

## Review

Review article

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## Features of the corrosion of coatings based on zinc alloys: oxidation products and the selective dissolution of zinc. Review

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### Abstract

The literature review analyses and systematizes the results of corrosion studies of widely used anti-corrosion zinc coatings based on various binary systems Zn-Al, Zn-Mg, Zn-Fe, Zn-Ni, Zn-Co. The patterns of corrosion, the role of selective dissolution and corrosion products in increasing the corrosion resistance of coatings in neutral chloride-containing environments have been studied. The analysis shows that the corrosion rate depends on the chemical and phase composition of zinc coatings, which is due to differences in the corrosion behavior of the phase components of the alloys. Selective dissolution has an ambiguous effect on the corrosion resistance of coatings. On the one hand, the process of selective dissolution of zinc can be accompanied by the formation of corrosion cracks, which reduces the corrosion resistance of the coating. On the other hand, a rough surface enriched with an electropositive alloying component is formed. As a result, roughness stimulates the deposition of a denser and more compact layer of corrosion products, which reduces the access of oxygen and other electrolyte components to the coating's surface. Under certain conditions, a film of corrosion products can provide additional resistance to the corrosion process due to low electrical conductivity. With the uniform dissolution of coatings, both the co-precipitation of complex compounds of zinc and alloying metals and the doping of the product layer with oxides or hydroxides of alloying metals occur. This also results in increased compactness and reduced electrical conductivity, which increases the corrosion resistance of the coatings. The purpose of the article: an overview of the results of studies of corrosion of zinc coatings, physical and chemical features of the formation and composition of the layer of corrosion products, the influence of corrosion products and selective dissolution on the corrosion resistance of coatings.

A review of the results of studies relating to the corrosion of zinc coatings was carried out, taking into account the formation of a protective layer of corrosion products and the selective dissolution of zinc. The corrosion of zinc coatings is influenced by the structure and phase composition of the coatings, the selective dissolution of zinc, as well as the nature of the layer of corrosion products. The corrosion resistance of zinc coatings increases if a compact layer of corrosion products with low electrical conductivity is formed. The selective dissolution of zinc can have a positive effect on its protective ability due to the formation of a rough surface, which promotes the deposition of a denser layer of corrosion products. In the case of the uniform dissolution of zinc alloy coatings, alloying metals are able to integrate into the structure of zinc corrosion products, which makes the layer more compact and leads to a decrease in its electrical conductivity, significantly increasing the corrosion resistance of the coatings.

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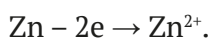
## 1. Introduction

Zinc and its alloys are widely used to protect structural materials and products from corrosion in various industries. Protective zinc coatings are produced by cathodic deposition, immersion in molten zinc, thermal diffusion methods and gas dynamic spraying using zinc powders, as well as their introduction into paint compositions. Regardless of the production method, the corrosion behavior of zinc coatings strongly depends on the composition, morphology and structure of the layer of corrosion products (CP), the physicochemical properties of which often determine the high corrosion resistance of zinc coatings. In addition to zinc oxide (ZnO) and zinc hydroxide ( $\text{Zn}(\text{OH})_2$ ), depending on the chemical composition of the corrosive environment, the CP layer may include various basic zinc salts [1–4]. In addition, corrosion of zinc alloys can proceed through the mechanism of selective dissolution (SD) [5]. In this case, the accumulation of an alloying component on the surface of the alloy is possible, which has an additional effect on the physicochemical properties of the protective layer and the corrosion resistance of coatings. The degradation processes of zinc coatings play a special role in microelectronics, where they can be used as an intermediate layer, for example, at nickel-plating of aluminum contact pads. Considering that the possibility of the formation of zinc alloys with nickel and aluminum cannot be excluded, along with the formation of zinc oxidation products, it is necessary to take into account the probability of its selective dissolution.

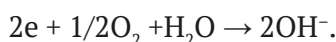
The study provides a review of the results of investigation of the patterns of formation of a protective layer of zinc corrosion products, which ensures the corrosion resistance of zinc-based coatings, taking into account the phenomenon of selective dissolution.

## 2. Corrosion of zinc

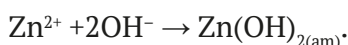
The process of the corrosive degradation of zinc includes its electrochemical oxidation at the anodic areas of the coating:



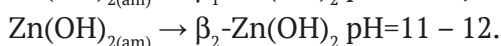
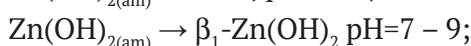
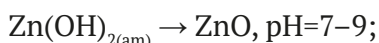
At the cathode sites in a neutral and alkaline aqueous environment, the reduction of oxygen dissolved in water occurs:



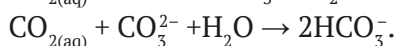
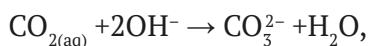
Accumulation of  $\text{Zn}^{2+}$  and  $\text{OH}^-$  ions in the surface layer of the solution leads to the rapid formation of zinc hydroxide precipitate:



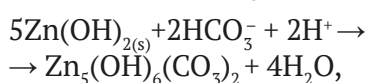
Being amorphous, it is capable of transformation into various products, the nature of which depends on the pH of the environment [6]:



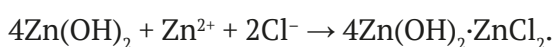
Subsequent transformations of  $\text{Zn}(\text{OH})_2$  mainly depend on the chemical composition of the medium, in particular, on the presence of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  ions, and products of reactions of dissolved  $\text{CO}_2$  with water:



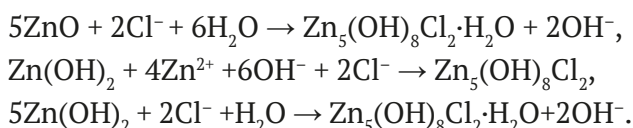
The latter, reacting with  $\text{Zn}(\text{OH})_2$  hydroxide, quickly (within several hours) form hydrozincite (HZ) or zinc hydroxycarbonate  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  ( $3\text{Zn}(\text{OH})_2 \cdot 2\text{Zn}(\text{CO}_3)_2$ ) [7, 8]:



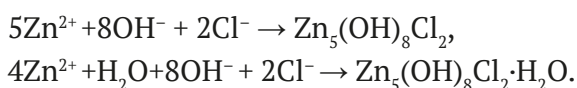
as well as zinc hydroxycarbonate monohydrate  $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ . In environments with a relatively high content of chloride ions, HZ transforms into simoncolleite (SC) or zinc hydroxychloride  $\text{Zn}_5\text{Cl}_2(\text{OH})_8 \cdot \text{H}_2\text{O}$  ( $4\text{Zn}(\text{OH})_2 \cdot \text{ZnCl}_2$ ) within a few days. If the  $\text{Cl}^-$  concentration in a solution is higher than 0.01 M and  $\text{pH} \approx 7$ , and  $\text{CO}_2$  is absent or its concentration is insignificant, then SC is formed directly from ZnO or  $\text{Zn}(\text{OH})_2$  [9–12]:



The formation of SC is also described by other chemical reactions, for example [9–12]:



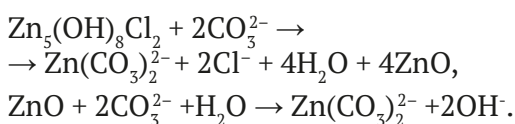
In addition, the formation of simoncolleite is also considered as chemical precipitation from an ion-saturated solution near the surface of a corroding metal [8, 13]:



The SC can transform into gordaite  $\text{NaZn}_4\text{Cl}_2(\text{OH})_6\text{SO}_4 \cdot 6\text{H}_2\text{O}$  with prolonged exposure for several years under the influence of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ .

Simoncolleite serves as a cathodic corrosion inhibitor of Zn, in the form of a dense protective layer, impeding both volumetric and intercrystalline diffusion of  $\text{O}_2$ . The corrosion of Zn is often local, which affects the homogeneity of the layer of products of the corrosion process. Thus, in chloride-containing media, the anodic areas are acidified, and the concentration of  $\text{Cl}^-$  ions increases near them, which contributes to the formation of predominantly simoncolleite [14, 15]. The cathode areas have a higher pH due to the reduction of dissolved  $\text{O}_2$ , as a result of which hydrozincite is formed on them [14, 15].

Simoncolleite is stable at relatively high  $\text{Cl}^-$  concentration in solution and in the absence of excess of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . As the pH increases, it transforms into the less compact ZnO oxide. In the presence of  $\text{HCO}_3^-$  ions SC transforms into sodium-zinc carbonate  $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4$  (at 0.5–1.0 M  $\text{HCO}_3^-$ ) or hydrozincite (at 0.05 M  $\text{HCO}_3^-$ ) [16]. With increasing  $\text{CO}_3^{2-}$  concentration zinc CP can transform into soluble carbonate complexes [16]:



All these factors contribute to a decrease in the degree of protection of zinc.

### 3. Corrosion of alloy coatings based on Zn-Al and Zn-Mg

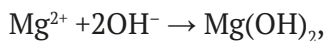
Coatings with zinc alloys of the Zn-Al system of the “Galvalume” (GL) type (55 wt. % Al) and “Galfan” (GF) (5 wt. % Al + mischmetal additive) allow to provide corrosion resistance 2–4 times

higher compared to zinc [17]. The microstructure of coatings obtained from Galfan and Galvalume alloys is different. In GF, the basis is the matrix of the  $\eta$ -phase is a solid solution of iron in zinc with a Fe concentration of 0.03 wt. %, and Al is present in the form of point inclusions ( $\beta$ -Al). In GL, the core consists of dendrites with a high Al content, and the interdendritic spaces are enriched with zinc [7, 18–22].

Differences in the microstructure of heterophase alloys of the Zn-Al system have a significant impact on their corrosion behavior. Thus, the process in the case of Galvalume alloys in a chloride environment starts on zinc-rich surface areas. Predominant dissolution of Zn from interdendritic regions occurs, while the phase enriched in Al has a more positive potential and accelerates corrosion of the coating, acting as a cathode [18]. At the same time, an increase in Al concentration in the alloy leads to the appearance of compounds such as  $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ , and  $\text{Al}(\text{OH})_3$  in the form of a thin film among CP. Local islands of mixed corrosion products of complex composition  $\text{Zn}_2\text{Al}(\text{OH})_6\text{Cl} \cdot \text{H}_2\text{O}$  and  $\text{Zn}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  are formed predominantly on zinc-rich interdendritic regions [7, 22]. With a high  $\text{Cl}^-$  content aluminum hydroxy compounds transform into aluminum oxychloride  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  [21]. Corrosion of Galfan-type alloys, characterized by a low aluminum content, is similar to the process involving metallic Zn. Indeed, the dissolution of the  $\eta$ -phase leads to the formation of CP characteristic of zinc, including  $\text{ZnO}$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ . When areas containing Al are dissolved,  $\text{Zn}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  or  $\text{Zn}_2\text{Al}(\text{OH})_6\text{Cl} \cdot \text{H}_2\text{O}$  appear among the corrosion products, similarly with the GL type coatings [7, 22].

The inclusion of aluminum compounds in the composition of corrosion products contributes to the formation of a denser protective layer, which ultimately leads to an increase in the protective effect and an increase in the corrosion resistance of coatings based on alloys of the Zn-Al system. An additional effect is exerted by the selective dissolution of zinc from the heterophase surface, which leads to an increase in roughness and creates topologically favorable conditions for the deposition of CP, forming a protective layer [19, 20, 22].

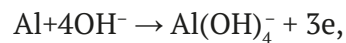
The microstructure of Zn,Al coatings changes with the introduction of magnesium and silicon. At a relatively low magnesium concentration, dendrites of an aluminum-based solid solution are formed, and in the interdendritic region, relatively rich in Zn, the formation of a dense intermetallic  $MgZn_2$  phase is observed. High Mg content and Si additive (0.4 wt. %) provide the formation of the  $Mg_2Si$  phase in the coating and also contribute to an increase in the thickness of the coating. During the corrosion of alloys,  $MgZn_2$  intermetallic compound acts as an anode and dissolves with the formation of  $Zn^{2+}$  and  $Mg^{2+}$  ions, and on the surface of the dendritic phase enriched in Al,  $O_2$  is reduced with release of  $OH^-$  ions. Magnesium ions can appear in the near-electrode layer as a result of selective dissolution, further increasing the corrosion resistance of the alloy [23]. Diffusion of  $Mg^{2+}$  ions into the near-cathode zone of the solution leads to the formation of a compact and dense precipitate of magnesium hydroxide [7]:



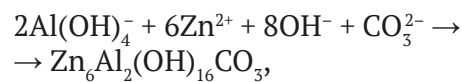
which contributes to the creation of a barrier for the diffusion of oxygen to the surface of the alloy [9, 23], suppressing the reaction of its reduction and slowing down the corrosion process. In addition to the formation of a protective deposit, the role of  $Mg^{2+}$  in increasing corrosion resistance is associated with neutralization of  $OH^-$  and  $CO_3^{2-}$  [9, 23]. The binding of  $OH^-$  into  $Mg(OH)_2$  hydroxide leads to buffering of the pH of the near-electrode layer, which creates favorable conditions for the precipitation of simoncolleite, since  $OH^-$  ions lead to alkaline destruction of SC. In turn,  $CO_3^{2-}$  binding into insoluble  $MgCO_3$  prevents the transition of SC into hydrozincite [24]. According to an alternative approach [25–27], the presence of  $Mg^{2+}$  does not affect the formation of SC, and the positive contribution of magnesium to the protective effect of CP is the formation of mixed oxides such as  $Zn_{(1-x)}Mg_xO$ . As a result, the amount of  $OH^-$  groups and a negative charge on the surface of the barrier layer increase [25, 26], therefore, the electron work function increases, the electrical resistivity of the layer increases, and the rate of charge transfer and corrosion in general, on the contrary, decreases. Regardless of the mechanism of action, magnesium compounds

increase the protective ability of the barrier layer of corrosion products, as a result the corrosion resistance of the coating increases.

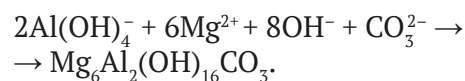
During the corrosion of zinc coatings with Al and Mg additives, the co-precipitation of double layered hydroxides, which additionally prevent the diffusion of  $O_2$  to the metal surface is also possible. The mechanism of their formation involves the dissolution of aluminum from dendrites without the formation of a protective layer:



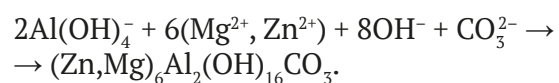
The presence of  $Zn^{2+}$  and  $Mg^{2+}$  ions in the medium determines the possibility of coprecipitation of hydroxide compounds of zinc, magnesium, and aluminum. According to [29, 30], the ZnAlMg coating corroded in salt spray, transforms into a stable, durable, aluminum-rich protective layer, identified as zinc aluminum carbonate hydroxide,  $Zn_6Al_2(OH)_{16}CO_3$ :



which protects the steel base from corrosion and is the main reason for the increased corrosion resistance of the ZnMgAl coating. The participation of magnesium in the coprecipitation of double layered hydroxides is possible [31]:



as well as the formation of even more complex compounds:



It was shown in [32] that the formation of double layered hydroxides has a positive effect on increasing the corrosion resistance of coatings. The authors of [31] noted that the formation of these compounds reduces the alkalization of the CP layer, which prevents the decomposition of already formed products. At the same time, the corrosion process only slows down, since with increasing exposure time in a corrosive environment, zinc CP were revealed in the protective layer.

The undissolved residual aluminum “skeleton” can further enhance the protective function of the CP barrier layer [33, 34].

In studies [35–38], the influence of small (0.05–0.1 mass. %) rare earth metal (REM) additives on the corrosion resistance of “hot” zinc coatings, based on Zn–Al alloys (5 wt. %) was studied. It has been shown [15, 35] that the modified coating of the composition Zn-4.9Al-0.1REM was characterized by a 2.5 times lower rate of chloride corrosion compared to zinc. The main reasons for the increase in corrosion resistance are believed to be the formation of a dense fine-grained structure of the coating [35], as well as inhibition of the transformation of simoncolleite  $Zn_5(OH)_8Cl_2 \cdot H_2O$  into hydrozincite  $Zn_5(OH)_6(CO_3)_2$  [39] and a decrease in the electrical conductivity and ion-exchange properties of the protective layer of zinc CP in the presence of rare-earth metals [40].

#### 4. Corrosion of alloy coatings based on Zn-Fe

Coatings from alloys of the Zn-Fe system are produced by electrodeposition, immersion in molten zinc, the additional heat treatment of “hot” coatings, and thermal diffusion saturation from zinc powders. Phase composition of Zn,Fe coatings may include the following phases:  $\eta$ -phase (0.03 wt. % Fe),  $\zeta$ -phase ( $FeZn_{13}$  5.0–6.0 wt. % Fe);  $\delta$ -phase ( $FeZn_{10}$  7.0–11.5 wt. % Fe);  $\Gamma_1$ -phase ( $Fe_5Zn_{21}$  17.0–19.5 wt. % Fe);  $\Gamma$ -phase ( $Fe_3Zn_{10}$  23.5–28.0 wt. % Fe) [41]. Moreover, in the case of “hot” coatings, the surface layers predominantly consist of zinc-rich  $\eta$ - and  $\zeta$ -phases, while annealed and thermal diffusion coatings are represented mainly by the  $\delta$ -phase  $FeZn_{10}$ .

The corrosion rate of Zn,Fe coatings depends nonlinearly on the Fe concentration. Galvanic materials Zn-Fe coatings with iron concentration from 10 to 25 wt. % are characterized by significant corrosion resistance. [42–45]. An increase in the Fe content above 20 wt. % leads to an acceleration of corrosion, and according to data [45–59], the lower rate of the process was observed at an iron concentration of 10 wt. %. It should be noted that this optimal iron concentration in most cases corresponds to Zn,Fe coatings that have undergone additional annealing. The observed effect can be associated with the features of the crystal structure and the corrosion behavior of the  $\delta$ -phase. In addition, it was assumed [47] that at a concentration of 10 wt. % Fe inhibits

the reduction reactions of  $O_2$  in a neutral NaCl solution due to the formation of a barrier layer based on  $Zn(OH)_2$ , uniformly distributed over the surface of the coating and, unlike semiconductor ZnO [48], characterized by extremely low electronic conductivity [47, 51].

Corrosion of Zn,Fe coatings is accompanied by selective dissolution of Zn and leads to the enrichment of the surface with iron and its morphological development, which has a positive effect on the growth and morphology of corrosion products [47, 54], forming a fairly dense layer with low values of porosity [57], ionic conductivity, and, consequently, the corrosion rate [55, 60]. Moreover, according to various authors, the composition of CP of Zn,Fe coatings and pure zinc is similar and includes ZnO,  $Zn(OH)_2$ , SC and HZ [55, 61–63]. With prolonged exposure in the CP layer, the appearance of iron compounds is observed, for example,  $FeOOH$  of various modifications [59, 63–66],  $Fe_2O_3$  [66, 67] or  $Fe_3O_4$  [68] depending on the conditions of the corrosion process. Some assumptions about the influence of iron on the composition or properties of the CP film were proposed by the authors [69–71] based on data obtained using the chemical coprecipitation of synthetic CP from two electrolyte systems:  $ZnCl_2$ - $FeCl_2$  and  $ZnCl_2$ - $FeCl_3$ . Thus, in a solution with the addition of  $Fe^{2+}$  as its concentration increases, the morphology of the precipitate changes: first, small scattered agglomerates are formed, then sheets, which become thinner and again transform into small aggregates. According to X-ray diffraction data, the sheets are SC, and the thin sheets are complex zinc-iron hydroxychloride:  $[Zn_{(1-x)}Fe(III)_x(OH)_2]^{x+}[Cl^-]_x \cdot nH_2O$  [72]. At a molar ratio of  $Fe/(Zn+Fe) = 0.6–0.8$ , the precipitate is X-ray amorphous. With a further increase in iron concentration, ferrite  $ZnFe_2O_4$  and then magnetite  $Fe_3O_4$  appear in the precipitate.

In solution with the addition of  $Fe^{3+}$  only small agglomerates of ZnO particles are formed, and SC precipitation does not occur. In this case, due to the proximity of ionic radii and the electronegativity of iron and zinc, a fairly stable compact layer based on trioctahedral hydroxides can be formed [69–72].

The addition of simoncolleite to solutions from which iron hydroxide  $\beta$ - $FeOOH$  was

precipitated inhibits the crystallization and growth of hydroxide particles [73]. At the same time, no incorporation of Zn into the structure of  $\beta$ -FeOOH was detected, but the compact amorphous precipitate of  $\beta$ -FeOOH particles was characterized by low adsorption capacity with respect to  $H_2O$  and  $CO_2$ . The effect is explained by the fact that zinc CP, when dissolved, increases the pH of solutions, enhancing the hydrolysis of  $Fe^{3+}$  with the formation of hydroxo complexes  $Fe(OH)_x^{(3-x)+}$ , which condense into amorphous iron oxides/hydroxides. The adsorption of  $Zn^{2+}$  ions on them inhibits the crystallization of  $\beta$ -FeOOH particles, as a result, the precipitate becomes amorphous and more compact [73], and the rate of the corrosion of Zn,Fe coating decreases.

### 5. Corrosion of Zn-Ni, Zn-Co coatings

Coatings based on alloys of the Zn-Ni and Zn-Co systems are obtained by electrodeposition from solutions of zinc salts with the addition of nickel or cobalt salts [74–76]. At a Ni concentration of less than 5 at. % Zn,Ni coatings consist predominantly  $\eta$ -phase, with increasing Ni concentration from 10 to 15 at. %, the presence of  $\delta$ -phase ( $Ni_5Zn_{22}$ ) and  $\gamma$ -phase ( $Ni_5Zn_{21}$ ) is possible and at Ni concentrations above 15 at. % the appearance of the  $\alpha$ -phase is possible [77]. In Zn,Co coatings, the presence of both solid solutions of cobalt in zinc and the  $\gamma$ -phase ( $Co_5Zn_{21}$ ) is possible.

Similar to alloys of the Zn-Fe system, the corrosion rate of Zn,Ni and Zn,Co coatings nonlinearly depends on the concentration of the alloying metal. Among Zn,Ni coatings, systems with a nickel concentration of 10–15 wt. % have the highest corrosion resistance [77–84]. In this case, the corrosion current of the alloy with a concentration of 15 wt. % is two times lower compared to the alloy with 22 wt. % [80, 85]. The effect is associated with the presence of a cubic  $\gamma$ -phase ( $Ni_5Zn_{21}$ ) [80, 85, 86], and with the fact that in this concentration range the alloy is homogeneous [83]. The highest corrosion resistance of Zn,Co coatings is observed in the cobalt concentration range of 10–20 wt. % ZnNi [87, 88], also corresponding to one  $\gamma$ -phase ( $Co_5Zn_{21}$ ) [87], characterized by high corrosion resistance [89].

Zn-Ni coatings are noticeably susceptible to the selective dissolution of zinc. As a result, the

surface is enriched with nickel, and the formation of a  $\beta$ - or  $\alpha$ -phase cannot be excluded [83, 90]. According to [91, 92] the initial corrosion rate of Zn,Ni coatings is higher than that of pure Zn coatings since Ni accumulation stimulates the cathodic reaction. The development of the corrosion process causes the formation of cracks that can reach the steel substrate [90–92], and also leads to a further increase in the relative content of Ni in the corrosion products and/or in the alloying coating layers. As the area of the substrate in contact with the electrolyte and the surface fraction of nickel increase due to the increase of cracks, the resistance of the coating to galvanic corrosion decreases. According to [93], Zn-Ni alloys containing 14 wt. % Ni and lower, show longer galvanic protection of the steel substrate compared to coatings where the Ni concentration is higher than 18 wt. %.

Selective dissolution can also have a positive effect on the corrosion resistance of Zn,Ni and Zn,Co coatings due to the formation of the composite [94–96], consisting of corrosion products and a metal phase enriched in Ni or Co [95] on the surface. As in the case of other zinc alloys, an increase in roughness during SD has a positive effect on the formation of a compact dense CP layer characterized by high resistance [97–99].

The relatively high corrosion resistance of Zn,Ni and Zn,Co coatings is also associated with the peculiarities of the formation of corrosion products. Thus, it is assumed [100, 101] that in the presence of Co, the dissolution of Zn is accelerated, and, consequently, the formation of simoncolleite, due to which the corrosion resistance increases. The nickel component, according to [102], slows down the crystallization of the layered structure of SC during the corrosion of Zn,Ni alloys. The substitution of zinc by nickel occurs in the SC structure, the size and thickness of crystallites decreases, and the layered structure is disrupted. As a result, complex precipitates that have a low adsorption capacity with respect to corrosive gases are formed [102]. Similarly, during the corrosion of Zn-Co coatings, among CP double hydroxide of zinc and cobalt  $Zn_2Co_3(OH)_{10} \cdot 2H_2O$  was found along with simoncolleite [103]. Over time, the proportion of SC in corrosion products decreases, and  $\alpha$ - $Co(OH)_2$ ,  $CoCl_2 \cdot H_2O$ , and ZnO appears. The formation of complex compounds

with zinc atoms substituted by Ni and Co, according to the authors, leads to increased compactness and improved barrier properties of corrosion products. Wherein the authors of [104] note that even at a concentration in the coating of less than 1 wt. %, Co prevents the conversion of  $\text{Zn}(\text{OH})_2$  into ZnO. For this reason, the CP of the Zn-Co system alloy includes a very small amount of ZnO compared to the corrosion products of pure Zn. A similar effect was observed when studying the corrosion products of Zn-Ni coatings [105]. Considering the fact that unlike loose semiconductor ZnO, zinc hydroxide is compact and has low electrical conductivity, this composition of the corrosion products of Zn,Co coatings contributes to effective corrosion inhibition [104].

## 6. Conclusions

The corrosion of coatings based on zinc alloys occurs via a complex mechanism, which includes a number of both electrochemical and chemical processes. The key factors that influence the corrosion resistance of coatings are the microstructure and phase composition of the coatings; selective dissolution of zinc; and the chemical nature and properties of corrosion products.

Coatings with surface layers heterogeneous in phase composition have lower corrosion resistance compared to homogeneous materials. The role of selective dissolution of zinc from alloys is not so clear. Selective dissolution of zinc from alloys can have both a positive effect on the durability of the coating and stimulate its further oxidation. The latter occurs due to the appearance of corrosion cracks, through which the electrolyte reaches the surface of the protected product. In this case, the galvanic protection of the product may decrease due to the accumulation of positive metal and the improvement of the electrode potential of the coating. At the same time, as a result of selective dissolution, the surface of the coating becomes rough, which provides a high density of active nucleation centers on which corrosion products crystallize, which have a protective effect on the coating.

The corrosion products of zinc coatings are predominantly zinc oxide ZnO and zinc hydroxide  $\text{Zn}(\text{OH})_2$ , as well as basic salts with a complex

layered structure. The protective effect of the barrier layer of corrosion products is determined by increased compactness, the formation of a denser film, and low electrical conductivity. In the first case, the film creates a mechanical barrier to the diffusion of aggressive components of the electrolyte and oxygen, in the second case it creates additional resistance, slowing down the transfer of electrons and reducing the rate of the corrosion process as a whole.

With prolonged corrosion of coatings, selective dissolution of zinc is replaced by joint oxidation of the alloy metals. The alloying metal oxidizes and accumulates in the layer of corrosion products in the form of various compounds. Its effect on the physicochemical characteristics of zinc corrosion products and the increase in corrosion resistance can be different. Metal ions are able to integrate into the structure of basic zinc salts, forming complex layered compounds. In addition, the doping of the film of zinc corrosion products with oxides and hydroxides of alloying metals may occur. An increase in the compactness of the film of zinc corrosion products and a decrease in its electrical conductivity occur, which leads to an increase in the corrosion resistance of the coating.

## Author contributions

Biryukov A. I. – idea, review concept, text writing, final conclusions. Kozaderov O. A. – text writing, scientific editing of the text, final conclusions. Batmanova T. V. – selection and systematization of material, conducting research.

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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