Protective metal matrix coating with nanocomponents

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Abstract. Experience of nanocrystalline chromium, titanium, silicon carbides and borides components application as nickel, zinc, chromium based electrodeposited composite coating is generalized. Electrodepositing conditions are determined. Structure and physicochemical properties of coatings, namely micro-hardness, adhesion to steel base, inherent stresses, heat resistance, corrosion currents, enduring quality, and their change during isothermal annealing are studied. As is shown, nanocomponents act as metal matrix modifier. Technological and economic feasibility study to evaluate expediency of replacing high priced nano-diamonds with nanocrystalline borides and carbides is undertaken.

1. Introduction

Increase in materials operation requirements stimulates surface hardening investigations. In this regard, development of environment friendly new material hardening technologies targeted on change in structure-phase state, physical and mechanical properties of surface layers, having advantages in comparison with traditional electroplating technology, thermo-mechanical, thermo-chemical processing, as well as impact methods, based on use of concentrated energy streams is on top of scientific agenda.

In addition, there is a stable interest to high-temperature extra-hard materials (diamonds, borides, carbides, nitrides, etc.) among developers of innovative hardening technologies. Analysis of scientific publications devoted to surface hardening implemented in various technological options, interactions with authors and research executors proves technological and economic feasibility of nanoscale materials (powders with particle size of less than 100 nm) application.

The paper is aimed at summarizing experience gained and the results achieved by the authors in development of technologies of nanodispersed boride, chromium, titanium and silicon carbides application as components of galvanic metal matrix composite coatings.

2. Production of borides and carbides nanopowders

Plated coating is extremely widely used in modern machine engineering technologies. Level of conventional electroplating technologies and equipment design is almost at its peak. However, modern
material science challenges investigators with a number of tasks in surface hardening of parts of machines and mechanisms, providing them with higher mechanical, anticorrosion, antifriction and aesthetic properties, which is impossible to do by means of conventional electroplating, that has determined active development of new research in this field.

One of these new research directions is galvanic composite coatings creation (GCC). The group includes coatings deposited as a thin layer on the articles with conductive surfaces made of electrolytes containing internal phase. New composite coatings are designed based on matrix of chromium, nickel, zinc, copper, gold, silver etc. Technology of composite electrodepositing was developed within scientific schools of Professor R.S. Saifullin (KSTU), Professor G.V. Khaldeev (PSU), Professor T.E. Tsupak (Dmitry Mendeleev University of Chemical Technology of Russia), Professor V.Yu. Dolmatov (SPbSTU) [1-5].

In composite electrodepositing micropowders of diamonds, transition metals carbides, borides, nitrides, silicides of 1 - 10 microns are traditionally used. Powders of such grain significantly enhance hardness and wear resistance of composite coatings. However relatively high particle size of powders and relevant uneven distribution of particles in volume of matrix leads to increased porosity of composite and, as a consequence, reduction of thermal and heat and corrosion resistance. These conditions determine feasibility of nano-disperse diamonds, borides and carbides technological application in electrodepositing.

Industrial technologies of synthesis and application of nano-size diamonds, or nanodiamonds, are presented by the authors [6-10]. Production includes detonation synthesis, chemical cleaning and conditioning of the product. Nano-diamonds appeared to be complex objects of triplex structure comprising of diamond nucleus of 4-6 nm size, transition shell around nucleus comprising of carbon X-ray amorphous structures of 0.4 - 1.0 nm thickness, surface layer consisting of carbon, nitrogen, oxygen, hydrogen atoms. Acceptable content of the main impurity – oxidized carbon – is up to 0.5 - 1.0%. Being introduced in materials nano-diamonds always play the role of high intensity structure forming agent, providing dispersion strengthening of composition. Optimal price - quality ratio of the product with nano-diamonds is achieved, according to developers, due to relatively low cost of nano-diamonds as compared to diamonds of static synthesis and positive effect after introducing nano-diamond additives into material, that is usually up to 1.0%. Despite the large number of emerging applications of nano-diamonds, currently leading are three main areas: approximately 70% of nano-diamonds are used in finish polishing, 25% - in electroplating, and about 5% - in oil compositions. Electrochemical composite coatings based on chromium, nickel, tin, zinc, copper, gold, silver, aluminum, iron and various alloys are developed using nano-diamonds. Introduction of nanomaterials in electrodeposited coating significantly increases its micro-hardness, enduring quality, corrosion resistance, improves its exterior appearance, reduces porosity.

Along with advantages and benefits of nano-diamonds application in GCC technology, electroplating experts note a number of problems in their application, namely: extremely high level of dispersion, defined by the way of obtaining, more than demanded field of application; associated delivery of nanodiamonds to the consumer in form of water base suspension, significant tendency to coagulation, rapid loss of sedimentation stability, need of implementation of complex multistage technology of electrolyte preparation and application, limited life of chrome-diamond coatings at high temperatures (over 473 - 573 K) due to destruction reasoned by oxidation of nanodiamond particles, impregnated in the surface layers of chrome matrix, during heating of the operating tool in operation.

Titanium, chromium and silicon borides and carbides nanopowders industrial production technology is described by the authors [11-12]. Manufacturing process includes plasma synthesis and, if necessary, nanopowders refining. Table 1 summarizes parameters of borides and carbides forming in conditions of three-jet vertical once-through reactor of 150 kW capacity and basic characteristics of borides and carbides. It can be seen that, by the main phases content and level of dispersion, introduced materials generally meet requirements on components of metal matrix composite coatings:

- level of dispersion of 30 - 60 nm predetermining creation of micro-regular distribution of particles in the matrix, stability of suspensions of which the coatings are deposited, and the
most complete manifestation of particles activity (chemical interaction with matrix, diffusion processes development, material hardening and improvement of its corrosion resistance);

- phase composition homogeneity, determining identity of particles behaviour in electrolyte and coating, local reproducibility of coating properties;
- homogeneity of chemical composition, suggesting minimum amount of impurities, especially free carbon: not always insurmountable technological difficulties are found when using nanocarbides with high content of free carbon;
- controlled state of the particles surface (gas saturation, presence of oxide films, etc.) having significant impact on developing such negative processes in electrolyte -suspension as liquid coalescence;
- high corrosion resistance, ensuring consistent suspensions composition and technological parameters of electrodepositing;
- high thermal oxidation stability, providing such an important operational characteristics of the coating, as scaling resistance.

3. Metal matrix composite coatings with nanocomponents
The main characteristics of coatings with nanocomponents: chrome, nickel - silicon carbide, nickel - carbonitride, chromium boride, nickel - carbide, titanium boride, zinc - chromium boride are given below (Table 2). Terms of electrodepositing, structure and properties of coatings are specified [13-15]. Analysis of the results indicates identity of composite chromium, nickel and zinc plating processes, and reveals the following main factors of raising coatings operational properties:

- borides and carbides nanopowders are represented by particles similar in shape to spherical or oval, having no sharp edges; they have high chemical and ad-sorption activity and, form electrolyte suspensions resistant to sedimentation and coagulation; due to small weight and size effectively are transferred to coated surface;
- during electrodeposition boride and carbide particles suspended in electrolyte interact with growing sediment surface due to hydrodynamic, molecular, electrostatic forces, that leads to formation of composite coating;
- during electrolytic deposition of chromium, nickel and zinc nanoparticles act as crystal seeds from which metal crystallization begins; due to large number of particles, involved in the process, crystallization is of massive multigerm nature and generated coating has small size of structural fragments, distinctive matte colour and are practically non-porous;
- synergy of particles non-inertial mass transfer and massive metals crystallization ensures regular deposition of coatings on equipotential surfaces;
- small size of metal crystallite particles provides precise duplication of surface micro-relief that increases general surface, and composite coating to base adhesive strength;
- improvement of coating quality, i.e. its corrosion resistance and micro hardness is achieved at low content of borides and carbides in coating (0.5 - 1.0%), which makes the process economically feasible.

Consequently, unlike micropowders, borides and carbides nanopowders are not only a filling material or the second phase, they also act as a strong modifier and a structure forming agent in electro-crystallization of metals, which leads to formation of highly dispersed nonporous structure of coating with increased corrosion resistance, micro-hardness and enduring quality.

Table 1. Parameters of borides and carbides forming and basic characteristics of nanopowders.

| Parameters of synthesis and its characteristics | CrB₂ | Cr₂(C₀.₈N₀.₂)₂ | TiB₂ | TiC | SiC |
|------------------------------------------------|------|---------------|------|-----|-----|
| Composition of the coolant gas,% vol.:         |      |               |      |     |     |
| - nitrogen / hydrogen / methane                | 74/25/1 | 99/−/1      | 74/25/1 | 99/−/1 | 99/−/1 |
| Technological variant of synthesis             | Cr+H₂ | Cr+CH₄        | Ti+H₂ | Ti+CH₄ | Si+CH₄ |
| Performance on feed, kg / h                    | 3.6   | 3.1           | 3.6  | 3.2  | 3.0  |
temperatures above 473 - 573 K. Enduring quality, micro-hardness, corrosion resistance, longer service life when operating under chromium, nickel and zinc with diamond, carbide and boride nanocomponents (Tables 3 - 5). It can be chrome, nickel and zinc plating comparison of characteristics of composite coatings based on

** Determined after exposure in the air for 24 h.**

* Calculated with value of specific surface;

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

| Coatings       | Micro-hardness ±0.3 GPa | Adhesive strength, MPa | Enduring quality** | Oxidation speed** T=1173K | Inherent stresses, MPa | Corrosion currents, μA/cm² |
|----------------|-------------------------|------------------------|--------------------|---------------------------|------------------------|-----------------------------|
| Chromium       | 5.4                     | 27.9-28.8              | 1                  | *                         | *                      | *                          |
| Cr - SiC NP    | 9.7                     | 29.3-30.4              | 2.5                | *                         | *                      | *                          |
| Cr - SiC MP    | 8.9                     | 28.4-29.2              | 2.2                |                           |                        |                            |
| Nickel         | 2.2                     | 29.1-30.3              | 1                  | 2.55                      | 1.36                   | 0.17                        |
| Ni -           | 4.5                     | 29.8-32.1              | 1.72               | 1                         | 0.50                   | 0.02                        |
| Cr₃(N₀₃N₂)₂NP  | 3.2                     | 28.9-30.2              | 1.54               | 1.34                      | 0.78                   | 0.11                        |
| Ni - Cr₃C₂MP   | 4.6                     | 31.2-33.3              | 1.69               | 1                         | 0.41                   | 0.02                        |
| Ni - Cr₂B₂NP  | 3.5                     | 29.8-30.6              | 1.52               | 1.17                      | 0.72                   | 0.10                        |
| Ni - Cr₂B₂MP  | 4.4                     | 30.7-32.8              | 1.70               | 1                         | 0.52                   | 0.03                        |
| Ni - TiC NP    | 3.3                     | 29.2-29.6              | 1.50               | 1.31                      | 0.78                   | 0.12                        |
| Ni - TiC MP    | 5.3                     | 29.5-32.2              | 1.76               | 1                         | 0.54                   | 0.02                        |
| Ni - TiB₂NP    | 3.3                     | 29.1-31.2              | 1.47               | 1.24                      | 0.79                   | 0.11                        |
| Ni - TiB₂ MP   |                         |                        |                    |                           |                        |                             |
| Zinc           | 1.0                     | *                      | *                  | *                         | *                      | 1.0**                       |
| Zn - Cr₂B₂NP  | 1.2                     | *                      | *                  | *                         | *                      | 2.3**                       |

* not evaluated;  
** relative values are given;  
*** corrosion resistance according to GOST 9.308-85 is provided, relative values  
NP - nanopowder  
MP - micropowder

To assess possibility of replacing nano-diamonds with nanopowders of carbides and borides in chrome, nickel and zinc plating comparison of characteristics of composite coatings based on chromium, nickel and zinc with diamond, carbide and boride nanocomponents (Tables 3 - 5). It can be seen (Table 3) that chromium carbide coatings have comparable to chromium-diamond coatings enduring quality, micro-hardness, corrosion resistance, longer service life when operating under temperatures above 473 - 573 K.
Table 3. Comparative characteristics of coatings based on chromium – with SiC silicon carbide and diamond nanopowders.

| Electrodeposition conditions and achieved results | Technologic options | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------------------------------------|---------------------|---|---|---|---|---|---|
| Electrolyte composition, kg/m³                  | Chromic anhydride   | 250| 250| 250| 250| 250| 260|
|                                               | Sulphuric acid      | 3 | 3 | 3 | 3 | 3 | 0.3 |
|                                               | Trivalent chromium  | 8 | 8 | 8 | 8 | 8 | -  |
|                                               | Potassium fluorosilicate | - | - | - | - | 19 |    |
|                                               | Barium sulfate      | - | - | - | - | 7 |    |
|                                               | Silicon carbide NP  | 4 | 6 | 7 | 8 | 10 | 7  |
|                                               | Diamond NP          | - | - | - | - | 20 |    |
| Electrodepositing mode                        | Temperature, K       | 328| 328| 328| 328| 328| 331|
|                                               | Current density A/dm² | 55 | 55 | 55 | 55 | 55 | 55 |
| Results                                       | Enduring quality*    | 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 when operating at temperatures above 473-573K* | 1.1 | 1.50 | 1.70 | 2.00 | 2.06 | 1.0 |
|                                               | Cost of 1m³ of electrolyte suspension * | 0.13 | 0.16 | 0.18 | 0.20 | 0.23 | 1.0 |

* Enduring quality, corrosion resistance, service life when operating at temperatures above 473-573K, cost of 1m³ of electrolyte suspension are given relatively to option 6, for which values of these indexes are taken as 1.0.

Table 4. Comparative performance indicators of nickel-based coatings with diamond (ND) and chromium carbide (KBKh) nanopowders.

| Electrodeposition conditions and achieved results | Options | Ni | Ni+ND | Ni+KBKh |
|------------------------------------------------|---------|----|-------|---------|
| Electrolyte composition, kg/m³                  |         |    |       |         |
| Nickel sulfate heptahydrate                     |         | 245| 245   | 245     |
| Boric acid                                      |         | 30 | 30    | 30      |
| Sodium chloride                                 |         | 20 | 20    | 20      |
| Sodium fluoride                                 |         | 6  | 6     | 6       |
| Diamond NP                                      |         | -  | 10    | -       |
| Chromium carbide NP                             |         | -  | -     | 10      |
| Electrolyte suspension preparation duration of nanopowder and electrolyte mixing time, h |         | -  | 40–80 | 0.5     |
| Duration of ultrasonic treatment at 20 kHz, h  |         | -  | 1–2   | -       |
| Cathodic current density kA/m²                  |         | -  | 0.01–0.02 | 0.01–0.02 |
| Duration of electrolyte suspension processing, h |         | -  | 2     | 2       |
| Electrolysis conditions                        |         |    |       |         |
| Electrolyte temperature, °C                    |         | 50–55| 50–55| 50–55   |
| Electrolyte pH                                 |         | 5.0–5.5| 5.0–5.5| 5.0–5.5 |
| Cathodic current density kA/m²                 |         | 0.5 | 0.5   | 1       |
| Volume of nickel plating baths, m³              |         | 0.6 | 0.6   | 0.6     |
| Electrolyte agitation                          |         | no | present | present |
| Results                                        |         |    |       |         |
| Coating thickness, μm                           |         | 40 | 40    | 40      |
| Nanopowder content in coating, %               |         | -  | 0.74  | 0.77    |
| Micro-hardness (P = 0.49N) ± 0.21, hPa        |         | 2.0 | 5.2   | 6.0     |
| Increase of enduring quality, relative units   |         | 1.0 | 3.0   | 3.5     |
Increase of corrosion resistance, relative units 1.0 16.7 12.2
Service life of threadlike sensor of stranding machines, months 4 11.5 12
Cost of 1 m³ of electrolyte suspension relative units - 1 7.5

When replacing nano-diamonds with nanoscale boride and chromium carbide at nickel and zinc plating, fine grained structure coatings, almost nonporous with comparable corrosion resistance are obtained (Tables 4 and 5). Consequently, nanopowders of carbides and borides can be used in chrome, nickel and zinc composite electroplating.

4. Economic evaluation

Table 5. Comparative performance indicators of zinc-based coatings with diamond nanopowders (ND) and chromium carbide (KBKh).

| Electrodeposition conditions and achieved results | Options                | Zn | Zn + ND | Zn + KBKh |
|-------------------------------------------------|------------------------|----|---------|-----------|
| Electrolyte composition, kg/m³                  | Zinc oxide             | 10 | 10      | 10        |
| Sodium hydroxide                                | 100                    | 100|         |           |
| Organic additive                                | 4                      | 4  |        |           |
| Diamond NP                                      | -                      | 10 | -       |           |
| Chromium carbide NP                             | -                      | -  | 10      |           |
| Electrolyte duration of nanopowder and electrolyte mixing time, h | -                      | 40| -0.5 | 0.5       |
| Duration of ultrasonic treatment at 20 kHz, h   | -                      | 1-2| -      | -         |
| Electrolyzing cathodic current density kA/m²    | -                      | 0.01-0.02 | 0.01-0.02 |
| Duration of electrolyte suspension processing, h | -                      | 2 | 2      | 2         |
| Electrolysis conditions                         | Electrolyte temperature, °C | 25-28| 25-28 | 25-28     |
| Cathodic current density kA/m²                  | 0.2                    | 0.2| 0.5    |           |
| Volume of nickel plating baths, m³              | 0.5                    | 0.5| 0.5    |           |
| Electrolyte agitation                           | no                     | yes| yes    | yes       |
| Results                                         | Coating thickness, μm  | 10 | 10      | 10        |
| Nanopowder content in coating, %                | -                      | 0.70| 0.64  |
| Micro-hardness (P = 0.2N) ± 0.10, hPA           | 1.00                   | 1.30| 1.20  |
| Corrosion resistance, h                         | 40                     | 95 | 90     |           |
| Service life of mold knives, months             | 1                      | 4  | 4      |           |
| Cost of 1 m³ of electrolyte suspension relative units | -                      | 650| 85     |           |
| Composition of solution for phosphate treatment, kg/m³ | Zinc oxide             | 10 | 10      | 10        |
| Sodium phosphate                                | 50                     | 50 | 50     |           |
| Sodium nitrate                                  | 10                     | 10 | 10     |           |
| Phosphate treatment Temperature °C              | 70–75                  | 70–75| 70–75 |           |
| Conditions                                      | Duration, h             | 0.5| 0.5    | 0.5       |
| Results                                         | Corrosion resistance, h | 52 | 205    | 200       |
| Service life of mold knives, months             | 1                      | 10 | 10     |           |

* Corrosion resistance of coating is provided based on GOST 9.308-85 by means of neutral salt spray testing (5% solution of sodium chloride at temperature 35°C).

electrolyte suspension preparation is significantly simplified and accelerated; deposition rate is increased by 2.5 times; cost of 1 m³ of electrolyte suspension is reduced by 8-10 times. Replacing of 1 tonne of nano-diamonds by nanopowders of borides and carbides gives economic efficiency of 135 mln rub.
5. Conclusions
Analysis of results of research in nanosize diamonds, borides and carbides application in electroplating metal matrix composite coatings production shows that combination of nanosize state with specifically shaped set of properties inherent to introduced borides and carbides provides sustainable achievement of parametric, concentration, structural and economic effects when they are introduced instead of diamonds, that proves their high competitiveness in domestic and global electroplating technology.

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7. References
[1] Sayfullin P S 2009 Proc. of Kaz. Tech. Univ. 6 80 – 90
[2] Desyatkova G I, Yagodkina L M et al 2002 Metals Protection 38 (5) 525–529
[3] Tsupak T E 2008 High Productive Processes of Electroplating of Nickel, Alloy Nickel – Phosphorus from Electrolytes Containing Carbon Acids (Moscow) abstr. PhD thes. p 40
[4] Dolmatov V Yu 2006 Proc. Int. Conf. on Nanotechnologies – to the Production (M.: Yanus-K) pp 113–151
[5] Dolmatov V Yu 2003 Ultra Dispersed Diamonds of Detonation Synthesis (St. Petersburg: SPbGPU) p 344
[6] Dolmatov V Yu 2005 Proc. 4th Int. Conf. MP3-IV (Tsukuba Science City, Ibraki, Japan) (Singapore: Institute of Materials) pp 284–286
[7] Burkat G K, Dolmatov V Y et al 2005 Composite Chrome-diamond Coating, Coating Layer and Manufacturing Method of thereof appl. for Pat. Rep. of Korea No. 10-2005-0037999
[8] Loubnin E N, Pimenov S M et al 1999 New Diamond Frontier Carbon Technology 9 (4) 273–282
[9] Pyzyr A P, Dolmatov V Yu et al 2004 Diamond and Related Materials 13 2020–23
[10] Ilyushin M A, Tselinsky I V et al 2005 Central European Journal of Energetic, Warsaw, Materials 1 21–33
[11] Efimova K A, Galevskii G V et al 2015 IOP Conf. Series: Materials Science and Engineering 91 1–10
[12] Galevskii G V, Rudneva V V et al 2015 IOP Conf. Series: Materials Science and Engineering 91 1–5
[13] Rudneva V V Galevskii G V 2007 Steel in Translation 37 (3) 224–227
[14] Rudneva V V, Galevskii G V and Kozyrev N A 2015 IOP Conf. Series: Materials Science and Engineering 91 1–11
[15] Efimova K A, Galevskii G V et al 2015 IOP Conf. Series: Materials Science and Engineering 91 1–8