Nickel and titanium nanoboride composite coating

K A Efimova1, G V Galevsky2, V V Rudneva2, N A Kozyrev2, E G Orshanskaya3

1Postgraduate student, Siberian State Industrial University, 654007, Novokuznetsk, 42, Kirov str.
2Doctor of Engineering, Professor, Siberian State Industrial University, 654007, Novokuznetsk, 42, Kirov str.
3Doctor of Pedagogy, Professor, Siberian State Industrial University, 654007, Novokuznetsk, 42, Kirov str.
e-mail: kafcmet@sibsiu.ru

Abstract. Electrodeposition conditions, structural-physical and mechanical properties (microhardness, cohesion with a base, wear resistance, corrosion currents) of electroplated composite coatings on the base of nickel with nano and micro-powders of titanium boride are investigated. It has been found out that electro-crystallization of nickel with boride nano-particles is the cause of coating formation with structural fragments of small sizes, low porosity and improved physical and mechanical properties. Titanium nano-boride is a component of composite coating, as well as an effective modifier of nickel matrix. Nano-boride of the electrolyte improves efficiency of the latter due to increased permissible upper limit of the cathodic current density.

Introduction
Electrodeposited or galvanic composite coatings (GCC) are formed as a thin layer in the course of metals deposition on the products with electro-conductive surface made up of electrolytes-suspensions with a dispersed phase. Service characteristics of coating are improved due to particles. Improvement of GCC service characteristics necessitates enhancing the dispersion level of strengthening phase. For this reason experts dealing with GCC technology always use materials with high dispersion including nano-level ones as a strengthening phase [1 – 8].

Purpose and objectives of research
This research is aimed at revealing peculiarities of nickel GCC formation and properties, its strengthening phase is made up of nano- and micro-powders of titanium boride, which is a synthetic superhard, high heat, and high temperature material needed in protective coatings technology. Galvanic nickel coatings are the most utilized ones in various industries; their usage amounts to 75% of overall total electroplated deposited metals.

Materials and methods of experiments
For hardening nickel matrix we used nano-powder of titanium boride (NP TiB2), which was obtained through boriding metal powder of titanium in nitrogen plasma flow, and its micro-powder (MP TiB2), produced in the course of self-spreading high-temperature synthesis. TiB2 concentration in nanopowder is 92.81%, and 94.12% in micro-powder, specific surface area of powders is 46000 and...
1000 m²/kg, dimensional range of particles is 0.01–0.07 and 3–7 µm. Micro-photographs of nano- and micro-powders, made by transmission and scanning electron microscopy (TEM, SEM), are depicted in Figure 1.

The research into parameters of GCC deposition was carried out in standard nickel-plating electrolyte, containing NiSO₄·7H₂O – 245, H₃BO₃ – 30, NaCl – 20, NaF – 6 kg/m³ in the following conditions: pH 5.0–5.5, temperature 323 K, cathodic density of current 0.1–1.2 kA/m², powder concentration 1–100 kg/m³, constant mixing of electrolyte. Steel (St. 3) samples with surface area 2.0·10⁻³ m² were used as cathodes. 0.08 х 0.1 m nickel plates were used as anodes.

Fine structure of GCC with nano-powder was tested by electron microscopy and energy-dispersive spectrometry. For investigation of basic morphological types of micro- and nano-powders, identification of their form and linear features we used field emission scanning electron microscope JSM – 6700F with an appliance for energy-dispersion spectrometry JED – 2300F, equipped by high-power conic objective lens. This objective lens provides guaranteed resolution 1.0 nm at accelerating voltage 20 kW and 2.2 nm at 1 kW. The first stage of investigation focused on formation of surface microrelief in secondary electrons. Then, in conditions of relatively small but sufficient (x 2000 – x 3000) magnification for identifying all objects we checked the surface of prepared samples totally in order to find their most typical zones. These areas were tested more precisely to define form, length and diameter of micro- and nano-objects. Identification of element composition of GCC samples was performed by energy-dispersion spectrometry with scanning electron microscope JSM – 6480 LV with an appliance for energy-dispersion spectrometry INCA. This method taken with scanning electron microscopy makes it possible to carry out a quantitative elementary analysis, ranging from boron to uranium and in quantity 1–3 cubic µm. Sensitivity of the method is 0.1 atomic %. Relative error of measurement is 5 %.

Cathodic current efficiency of nickel is determined gravimetrically by copper coulometer, connected in-series with electrolyzer.

Titanium boride concentration in composite coatings was determined gravimetrically after their dissolution in 10 % HNO₃ solution (GOST 5744 – 94). Percentage of boride concentration in matrix was calculated as relation of insoluble residual mass to the mass of coating.

Microhardness of coating was measured by microhardness testing instrument PMT – 3 and involved static hardness indentation perpendicularly to coating layer subject to 0.49 N load. Microhardness of coatings was determined on samples 40 µm thick according to 5 – 6 measurements of imprint diagonal.
Figure 1. PEM microphotographs of titanium boride nano-powder (a) and micro-powder (b), SEM of titanium boride nano-powder (c – ensemble of particles and aggregates; d – morphological structure of aggregate; e – separate particles)

Internal stresses of coatings were measured by deformation method of elastic cathode. Coating cohesion with steel base was assessed by the method of shear loading; samples were glued together with BK – 9 glue, bonding area was $0.35 \cdot 10^{-4}$ m², layer thickness – $0.5 \cdot 10^{-3}$ m, after drying they were tested by P – 0.5 tension testing machine for 24 hours. Protective capability of coatings was assessed according to coating-base corrosion currents, determined by Rosenfeld method in a neutral electrolyte.

For investigation of changing GCC properties when isothermal annealing GCC samples were placed into quartz vessels, vacuumized and sealed. Then, the vessels were placed into electric-tube furnace, which provided heating rate up to needed temperature about 0.1 degree/s, there samples were kept for 120 minutes at each temperature. The research focused on the effect of temperature and temporal annealing conditions on microhardness and strength of GCC-steel base cohesion.

Methods to determine titanium boride concentration in coatings, their microhardness, fine structure, internal stresses, and cohesion with base, corrosion currents between them and the base are described in papers [9–11] in detail.

**Results of research and discussion**

The investigation focused on effect of cathode density of current and powders concentration in electrolyte on titanium boride concentration in coatings and their microhardness.

| Cathode density of current, kA/m² | Strengthening phase concentration in GCC, % |  |
|----------------------------------|--------------------------------------------|---|
|                                  | NP TiB₂                                    | MP TiB₂ |  |
| 0.1                              | 0.31                                       | 0.59     |  |
| 0.3                              | 0.36                                       | 0.73     |  |
| 0.5                              | 0.41                                       | 0.91     |  |
| 0.7                              | 0.52                                       | 1.32     |  |
| 1.0                              | 0.57                                       |         |  |
| 1.2                              | defective coatings                         |         |  |
Table 2. The relation of strengthening phase concentration in GCC and their microhardness to powder concentration in electrolyte

| NP, MP concentration in electrolyte, kg/m³ | Strengthening phase concentration in GCC, % | Microhardness ± 0.3 GPa |
|-------------------------------------------|-------------------------------------------|------------------------|
|                                           | NP TiB₂                                  | MP TiB₂                |
| 2.0                                       | 0.22/3.0                                 | 0.33/2.9               |
| 5.0                                       | 0.30/3.4                                 | 0.60/2.9               |
| 10.0                                      | 0.51/4.8                                 | 1.18/3.1               |
| 15.0                                      | 0.60/5.3                                 | 1.32/3.3               |
| 30.0                                      | 0.61/5.2                                 | 1.73/3.3               |
| 45.0                                      | 0.59/5.1                                 | 2.01/3.6               |
| 60.0                                      | 0.52/4.7                                 | 2.32/3.8               |
| 80.0                                      | 0.52/4.8                                 | 3.01/4.1               |
| 100.0                                     | not tested                               | 3.12/4.0               |

The research into the effect of cathode density on strengthening phase concentration in a coating was conducted in the following conditions: pH of electrolyte 5.0, temperature 323 K, and strengthening phase concentration 15 kg/m³. The results are provided in Table 1. As one can see, the increase in cathode density of current within the limit 0.1 – 1.0 kA/m² for nano-powder and 0.7 kA/m² for micro-powder causes growth of strengthening phase concentration in a coating: for NP TiB₂ from 0.31 to 0.60; MP TiB₂ from 0.59 to 1.32 %. With strengthening nano-disperse phase the upper limit of operating current density of electrolyte is 1.0 kA/m², it’s higher than that for making nickel coatings in this electrolyte (0.5 kA/m²). Therefore, the electrolyte with nano-powder is more efficient; and more promising one for worn surfaces restoration, respectively.

The influence of powders concentration in electrolyte on strengthening phase concentration in a coating was tested in the following conditions: pH of electrolyte – 5.0, temperature 323 K, and cathodic density of current 1.0 kA/m² for nano-powder; and 0.7 kA/m² – for micro-powder. The results are provided in Table 2. As one can see, growing concentration of nanopowder in electrolyte-suspension up to 15 kg/m³ results in its increase in GCC, further, there is practically no change when concentration amounts to 15–45 kg/m³, and a slight decrease is possible in the range 45–80 kg/m³. When micro-powder is added to electrolyte in concentration 2–100 kg/m³ its concentration goes up in a coating from 0.53 to 3.12 %. As the consequence, the bigger coarseness of titanium boride powder is the higher concentration of strengthening phase is needed for nickel matrix saturation.

Thus, we suggest that nano-powder is more reasonable to use than micro-powder for composite coatings manufacture. Optimal conditions of GCC nickel – NP titanium boride deposition are as follows: TiB₂ concentration 15 kg/m³, cathodic density of current 0.9–1.0 kA/m² temperature 323 K, pH – 5.0–5.5, and constant mixing electrolyte. Nickel current efficiency in these conditions is 92–94%.

The structure and main characteristics (hardness, cohesion with steel base, internal stresses, corrosion currents) of nickel composite coating containing nano- and micro-powder of titanium boride were tested, as well as those of pure nickel coating, i.d. nickel matrix. Deposition of GCC Ni – NP TiB₂ was performed with nano-powder concentration in electrolyte 15 kg/m³ and cathodic density 1.0 kA/m². When GCC Ni – MP TiB₂ depositing concentration of micro-powder in electrolyte was 80 kg/m³, cathodic density of current – 0.7 kA/m². For deposition of pure nickel coatings electrolyte of the same composition was used, without disperse phase.

Analysis of energy-disperse spectra of electrodeposited nickel and GCC confirms that they contain Ni, O and Ni, Ti, B, O. Quantitative relations are quite acceptable ones (Table 3). Here, for elements to be identified rather even distribution is typical in 30 µm coating (Fig. 2), i.d. its composite character is confirmed.
Table 3. Element chemical composition of electrodeposited nickel (specter 1) and GCC Ni – NP TiB₂ (spectra 2-4)

| Element | Specter 1 | Specter 2 | Specter 3 | Specter 4 |
|---------|-----------|-----------|-----------|-----------|
| Ni      | 98.20     | 97.67     | 97.65     | 97.69     |
| O       | 1.80      | 1.71      | 1.79      | 1.72      |
| Ti      | 0.42      | 0.40      | 0.42      |           |
| B       | 0.20      | 0.18      | 0.18      |           |

Figure 2. Results of micro-roentgen spectral analysis of basic elements distribution in GCC Ni – NP TiB₂

Microhardness of GCC is determined by strengthening phase concentration in it and dimensions of its particles (Table 2). Microhardness of GCC Ni – TiB₂ is 5.1–5.3 GPa, it’s 2–2.3 higher than that of nickel matrix, and 1.4 times higher than that of GCC with MP TiB₂. Cohesion of GCC Ni – NP TiB₂ with steel base is 29.5–33.1 MPa. Isothermal annealing of GCC Ni – NP TiB₂ in vacuum in temperature range 473 – 1273 K facilitates microhardness increase in GCC (Fig. 3). However, the character of temperature dependence of microhardness for GCC under consideration is different. For instance, for GCC Ni – MP TiB₂ (curve 2, Figure 3) microhardness rises monotonously from 3.8 to 5.2 GPa when annealing temperature rising from 473 to 1273. Microhardness of GCC Ni – NP TiB₂ (curve 1, Fig. 3) in temperature range 473 – 873 K grows from 5.1 to 6.2 GPa, but in temperature range 873 – 1273 K hardly changes practically. Here, to achieve maximum microhardness of GCC Ni – NP TiB₂ 60 – 75 minute annealing is sufficient (curve 1, Fig. 4), whereas for GCC – MP TiB₂ annealing for 120 minutes is required (curve 2, Fig. 4).

Figure 3. The dependence of microhardness of GCC Ni – NP TiB₂ (1) and Ni – MP TiB₂ (2) on temperature of 2 hour annealing in vacuum
The strength of GCC Ni – NP TiB$_2$ cohesion with the base, which was annealed in vacuum at temperature 873 K for 75 minutes, increased 1.4 times in comparison to non-annealed ones and was 42.3 – 45.2 MPa.

Disperse particles in a coating reduce internal stresses, especially when titanium boride nano-powder is used. For instance, internal stresses of 40 µm thick composite coating with micro-powder TiB$_2$ are 1.5 times and with nano-particles 3.4 times smaller than those of pure nickel (Table 4). Obviously, the reason for it is a more fine-disperse structure of growing sediment due to evenly distributed particles of disperse phase in it. Coarse particles of micro-powder as if compared with NP cause uneven deformation of a matrix including big groups of grains, therefore, increasing internal stresses and reducing corrosion characteristics.

Corrosion currents arising in coating – steel base spacing are far lower than in nickel matrix (Table 4). In 40 µm coating, made of micro-powder, corrosion currents are 2.3 times lower than in pure nickel, and in a coating made of nano-powder – 11.9 times lower, it means, that practically pore-free GCC Ni – NP TiB$_2$, form and provide high protective characteristics (Figure 5).
Figure 5. Microphotographs of electrodeposited nickel surface (a) and ГКП Ni – NP TiB₂ (b)

Table 4. The dependence of internal stresses and corrosion currents on coating thickness

| Coating thickness, µm | Ni | Ni – NP TiB₂ | Ni – MP TiB₂ | Ni | Ni – NP TiB₂ | Ni – MP TiB₂ |
|----------------------|----|-------------|-------------|----|-------------|-------------|
| 5                    | 936| 351         | 578         | 0.304| 0.088       | 0.167       |
| 10                   | 692| 159         | 323         | 0.265| 0.061       | 0.154       |
| 20                   | 361| 62          | 146         | 0.205| 0.047       | 0.139       |
| 30                   | 127| 54          | 79          | 0.173| 0.022       | 0.102       |
| 40                   | 101| 30          | 69          | 0.167| 0.014       | 0.072       |

Thus, nano-particles of titanium boride have significant chemical and adsorptive energy, form sedimentation and coagulation stable electrolytes-suspensions and can be easily transferred to surfaced area due to low mass. In course of electrodeposition of nickel nano-particles of boride are centers of crystallization. As a great number of boride nano-particles take part in this process, the character of crystallization is mass multinuclear one. Coatings have small dimensions of structure elements, typical matt colour and low porosity. Small particles of boride and nickel crystallite provide exact imitation of surface micro-relief. Relatively low concentration of strengthening phase in coating Ni – NP TiB₂ is the reason of its considerably low consumption per 1 m² of processed surface and helps to keep valuable properties of a matrix. Low concentration of nano-powder in electrolyte simplifies maintenance of electroplating baths and reduces titanium boride losses caused by electrolyte carry-over on workpieces. Titanium boride raises electrolyte efficiency due to increased upper limit of cathodic density of current. These properties of GCC Ni – NP TiB₂ are the reason to recommend them for anticorrosion protection of workpieces, and after thermal treatment – for strengthening workpieces, running at full capacity in conditions of sliding friction at mean circular velocities (1.5–2.5 m/s) and low specific loads (5–6 MPa) (shafts, bushes, sliding bearings, spindles etc.).

Conclusions

When electrodepositing nickel from electrolyte-suspension, nano-powder of titanium boride is a component of a composite coating nickel – titanium boride and an efficient modifier at the same time. As the result, coatings are formed with fine-grain pore-free structure and high operational services.
Technological advantages of nickel galvanic composite coatings including nano-titanium boride have been revealed, as well as engineering spheres of their most efficient application.

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