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Nanosized Borides and Carbides for Electroplating. Metal-Matrix Coatings: Specifications, Performance Evaluation

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Abstract. This paper summarizes experience of application of nano-sized carbides and borides of titanium and chromium, silicon carbide as components of electro-depositable coating compositions based on nickel, zinc, and chromium. Basic physical and mechanical properties of the coatings are determined. Technological and economic evaluation is completed; practicability of high-cost nano-diamonds substitution for nano-sized borides and carbides is justified.

1. Introduction.

Rise of operational requirements for materials is constantly encouraging developments in the field of surface hardening. Therefore, currently an urgent problem is development of environmentally friendly new techniques of material hardening by means of changing structural-phase state and physical-mechanical specifications of surface layers.

These techniques have some advantages in comparison with conventional electroplating, thermo-mechanical and chemical-thermal processes as well as with methods of concentrated energy flux exposure. Developers of innovative hardening techniques turn to high-temperature ultra-hard materials (diamond, borides, carbides, nitrides and others). Analysis of scientific and applied studies on various methods of surface hardening and cooperation with authors and developers, confirms technological and economic practicability of use of nanoscale materials, i.e. powders with a particle size less than 100 nm.

The objective of this work is analysis and synthesis of experience and results of use of nano-dispersed borides and carbides of chromium, titanium and silicon as components of galvanic composite metal-matrix coatings.

2. Manufacture of nanopowders borides and carbides

Electroplating is extensively used in modern engineering technology. Electroplating conventional techniques and equipment have almost reached the peak of development. Modern industry requires new techniques of surface hardening of machine parts and mechanisms, giving them increased mechanical, corrosion-resistant, anti-friction and aesthetic properties. This problem can not be solved by conventional electroplating. Therefore active developments of innovative hardening methods are conducted.

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Galvanic composite coating (GCC) is one of the innovative techniques. These coatings are deposited as a thin electrolyte layer, containing a dispersed phase, to items with conductive surface. New composite coatings are based on matrices of chromium, nickel, zinc, copper, gold, silver and others. Composite plating technology has been developed by scientific Schools of professors R.S. Saifullin (KSTU), G.V. Khaldeev (PSU), T.E. Tsupak (UCTR) V.Yu.Dolmatov (SPbSPU).

1 - 10 micron micropowders of diamonds, carbides, borides, nitrides, and silicides of transition metals are conventionally used for composite electroplating. Powders of such granularity significantly increase hardness and wear resistance of composite coatings. However, relatively large particles are unevenly distributed in the matrix volume; that causes increased composite porosity and, as a consequence, reduces thermal resistance, heat resistance and corrosion resistance. These weaknesses have questioned practicability of nano-dispersed diamonds, borides and carbides use for electroplating.

[1-5] represent nanodiamond synthesis technology and application. Manufacturing involves detonation synthesis, product chemical cleaning and conditioning. A nanodiamond is a complex object with three-layer structure consisting of 4-6 nm diamond core, a transition shell of 0.4-1.0 nm X-ray amorphous carbon structures, a surface layer consisting of carbon, nitrogen, oxygen and hydrogen. Acceptable content of the main impurity, oxidized carbon, is 0.5-1.0%. Impregnared in materials, nanodiamonds are structure-forming agents, providing precipitation hardening of the composition.

Relatively low cost of nanodiamonds, compared with static synthetic diamonds, aids optimal "quality-to-price" ratio. A positive effect is achieved by impregnating as much as 1.0% of nanodiamonds into the material. There are many areas of application of nanodiamonds; these are three main ones: finish polishing (approximately 70%), electroplating (25%) and oil compositions (about 5%). Nanodiamonds are used in electrochemical composite coatings based on chromium, nickel, tin, zinc, copper, gold, silver, aluminum, iron, various alloys.

Nanomaterials, impregnated into electroplated coatings, greatly increase micro-hardness, wear resistance, corrosion resistance, improve exterior view and reduce porosity. Along with the advantages of nanodiamonds in GCC technology there is a number of significant weaknesses. Professionals-electroplaters note an extremely high level of dispersion, specified by the manufacturing method, because of which the nanodiamonds are supplied as an aqueous suspension; a significant tendency to coagulation; rapid loss of sedimentation stability; multioperational complex technology of electrolyte preparation and operation; chrome-diamond coating limited lifetime, caused by oxidation of nanodiamond particles, impregnated to the surface layers of chromium matrix, at temperatures above 473-573 K.

Manufacturing technology for nanopowders of borides and carbides of titanium, chromium and silicon is described in [6]. The procedure includes plasma synthesis and, if appropriate, refining.

Table 1 shows parameters of boride- and carbide-formation in conditions of the three-jet vertical continuous-flow reactor with 150 kW capacity as well as general properties of borides and carbides. It can be seen that basic phase content and dispersion grade of the materials comply with specifications for components of metal-matrix composite coatings:

- 30-60 nm dispersion grade, wherein particles in the matrix are distributed micro-uniformly, stability of depositing suspensions, and the most complete activity of the particles (chemical interaction with the matrix, diffusion processes, material hardening and corrosion resistance improving);
- homogeneity of phase composition, which determines the identity of particle behavior in the electrolyte and coating, local reproducibility of performance properties of the coating;
- homogeneity of chemical composition, with a minimum amount of impurities, primarily free carbon (there are some technical difficulties when using nano-carbides with a high content of free carbon);
- controlled state of particle surfaces (gas content, presence of oxide films, etc.), which significantly impact on the development of liquid coalescence in the electrolyte-suspension;

- high corrosion resistance provides constant suspension compositions and electroplating parameters;
- high thermal stability provides scaling resistance.

Metal-matrix composite coatings with nano-components

The following are basic specifications of coatings with nano-components: chrome, nickel - silicon carbide, nickel - carbonitride, boride, chromium, nickel - carbide, titanium boride, zinc - chromium boride (Table. 2). Electroplating conditions, structure and properties of coatings are described in detail in [6-11]. Analysis of the results reveals identity of procedures of composite chromium plating, nickel plating and galvanizing as well as some basic factors of improving of coating service properties:

– boride and carbide nanopowder particles are spherical or oval without sharp edges; have high chemical adsorption activity, form electrolyte-suspensions, stable to sedimentation and coagulation; the particles, because of their small size and weight, are effectively transferred to the surface;

– during electroplating, suspended boride and carbide particles interact with a growing surface sediment through hydrodynamic, molecular and electrostatic forces; that leads to formation of the composite coating;

– when electroplating of chromium, nickel and zinc, nanoparticles are centers of metal crystallization; in consequence of large number of particles, crystallization has a multicelled nature; and the resulting coatings have small dimensions of structural fragments, specific matt appearance and are almost non-porous;

- aggregate of almost non-inertial particle mass transfer and mass crystallization ensures uniform depositing of metal coatings on equipotential surfaces;

– a small size of metal crystallite particles provides an exact copy of the surface micro-topography; that increases the general surface and composite coating adhesion to the substrate;

– coating quality, namely corrosion resistance and micro-hardness, is achieved at a low boride and carbide content in the coating (0.5 - 1.0)%, thereby reducing production costs.

Therefore, unlike micropowders, boride and carbide nanopowders are not only filling matter and second phase, but strong modifiers or structure-forming agents in the metal electro-crystallization procedure. They form a superfine non-porous coating structure with improved corrosion resistance, wear resistance and micro-hardness.

Table 1. Parameters of boride- and carbide formation and general specifications of nanopowders

Synthesis parameters and Specifications	CrB_2	$Cr_3(C_{0,8}N_{0,2})_2$	TiB_2	TiC	SiC
Composition of gas - heat-transfer agent, % vol.: - Nitrogen/hydrogen/methane	74/25/1	99/–/1	74/25/1	99/–/1	99/–/1
Technology option of synthesis	$Cr+B+H_2$	$Cr+CH_4$	$Ti+B+H_2$	$Ti+CH_4$	$Si+CH_4$
Productivity on raw materials, kg / h	3.6	3.1	3.6	3.2	3.0
Boron amount in charge, % of stoichiometric	100-120	–	100-120	–	–
Carbide constituent amount, % of stoichiometric	–	120-140	–	120-140	120-140
Plasma flow initial temperature, K	н.м. 5400	н.м. 5400	н.м. 5400	н.м. 5400	н.м. 5400
Hardening temperature, K	2600-2800	2000-2200	2600-2800	2600-2800	2800-3000

Synthesis parameters and Specifications	CrB_2	$Cr_3(C_{0,8}N_{0,2})_2$	TiB_2	TiC	SiC
Phase content	CrB_2	$Cr_3(C_{0.8}N_{0.2})_2$	TiB_2	TiC	β-SiC
Basic phase content, %	92-93	92-93.5	92-93	93-93.5	91-92
Basic phase output, %	91-92	90.5-91.5	91.5-92.5	92-92.5	87-90
Productivity kg/h	3.0	3.4	3.4	3.7	4.05
Intensity kg/ $\cdot m^3$	1364	2010	1980	2105	2200
Specific surface, m^2/kg	33000-35000	31000-35000	46000-48000	33000-35000	40000-44000
Size * of particles, nm	42.0	34.0	36.0	35.0	55.0
Particle shape	spherical	spherical	spherical	faceted cube	faceted
Oxidation ** of nanopowder $x10^7$, kg O_2/m^2	9.0-9.7	8.0-10.0	5.8-7.6	8.5-9.5	6.5-8.0
* - calculated on the specific surface value; ** - measured after exposure in air for 24 h.					

Table 2. Basic physical and mechanical specifications of composite coatings with nanocomponents

Coatings	Specifications					
	Micro-hardness ±0,3 hPa	Adhesion , MPa	Wear resistance**	Oxidation rate ** T=1173K	Inner stress, MPa	Corroding current, mcA/cm^2
Chrome	5.4	27.9-28.8	1			
Cr – NP SiC	9.7	29.3-30.4	2.5	*	*	*
Cr – MP SiC	8.9	28.4-29.2	2.2			
Nickel	2.2	29.1-30.3	1	2.55	1.36	0.17
Ni – NP	4.5	29.8-32.1	1.72	1	0.50	0.02
$Cr_3(C_{0,8}N_{0,2})_2$	3.2	28.9-30.2	1.54	1.34	0.78	0.11
Ni – MP Cr_3C_2	4.6	31.2-33.3	1.69	1	0.41	0.02
Ni – NP CrB_2	3.5	29.8-30.6	1.52	1.17	0.72	0.10
Ni – MP CrB_2	4.4	30.7-32.8	1.70	1	0.52	0.03
Ni – NP TiC	3.3	29.2-29.6	1.50	1.31	0.78	0.12
Ni – MP TiC	5.3	29.5-32.2	1.76	1	0.54	0.02
Ni – NP TiB_2	3.3	29.1-31.2	1.47	1.24	0.79	0.11
Ni – MP TiB_2						
Zinc	1.0	*	*	*	*	1.0***
Zn – NP CrB_2	1.2					2.3***
* - not specified ** - relative values *** - corrosion resistance according to State Standard 9.308-85, relative values	NP – nanopowder MP – micropowder					

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A comparison of characteristics of composite coatings based on chromium, nickel and zinc, with diamond, carbide and boride nano-components has been performed (Table. 1,2,3) to assess the possibility of the carbide and boride nanopowders substitution by nanodiamonds in chrome plating, nickel plating and galvanizing. It can be seen (Table 3) that chromium carbide coatings have wear resistance, micro-hardness, corrosion resistance, service life comparable to chrome-diamond coatings when exploited in temperatures above 473-573 K.

If nanodiamonds are substituted by nanoscale boride and chromium carbide when nickel plating and galvanizing, fine-grained coatings substantially nonporous will be obtained with similar corrosion resistance. Consequently, carbide and boride nanopowders can be used in galvanic composite chromium and nickel electroplating and galvanizing.

Numerous studies confirm technological and economic practicability of substitution of nanodiamonds by nano- borides and carbides in the composite nickel plating, chrome plating and galvanizing.

Under similar performance and service life of reinforced parts, such substitution results in the following manufacturing and economic advantages: the electrolyte-suspension preparation procedure is significantly simplified and accelerated; 2.5-fold deposition rate increase;1 m^3 electrolyte-suspension cost diminishes by a factor of 8-10. Substitution of 1 ton of nanodiamonds by boride and carbide nanopowders brings economic efficiency of 135 million rubles.

Table 3. Comparative Specifications of coatings based on chrome with silicon carbide SiC and diamond nanopowders

Electroplating conditions and achieved results		Technological options					
		1	2	3	4	5	6
Electrolyte composition, kg/m^3	Chromic anhydride	250	250	250	250	250	260
	Sulphuric acid	3	3	3	3	3	0.3 4
	trivalent Chromium	8	8	8	8	8	-
	Potassium fluorosilicate	-	-	-	-	-	19
	Barium sulfate	-	-	-	-	-	7
	NP SiC	4	6	7	8	10	-
	NP diamond	-	-	-	-	-	20
Deposition mode	Temperature, K	328	328	328	328	328	331
	Current density, A/dm^2	55	55	55	55	55	55
Results	Wear resistance*	0.96	1.0	1.05	1.07	1.08	1.0
	Micro-hardness, hPa	8.9	9.0	9.1	9.15	9.15	9.0
	Corrosion resistance *	0.96	1.05	1.07	1.10	1.10	1.0
	Service life at T above 473-573 K*	1.1	1.50	1.70	2.00	2.06	1.0
	1 m^3 electrolyte suspension cost *	0.13	0.16	0.18	0.20	0.23	1.0

Note: * Wear resistance, corrosion resistance, service life and 1 m^3 electrolyte suspension cost are given in relation to option 6, for which values of these indicators are taken as 1.0.

3. Conclusion

The results of the comparative analysis of nanoscale diamonds, borides and carbides use in galvanic metal-matrix composite coatings show that use of nanoscale borides and carbides with formed set of specifications instead of nano-diamonds ensures achievement of stable parametric, concentration, structural and economic advantages; that testifies their high competitiveness in the domestic and international electroplating

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