Electrochemical technology for the formation of heterogeneous metal structures with increased corrosion resistance

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Abstract. Research into corrosion resistance of multilayer materials obtained by the method of potentiostatic pulse electrolysis was conducted. The purpose of the work was to select materials for the creation of multilayer steel coatings with high corrosion resistance, as well as to develop technology for their formation. The formation of galvanic coatings was carried out in stationary and potentiostatic pulse electrolysis modes. The study of corrosion resistance was carried out by accelerated methods in solutions simulating the marine environment. Corrosion resistance of samples made of St3 steel coated with nickel and zinc-nickel alloys of different compositions when using various electrolysis modes was studied. It has been experimentally proved that the potentiostatic mode of pulse electrolysis allows the formation of galvanic coatings with a zinc-nickel alloy of various compositions from one electrolyte. Based on the study of electrode potentials of coatings in various media, the composition of the outer and inner layers of a multilayer heterogeneous structure was substantiated. It was experimentally proved that the formation of multilayer coatings on the surface of steel could significantly increase the protective properties of these coatings. It was theoretically justified that the materials of the layers should have different values of electrode potentials, and the inner layer should have a more negative value of the potential than the outer one has.

1. Introduction
One of the most dangerous types of corrosion is pitting corrosion. We [1] have proposed and studied a multilayer corrosion-resistant material that implements the principle of pitting corrosion protection. The increase in corrosion resistance was provided by the specific architecture of the multilayer composite. Pitting corrosion develops predominantly under the influence of a corrosive medium in the outer layer made of high alloy steel. In case of end-to-end damage to the outer layer, the inner tread made of low-alloy carbon steel, due to the difference in electrochemical potentials, becomes a sacrificial layer. It transforms the corrosion mechanism of the multilayer material as a whole and slows down the pitting process of the outer layer. The third layer, similar in composition to the outer one, maintains integrity for a long time. The fourth layer is made of low alloy steel of increased strength and performs the functions of a bearing layer. The proposed multilayer systems were obtained by explosion welding and are thick materials that can be used, for example, as structural materials for creating chemical reactors in the production of mineral fertilizers, as well as for walls of highly active nuclear waste storage facilities.
Multilayer galvanic coatings are significantly thinner, but they also effectively protect parts from corrosion, including pitting corrosion. Considering the above, as well as analyzing numerous literature sources [2-16], we can conclude that it is most advisable to use multilayer coatings for the effective protection of steel against corrosion. Moreover, the materials of the layers should have different values of the electrode potential. Thus, the aim of this work was to develop the architecture of multilayer galvanic coatings obtained under various electrolysis conditions, which provides higher protection of the base metal from corrosion, compared with single-layer coatings.

2. Experimental results and their discussion
The material potentials of the layers can be changed by introducing electrolyte additives that would be included in the coating. The examples of such multilayer galvanic coatings are bi-nickel and tri-nickel plating [11-13]. The work [3] proposed the architecture of a multilayer coating with nickel and a nickel-phosphorus alloy formed by means of galvanic and chemical deposition, respectively. It has been experimentally established that the following corrosion architecture is the most corrosion-resistant coating, namely, steel/nickel-phosphorus (low phosphate)/nickel/nickel-phosphorus (high phosphate).

It is possible to vary values of the electrode potentials of the metal layers most widely by changing the nature of the metal. When choosing metals for a multilayer material, it is necessary to evaluate the possibility of combining them in accordance with GOST 9.005-72, and also take into account operating conditions (composition of the corrosive medium and temperature). The operating conditions will affect the value of the electrode potential of the layer, and determine its properties in relation to other layers and the base. So, a standard electrode potential of a nickel coating pre-activated in hydrochloric acid in seawater is -0.12 V. In this case, the nickel coating will be a cathode with respect to St3 steel. Passivation of the nickel coating in the environment of oxidizing agents (hypochlorites) leads to the potential shift to more positive values. So, a stationary potential of passivated nickel in seawater (pH 6.5-7.0) is +0.25 V, and it is +0.47 V in the alkaline environment (sodium hypochlorite solution, pH 10.0). These values are more positive compared not only with St3 steel, but also with copper. It has also been experimentally established that the corrosion resistance of electroplated coatings largely depends on the electrolysis mode [17-20].

One of the problems limiting the development of these technologies is the need to use their own electrolyte for each coating layer, which, together with the washing operations between these stages, will significantly increase the number of bathtubs in the line.

In addition to the above, difficulties arise in applying metals of different nature to each other. For example, zinc in an acidic nickel plating electrolyte undergoes intense corrosion, which does not allow the formation of a high-quality nickel coating. To solve this problem, hanging parts in a nickel bath under current is used [11, 12].

The formation of a two-layer coating with zinc and nickel on the St3 steel protects it from corrosion much more effectively than a single-layer coating with nickel. We have made the following samples: 1) St3 plates with a two-layer coating of 5 μm Zn + 5 μm Ni (Fe/Zn5.Ni5); 2) St3 plates coated with 10 μm Ni (Fe/Ni10).

These samples were immersed in a 0.5 M sodium chloride solution and kept at a temperature of 25±1°C. Red corrosion products on samples with a single-layer nickel coating were detected 2-3 hours later. Minor spots of red corrosion were detected on samples with a two-layer Zn5.Ni5 coating 120 hours later, and they did not increase in size for 330-340 hours.

It has been experimentally established that the application of rectangular-shaped potential pulses (the potentiostatic mode of pulse electrolysis [17, 20]) makes it possible to form coatings of various compositions from one solution by changing process parameters. Using this mode, it is possible to obtain several coating layers of various compositions on one sample for one immersion of the part.

To prove the effectiveness of multilayer coatings with zinc-nickel alloy in the marine environment, an experiment was conducted, the results of which are presented in table 1.
In the manufacture of samples with multilayer coatings, the layer materials were chosen so that the inner layer applied directly to the steel should have a more negative electrode potential than the next layer. The material of the outer layer with respect to the corrosive environment should have higher corrosion resistance and better decorative characteristics, which is important when finishing parts.

**Table 1.** The research results of the corrosion resistance of samples (St3 steel) with various coatings in a 3% sodium chloride solution at a temperature of 25±1°C.

| Coating          | Mode                | Time until the appearance of red corrosion products, h |
|------------------|---------------------|-------------------------------------------------------|
| Zn88-Ni6/Zn75-Ni6| Potentiostatic pulse| >1900                                                 |
| Zn88-Ni7/Zn75-Ni9| Potentiostatic pulse| >1900                                                 |
| Zn88-Ni12        | Potentiostatic pulse| 780-800                                               |
| Zn88-Ni12        | Stationary          | 720-740                                               |
| Zn75-Ni16        | Potentiostatic pulse| 560                                                   |
| Ni8              | Potentiostatic pulse| 310                                                   |

3. Conclusions
The obtained results prove that multilayer coatings with zinc-nickel alloy reliably protect steel from corrosion for a longer time compared to single-layer coatings of the same thickness. The stationary potential of the Zn88-Ni alloy in a sodium chloride solution has more negative values than the potential of the Zn75-Ni alloy. If there are pores in the outer layer, or when pitting develops and reaches the inner layer, a galvanic cell appears in which the anode will be the inner layer (Zn88-Ni).

The electrolysis mode also affects the corrosion resistance of the formed coatings. Coatings formed using the potentiostatic mode of pulse electrolysis, prevent the formation of red corrosion products for a longer time (compared with the stationary mode). This circumstance can be explained by the influence of the electrolysis mode on the morphological features of the coatings, in particular on uniformity, crystal size, and porosity.

Thus, using the zinc-nickel alloy as an example, it is proved that the use of the potentiostatic regime of pulse electrolysis allows the formation of coatings of various compositions from one electrolyte. To do this, it is necessary to carry out the process using the program mode: first, the process parameters are set for applying the inner layer, then after some time sufficient to form the layer of the required thickness, parameters are set for the formation of the next layer, etc. (figure 1). In this mode, one can get an almost unlimited number of layers:

\[\text{Fe/}(\text{Zn88-Ni/}Zn75-\text{Ni})_n/Zn75-\text{Ni}\]

**Figure 1.** An example of a five-layer Zn-Ni plating of carbon steel: 1 – base material (low alloy carbon steel), 2 – Zn-Ni alloy coating with 75% zinc content, 3 – Zn-Ni alloy coating with 88% zinc content.
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