Research of properties of zinc-iron coating when restoring places of indigenous supports of engines of transport and technological machines

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Abstract. This article presents the results of experimental studies to determine the relationship between electrolysis modes and the properties of electroplated coatings, which are used in mathematical modeling of the dynamics of the electrolytic process, described by a system of ordinary differential equations due to the complex relationship between the kinetics of chemical reactions, hydrodynamics and mass transfer in the electrolyte stream, the kinematics of electrode plates, as well as the influence on all these processes of the electric field of the pair “anode-cathode”. At the same time, a series of field experiments to restore the seats of the main bearings of the cylinder blocks with galvanic coatings served as the experimental base. The final result of this study is the procedure for constructing an optimal resource-saving mode of deposition of galvanic coatings, which are a zinc-iron alloy.

1. Introduction

Laboratory studies of the zinc-iron coating, providing a different content of components, in order to determine the behavior of the zinc-iron coating under conditions close to the operating conditions of the parts, give a zinc-iron coating.

Testing samples with zinc-iron coatings on them has an adhesion effect when pressing and pressing out; adhesion strength during prolonged operation in a production environment. The strength of the press joints is determined by the adhesion forces developing on the contact surface as the preload increases. But besides this, factors such as the material of the part, macro- and microgeometry of the mating surfaces, the presence of oxides, the contact area, the coating material, etc. influence the strength of the press joints. Thus, the actual contact area in turn depends on the surface parameters and the mechanical properties of the surface layer metal parts, the physical condition of which is mainly determined by the wear resistance of the parts.

When machining parts, the physical properties and parameters of the surface layer change. Voids appear on the surface of the part, an accumulation of small fragments of crystals resulting from plastic
deformation and other defects. The presence of these defects leads to a decrease in the friction forces [4, 5].

One of the ways to restore the crystal lattice and to obtain a homogeneous structure of the surface layer of the metal is galvanic deposition of metal coatings on the surface of the base metal.

Soft coatings, such as zinc and others, increase the actual contact area due to the low yield strength of the material and do not lower the fatigue strength of the main part. Such coatings create compressive residual stresses on the metal surface, the presence of which positively affects the fatigue strength of press joints.

When testing couples for press mating, the samples were coated at a changed concentration of components. As can be seen from Figure 1, the specific pressure varies depending on the average interference value and the percentage ratio of FeSO₄ / ZnSO₄. The dependence of the pressing-in and pressing-out on the preload value has the same character as for homogeneous conjugated parts.

So, with an increase in interference from 10 μcm to 30 μcm, the average specific pressure increases from 3.88 kg ∙ cm⁻² to 7.89 kg ∙ cm⁻² with a ratio of FeSO₄ / ZnSO₄= 0.1, but the value of the tightness of the press joints does not affect, because with large values of interference, breakdowns and seizures occur during pressing.

With a change in the concentration of the constituent components of the zinc-iron coating, the strength of the press joints also changes. With an increase in the iron content in the coating, a decrease in the specific pressure is observed, the friction coefficients during pressing and unpressing decrease from 0.56 when pressing to 0.17 when pressing.

This is because the plastic deformation of the coating is reduced and, therefore, the true contact area of the mating parts is reduced. In this case, there is a limit to the interference value at which the
strength of the layers of the zinc-iron alloy exceeds the yield strength. In this case, the forces of pressing and pressing out fall. Therefore, when testing for repressing was limited to the choice of only three values of interference.

Metallographic studies have established that galvanic coatings contribute to the formation of strong metal bonds in the contact zone of the mating surfaces of the press joints. In press joints, parts of which are coated with a zinc-iron alloy with a low iron content, traces of loosening of galvanic coatings are visible over the entire area of the interface without destroying the surface of the parts to be joined (Figure 2).

![Figure 2. Structure of a zinc-iron coating with an iron content of p to 5% based, x 500.](image)

Therefore, zinc-iron plating can be used in press joints, which are subjected to further repeated pressing. When pressing covered parts with soft galvanic coatings, the surfaces of the rollers and bushings did not collapse, and only thin coated films were present, and the strength of the press joints during repeated pressings did not decrease.

When testing samples with galvanic coatings for adhesion to the base, it was revealed: when applying a coating of zinc-iron alloy, the strength of press joints increases due to the occurrence of setting and due to an increase in the area of actual contact, and not due to interference; the friction coefficient during the formation of press joints from parts with different percentage composition of the coating components reaches during pressing up to 0.17 and during extrusion up to 0.56. With an increase in the iron content in the coating, the friction coefficient decreases; when pressing out a roller coated with a zinc-iron alloy with a low iron content, the galvanic coatings on the surface of the rollers and bushings were not destroyed. The strength of the press joints during repeated press-fits did not decrease; research results show that zinc-iron coatings can be used in the repair and restoration of weakened parts of press joints.

2. Metallographic and X-ray structural studies of the structure of zinc-iron coatings

The structure of electrolytic coatings was studied on the same samples that were used to determine microhardness. In this case, the samples were cut from the coating removed from the sample, installed in aluminum rings and filled with sulfur.

Electroplating consider the formation of coatings at the cathode as a process of crystallization of coatings, which proceeds in two stages [6, 7]:

1. The formation of crystallization centers (nuclei).
2. The growth of the formed crystallization centers.

The rate of each of these processes is determined by the conditions of electrolysis, the composition of the electrolyte and the electrolysis conditions. In this case, the higher the rate of formation of crystallization centers, i.e., the more crystals that appear on the cathode per unit time, the fewer crystals of the resulting coating.

Iron crystallizes from solutions of its salts at low temperatures and low cathodic current densities in the form of finely crystalline coatings.

Zinc, under similar conditions, gives larger crystalline coatings; however, it is noted that zinc forms dense continuous coatings in thin layers, as for the characteristics of the structures of zinc coatings obtained by hot galvanizing, it is known that iron delays the recrystallization of zinc and promotes the
production of hard riveted coatings. When the iron content exceeds 0.2 %, brittle intermetallic compounds FeZn$_4$ and FeZn$_3$ appear in zinc. The iron content above 0.2 % increases the brittleness so much that it is difficult to roll [1]. In contrast to the hot method, electrolytic galvanizing of iron does not form an alloy of metals.

The study of potential measurements and metallographic, X-ray diffraction analysis showed that, when iron and zinc are co-precipitated from aqueous solutions of their salts, the cathode zinc-iron coating does not contain a chemical compound of iron and zinc. Comparing the microstructure of the zinc-iron coating obtained at various concentrations of the components, all other things being equal, the electrolyte, as well as the electrolysis modes, made it possible to establish. That their microstructure is almost identical and determines a solid solution, the dispersion value, the structure of which depends on the percentage composition of the coating and the electrolysis conditions. Thus, with an increase in the iron content in the coating, the formation of a finely dispersed structure increases. With increasing process temperature, the structure of the coatings becomes more coarse.

The study of the microstructure showed that the nature of the structure of the coatings obtained at different current densities is the same, but there are differences in the size of the crystals (Figures 3-5). At a current density of $0.40 \div 2.00 \text{ A} \cdot \text{cm}^{-2}$, fine-crystalline coatings are obtained.

![Figure 3. Structure of zinc-iron coating with iron content in the coating = 40% x 500.](image)

![Figure 4. The structure of the zinc-iron coating obtained at an electrolyte temperature $= 90^\circ\text{C}$ x 500.](image)

a) cathodic current density $D_k = 0.40 \text{ A} \cdot \text{cm}^{-2}$  \quad  b) cathodic current density $D_k = 1.80 \text{ A} \cdot \text{cm}^{-2}$

![Figure 5. The structure of the zinc-iron coating obtained at various current densities x500.](image)

3. X-ray analysis
As a result of X-ray analysis of zinc-iron coating samples, depending on the percentage composition of the electrolyte components, changes in the cathode current density, electrolysis temperature and acidity of the electrolyte, the following was established: depending on changes in the concentration of zinc sulfate and iron sulfate in the electrolyte in all samples zinc is present in different amounts, increasing with increasing zinc sulfate in the electrolyte and with a decrease in cathodic current density. With an increase in iron sulfate in the electrolyte and an increase in the cathode current density, an insignificant amount of iron is observed.

As shown by chemical analysis, iron is contained in the coating, although in different percentages, depending on the electrolysis conditions. The seemingly contradiction between the results of chemical and radiographic analyzes can be explained by the formation of compact fine-crystalline coatings of zinc-iron alloy, the size of the crystals of which was influenced by mechanical activation. The resulting crystal lattices are significantly changed, which does not coincide with the tabular data (table 1) of the interplanar spacings of the iron and zinc crystal lattices obtained in the usual way.

It was found that the formation of chemical compounds of iron and zinc, depending on changes in the electrolyte composition and electrolysis conditions, is not observed, which is confirmed by the data given in table 1.

| Table 1. Interplanar spacings of the crystal lattice of zinc and iron. |
|---------------------------------------------------------------|
| Tabular data interplanar distances | Experimental data interplanar distances |
|-----------------------------------|----------------------------------------|
| 1                                 | 1.66 (8)                                |
| 1                                 | 2                                       |
| 1                                 | 2.06                                    |
| 1                                 | 1.879                                   |
| 1                                 | 1.68 (8)                                |
| 1                                 | 1.348                                   |
| 1                                 | 1.334                                   |
| 2                                 | 1.180                                   |

Where 1 – relative intensity of reflexes, α /n - interplanar distances.

Of particular note is the effect of mechanical smoothing of the coating surface when using an emery bar and brush on the structure of the cathode deposit. This is due to the following reasons: the next pass of the emery bar cuts off microroughnesses, maintaining the surface roughness at a constant level corresponding to the state of the bar surface. At the same time, mechanical activation of the coating surface occurs, which prevents the reduction of the number of surface growth points and the strengthening of crystals due to a violation of the crystal lattice of some crystals, removal of a passive film, lowering the release potential, removal of adhering hydrogen bubbles and an increase in the effective cathode surface, as well as a decrease in concentration polarization. In addition to mechanical activation, there is an “extrusion” of the cathode layer of the electrolyte and its replacement with a fresh one, rushing into the void behind the leaving bar. Such a forced electrolyte change significantly improves the conditions for supplying the growing surface with ions of discharging metals. Thus, when applying mechanical action on the cathode surface, factors appear that lead to the grinding of growing crystals. The high current densities used in this case lead to the formation of a large number of nuclei.

The mechanical activation of the surface, together with the forced supply of discharging metal ions, promotes the growth of the formed nuclei. Comparing the micrographs of the transverse sections of the cathode coatings of the zinc-iron alloy (Figure 6), obtained with the use of an emery bar and
without mechanical action on the surface of the cathode deposit, a significant grinding of crystals is clearly visible.

![Figure 6. X-ray plot of the zinc-iron coating obtained on a diffractometer.](image)

In this case, the coating has increased rigidity, which is associated with its fine-crystalline structure and a certain orientation of the crystals in the direction of movement of the bar and brush (Figure 7).

![Figure 7. The microrelief of the surface of the zinc-iron coating, obtained by contact in a flowing electrolyte with simultaneous smoothing with an emery bar, x1200.](image)

The replicas for electron microscopy were made by removing a plastic impression from the surface of a sample on which a carbon layer 1000 Å thick was sprayed in vacuum. The carbon replica was separated from the plastic by dissolution and was tinted with chrome. The resolution of the resulting replicas was 150-200 Å.

According to modern concepts, the process of electrocrystallization includes three successive stages: the transfer of ions from the volume of the electrolyte to the discharge sites; ion discharge and coating crystallization. Crystallization of the coating at the cathode is characterized by a number of processes, of which the formation of nuclei (crystallization centers) and their growth determine the structure of electroplating. The rate of each of these processes depends on the electrolysis conditions — composition, acidity and temperature of the electrolyte, cathode current density, presence of impurities and surfactants, anode rotation speed, electrolyte flow rate in the interelectrode space, cathode activation method, etc.

The main structural characteristic of electrolytic coatings, the grain size, depends on the ratio of the nucleation and crystal growth rates. Iron crystallizes from solutions of simple salts at low temperatures and low cathodic current densities in the form of finely crystalline coatings. Under similar conditions, zinc gives larger crystalline coatings, and alloying it with iron favorably affects the production of a fine-crystalline structure. When iron and zinc are co-precipitated from acidic aqueous solutions of their salts, the coatings do not contain a chemical compound of iron with zinc, but are a solid solution, the dispersion of the structure of which depends on the percentage of iron in the coating and electrodeposition conditions [2,3].

Studies have confirmed that the Zn-Fe precipitated alloy is a solid solution of iron in zinc. The concentration of iron in the coating is (0.4 ± 4.6%).
In parallel with electrochemical studies, the effect of surfactant additives on the microstructure and micrometry of coatings was studied. The studied additives were introduced into the electrolyte in an amount of 1.2.4 mg ∙ l⁻¹. The electrodeposition of the coating was carried out at \( D_k = 0.40 \text{ A} \cdot \text{cm}^{-2} \), \( pH = 2.5 \), temperature \( 25^0 \text{ C} \), anode rotation speed of \( 30 \text{ rpm} \cdot \text{min}^{-1} \), electrolyte flow rate of \( 2.5 \text{ m} \cdot \text{s}^{-1} \). The appearance of the coating was evaluated visually; the leveling ability of the electrolyte was judged by the distribution of the coating on the transverse microsection with grooves.

As a result of studies, it was found that the organic additive helps smooth out the sharp peaks and edges of crystallites. Coatings are obtained with a flat and smooth surface with accurate reproduction of the microrelief of the base and alignment of individual microroughnesses of the relief.

The results of metallographic and profilometric and X-ray diffraction studies make it possible to obtain fine-grained non-porous coatings. X-ray diffraction studies of coatings showed an extreme dispersion of the structure without separate reflexes of structural units (Figure 8). In addition, the presence of interference maxima indicates the texturing of the coating, which positively affects the mechanical properties of the coating. This can be explained by the action of surface-active substances on kinetics-electrode processes with inhibition of the electrochemical reaction and an increase in polarization.

It has been established by profilometric studies that crystalline roughness naturally increases with increasing coating thickness. The introduction of surface active substances into the electrolyte reduces the roughness coefficient and the faster, the higher the concentration of ZnSO₄ and FeSO₄ in the electrolyte. Based on the profilograms, the microlief of the surface of the coating is determined by various structural units (Figure 8). The largest elevations with a width of \( 50 \div 100 \text{ mcm} \) represent convection undulation and determine the roughness of shiny coatings. Small growth protrusions (\( 5 \div 10 \text{ mcm} \)) are monolithic crystalline splices that determine the roughness of matte coatings. Stepped and jagged intergrowths with a width of 25–30 mcm are predominant in the relief of semi-brilliant coatings. Metallographic studies at \( x500 \)-fold increase have shown that they have the form of spherulites or irregular tables with a tendency to hexagonal cutting and are most developed in thick coatings obtained from electrolyte with a minimum content organic additives. In this case, the inhibition of the growth of individual spherulites and the general leveling of the coating surface are apparently due to the adsorption properties of the organic additive and the rate of nucleation of the crystallization centers exceeds the rate of their development.
Figure 8. Radiographs and microstructure depending on the method plating, x 500, where: 1 - coating in the bath at $D_k = 0.5 \text{A} \cdot \text{cm}^{-2}$; 2 - coating with a rotating sample; 3 - coating in a flowing electrolyte; 4 - coating by contact with a brush and an emery bar in a flowing electrolyte; 5 - coating using surfactants.

The micromorphology of the surface is determined by the lamination, which determines the structure of the coating growth. Figure 9 shows that, regardless of the composition of the electrolyte, the front of the layer can be tortuous (a, c, h, k), straight (b, d, g) or step (e). With an increase in the concentration of the organic additive in the electrolyte, the thickness of the layers decreases markedly (c, h, k), vicinal mounds are revealed, giving rise to new layers. Often, growth layers have the appearance of irregular or tabular bursts, turning into a smooth surface. At times, damped growth stages from screw dislocations (h) are detected, which indicates an insignificant coating intensity and a sufficiently high polarization of the process.
Figure 9. The microrelief of the surface of the zinc-iron coating: a, b, c, d - depending on the method of coating; e, g, h, k - with the use of organic additives, x2500.

4. Conclusions
Based on the analysis of the microstructure of zinc-iron coatings obtained at various concentrations of electrolytes, electrolysis modes, as well as on the basis of X-ray diffraction analysis of these coatings, it was established: the structure of the electrolytic zinc-iron coating is a solid solution of zinc replacement with iron without any signs of chemical iron and zinc compounds; the dispersion of the structure of zinc-iron coatings depends on the specific conditions of electrolysis (concentration of components, electrolysis mode). The iron content in the coating favorably affects the microstructure of the coatings, making them finer grained compared with the microstructure of completely pure zinc coatings. The use of mechanical smoothing of the coating surface showed that mechanical activation of the surface results in dense microcrystalline coatings with increased stiffness and constant surface.

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