The role of dispersed phase in the formation of Ni – CEC

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Abstract. Composite electrochemical coatings make it possible to successfully solve many practical problems of surface hardening of structural parts, tooling and restoration of their wear parts. One of the factors influencing the structure and properties of composite coatings is characteristics of the dispersed phase (nature, concentration, dispersion). This paper presents the results of studying activation of titanium carbide by heat treatment method, which contributed to an increase in the main characteristics of nickel electroreduction. Barium sulfate is a promising dispersed material for composite coatings. This powder can be obtained with any dispersion as a result of an exchange reaction. In this work investigates the effect on the particle size of barium sulfate deposition conditions (time of mixing and pouring of reagents). The optimum conditions for obtaining barium sulfate are determined. Both powders can be used as a dispersed phase to obtain composite coatings with a nickel matrix.

1. Introduction
Composite electrochemical coatings (CEC) are widely used in instrumentation and mechanical engineering to impart special properties to the surface of metals. CECs are heterophase systems, cathode-deposited or isolated by chemical (current-free) reduction from solution, obtained by electrochemical and chemical means. CECs consist of a layer of metal or anodic oxide (matrix) in which particles of a solid (liquid, gas) are dispersed, called the dispersed phase (DP) or the second phase. Inclusion of DP particles imparts a complex of new properties to metal coatings (hardness, wear resistance, corrosion resistance, etc.). CECs make it possible to successfully solve many practical problems of surface hardening of structural parts, tooling and restoration of their wearing parts. The most widespread among CECs are coatings with a nickel matrix. Dispersed particles of various nature with sizes ranging from nanoscale to micrometer sizes are easily coprecipitated with nickel [1-4].

Recently, finely dispersed particles obtained by chemical reactions directly in the electrolyte or in solutions, electrolyte components, have been used as a dispersed phase.

Titanium carbide possesses unique physicochemical characteristics and is widely used for the manufacture of elements of jet aircraft engines and special coatings for missiles. It is included in various alloys to increase the strength of high-temperature steel materials; abrasive pastes used for polishing various tools and parts. The use of this substance in the electrode industry is of particular importance.

Particles of titanium carbide are widespread and often used as a dispersed phase to obtain CECs with various metal matrices. The use of titanium carbide nanopowders as the second phase makes it possible to obtain composite coatings that can be used for anticorrosive protection and hardening of parts that wear out at medium peripheral speeds and low specific loads.

Barium sulfate particles are a promising dispersed material that has many advantages (low
solubility, different dispersion). Finely dispersed barium sulfate particles produce compact and uniform coatings. The presence of BaSO₄ in nickel (copper) coatings helps to maintain their smoothness, prevents welding of moving contacts and facilitates sliding. Barium sulfate particles can be a model for studying the formation process and properties of composite electrochemical coatings based on copper and other metals in electrolytes. Also BaSO₄, obtained with the required particle size distribution, has a high reflectivity in the UV, visible and near-IR regions of the spectrum. This quality makes it possible to use such powders as pigments for thermoregulatory coatings of spacecraft exposed to the action of quanta of the solar spectrum, electrons, protons and other types of radiation [5].

The aim of the work was to study the properties of titanium carbide powder activated by heat treatment and obtain highly dispersed barium sulfate with the aim of using them as a dispersed phase for obtaining coatings with a nickel matrix.

2. Objects and research methods
To obtain nickel coatings, nickel-plating sulfate electrolyte of the following composition was used: NiSO₄⁺7H₂O 75 g/l, Na₂SO₄⁺10H₂O 45 g/l, H₃BO₃ 30 g/l, NaCl 10 g/l. The coatings were applied to steel samples. The following were used as particles of the second phase: titanium carbide powder, grade ‘clean’, d = 20–40 µm; titanium dioxide powder. Powder concentration - 5 g/l. Electrolysis mode: pH = 5.6–5.8; t = 20 ± 50°C; cathode current density = 2 and 3 A/dm². Nickel plates were used as anodes; electrolysis was carried out with constant stirring with a magnetic stirrer with a rotation frequency of 60 rpm. The charge yield of metal (CY) was calculated according to the Faraday law. The thickness of the coatings was determined by the gravimetric method in accordance with GOST 9.302-88. The chemical composition of powders and layers in the Fe-Ni system was determined using an X-ray fluorescence analyzer (XFA) of coatings (X-STRATA 980).

To prepare a solution of barium chloride and sodium sulfate, reagents were used that corresponded to GOST 4108-72 and GOST 4166. The concentration of barium chloride solution consisted of 1.5M, and sodium sulfate -1M. The process of precipitation of barium sulfate was carried out under various conditions: at a temperature of 20 ± 5°C; mixing time - 20 and 60 minutes and time of solution drainage: instant, 2; 3; 5 minutes. The conditions were chosen based on literature data [6]. The particle size of barium sulfate was determined using an Analysette 22 laser diffraction analyzer. This microanalyzer is designed for automatic express particle size analysis in suspensions in the range from 0.16 microns to 600 microns and reproduces the measurement of particle size distribution with high accuracy. The duration of one measurement is 5 minutes, the required sample amount is about 0.1 - 2 g. The micrographs were obtained on a Hitachi HT7700 transmission electron microscope (Japan) at an accelerating voltage of 100 kV. The samples were sonicated in ethanol and slurried onto a 300 mesh copper mesh covered with a continuous layer of carbon-sprayed formvar.

3. Experimental results and their discussion
For a comparative analysis of the data obtained, a theoretical calculation of the composition of powders was carried out, which showed that in TiC the content of titanium is about 80%, carbon is about 20%, the iron content is allowed up to 0.05%; in TiO₂ the titanium content is about 60%, the oxygen content is 40%; in TiO the titanium content is about 75%, the oxygen content is 25%. Activation by heat treatment was carried out in order to reduce the amount of free carbon in titanium carbide, since its high content negatively affects physical and mechanical properties of the products. X-ray fluorescence was used as the main research method. In [7], this method was used to estimate the thickness of coatings. Analysis of the TiC powder on an X-ray fluorescence analyzer showed that it contains 78% of Ti. The composition of the metal sample used for coating was also determined. Its composition is Fe 75%, Ni 1.16%, other substances 24%.

Heat treatment was carried out at a temperature of 800°C for 2 and 2.5 hours. All obtained samples had weight gain. The powder baked for 2 hours had a mixed shade of black with an interspersed lemon-yellow color, and the powder baked for 2.5 hours had a bright yellow color, which turned into a
pale lemon on cooling. The data obtained allowed us to make an assumption about the partial transition of TiC to TiO, which has a golden-yellow color, as well as the presence of different modifications of titanium dioxide in the baked powder. Presumably, the titanium dioxide obtained is in the rutile modification, but some of it can be presented in the form of anatase and brookite modifications.

The chemical behavior of the investigated powders in water and in nickel plating electrolyte was studied. As can be expected, the baked powder is more active than the unbaked powder. The weight loss in the electrolyte was 30% as compared to 20% for the unbaked powder.

Table 1 shows the results of X-ray fluorescence analysis of powders after treatment in a nickel plating electrolyte and water.

| Definition point number | Baked electrolyte | Baked water | Unbaked electrolyte | Unbaked water | Unbaked no |
|-------------------------|-------------------|-------------|---------------------|--------------|-----------|
| 1                       | 76.34             | 61.98       | 64.5                | 66.5         | 75.8      | 77.2      |
| 2                       | 68.9              | 59.6        | 57.24               | 79.1         | 86.61     | 79.55     |

The results obtained make it possible to confirm that the powder after heat treatment is titanium dioxide.

The coatings were obtained on a metal cathode in a background electrolyte and from electrolyte suspensions with activated powder at current densities of 2 A/dm$^2$ and 3 A/dm$^2$. The duration of electrolysis was calculated to obtain a coating with a thickness of 20 μm and was 49 min for a current density of 2 A/dm$^2$ and 33 min for 3 A/dm$^2$. The resulting coatings had a matte sheen.

Table 2 shows characteristics and compositions of the coatings obtained from the electrolyte-suspension with baked titanium carbide.

| Sample number | Current density, A/dm$^2$ | Current yield, % | Deposition rate, μm/min | Coating thickness, microns | Coating composition, % |
|---------------|---------------------------|------------------|-------------------------|-----------------------------|-----------------------|
| 1             | 2                         | 98               | 0.394                   | 13.3                        | Ni – 82.5             |
|               |                           |                  |                         |                             | Fe – 12.9             |
|               |                           |                  |                         |                             | Ti – 0.02             |
| 2             | 2                         | 97               | 0.390                   | 13.2                        | Ni – 96.6             |
|               |                           |                  |                         |                             | Fe – 1.3              |
|               |                           |                  |                         |                             | Ti – 0                |
| 3             | 3                         | 85               | 0.512                   | 17.19                       | Ni – 87.5             |
|               |                           |                  |                         |                             | Fe – 10.6             |
|               |                           |                  |                         |                             | Ti – 0.09             |
| 4             | 3                         | 93               | 0.561                   | 18.95                       | Ni – 98.9             |
|               |                           |                  |                         |                             | Fe – 7.6              |
|               |                           |                  |                         |                             | Ti – 0.44             |
| Background sample | 3                         | 72               | 0.434                   | 14.54                       | –                     |

As the studies have shown, the proportion of DP in the coatings is insignificant, but with an increase in the current density, the titanium content in the coatings increases. In addition, the current density also affects the deposition rate of particles - the higher the current density, the faster the
deposition proceeds. The low coprecipitation of the particles of baked titanium carbide with the matrix can be associated with their low dispersion, therefore, it is recommended to grind it before use.

Thus, our studies have shown that thermal activation of silicon carbide promotes intensification of deposition with a nickel matrix.

It is known from literature [8] that the main method for the production of barium sulfate is its precipitation from aqueous solutions of barium salts with sodium sulfate. The method is based on an exchange reaction.

The dispersion of powders is affected by the deposition conditions (concentration of the initial reagents, impurities, duration of mixing and rate of merging of the initial reagents) [10]. When obtaining barium sulfate, concentrated solutions of the initial reagents were used, since high concentrations of reagents create high supersaturations in the synthesis and ensure the precipitation of a highly dispersed product [10]. Concentrations of the reagents were selected in previous works [12].

The mixing time was 20 minutes (samples 1-4) and 60 minutes (samples 5-8). The ratio of components in all experiments was 1:1. The duration of mixing the reagent solutions was instantaneous (samples 1; 5), 2 min (samples 2; 6); 3 min (samples 3; 7); 5 min (samples 4; 8).

After the barium sulfate suspension was obtained, it was filtered, but the particles passed through the filter. Therefore, to separate BaSO₄ particles from the liquid, the suspension was heated to the temperature of liquid evaporation. The suspension was washed from chloride ions as follows: the suspension was allowed to stand, the clarified liquid was poured out, then distilled water was poured in and allowed to stand again. The process was repeated until a negative reaction for chloride ions was reached.

Sizes of the obtained BaSO₄ particles are presented in Table 3.

| Sample number | Particle content (%) in a given fraction (μm) | Average size, μm | Specific surface, 10⁻⁵ cm²/cm³ |
|---------------|---------------------------------------------|-----------------|------------------------------|
|               | ≤0.05 | 0.05-0.1 | 0.1-0.2 | 0.2-0.3 | 0.3-0.5 | 0.5-1 | 1-1.5 |               |
| Sample 1      | 0.00  | 8.77     | 50.01   | 30.19  | 9.74    | 1.30  | 0.00  | 0.20  | 3.6               |
| Sample 2      | 0.81  | 20.64    | 61.31   | 15.40  | 1.84    | 0.00  | 0.00  | 0.15  | 4.7               |
| Sample 3      | 0.00  | 7.99     | 44.34   | 30.59  | 13.57   | 3.34  | 0.17  | 0.22  | 3.4               |
| Sample 4      | 0.00  | 8.58     | 48.80   | 30.14  | 10.59   | 1.79  | 0.11  | 0.20  | 3.6               |
| Sample 5      | 0.00  | 9.34     | 53.19   | 28.94  | 7.86    | 0.68  | 0.00  | 0.19  | 3.7               |
| Sample 6      | 0.35  | 16.55    | 60.55   | 19.21  | 3.35    | 0.00  | 0.00  | 0.16  | 4.4               |
| Sample 7      | 0.39  | 17.24    | 60.38   | 18.61  | 3.24    | 0.15  | 0.00  | 0.16  | 4.5               |
| Sample 8      | 0.00  | 9.91     | 52.02   | 28.04  | 8.52    | 1.41  | 0.11  | 0.19  | 3.7               |

As can be seen from Table 3, all obtained samples are polydisperse. The presence of aggregates of different sizes indicates the random nature of the nucleation process. The content of particles with a size of 100-200 nm in all samples is about 50%. Samples 2; 6; 7 contain particles of less than 50 nm about 1%, there are no particles larger than 0.5 μm, their average size is 150 nm. Other samples (1; 3-5; 8) contain about 2% particles larger than 0.5 μm, and the average size of these particles is 200 nm. In samples 2; 6; 7, the highest content (~ 20%) of particles with a size less than 100 nm was found. It is possible that a decrease in the size of barium sulfate particles in samples 2 and 6 (150 and 160 nm) in comparison with other samples is associated with the time of decantation of the initial reagents (2 min) [10, 11]. From our data, the most optimum drainage time is 2 min. The duration of stirring the
suspension affects the dispersion of all obtained samples insignificantly.

In [11], it was shown that with a slow drainage of reagents, formation of larger aggregates is accelerated due to the presence of interlayer water in the salts, which facilitates diffusion processes. This position is confirmed by the data of experiments 3-5; 7; 8; in Table 1 and in Figure 2.

The following are photomicrographs of barium sulfate particles obtained using transmission electron microscopy in Figures 1 and 2. The photomicrographs obtained using transmission electron microscopy show that nanosized particles are formed in the system. The particles obtained after a 2-minute decantation of the initial reagents have sizes from 50 to 200 nm, but larger particles are also observed in the form of aggregates, Figure 1.

At a 5-minute time of decantation of initial reagents, the particles have a size from 100 to 400 nm. Figure 2 shows a phase between the aggregates in the state of the beginning of nucleation, and not in the crystalline form [9]. The forming crystals have the form of hexagonal prisms (Figures 1 and 2), and each of their faces increases in size by the layer-by-layer growth mechanism. The crystallization process of barium sulfate can be represented as follows: crystals nucleate homogeneously and grow molecularly. At the same time, agglomeration begins, and the aggregates turn into pseudo-single crystals. With prolonged stirring of the suspension, formation of aggregates will decrease; with a short time, vice versa. If the barium sulfate crystals did not agglomerate, their specific surface area would increase to 100 m$^2$/g [6].

In the literature, oxides and carbides are mainly used as DPs. In this work, barium sulfate particles of different dispersion were used as DPs. These particles are partially soluble in water (PR = 1.1 · 10$^{-10}$). Particles of BaSO$_4$ powder were added to the electrolyte in an amount of 5-25 g/L, sample 6. The size of these particles were from 50 to 200 nm. All coatings obtained were of good quality. For sample 6, the number of particles in the zinc matrix was 2.8%, with their concentration in the suspension electrolyte - 25 g/L.
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