COMPOSITE GALVANIC COATINGS BASED ON ZINC

N. A. Vysotskaya¹, B. N. Kabylbekova¹, K.A. Bekzhigitova², L.D. Aikozova³, G.M. Adyrbekova³, L.A. Zhurhabayeva³ and E. N. Abdulova²

¹Department of Metallurgy M. Auezov South Kazakhstan State University, 160012, Shymkent, Tauke khan Ave. 5
²Department of Chemistry and the Basics of Chemical Technology, M. Auezov South Kazakhstan State University, 160012, Shymkent, Tauke Khan Ave. 5
³Department of Chemistry M. Auezov South Kazakhstan State University, 160012, Shymkent, Tauke Khan Ave. 5
*E-mail: kabylbekova.b@list.ru

ABSTRACT
The research aims to modify the process of obtaining galvanic composite coatings based on zinc. The model used the usual parameters of the deposition process: current density, temperature, deposition time, and electrolyte composition. The novelty of the research is the gradual combination of surfactants in the electrodeposition process. At the first stage of obtaining a zinc coating, known additives (gelatin, thiourea) were used in the electrolyte at current densities of 0.5-3 A/dm². At the second stage, already on the obtained zinc coating, deposition from an electrolyte of similar composition was performed again, but using a surfactant (the conditional name of BGU-21) - the product of oil synthesis [R₂POHC(S) (NH₂)], having a high adsorption capacity and good solubility in the electrolyte.

Keywords: Composite Zinc Coatings, Thiourea, Gelatin, BGU-12, Energy Dispersion Analysis

INTRODUCTION
Currently, much attention is paid to modern electroplating technology based on obtaining high-quality composite coatings of metals, in particular, Nickel-cobalt-aluminum oxide, Nickel-diamond, zinc-diamond, polymer-metal oxide, Nickel-chromium diboride, Nickel coatings with quasi-crystalline particles, as well as composite coatings containing Nanodiamond powders. Composite coatings have high-quality decorative and functional properties: high strength, porosity, resistance to atmospheric and corrosion effects, high magnetic and electrical characteristics. Composite coatings are a metal matrix of any metal (zinc, cadmium, copper, nickel, chromium) containing a dispersed phase of solid particles. Increased wear resistance, adhesion strength to the base, and anti-corrosion properties of composite coatings are determined mainly by the dispersed phase, and the metal (substrate) only binds the dispersed particles to each other and the substrate surface. The authors of the research choose carbides, nitrides, corundum’s, or diamonds with sizes up to 5 microns for the composition, with their content in the matrix up to 20%. Of particular interest are methods for applying composite coatings with metals (zinc, copper, nickel, cadmium), which include successive deposition of coating layers from electrolytes using various surfactants.

EXPERIMENTAL
In the standard galvanizing electrolyte, we tested thiourea and gelatin as a surfactant in the current density mode from 0.5 to 3 A / dm², with a constantly fixed pH value and temperatures of 20°-40°C. Components for the preparation of the galvanizing electrolyte used to brand «Chemical clean» sodium sulfate, zinc sulfate, aluminum sulfate (or aluminum-potassium alum). Soda was used to degrease the electrodes, 0.1 n sulfuric acid solution was used to decapitate the surface of the electrodes before the
experiment and ethyl alcohol and surfactants (gelatin, thiourea, BGU-21) were used to dry the electrodes, the steel plate cathodes, and the anodes of electrolytic zinc. Before applying the zinc coating, steel samples were machined with sandpaper of increasing numbers to remove roughness, degreased with soda or a mixture of Ash, repeatedly washed with distilled water, dried with alcohol, and weighed on electronic scales. The measured surface of the steel samples (cathode) and the specified current density (from 0.5 to 3 A/dm²) were used to calculate the current strength for fixing on the ammeter. The temperature was measured with a conventional thermometer. The structure of zinc coatings was studied using an electron microscope. Based on the difference in the mass of zinc deposited and calculated theoretically according to Faraday’s law, the current output (CO) in % was calculated. To maintain the pH within 3.5-4.5, the electrolyte was adjusted by introducing a small amount of sulfuric acid into the electrolyte at a temperature of 20°C. The porosity of the zinc coating was determined by filter paper dipped in a solution (10 g of potassium Ferrocyanide and 15 g of sodium chloride in 1 l of water) by applying the paper to the surface of the sample. If there are pores in the zinc coating, Turnbull blue dots will be printed on the paper. Porosity in % was calculated from the number of printed pores per 1 cm². Obtaining zinc electroplating was carried out on an installation consisting of electrolyze, an ammeter, a rheostat, and a DC source with a total voltage of 220 V.

RESULTS AND DISCUSSION

The electrolyte was prepared from salts of the "Chemical clean" brand-zinc sulfate, sodium sulfate, aluminum sulfate, anodes made of high-purity electrolytic zinc, a steel cathode base. Table-1 shows the quality indicators of zinc coatings obtained from the galvanizing electrolyte with thiourea.

| Iᵦ, A/dm² | CO, % | Appearance of the Zinc Coating | Thickness, microns | Porous | The Data of Scanning Electron Microscope JSM-6490LV |
|-----------|-------|---------------------------------|-------------------|--------|--------------------------------------------------|
|           |       |                                 |                   |        | Impurities                                      | % Zn |
| 0.5       | 72.6  | Gray, Coarse                    | 11.8              | Porous | C, O, N, Fe, S                                  | 79.5 |
| 1         | 74.1  | Gray, Coarse                    | 14.5              | Porous | C, O, N, S, Fe                                  | 77.0 |
| 2.5       | 79.4  | Gray, Fine-grained              | 16.6              | Slightly porous | C, O, N, Fe, S                              | 81.5 |
| 3         | 66.2  | Dark around the edges with burned-on food | 13.3 | Porous | C, O, N, Fe, S                                  | 80.07 |

Zinc coatings, coarse-grained, porous, with low current output (65-79%). Moreover, with the increasing current density of the coating becomes a darker shade, peel off the substrate at the edges of the cover are formed by the burned-on food and dendrites. The elemental composition of zinc coatings described using an electron microscope of one of the zinc coating sites for current density conditions of 2.5 A / dm² is shown in Fig.-1.

| Elements | Weight % |
|----------|----------|
| C        | 8.62     |
| O        | 2.43     |
| N        | 2.21     |
| Fe       | 179      |
| S        | 2.9      |
| Zn       | 81.5     |
In a separate section, the structure of the zinc coating is shown, a burn is visible along the edge of the coating, and the porosity of the zinc coating is visible. The structure and elemental composition of the zinc coating obtained from an acidic electrolyte with the addition of gelatin at a current density of 2.5 A/dm² are shown in Fig.-2.

The structure of the zinc coating obtained with the addition of gelatin is much denser, slightly porous, and light in appearance. If you look at the elemental composition, the coating has a significantly higher weight content of zinc. If the first zinc coating is 81.5%, the second -90.1%. To obtain a composite coating, we selected a coating with the addition of gelatin.

The electrolyte of the same composition as in the first two described experiments, but with the addition of BGU-21, was subjected to electrolysis. The obtained data on the composition and quality of the coating is shown in Table-2 and Fig.-3.

![Fig.-2: Zinc Coating and its Elemental Composition From An Electrolyte with Gelatin](image)

### Table -2: Quality of Zinc Coatings in the Electrolyte with the Addition of BGU-21 and WT Zinc

| $I_k$, A/dm² | CO, % | Appearance of the Zinc Coating | Thickness, microns | Porous | Data of Scanning Electron Microscope JSM-6490LV | Impurities | % Zn |
|--------------|-------|-------------------------------|-------------------|--------|-----------------------------------------------|------------|------|
| 0.5          | 72.6  | Gray, Coarse                  | 13.8              | Porous | C, O, P, N, Fe, S                          | 79.5       |
| 1            | 84.1  | Gray, Fine-grained            | 17.1              | Weakly porous | C, O, N, S, Fe, P                      | 82.0       |
| 2.5          | 92.4  | Light, Fine-grained           | 22.6              | Nonporous | C, O, N, Fe, S                           | 95.9       |
| 3            | 86.2  | Dark, Exfoliates at the edges | 13.3              | Porous   | C, O, N, Fe, S, P                        | 82.07      |

Figure-3 shows the appearance of the composite zinc coating obtained on the substrate already obtained (Fig.-2), at a current density of 2.5 A/dm². The coating is light, fine-grained, dense, and non-porous.

![Fig.-3: Zinc Coating and its Elemental Composition From the Electrolyte with BGU-21](image)
Of particular note is the zinc content in the coating. Its amount is more significant than the coating obtained with the addition of gelatin. To calculate the thickness of composite coatings, the values of the current output, the density of zinc and its electrochemical equivalent were used. The table shows that the thickness of the coating with surfactant BGU-21, obtained at a current density of 2A/dm², is 22.6 microns. For comparison, we conducted studies on the effect of surfactants in the electrolyte at a higher temperature -40°C. On a pre-prepared substrate with the addition of thiourea, a zinc coating was deposited in an electrolyte with the addition of BGU-21. Table-3 shows the quality indicators of the resulting composite zinc coating.

Table-3: Quality of Zinc Coatings in the Electrolyte with the Addition of BGU-21, W at the Electrolyte Temperature of 40°C

| I₀, A/dm² | CO₂, % | Appearance of the Zinc Coating | Thickness, microns | Porous | Data of Scanning Electron Microscope JSM-6490LV | Impurities | % Zn |
|-----------|--------|--------------------------------|-------------------|--------|-----------------------------------------------|------------|------|
| 0.5       | 70.1   | Dark, Coarse-grained           | 11.8              | Porous | C, O, P, N, Fe, S                           | 74.9       |      |
| 1         | 78.1   | Dark Grey, Coarse-grained      | 14.7              | Weakly Porous | C, O, N, S, Fe, P                        | 77.2       |      |
| 2.5       | 81.4   | Gray, Fine-grained             | 17.4              | Weakly Porous | C, O, N, P, Fe, S                         | 82.05      |      |
| 3         | 76.2   | Dark with Dendrites            | 12.9              | Porous | C, O, N, Fe, S, P                          | 73.9       |      |

As can be seen from the table, the temperature adversely affects the quality of the obtained zinc coatings. In the range of current densities studied, the coatings are dark and very porous (figure 4).

Based on the results of porosity, color, coating thickness, and current output, we can draw the following conclusions.

**CONCLUSION**

1. The process of obtaining a composite zinc coating on a substrate previously obtained from an electrolyte with a surfactant is investigated.
2. A high-quality composite zinc coating was obtained on the prepared substrate with the addition of BGU-12 in the electrolyte.
3. The composition of the composite zinc coating was determined using a scanning electron microscope of the JSM-6490LV brand with energy-dispersive microanalysis systems.
4. It can be assumed that the resulting composite zinc coatings will protect metal products operated in aggressive environments from corrosion.

**REFERENCES**

1. Vakhidov R.S., Vysotskaya N.A., Averbukh M.E., Materials of the XI Mendeleevskoy Congress on the Subject and Application of Chemistry, Alma-Ata: Nauka, pp.277-280 (1975)
2. Kuz'mar I., Lanin V., Pas N., Khmyl A., *Technologies in The Electronic Industry*, 6(20), 22(2006)
3. V.V. Ivanov, V.I. Balakai, A.V. Arzumanova, A.V. Starunov, K.V. Murzenko, I.V. Balakay, *Modern High Technology*, **10**(2), 253(2016).
4. V.V. Kuznetsov, T.V. Pshenichkina, *Electrochemistry*, **46**(7), 423(2010).
5. S.P. Sidelnikova, G.P. Globa, *Electrochemistry*, **47**(3), 391(2011).
6. A.L. Maslov, N.I. Polushin, N.N. Stepireva, V.V. Zhuravlev, KZ Patent 2487201 (2019).
7. O.A. Chulkov, I.M. Zharsky, V.K. Karagulkin, RB Patent 9169 (2007).
8. V.I. Balakai, I.V. Balakai, Yu.Ya. Gerasimenko, RF Patent 2297476 (2006).
9. Yu.V. Trubnikov, S.S. Klimenko, D.A. Gruzdev, A.K. Novikov, RB Patent 7140 (2005).
10. V.M. Rudoi, T.N. Ostanina, A.B. Darintseva, N.I. Ostanin, I.A. Alikhanova, S.L. Demakov, A.S. Prokofieva, *Electrochemistry*, **46**(6), 747(2010).
11. V.M. Shevko, A.D. Badikova, D.D. Amanov, G.E. Karataeva, B.A. Lavrov, *Rasayan Journal of Chemistry*, **11**(3), 1050(2018), [DOI:10.31788/RJC.2018.1132038] [RJC-5841/2020]