Composite electrochemical nickel coatings with dispersed particles

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Abstract. The composition of electrochemical coatings of nickel-zirconium dioxide, the peculiarities of their morphology were investigated. It was shown that depending on the dispersion and the method of preparation (plasma-chemical method and deposition method) of the dispersed phase, the content of inclusions in coatings varies from 0.2 to 1%, in the case of the plasma-chemical method and from 0.3 to 2%, in the case of particles obtained by the deposition method. Nickel-zirconium coatings are characterized by increased microhardness, corrosion resistance, and wear resistance compared to control precipitates by 1.4; 2.4 and 1.2 times respectively.

1. Introduction
At present, technological requirements for materials used in such industries as medicine, aviation, chemical and machine-building industry, etc. are increasing. High values of heat and electrical conductivity, wear resistance, plasticity are required, and it is very useful if the materials are heat-resistant, have chemical durability and hardness. In this regard, composite electrochemical coatings (CEC) are being developed to improve the performance characteristics of the materials used [1, 2]. Coatings are obtained by electro-deposition of a metal (matrix) with a dispersed phase (DP). The most common use of nickel as a matrix material is due to its physical and chemical properties. It readily forms coatings with many particles used as the dispersed phase. Nickel coatings are not able to sufficiently electrochemically protect iron from corrosion. The main condition for ensuring the protection of iron from the effects of the external environment is non-porous nickel coatings.

Obtaining a non-porous nickel coating is difficult due to the crystalline heterogeneity of the surface of the base metal and the presence of various machining defects in it. One of the ways to eliminate porosity is dispersion of nanoparticles in a metal matrix [3]. The dispersed phase is evenly distributed in the nickel matrix, thereby preventing the oxidation of iron by reducing the porosity of the coatings.

In this paper, zirconium dioxide is used as the dispersed phase. It is known [4] that these particles contribute to the improvement of the operational characteristics of coatings.

In this regard, the topical issues considered in this paper are the studies of the possibility of obtaining CEC with a nickel matrix with DP of zirconium dioxide of different dispersion.
2. Methodology of the experiment

For the study, the following composition of nickel-plating sulphate electrolyte was used, g/dm³:
NiSO₄·7H₂O - 75; Na₂SO₄·10H₂O - 50; H₃BO₃ - 30; NaCl - 10. Conditions for obtaining CEC from this electrolyte: \( i_k = 2A/dm²; \) pH=5.6-5.8; t=20±2°C. The concentration of DP in the electrolyte is applied in the range from 0.1 to 50 g/dm³. The thickness of the formed coatings is 20 microns. Copper and steel samples served as cathodes, nickel plates served as anodes. The pH of the suspensions and electrolyte was measured using a pH meter, pH-150M, until the readings stabilized for about 4 minutes. The viscosity of the electrolyte suspensions was measured according to GOST 33-2016 using a capillary glass viscometer VPZh-2 type.

The determination of the density of electrolyte suspensions was performed by a hydrometer according to GOST 3900-85. Particle size determination was performed by laser diffraction using a Horiba LA-950-V2 laser analyser, in accordance with GOST 8.777-2011. An x-ray powder analysis method was carried out in a step-scanning mode on a Bruker D8 ADVANCE diffractometer with Breug-Brentano focusing using monochromatic Cu-radiation. The current output of nickel was measured coulometrically. The number of inclusions of the dispersed phase in the coatings was determined by the direct method. The elemental composition of Ni-ZrO₂ coatings was carried out by X-ray fluorescence analysis in accordance with ISO 3497, using "X-STRATA 980 GMFMINI" analyser. The porosity of the coatings was determined according to GOST 9.302-88. The change in the mass of the coatings was established in accordance with GOST 9.90885 in 3% NaCl solution for one week. Polarization measurements were carried out in a YaSE-1 cell in a potentiodynamic mode using an IPC-2000 potentiostat-galvanostat. Potential sweep rate is 10 mV/s. A platinum plate was used as a working electrode (S=6 mm²).

A silver chloride electrode served as a reference electrode, and platinum (S=3 cm²) served as an auxiliary electrode. The polarization curves of nickel electro reduction were recorded on freshly precipitated nickel with a thickness of \( \delta = 2 \) μm. The microhardness of the coatings was determined using a PMT-3 microhardness meter according to GOST 9.450-76 (with a load of 70 gf). To study the morphology of nickel coatings, the method of raster electron microscopy and elemental analysis (REM-EDAR) was used. The survey was carried out using a REM-100U microscope with an EDAR-energy-dispersive analyser. The wear resistance of the coatings was determined by friction of the test (steel cylinder coated with Ni-ZrO₂ (\( \delta = 100 \) μm)) and reference samples (nickel surface (\( \delta = 100 \) μm)) on the surface with abrasive particles fixed on it at static load P = 0.94 MPa, according to GOST 17367-71.

3. Research results and discussion

Zirconium dioxide particles of various dispersity and method of preparation were used as DP for modifying the electrolyte. The method of diffraction of laser radiation showed that the particles of the dispersed phase of the MRTU brand, obtained by the deposition method, have a size of from 1 to 100 μm, the particles obtained by the plasma-chemical method - from 50 nm to 60 μm.

X-ray phase analysis showed that both species of zirconium dioxide particles contain tetragonal and monoclinic syngonies with a predominance of monoclinic thermodynamically stable up to 1170°C [5].

It has been established (table 1) that the density and viscosity of electrolyte suspensions increase with increasing particle concentration, and these indicators become more important due to smaller particles, i.e. plasma particles. It is known that there is a linear relationship between the viscosity of the system and the content of the dispersed phase in it, which is confirmed by experimental data.
Table 1. Physico-chemical properties of the suspension for the electrodeposition of the Ni CEC – DP.

| C (micro-particles), g/dm³ | ν, mm²/s | ρ, kg/m³ | C (plasma-particles), g/dm³ | ν, mm²/s | ρ, kg/m³ |
|---------------------------|----------|----------|-----------------------------|----------|----------|
| 0                         | 1.592    | 1076     | 0                           | 1.592    | 1076     |
| 1                         | 1.594    | 1077     | 1                           | 1.636    | 1078     |
| 3                         | 1.605    | 1078     | 3                           | 1.64     | 1080     |
| 5                         | 1.630    | 1080     | 5                           | 1.659    | 1083     |
| 10                        | 1.661    | 1082     | 10                          | 1.675    | 1086     |
| 15                        | 1.690    | 1088     | 15                          | 1.702    | 1096     |
| 25                        | 1.709    | 1096     | 25                          | 1.722    | 1100     |
| 35                        | 1.718    | 1105     | 30                          | 1.74     | 1105     |
| 50                        | 1.735    | 1115     | 50                          | 1.76     | 1117     |

The possibility of obtaining composite coatings of Ni-zirconium dioxide with different DP contents of both species was investigated. The optimum current density for obtaining high quality Ni-ZrO₂ coatings was determined. From the current density range from 1 to 4 A/dm², a current density of 2 A/dm² was chosen, since this value corresponds to a maximum current efficiency of 87.5% and dense nickel coatings with a minimum number of pores. The number of inclusions in the nickel matrix of plasma particles in a wide range of concentrations ranges from 0.2 to 1%, and of microparticles from 0.3 to 2% (table 2).

Table 2. The dependence of the number of inclusions of the dispersed phase in the nickel matrix and porosity on the concentration of particles in the electrolyte suspension and their dispersion.

| C (micro-particles), g/dm³ | aₘ, % | Porosity, pores/cm² | C (plasma-particles), g/dm³ | aₘ, % | Porosity, pores/cm² |
|---------------------------|-------|---------------------|-----------------------------|-------|---------------------|
| 0                         | 0     | 7                   | 0                           | 0     | 7                   |
| 1                         | 0.33  | 6                   | 1                           | 0.26  | 7                   |
| 5                         | 0.86  | 5                   | 5                           | 0.36  | 5                   |
| 10                        | 1.47  | 3                   | 10                          | 0.57  | 4                   |
| 15                        | 1.56  | 3                   | 15                          | 0.78  | 3                   |
| 25                        | 1.76  | 2                   | 25                          | 0.88  | 1                   |
| 35                        | 1.85  | 1                   | 30                          | 0.95  | 1                   |
| 50                        | 1.89  | 1                   | 50                          | 1.01  | 1                   |

The method of X-ray fluorescence analysis shows the uneven distribution of zirconium in the nickel coating. The greatest amount of zirconium is contained in the lower part of the coating, and the smallest in the upper, probably this is due to the uneven mixing of the suspension.

The dependences of physicochemical and mechanical properties on the DP content in coatings are illustrated in tables 3 and 4. It can be seen that the microhardness of Ni-DP precipitates increases from 1741 to 2404 MPa with an increase in the concentration of zirconium dioxide in the CEC to 1.89% in the case of microparticles and to 2110 MPa with the content of ZrO₂ in the CEP is up to 1% in the case of plasma particles. This is probably due to the fact that the particles under consideration contribute to the compaction of the sediment and the formation of fine-crystalline coatings, as it can be seen in
While going from the control coating (figure 1), which has a surface with parallel textural grooves and sparse microglobulas 5-10 micron to CEC microstructure changes noticeably. The surface of composite coatings with microparticles (figure 2) becomes slightly corrugated and is formed by microglobules with a size of 1-5 μm and rod-needle-like structures with a length of 20-50 μm. In the case of plasma particles, the surface takes on a different appearance (figure 3). The surface becomes pseudo-corrugated with parallel textural grooves, covered with densely located microglobules of 2-5 μm in size, but unlike CEC Ni-ZrO₂ (microparticles), rod-like structures are contained to a lesser extent.

| Table 3. | Influence of concentration and degree of dispersion of ZrO₂ particles on microhardness and corrosion rate of nickel coatings. |
|----------|---------------------------------------------------------------------------------------------------------------------|
| C | N, MPa | K, g/m²·h | C | N, MPa | K, g/m²·h |
|---|---|---|---|---|---|
| 0 | 1741 | 0.043 | 0 | 1741 | 0.043 |
| 5 | 1773 | 0.033 | 5 | 1749 | 0.034 |
| 10 | 1872 | 0.030 | 10 | 1969 | 0.027 |
| 15 | 1896 | 0.028 | 15 | 1989 | 0.025 |
| 25 | 2165 | 0.023 | 25 | 2017 | 0.022 |
| 35 | 2341 | 0.02 | 30 | 2068 | 0.021 |
| 50 | 2404 | 0.02 | 50 | 2110 | 0.018 |

| Table 4. | Wear resistance of nickel coatings. |
|----------|---------------------------------------------------------------|
| Type of test sample | Wear of coatings, g |
| Reference sample | 0.0345 |
| CEC with microparticles, concentration in ES 35 g/dm³ | 0.03 |
| Reference sample | 0.0358 |
| CEC with plasmaparticles, concentration in ES 50 g/dm³ | 0.0311 |

Comparison of the protective ability of Ni and CEC on its basis shows a decrease in the mass corrosion rate for the Ni-ZrO₂ CEC and an increase in its protective function (table 3). It is possible that the improvement in the corrosion resistance of CEC is associated with a change in the morphology of the coatings and a decrease in their porosity (table 2). With the introduction of particles of zirconium dioxide of different degrees of dispersion in the electrolyte suspension, the porosity of the coatings is reduced in both cases. For CEC with microparticles, the minimum number of pores corresponds to concentrations of 35 and 50 g/l and is 1 pores/cm². The introduction of plasma particles makes it possible to obtain coatings with a given minimum number of pores already at c = 25 g/l.

The most important property that ensures the performance of hardened and reconditioned parts is wear resistance. Zirconia particles reduce the wear resistance of the nickel coating by a factor of 1.2 both in the case of plasma and micro-order particles. This is due to the inclusions of solid particles of zirconium dioxide in the nickel matrix (table 4).
Figure 1. Electron microscopic photographs of the surface of the control nickel coating.

Figure 2. Electron microscopic photographs of the surface of a nickel coating with microorder ZrO$_2$ particles, c = 15 g/dm$^3$.

Figure 3. Electron microscopic photographs of the surface of a nickel coating with plasma ZrO$_2$ particles, c = 50 g/dm$^3$.

The cathodic polarization curves of the electrolyte suspensions were photographed (figure 4). The process of electrodeposition proceeds with depolarization at low current densities, presumably due to the fact that the particles activate the surface. At the same potential, the current strength is higher for the CEC, which indicates an increase in the rate of the cathodic process.

Figure 4. Cathodic polarization curves in the electrolyte nickel-plating depending on the concentration of micro- and plasma particles ZrO$_2$. Concentration of ZrO$_2$ (plasma), g/dm$^3$: ○ – 0; ■ – 1; ▲ – 15. Concentration of ZrO$_2$ (micro), g/dm$^3$: ● – 0; x – 1; + – 15.
4. Conclusions
It was established that, regardless of the dispersion of the second phase, co-precipitation of zirconium dioxide particles with a nickel matrix from this electrolyte occurs. The maximum number of inclusions of plasma particles equal to 1% is observed at a concentration of 50 g/l, the content of inclusions of microparticles at a given concentration is 2%.

The introduction of both types of ZrO$_2$ powders into the coating leads to an improvement in their performance characteristics. It was established that the microhardness of the nickel matrix increases with an increase in the number of inclusions by 1.4 times, wear resistance - by 1.2 times, corrosion resistance - by 2.4 times.

The effect of zirconia particles on the morphology of the coatings is shown. Nickel grain is crushed and fine crystalline coatings are formed.

References
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