

# CORROSION PROPERTIES OF DIFFUSIONAL ZINC COATINGS OBTAINED BY NANOGALVANIZING

Galim R. G.<sup>1</sup>, Biryukov A. I.<sup>2</sup>, Zakharyevich D. A.<sup>2</sup>, Batmanova T. V.<sup>2</sup>, Yankov E.<sup>3</sup>, Fiskuchev S.<sup>4</sup>,

<sup>1</sup>LLC "VIKA-GAL", Chelyabinsk, Russia

<sup>2</sup>Chelyabinsk state university, Chelyabinsk, Russia

<sup>3</sup>University of Ruse, Dept. Material Science and Technology, Ruse, 8 Studentska Str., Bulgaria

<sup>4</sup>Chief Termoserviz OOD, Ruse, Bulgaria

st4857@yandex.ru

**Abstract:** Corrosion properties of diffusional zinc coatings with various surface compositions, obtained by nanogalvanizing technology, are studied in model oilfield and aggressive chloride-containing media. A complex of physical and chemical methods for studying corrosion behavior, including polarization measurements, X-ray diffraction analysis and SEM, was used in the work. Corrosion resistance of diffusional zinc coatings obtained by nanogalvanizing is determined by the composition, texture and thickness of the coating.

**KEYWORDS:** CORROSION, DIFFUSIONAL ZINC COATING, NANOGALVANIZING, SIMONKOLLEITE

## 1. Introduction

The technology of diffusional galvanizing (DG, also known as sherardizing) is currently gaining popularity as a method of protecting steel products from corrosion damage. DG coatings have both high corrosion resistance and good mechanical properties (microhardness, ductility, etc.). With the help of thermal diffusion galvanizing, coatings of different phase composition are obtained, providing protection of products under conditions that were previously considered too aggressive for zinc. The author developed the technology of DG in zinc powders with a nanocrystallized particle surface [1], so-called nanogalvanizing. The technology of DG with nanocrystallized zinc powders allows galvanizing in a wide range of temperatures (400-700°C) and adjusting the distribution profile of zinc concentration across the thickness of the coating. In Fig. 1 shows the distribution of zinc in the thickness of the coating for a DG coating sample with a thickness of 45  $\mu\text{m}$  consisting primarily of  $\delta$ -phase  $\text{FeZn}_{7-10}$ .

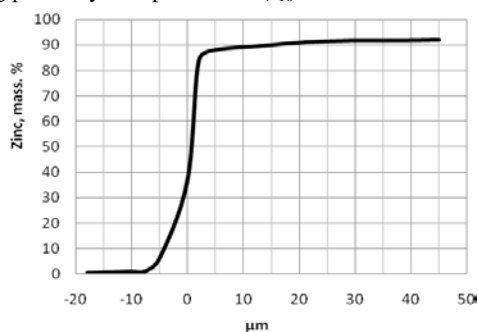


Fig. 1. Distribution of zinc by coating thickness

The resulting coatings, depending on the composition, can provide high corrosion resistance of the products to be protected in media containing chloride ions and hydrogen sulfide [2]. The researchers from Chelyabinsk state university, "VIKA-GAL" and "Termo serviz" companies have been conducting joint research to optimize the composition and structure of DG coatings for various conditions of operation of galvanized products since 2006.

## 2. Experimental

To optimize the distribution profile of the zinc concentration and the structural state of the coating, studies carried out on the effect of the composition and structural state of the coating layers on their corrosive behavior were. In the work, diffusion-galvanized carbon steel samples galvanized by the

procedure [1] at a temperature of 450°C for 3 hours were investigated.

The gravimetry and various electrochemical methods were used as methods for investigating the corrosion behavior. Polarization curves of the coatings under investigation were obtained with the help of the potentiostat-galvanostat P-30J (Elins). The corrosion products formed on the surface of the DG coatings, were studied by X-ray diffraction and scanning electron microscopy. X-ray diffraction analysis was performed on a DRON-3 diffractometer, Cu K $\alpha$ -radiation, in the range  $20^\circ \leq 2\theta \leq 60^\circ$  at scanning rate of 1-2  $^\circ/\text{min}$ . A scanning electron microscope "JEOL" JSM-6460 LV with an energy dispersive spectrometer "Oxford Instruments" was used to study the morphology of corrosion products and chemical microanalysis.

Investigation of corrosion behavior was carried out in model oilfield and aggressive chloride-containing media. As model oilfields media the highly mineralized solutions containing chloride, sulfate ions and metal ions, saturated with carbon dioxide or hydrogen sulfide were used. A solution of 3% sodium chloride was also used as the model corrosive medium.

To study the effect of the layer-by-layer distribution of zinc and the structural features of the DG coating layers on their corrosion behavior, the initial coating was etched in a 6% solution of nitric acid during time various intervals to obtain a series of samples with successively decreasing coating thickness in steps of 5  $\mu\text{m}$ . The thickness of the removed layer for each etching was determined from the difference in mass before and after etching. After etching, photometric determination of iron (III) content in etching solutions at  $\lambda = 400 \text{ nm}$  and  $l = 0.5 \text{ cm}$  with salicylic acid was carried out. According to the obtained data, the percentage of iron (III) in the layers of iron-zinc coating was calculated. After etching, the samples were washed with distilled water and degreased with acetone.

Data on corrosion behavior, structural features are given depending on the depth of the layers (thickness) calculated from the surface of the coating.

X-ray diagrams of all samples contain the maxima of the  $\delta$ -phase  $\text{FeZn}_{7-10}$  only. However, the diffraction pattern changes with thickness. As was shown earlier [3], this is due to the lack of a  $\delta$ -phase texture, typical for hot-dip zinc coatings, in diffusional coatings with thicknesses more than 30  $\mu\text{m}$ . On the X-ray diagram of the original coating (without etching) there are maxima with a high third Miller index: (1.4.14) and (3.0.22). After the third and fourth etching, these maxima almost disappear, while the relative intensity of the maxima with the zero third index, for example, (330) and (500), increases. Subsequent etching of the coating leads to a further increase in the relative intensity of the maxima with a zero third index.

Thus, on the surface of the initial coating  $\delta$ -phase crystals of different orientations are present, whereas in coating layers below 15  $\mu\text{m}$  crystals with a 6th-order axis  $c$  directed parallel to the coating surface prevail.

The results of the studies show that the corrosion resistance of the DG coating is high enough both in solutions of 3% sodium chloride and in model oilfield environments.

Based on the results of gravimetric tests, it is established that the corrosion rate of the DG samples of coatings represented by the  $\delta$ -phase in the 3% NaCl medium is 0.02  $\text{g}/(\text{m}^2 \cdot \text{hour})$ , while the corrosion rate of zinc and hot-dip zinc coatings is 0.04 and 0.05  $\text{g}/(\text{m}^2 \cdot \text{hour})$ , respectively.

X-ray diffraction analysis of corrosion products after prolonged exposure (30 days) in chloride-containing media shows that zinc hydroxochloride - simonkolleite is present on the surface of both zinc and zinc coatings obtained by various methods. However, the rate of its formation on the DG coatings is twice higher than on zinc or zinc coatings obtained from the melt [4].

Simonkolleite as a corrosion product of DG coatings is also detected after the samples are held in the NACE model oilfield (5% NaCl + 0.5%  $\text{CH}_3\text{COOH}$  + 0.3%  $\text{H}_2\text{S}$  +  $\text{CO}_2$ ). During 720 hours the DG coating was preserved only on samples whose surface after galvanizing was formed by a  $\delta$  phase with a Zn content of more than 90%. When studying the surface of samples that were tested in NACE medium using scanning electron microscopy, the morphology characteristic of simonkolleite was described by the authors in [5].

In the study of samples subjected to layer-by-layer etching, the following results were obtained. It is noted that the concentration of iron increases with the thickness of the layers, i.e. as they approach the substrate, but this growth occurs exponentially. A peculiar inflection point is 25-30  $\mu\text{m}$ , at this depth there is a sharp increase in the concentration of iron. Minima of etching rate are observed at depths of 15 and 30 microns.

The steady-state potential of the DG coating samples in a 3% NaCl medium becomes more positive when approaching the substrate material. The steady-state potential of the substrate - carbon steel is equal to -0.38 V (according to the standard hydrogen electrode). However, even at a depth of 45  $\mu\text{m}$ , the potential is more negative than the potential of the steel.

The dependence of the corrosion current on the thickness of the coating is not linear. Two characteristic points, at 15 and 30-40  $\mu\text{m}$  can be seen. At the first point, the corrosion current is reduced by a factor of two compared to the value characteristic for neighboring regions. In the region of 30-40  $\mu\text{m}$ , a sharp jump occurs, followed by a strong decrease in the corrosion current compared to the substrate material. In addition, at a thickness of 40  $\mu\text{m}$ , the stationary potential shifts to a more positive region, the shape of the cathode curve changes, which may indicate a change in the depolarizer in the corrosion process.

For long-term corrosion study, the samples were immersed in a solution of 3% NaCl for certain time intervals (5, 10 and 30 days) and the effect of the resulting corrosion products on the polarization curves and the value of the corrosion current was studied. Based on the change of the corrosion current as function of the test time, the following regions can be distinguished: 5-10  $\mu\text{m}$ : the corrosion current decreases linearly with time; 20 - 25  $\mu\text{m}$ : corrosion current decreases for 10 days, and then it starts to increase. For a thickness of 15  $\mu\text{m}$  there is an increase in current at small test times. For a thickness of 30  $\mu\text{m}$ , the corrosion current decreases sharply on the fifth day.

Thus, the dependencies of the corrosion current on the test time gives two characteristic points - 15 and 30  $\mu\text{m}$ , where the properties of the coating vary nonlinearly. These points also correspond to extrema on the dependence of the etching rate on the thickness of the coating.

Reduction of the corrosion current from the surface of the coating to a thickness of 15  $\mu\text{m}$  is probably due to an increase in the concentration of iron in the layers, as well as to the non-textured state of the  $\delta$  phase. Then, along with the enhancement of the

texture of the coating layers, despite the high iron content, the corrosion current is increased till a thickness of 30  $\mu\text{m}$ . A sharp decrease in the corrosion current and a change in the shape of the polarization curve at a thickness greater than 30  $\mu\text{m}$ , despite the increase in texture, can be related to the transition state of the coating at a given point.

After 30 days of test, according to X-ray diffraction analysis, simonkolleite is formed on all layers of the coating. According to the scanning electron microscopy, the surface is covered with a uniform film of corrosion products (Fig. 2). The iron content on the surface of all the samples is in the range from 0.7 to 1.3 at. %, The maximum content also corresponds to a thickness of 30  $\mu\text{m}$ . The zinc content is actually at the same level and is about 40 at. %.

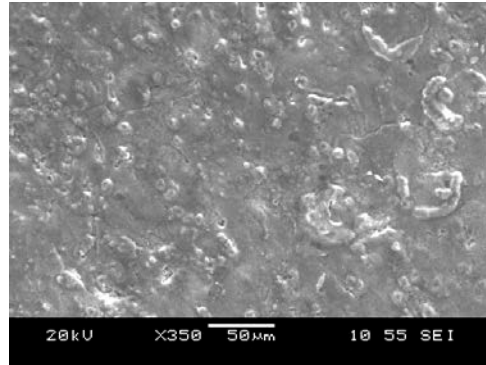


Fig.2. SEM image of the sample surface with a layer depth of 30  $\mu\text{m}$  after 30 days in a 3% NaCl solution

### 3. Conclusion

Diffusional zinc coatings, whose phase composition is represented by the  $\delta$ -phase, exhibit higher corrosion resistance than pure zinc (galvanic zinc coatings) and zinc coatings obtained from the melt.

In a 3% solution of sodium chloride, the DG coating layers have different corrosion behavior. Increased corrosion resistance of the upper layers is due to an increased content of zinc, and absence of a texture of the  $\delta$ -phase.

The formation of simonkolleite as the main product of corrosion along the entire thickness of the coating provides increased corrosion resistance of DG coatings.

1. Galin R. G., Modified zinc powder Patent 2170643 Russian, MPK B22F1/02, C23C10/28; statement. 10.12.2000; Publ. 20.07.2001 - 3 p.
2. Galin R. G., Corrosion resistance of thermodiffusion zinc coatings in hydrogen sulfide-containing media / R. G. Galin, A. G. Gumerov, M. H. Sultanov, D. A. Zakharyevich, A. I. Biryukov // Problems of collecting, preparing and transporting oil and oil products. - 2014. - 1 (95). - pp. 86 - 92.
3. Galin R. G. Formation and Structure of Diffusion Zinc Coatings Formed in Nanocrystallized Zinc Powders / R.G. Galin, D. A. Zakharyevich, S. V. Rushchitz // Materials Science Forum. - 2016. - Vol.870. - pp 404 - 408.
4. Biryukov A. I., Formation and structure of simonkolleite on the surface of thermodiffusion zinc coatings in chloride-containing media / A. I. Biryukov, R. G. Galin, D. A. Zakharyevich, A. P. Tronov // Corrosion. Materials, protection. - 2016. - №9. - p.28
5. Mahmoudiana M.R., Basirun W.J., Alias Y., Ebadi M. Facile fabrication of  $\text{Zn}/\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  flower-like nanostructure on the surface of Zn coated with poly (N-methyl pyrrole) // Applied Surface Science. 2011. - V.257. P.10539- 10544.