Influence of annealing on corrosion properties of electroplated coatings

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Abstract. The paper discusses the features of the conditions of electroplating and heat treatment of traditional electroplated coatings to ensure the best anti-corrosion protection in the conditions of oil fields in Western and Eastern Siberia. The patterns of formation of the structures of the obtained coatings are given. Recommendations on the use of protective coatings are given, taking into account the climatic conditions of their operation.

1. Introduction
Modern electroplated coatings have a wide range of properties and are actively used as protective ones, including protection of oilfield equipment operating under harsh climatic conditions. Traditional methods of coating allow obtaining various types of structures after electrodeposition, which certainly affects their properties. However, the formation of the structure of coatings can be considered more widely by conducting heat treatment after electroplating.

As the object of study, coatings traditionally used as protective materials were taken: nickel, chromium, cadmium and zinc [1].

2. Material and methods of research
Coatings were obtained in factory conditions in industrial baths and from traditional electrolytes. The composition of electrolytes and the parameters of electrodeposition are shown in Table 1.

Annealing of the coatings was carried out in the argon shield at temperatures not exceeding the recrystallization temperature.

The corrosion rate was evaluated in gravimetric tests in media recommended by GOST, as well as in media consisting of produced water from various oil fields in Western and Eastern Siberia. The compositions of corrosive media are shown in Table 2.

Hardness was determined on a PMT-3M microhardness meter by the reconstructed imprint method.

The structure was investigated using optical and electron microscopy on Olympus GX51F and JEOL JSM-6510A microscopes.

X-ray diffraction analysis was performed using a DRON-7 X-ray diffractometer.
Table 1. The composition of electrolytes and modes of electrodeposition of the studied coatings.

| Coating material | Electrolyte composition, g/l | Deposition modes |
|------------------|------------------------------|------------------|
| Cd               | CdO – 20-40                  | Temperature – 15-30 °C |
|                  | NaCN - 80-130                | Cathode current density – 0.5-2 A/dm² + chromating |
|                  | NaOH – 20-30                 |                  |
|                  | (C₆H₁₀O₅)n – 1-2             |                  |
| Zn               | ZnO – 20-45                  | Temperature – 15-40 °C |
|                  | NaCN – 40-70                 | Cathode current density – 0.5-3 A/ dm² + chromating |
| Ni               | NiSO₄ – 200-220              | Temperature – 40 – 60 °C |
|                  | H₃BO₃ – 25-30                | Cathode current density – 20-70 A/ dm² |
|                  | NaCl – 8-10                  |                  |

Table 2. Composition of corrosive media

| Medium / field   | pH   | The content of ions, mg/l | Total mineralization |
|------------------|------|---------------------------|----------------------|
|                  |      | Cl | HCO₃⁻ | SO₄²⁻ | Ca²⁺ | Mg²⁺ | Na⁺+K⁺ | Fe total | mg/l | Mg-equiv/l |
| Kalchinskoye     | 8.03 | 5751 | 3416 | 5.6 | 72 | 7.8 | 4918.92 | 0.08 | 14171 | 419.1 |
| Ety-Purovskoye   | 7    | 4468 | 549  | 8   | 276 | 12  | 2725    | 0    | 8038  | 258.8 |
| Kuyumbinskoye    | 4.26 | 188150 | 28.06 | 170 | 42000 | 8640 | 57244.7 | 1.32 | 296234 | 10413.8 |

3. Results and discussion

The type of structure obtained after electrodeposition of coatings is significantly different. So, for example, during electrodeposition of refractory metals (chromium and nickel) with a high overvoltage of the cathode a cellular structure is formed, and with decreasing current density it may be subgrain or even monoblock.

During the deposition of coatings of relatively low-melting-point metals (zinc and cadmium), only subgrain or monoblock structures are formed, and a cellular one is not.

The corrosion rate during the “tightening” of electrodeposition modes increases. For example, when moving from a monoblock structure to a subgrain, the corrosion rate increases on average by 20%.

Annealing of the obtained coatings leads to a transformation of the structure and a significant change in the properties of the coatings [2]. When conducting corrosion tests, the dependences of the corrosion rate on the annealing temperature were obtained (Figure 1).

It can be noted that during annealing of electroplated low-melting-point materials, such as zinc and cadmium, at temperatures not exceeding 150 °C, there are no significant changes in the corrosion rate. However, annealing at these temperatures makes it possible to stabilize the properties of the coatings and reduce the internal stresses arising during electrodeposition. Heating to temperatures higher than the homologous temperature of recrystallization significantly increases the corrosion rate, which can be explained by the appearance of secondary porosity in the coatings.
**Figure 1.** Change of the corrosion rate from annealing temperature

a) zinc; b) chromium; c) cadmium; d) nickel. (corrosive media: ▲ – 3%NaCl+ CH₃COOH; ○ – 3% NaCl; ■ – Kalchinskoye field; □ – Ety-Purovskoye field; ● – Kuyumbinskoye field).
When chromium is annealed, an increase in the corrosion rate is observed at temperatures close to the recrystallization temperatures. When nickel is annealed, the maximum increase in the corrosion rate occurs at a temperature of 100 °C, which corresponds to the polygonization temperature and can be explained by the redistribution of atomic-crystal defects [3].

It should also be noted that the best results for corrosion resistance in produced water with a pH of 4.6 and total mineralization of 296.234 g / l are observed for coatings of zinc and cadmium, for coatings of nickel and chromium in these media the worst result is observed. With an increase in pH and a decrease in water salinity, the opposite result is observed: the worst value of corrosion resistance is in low-melting-point coatings, the best is in refractory ones.

4. Conclusion
A key factor affecting the corrosion rate in the produced waters of oil fields is the pH of the medium.

Taking into account the natural and climatic features of the fields, their water cut and the composition of produced water, it is possible to increase the corrosion resistance of oilfield equipment using protective coatings.

By analyzing the data obtained, it can be concluded that by changing the annealing parameters of galvanic coatings, it is possible to choose the most suitable parameters for specific operating conditions.

References
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Acknowledgments
This work was financially supported by Transneft.