The design and properties of galvanic anticorrosive coatings for important precision parts of farming equipment

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Abstract. The paper explores the possibility of using a number of nickel alloys in multilayer coatings to decrease nickel consumption and preserve the functional effect of the coating. The following is proved by the graphical calculation technique using experimental data on the galvanic properties of the multilayer coating parts. Nickel-iron, nickel-phosphorus and nickel-tin alloy can be applied as a lower coating layer rather than semi-shiny, shiny or composite nickel. It is advisable to use a nickel-iron alloy as the middle (second) layer, and the concentration of iron depends on the composition of the first and third layers. If a nickel-iron alloy is applied as the material of the first layer, then the second layer may be semi-shiny (N$_{s-sh}$) or shiny (N$_{sh}$) nickel. The substitution of nickel layers for nickel alloys allows to considerably (about 10%) decrease the cost of a multilayer coating, while the protective properties are remaining the same. The application of the same nickel-containing alloys as single-layer anticorrosive coatings shows a lower level of protective properties.

1. Introduction
The farming equipment, as a rule, is used in unfavorable conditions. Therefore, as a result of contact with the soil, fuels and lubricants, fertilizers, pesticides, metal parts of the mechanisms corrode and, as a result, break down. The use of protective coatings on the surface of parts may enhance the service life of farming equipment by up to 10-15% [Astana, 2017; Astanin, 2016; Vakana, 1986]. Hydraulic systems are an essential part of farming machinery [Stekolnikova, 2017]. Nearly 50% of all breakdowns of farming equipment are failures of the hydraulic system [Kruglikov, 1967]. This system is responsible for lifting, lowering, and driving the working devices of trailed, semi-chain, attachments and farming machinery. A premature corrosion wear of such crucial and expensive parts (for example, spools) results in the failure of the equipment. To increase the duration of operation of these parts, one of the ways is to use protective coatings. MEC (multilayer electroplating coatings) occupy a special place among them. These coatings are distinguished by high mechanical and anticorrosive properties. Besides, the most widespread are multilayer coatings, which consist of layers of nickel with a copper or chrome sublayer and an upper layer of cobalt [Asier Salisio-Paz, 2019; Kanut Sherwin, 2020; Song, 2013; Makarova, 2018]. All the developed techniques are based on the principle of electrochemical protection of the underlying layers of the coating with overlying layers [Los, 2013; Perelgin, 2015; Vinogradova, 2013; Huawei, 2020].

A single-layer nickel coating on steel has a less electronegative potential. Thus, it protects iron only mechanically. Its shielding qualities are defined only by thickness and integrity [Authovich, 2017; Encyclopedia of Mechanical Engineering XXL]. In a two-layer coating, the first layer of nickel (matte or semi-shiny) is precipitated from a standard electrolyte and does not include extraneous additives.
The second layer of nickel of a two-layer coating is deposited from an electrolyte for brilliant nickel plating, which consists of organic sulfur-holding brightening agents. Sulfur in the composition of the shiny layer displaces its electrode potential by 60-80 mV towards electronegative values compared to the first layer. The first and second layers generate a galvanic pair in which the shiny layer is the anode and protects the first layer from corrosion [Rena Ta Orin A Kova, 2006]. The coatings with three or more layers have a higher corrosion resistance than the two-layer. After the deposition of the first layer, the middle layer of nickel (high-sulfur) with a high sulfur content is precipitated. This layer has the most electronegative potential and protects the nickel layers contacting it from corrosion. The last layer of the coating is a compound consisting of nickel and inert kaolin particles. There is a layer of chromium between the last nickel-containing layer and the steel surface [Rena Ta Orin A Kova, 2006].

The disadvantage of multilayer coatings is the high cost, which restricts their wide application, despite the functional qualities. Therefore, it is essential to decrease the consumption of non-ferrous metals and, simultaneously, the preservation or improvement of the protective properties of the coating [Rudenok, 1984].

This article studies the possibility of using a number of nickel alloys in multilayer coatings to decrease nickel consumption and to preserve the basic principle of the functional coating effect.

2. Materials and methods

The multilayer coatings were the objects of the study. The coatings included layers of chromium (Ch), nickel (high-sulfur nickel (N_s), semi - shiny nickel (N_s-sh), shiny nickel (N_sh), composite nickel (N_com) and nickel alloys: (Ni-65%Sn (NO65), Ni-12%P(NF12), Ni-20-60%Fe (NI20)).

The corrosion tests were performed in ACC solution, which consisted of 0.86 mol/l of sodium chloride with the addition of acetic acid to get a solution with a pH of 3.24 [Kudryavtsev, 1970].

To choose the composition of the coating with the highest protective properties, a graphical technique based on experimental electrochemical data was applied [Rudenok, 1984].

3. Results and discussion

The multilayer coatings were introduced in the form of a multielectrode short-closed system. The graphical calculation was done under experimental cathode and anode polarization curves for each component of the coating (figure 1, figure 2).

Instead of the current density, the currents for each layer were used in the calculation, considering its surface. The calculation was made for a conditional cylindrical cavity in the coating. The surfaces of the layers in the cavity were correlated as the thicknesses of these layers. Porosity of the last layer of chromium and other layers applied to the composite nickel layer (N_com), were fixed at the same level. The number of cavities in microporous chromium is 5·10⁵ cav·cm². The structure of the composite layer, in addition to nickel, included kaolin particles, the average size of which is 2·10⁻⁸ cm². Therefore, the surface of the particles in the cavities on 1 cm² of layer is equal to 10² cm². Therefore, there are 100 units of chromium surface per unit of nickel coating surface in the cavities. According to these arguments, the ratio of the surfaces of the layers in the cavity was S_l: S_s : S_sh = 1 : 0.1 : 1 : 100. Meanwhile, the presence of a thin composite layer was not considered, since its electrochemical properties are close to the properties of a shiny nickel layer.

A five-layer coating with a ratio of layer thicknesses was selected as the model:

layer order  
N_s-sh - N_s - N_sh - N_com - Ch  
thickness, microns  
10 1 10 2 0.25

In case of replacement of chromium with nickel alloy, the thickness of the fifth layer was raised to 1 micron. The electrochemical characteristics of layers of different composition are given in Table 1.

| Electrochemical character-NT | NPh | N_s-sh | N_sh | N_com | NI20 | NI 43 | NI 57 | N_s |
|-----------------------------|-----|--------|------|-------|------|-------|-------|-----|

Table 1. The electrochemical compositions of layers of nickel and nickel alloys.
In Table 1: $E_{cp}$ – nickel or alloy corrosion potential; $E_{s}$ – corrosion potential of the steel – single-layer coating system with the appropriate metal or alloy (10 microns thick); $I_{cont}$ – contact corrosion current of the steel-coating system; $P$ – porosity. $E_{st}$ – $-360$ mV. According to [15], the value $i$ of the protective abilities of materials.

The findings of the graphical calculation of the protective ability of a multilayer coating for various combinations of metals and alloys in them are presented in comparison with the standard system (1) are shown in Table 2. According to the change in the total anode current in the coating ($I_{Σ}$) and its rearrangement between the individual layers of the coating, depending on their electrochemical properties, it is feasible to assess the behavior of these layers during corrosion. Based on this, it is possible to choose the composition of the multilayer coating with the best anticorrosive properties.

Figure 3 illustrates an example of constructing a diagram for system 1 (table 2). The arrangement of the anode curves in the diagram is the following: the total anode current does not contain the current of dissolution of the lower layer. Generally, all cathode curves should also be summed up. In this case, the role of the cathode is fulfilled by chromium. In the case of the total potential of the system, due to the different anode polarizability of the electrodes, the second layer dilutes at the highest rate. The dissolution rate of the third layer is much lower, and the lower layer is effectively protected from corrosion.

For system 2, irrespective of the type of the third layer, the dissolution current of the second layer is 65-85% of the total current. Replacement in the second layer of nickel $N_s$ to the nickel-iron alloy (2) with lower electrochemical activity results in accelerated dissolution of the third layer.

With subsequent replacement of nickel $N_{s-sh}$ to the nickel-iron alloy NI20, the first layer is not completely protected (4), especially if the third layer has iron in its structure (5).

Owing to the positive values of the anode potential, the nickel-phosphorus alloy in the lower layer (6) is protected by the upper layers with various combinations of layers of multilayer coating. Since the cathode process on nickel-tin and nickel-phosphorus alloys is simplified compared to the process on chromium, the replacement of chromium with these alloys is ineffective. Some systems have a total dissolution current several times higher than the standard system (7). Nevertheless, if two layers of nickel-phosphorus alloy are separated by a layer of nickel $N_{s-sh}$, then the total current of the system with the top layer of nickel-tin is less than that of the system with chromium (8). Meanwhile, the lower layer of the coating is poorly protected.
Figure 1. Cathode polarization curves in ACC solution for alloys: NT65 (1), NPh12(2), NI57 (3), NI20 (5), NID43 (6); nickel: Ns-sh (4), Nsh (7), Ns (8); chromium – Ch(9).

Figure 2. Anodic polarization curves in ACC solution for alloys: NT 65 (1), NPh12(2), NI57 (7), NI20 (4), NI43 (5), NI60 (8); nickel: Ns-sh (3), Nsh (6), Ns (9).

Figure 3. Graphical corrosion rate calculation of the MEC: Ns-sh-Ns-NI20-Ncom-Ch. Anode polarization curves for: Ns-sh(1), NI20 (2), Ncom (3), Ns (4); total anode curve (5), cathode polarization curve Ch.
Table 2. The layer sequence and the characteristics of the protective ability of the MEC.

| System No. | MEC system (layer number from the base) | Corrosion currents of layers and total current, µA |
|------------|----------------------------------------|--------------------------------------------------|
| 1          | Ns-sh Ns N20 Ncom Ch                   | I1 300 I2 15 I3 35 I4 350                      |
| 2          | Ns-sh Ns Nsh Ncom Ch                   | I1 250 I2 125 I3 - I4 375                      |
| 3          | Ns-sh Ni57 Nsh Ncom Ch                 | I1 30 I2 300 I3 - I4 330                      |
| 4          | Ni20 Ns Nsh Ncom Ch                   | I1 5 230 I2 100 I3 - I4 335                      |
| 5          | Ni20 Ni57 Ni20 Ncom Ch                 | I1 75 I2 135 I3 75 I4 - I5 285                  |
| 6          | NPh Ns Nsh Ncom NPh                    | I1 - I2 250 I3 110 - I4 360                     |
| 7          | Ns-sh Ni57 Nsh Ncom NPh                | I1 - I2 - I3 - I4 1000                         |
| 8          | NPh Ns-sh NPh                          | I1 NT 70 I2 20 I3 - I4 110                    |

4. Conclusion
Nickel-iron alloy with a low iron content, as well as nickel-phosphorus and nickel-tin alloys may be applied as the lower layer of a multilayer anticorrosive coating, additionally to semi-shiny, shiny or composite nickel. It is advisable to apply a nickel-iron alloy as the middle (second) layer. Its iron content is defined by the composition of the first and third layers. If the first layer is nickel-phosphorus, then the second layer may be semi-shiny nickel Ns-sh or shiny nickel Nsh. The substitution of nickel layers for nickel alloys essentially decreases the cost of multilayer coatings while preserving functional properties. The choice of materials of multifunctional galvanic coatings for anticorrosive protection of precision parts of farming equipment may be fulfilled under a graphical calculation. It is required to consider the electrochemical properties of materials of different composition.

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