

[22] Dolmatov, V.Yu. (inventor), 2014. Nanodiamond and the method of its production. WO Patent. 2007078210. 2007 July 12. https://patentscope.wipo.int/search/ru/detail.jsf?docId=WO2007078210&_cid=P11-MCYRK5-10946-1

[23] Dolmatov, V.Yu., Ozerin, A.N., Kulakova, I.I., et al., 2020. Detonation nanodiamonds: New aspects in the theory and practice of synthesis, properties and applications. Russian Chemical Reviews. 89(12), 1428–1462. DOI: https://doi.org/10.1070/RCR4924

[24] Gubarevich T.M., Larionova I.S., Sataev R.R., Dolmatov, V.Yu., Pyaterikov V.F. (inventors), 1993. Method of treatment of ultradispersed diamond from nondiamond carbon. Russian Federation (USSR data) Patent 01819851. 1993 June 07. https://patentscope.wipo.int/search/ru/detail.jsf?docId=SU29227006&_cid=P11-MCYQW6-83202-1

[25] Ovidko, I.A., 2009. Theories of grain growth and methods of its suppression in nanocrystalline and polycrystalline materials. Materials Physics and Mechanics. 11(2), 174–199.