Corrosion of diffusion iron–zinc coatings (δ -phase) in an alkaline medium

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Abstract

The corrosion behaviour of diffusion iron–zinc coatings of various thickness and chemical composition in an alkaline medium was studied, using gravimetric measurements, electrode potential measurement, scanning electron microscopy, X-ray spectral and diffraction analysis. The study of corrosion of metal alloys and coatings in alkaline media is of interest both from the point of view of corrosion protection of structures in aggressive alkaline solutions and from the point of view of using selective dissolution of components to obtain promising nanosized materials. Diffusion iron–zinc coatings were obtained using zinc powders, the particles of which were coated with a nanostructured porous zinc oxide layer. This approach can significantly improve the efficiency of the galvanizing process. It is shown in the work that the main component of the coatings is the δ -phase. Corrosion of the δ -phase in an alkaline medium is accompanied by the predominant dissolution of zinc. The minimum corrosion rate is observed for diffusion iron–zinc coatings formed by the δ -phase with a zinc content on the surface of ~90 at.% and thickness 50 μm . Selective corrosion of diffusion iron–zinc coatings proceeds with the morphological development of the surface with the formation of numerous cracks and pores, which accelerates the corrosion process.

Keywords: *diffusion iron–zinc coatings, selective dissolution, selective corrosion.*

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1. Introduction

The issues of clarifying the mechanism of zinc dissolution in alkalis [1–3], alkaline zinc passivation [4, 5], the use of zinc in alkaline power sources [6–8], as well as corrosion of zinc alloys in an alkali, including iron–zinc coatings are currently of importance [9–12].

It is known that zinc in strongly alkaline solutions is oxidized with the formation of complex zincate ions $\text{Zn}(\text{OH})_4^{2-}$. The mechanism of this process, according to various

sources, includes the adsorption of zinc ions Zn_{ad}^+ or $\text{Zn}_{\text{ad}}^{2+}$, sequential formation of complex compounds from $\text{Zn}(\text{OH})^+$ to $\text{Zn}(\text{OH})_4^{2-}$ with a delayed stage of the removal of second electron, and surface diffusion of adsorbed $\text{Zn}(\text{OH})_{\text{ad}}$ particles. Under stationary conditions, the rate of the process is limited by the diffusion of zincate from the surface of the zinc electrode into the alkali solution [13].

Anodic dissolution of zinc in alkalis can be accompanied by its passivation. In this case, a characteristic decrease in current is observed on the polarization curves. The generally accepted mechanism for zinc passivation involves the oxidation of Zn with the formation of ZnO or $\text{Zn}(\text{OH})_2$, their dissolution with the formation of $\text{Zn}(\text{OH})_3^-$ or $\text{Zn}(\text{OH})_4^{2-}$ and with the saturation of the solution a passivating ZnO/ $\text{Zn}(\text{OH})_2$ film is formed on the surface.

In contrast to zinc, the corrosion behaviour of Fe-Zn alloys in strongly alkaline solutions is not fully described. In such studies authors often investigated zinc coatings obtained by the hot-dip galvanizing method [14–17]. It is known that their surface layers consist mainly of η and ζ phases with a high zinc content [18, 19]. As a consequence, their corrosion behaviour is interpreted based on the concept of corrosion of pure zinc; however, this approach is unsuitable for a description of the δ -phase with a higher iron content. In this case, iron–zinc coatings based on the δ -phase have a higher corrosion resistance compared to the η - and ζ -phases [20–23]. In addition, research is often carried out in carbonate solutions. In this case, hydrozincite is formed as a corrosion product [15], which makes the study of the alloy dissolution process more difficult.

The study of the corrosion behaviour of Fe-Zn alloys in strongly alkaline solutions is also interesting for the production of promising nanosized materials by the selective dissolution of zinc (dezincification). A similar dealumination process with the involvement of iron, nickel, and cobalt aluminides [24–29], leading to the formation of nanoporous metal films consisting of highly developed Fe, Ni, or Co is the basis for the production of Raney catalysts. The corrosion rate non-linearly depends on the phase composition of aluminides [26, 27, 29]. In concentrated alkali solutions, a highly active surface layer can be oxidized by atmospheric oxygen with the formation of nanosized Fe, Ni, Co oxides [24].

Here, the objects of study were Fe–Zn coatings (δ -phase) obtained by diffusion saturation in zinc powder, the particles of which were coated with nanostructured zinc oxide [30, 31]. The coatings consisted of layers of Fe–Zn phases with Zn concentration gradually increasing with the increase in the coating thickness [18, 20].

The aim of the work was the investigation of the corrosion behavior of diffusion iron–zinc coatings (δ -phases) of various thickness and chemical composition in alkaline solutions and the study of the composition and structure of their corrosion products.

2. Materials and methods

2.1. Materials

The objects of study were Fe-Zn coatings of 5–100 μm in thickness, deposited on a carbon steel substrate (steel 20) by diffusion saturation. The surfaces of the steel discs ($d=20.0\pm1.0$ mm) were polished with fine sandpaper (P1000), their dimensions were measured, and they were weighed with a precision of up to 0.0001 g. Further, samples with zinc powder, the particles of which were coated with nanostructured zinc oxide, were placed in a sealed container of a thermal diffusion galvanizing unit. The exposure time varied from 0.5 to 3.0 h, depending on the required thickness of the resulting coatings. Then the weight of the sample was measured again, and the thickness of the coatings was calculated based on the difference in weight. The surfaces of the obtained coatings were ground with sandpaper (P2500), polished with a cloth with an aqueous suspension of chromium oxide (III), and then the surfaces were washed with distilled water and dried with filter paper. Prior to the research, the samples were degreased with isopropyl alcohol. The corrosion behaviour of the obtained coatings was studied in 5 M NaOH solutions.

2.2. Methods

The surface morphology was examined using a Jeol JSM7001F scanning electron microscope (SEM) with energy dispersive fluorescence spectrometer Oxford INCA X-max 80 for chemical analysis. The X-ray diffraction analysis of the coatings was carried out using DRON-3 diffractometer with Co K_{α} -radiation, within an angle range of $20^{\circ}\leq 2\theta\leq 60^{\circ}$ at $2^{\circ}/\text{min}$.

The corrosion rate was measured by gravimetric method. The method was used by a number of authors to study the corrosion behavior of zinc-based coatings [32–35]. The samples were weighed before testing with a precision of up to 0.0001 g and immersed in a solution of 5 M NaOH. After exposure (for 30, 90, and 150 min), the samples were removed from the corrosive medium, washed with distilled water, dried at room temperature, and weighed with the same precision. The difference in weight before and after the exposure was used to calculate the corrosion rate in $\text{g}/(\text{m}^2\cdot\text{min})$.

The transient of the corrosion potential of the coatings was obtained using P-30J potentiostat/galvanostat, operating in the voltmeter mode relative to a silver chloride reference electrode for 60–120 min.

3. Results and Discussion

3.1. Phase composition of the coatings

XRD patterns of diffusion iron–zinc coatings of various thickness are shown in Figure 1. Zinc concentration in the surface layers of coatings of various thicknesses are shown in Table 1.

Table 1. Chemical composition of diffusion iron–zinc coatings of various thicknesses.

Thickness, μm	10	20	25	30	35	55	70
Zn, wt. %	86.5	88.6	90.3	91.5	91.7	92.1	92.5

Figure 1. XRD patterns of diffusion iron–zinc coatings of various thicknesses.

As can be seen in the XRD patterns of the coatings, regardless of their thickness, in the angular region of $2\theta = 48\text{--}52^\circ$ there were peaks corresponding to Fe–Zn phases. The predominant peaks were the δ -phase peaks of the composition FeZn_{7-10} . There were no reflections of pure zinc or peaks of the ζ -phase (FeZn_{13}) or zinc oxide on the surface of the coatings. The peak at $2\theta = 52.5^\circ$ was revealed in the XRD patterns of the coatings with thicknesses of 10 and 20 μm . Its intensity decreased with increasing thickness, and in the XRD patterns of coatings with a thickness of $\geq 30\text{--}35\text{ }\mu\text{m}$, it was absent. This peak corresponds to pure iron and its appearance in the XRD of thin coatings can be explained by the influence of the steel substrate. Between the peaks at 48° and 49.5° , which uniquely belong to the δ -phase, one more reflex was detected (angle $2\theta = 49.0\text{--}49.1^\circ$). Its intensity increased with an increase in the thickness of the coating, and, consequently, with the zinc concentration on the surface. Probably, it was associated with a change in the texture of the δ -phase in the coating [20, 23, 31]. Thus, the surface layers of diffusion zinc coatings with a thickness from 10 to 70 μm , with a zinc concentration in the surface layers from 88.0 to 93.0 wt.%, consisted mainly of the δ -phase, which is consistent with previous studies [20, 31].

3.2. Corrosion rate of coatings

The dependence of the corrosion rate of coatings on the thickness and time of exposure in an alkaline solution is shown in Figure 2. It can be seen that the corrosion rate increased with an increase in the exposure time. After exposure for 150 min, the corrosion rate of coatings

(10 and 20 μm) did not increase, which was probably associated with the almost complete dissolution of the coating. The minimum corrosion rate ($<0.4 \text{ g}/(\text{m}^2 \cdot \text{h})$) was characteristic for coatings with a thickness from 25 to 50 μm after a 30 min exposure. With an increase in thickness to 60–70 μm , the corrosion rate increased by almost 2–3 times. Regardless of the exposure time, coatings with a thickness of 50 μm had the lowest corrosion rate. The corrosion rate corresponded to a zinc concentration of 91–92 wt.% in the upper layers of the coating, which also corresponded to the δ -phase in the Fe-Zn system [18].

Figure 2. Dependences of the corrosion rate of diffusion iron–zinc coatings on the thickness in 5 M NaOH.

A similar dependence of the corrosion rate on the thickness of the Fe-Zn coating, and on the composition, was observed in other corrosive media [36, 37]. The minimum corrosion rate in neutral media is explained by a decrease in the rate of oxygen reduction or by the protective properties of dense corrosion products [38]. However, in acidic and strongly alkaline media, their formation is unlikely. The presence of a minimum in the dependences of the corrosion rate on the composition in studies [38, 39] was shown for Ni-Zn coatings and explained by the differences in the corrosion behaviour of the phases present in the coating. The diffusion coatings investigated in this study are characterized by the same phase composition and mainly include the δ -phase. Probably, the features of their corrosive behaviour in an alkaline medium can be explained as follows. Diffusion Fe-Zn coatings have an uneven dissolution, complicated by the selective dissolution of zinc [40–42]. During corrosion, the formation of numerous cracks and pores occurs [41]. The presence of cracks and pores provides galvanic connection and the appearance of corrosion micropairs between the overlying (with a more negative potential) and underlying (with a more positive

potential) coating layers, leading to an increase in the corrosion dissolution rate of the coating. At the same time, for thin coatings, a faster increase in the corrosion rate was characteristic, probably because cracks and pores reach the steel substrate faster. In addition, their appearance significantly increased the true surface area, which further increases the intensity of corrosion processes. An increase in the thickness of the coating caused both an increase in the concentration of zinc and an increase in the layer of the δ -phase. An increase in the concentration of zinc, active in terms of corrosion, led to an increase in the corrosion rate of the coating.

3.3 Corrosion potential

Dependences of the corrosion potential of the obtained coatings on the duration of exposure in 5 M NaOH solution are shown in Figure 3.

Figure 3. Dependence of electrode potentials of iron–zinc coatings of different thickness in 5 M NaOH over time.

The initial value of the potential of the coatings was by 20–50 mV more positive than the potential of pure zinc (-1.52 V), which was probably due to the presence of a more electropositive metal, specifically iron. Over time the potential of pure zinc reduced by 30 mV and afterwards a constant potential was established. The potential of the coatings shifted in the positive direction during the first 0.5–1.0 h. This may be due to the predominant dissolution of zinc from the δ -phase of the coating. Next, a constant potential value was established which did not depend on the thickness of the coating and was ~ -1.40 V. The first plateau appeared on the graphs; the length of plateau increased with the thickness of the coating. In the case of thin coatings (thickness < 10 μm), the plateau was not expressed and had a slight delay in the increase of potential. This region on the curves can

be attributed to the dissolution of the δ -phase. It should be noted that the time for the potential to reach the first plateau increased with an increase in the thickness.

Further, a repeated sharp increase of the potential was observed. In this case, the rate of shift of the potential did not depend on the thickness (for all coatings, this process takes 60 min). The constant potential was established, which, like the first plateau, did not depend on the thickness and was -1.15 V. This potential was 740 mV less than the potential of the steel substrate in 5 M NaOH ($-0.41 \dots -0.51$ V), which can be explained by the influence of incompletely dissolved zinc and by the oxidation of highly active iron formed as a result of the selective dissolution of zinc. In addition, during the diffusion iron–zinc coating process, an extended zone of a solid zinc solution in iron was formed in the steel substrate, which was also characterized by a lower electrode potential in comparison with Fe. In this case, a constant corrosion rate was established, or (as in the case of thin coatings) it decreased.

3.4. Evolution of the surface morphology after dissolution in alkali

SEM images of the surface coating after etching in 5 M NaOH are shown in Figure 4. We chose the time intervals for studying the surface morphology according to the inflection points on the dependences of the electrode potential on time. Whenever possible, the SEM holding time is close to the weight test.

It can be seen that already after 10 min of etching, the morphological development of the surface occurred due to the formation of a large number of pores, ranging in size from 0.2 to 1.0 μm (Figure 4 a and e). In addition, cracks with a width of 80–100 nm appeared on the surface of the coating. The zinc concentration after etching decreased to 88.7 at.%.

In this case, a sharp increase in the potential was observed on the dependence of potential over time, which can be explained by the selective dissolution of zinc. As the exposure time was increased to 40 min, the cracks increased in size up to 0.7–1.0 μm (Figure 4 b), penetrating the entire coating. The entire surface was covered with pores, the size of which also increased. The approach to the first plateau was observed on dependence of the potential over time after 40 min. Probably, the dissolution of the δ -phase, accompanied by both the development of the surface and the predominant dissolution of zinc occurred. The zinc concentration after 40 min of etching was 84 at.%, which is below the concentration range of the δ -phase, according to the phase diagram of the Fe-Zn system [18].

A further increase in the etching time to 120 min did not lead to a significant increase in the width of cracks, but their number increased (Figure 4 c and d). Branches from large and wide cracks, connected and dividing the surface into sections with a size of ~ 10 μm appeared. A large number of smaller cracks appeared within these areas. The etching depth after 120 min was 13 μm , the zinc concentration, according to X-ray spectral analysis data, decreased to 27 at.%, which corresponded to the concentration of zinc in the Γ -phase [18]. However, the fact that deep cracks can interfere with the determination of the chemical composition should be taken into account: they expose the underlying layers of the coating where the concentration of iron is much higher. Regarding the dependences of potential over time, this moment corresponded to a significant shift of the potential to the positive region

and the approach to the second plateau. In this case, the corrosion rate increased, which can be explained by the appearance of a galvanic connection between the upper and lower layers of the coating, which is effected through the deep cracks. The significantly different electrode potentials of the layers led to increased corrosion, which accelerated the dissolution of the coating. SEM images of the coating after etching for 10 and 120 min at high magnification are shown in Figure 4 e and f. It can be seen that the pores were of the same size; however, at 120 min of etching, their number was much higher. They coalesced and caused the appearance of cracks.

Figure 4. SEM images of the surface of diffusion iron–zinc coatings with a thickness of 10–15 μm after exposure in 5 M NaOH: a – 10 min; b – 40 min; c – 100 min; d – 120 min; e – exposure 10 min ($\times 10,000$); f – exposure 120 min ($\times 10,000$).

3.5. Coating corrosion products

SEM images of coating with a thickness of 10 μm after exposure in 5 M NaOH for 100 min are shown in Figure 5.

Areas filled with clusters of octahedral crystals with average face sizes of 500–800 nm could be seen on the surface after prolonged etching. The crystals were located on the porous substrate formed by etching the coating with a pore diameter of 100–200 nm. The formation of such crystals was not observed on coatings with a lower iron content, which suggests that the crystals were either magnetite Fe_3O_4 [24, 25] or zinc ferrite. The oxide can be a product of the oxidation of highly active iron, formed during the selective dissolution of zinc from the iron–zinc coating by atmospheric oxygen.

Figure 5. SEM images of the surface of diffusion iron–zinc coating with a thickness of 10 μm after exposure for 100 min in 5 M NaOH.

4. Conclusions

Diffusion iron–zinc coatings are subjected to the predominant dissolution of zinc during corrosion in a strongly alkaline medium. In this case, the dezincification of the δ -phase of diffusion iron–zinc coatings is accompanied by the morphological development of the surface with the formation of cracks and pores, accelerating the corrosion of the coating. The minimum corrosion rate was observed for coatings formed by the δ -phase with a zinc content on the surface of ~ 90 at. %.

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References

1. M. Mokaddem, P. Volovitch and K. Ogle, The anodic dissolution of zinc and zinc alloys in alkaline solution. I. Oxide formation on electrogalvanized steel, *Electrochim. Acta*, 2010, **55**, no. 27, 7867–7875. doi: [10.1016/j.electacta.2010.02.020](https://doi.org/10.1016/j.electacta.2010.02.020)
2. M. Mouanga, P. Berçot and J.Y. Rauch, Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions. Part I: Corrosion layer characterization, *Corros. Sci.*, 2010, **52**, no. 12, 3984–3992. doi: [10.1016/j.corsci.2010.08.003](https://doi.org/10.1016/j.corsci.2010.08.003)
3. L.A. Nedobezhkina and I.V. Protasova, Peculiarities of zinc dissolution during anodic polarization in sodium hydroxide solutions, *Condensed Matter and Interphases*, 2016, **18**, no. 1, 91–101 (in Russian).
4. S. Thomas, I.S. Cole, M. Sridhar and N. Birbilis, Revisiting zinc passivation in alkaline solutions, *Electrochim. Acta*, 2013, **97**, 192–201. doi: [10.1016/j.electacta.2013.03.008](https://doi.org/10.1016/j.electacta.2013.03.008)
5. M. Bockelmann, L. Reining, U. Kunz and T. Turek, Electrochemical characterization and mathematical modeling of zinc passivation in alkaline solutions: A review, *Electrochim. Acta*, 2017, **237**, 276–298. doi: [10.1016/j.electacta.2017.03.143](https://doi.org/10.1016/j.electacta.2017.03.143)
6. A. Mainar, O. Leonet, M. Bengoechea, I. Boyano, I. de Meatza, A. Kvasha, A. Guerfi and J. Blázquez, Alkaline aqueous electrolytes for secondary zinc–air batteries: an overview, *Int. J. Energy Res.*, 2016, **40**, no. 8, 1032–1049. doi: [10.1002/er.3499](https://doi.org/10.1002/er.3499)

7. X. Wei, D. Desai, G.G. Yadav, D.E. Turney, A. Couzis and S. Banerjee, Impact of anode substrates on electrodeposited zinc over cycling in zinc-anode rechargeable alkaline batteries, *Electrochim. Acta*, 2016, **212**, 603–613. doi: [10.1016/j.electacta.2016.07.041](https://doi.org/10.1016/j.electacta.2016.07.041)
8. D.E. Turney, J.W. Gallaway, G.G. Yadav, R. Ramirez, M. Nyce, S. Banerjee and X. Wei, Rechargeable zinc alkaline anodes for long-cycle energy storage, *Chem. Mater.*, 2017, **29**, no. 11, 4819–4832. doi: [10.1021/acs.chemmater.7b00754](https://doi.org/10.1021/acs.chemmater.7b00754)
9. T.N. Vu, M. Mokaddem, P. Volovitch and K. Ogle, The anodic dissolution of zinc and zinc alloys in alkaline solution. II. Al and Zn partial dissolution from 5% Al–Zn coatings, *Electrochim. Acta*, 2012, **74**, 130–138. doi: [10.1016/j.electacta.2012.04.037](https://doi.org/10.1016/j.electacta.2012.04.037)
10. A.R. El-Sayed, H.S. Mohran and H.M. Abd El-Lateef, Corrosion study of zinc, nickel, and zinc-nickel alloys in alkaline solutions by Tafel plot and impedance techniques, *Metall. Mater. Trans. A*, 2012, **43**, no. 2, 619–632. doi: [10.1007/s11661-011-0908-4](https://doi.org/10.1007/s11661-011-0908-4)
11. V.I. Korobov, L.V. Petrenko and V. Poltavets, Effect of phase composition on the anodic dissolution and passivation of zinc-based alloys, *Univers. J. Chem.*, 2014, **2**, no. 5, 76–85.
12. M.F.M. Nazeri and A.A. Mohamad, Corrosion resistance of ternary Sn-9Zn-xIn solder joint in alkaline solution, *J. Alloys Compd.*, 2016, **661**, 516–525. doi: [10.1016/j.jallcom.2015.11.184](https://doi.org/10.1016/j.jallcom.2015.11.184)
13. X.G. Zhang, *Corrosion and electrochemistry of zinc*, Springer Science & Business Media, 1996, 262.
14. Z.Q. Tan and C.M. Hansson, Effect of surface condition on the initial corrosion of galvanized reinforcing steel embedded in concrete, *Corros. Sci.*, 2008, **50**, no. 9, 2512–2522. doi: [10.1016/j.corsci.2008.06.035](https://doi.org/10.1016/j.corsci.2008.06.035)
15. S.B. Farina and G.S. Duffó, Corrosion of zinc in simulated carbonated concrete pore solutions, *Electrochim. Acta*, 2007, **52**, no. 16, 5131–5139. doi: [10.1016/j.electacta.2007.01.014](https://doi.org/10.1016/j.electacta.2007.01.014)
16. P. Pokorný, P. Tej and M. Kouřil, Evaluation of the impact of corrosion of hot-dip galvanized reinforcement on bond strength with concrete – A review, *Constr. Build. Mater.*, 2017, **132**, 271–289. doi: [10.1016/j.conbuildmat.2016.11.096](https://doi.org/10.1016/j.conbuildmat.2016.11.096)
17. V.D.F. Lins, K.B. Batista, M.D.M. de Castro, C.G.F. Costa and R.M.V. Paranhos, Corrosion resistance of Fe–Zn surfaces of galvanized steel revealed after coulometric stripping in acid, alkaline and saline media, *Corros. Eng., Sci. Technol.*, 2016, **51**, no. 3, 223–231. doi: [10.1179/1743278215Y.0000000052](https://doi.org/10.1179/1743278215Y.0000000052)
18. A.R. Marder, The metallurgy of zinc-coated steel, *Prog. Mater. Sci.*, 2000, **45**, no. 3, 191–271. doi: [10.1016/S0079-6425\(98\)00006-1](https://doi.org/10.1016/S0079-6425(98)00006-1)
19. E.V. Proskurkin and N.S. Gorbunov, *Galvanizing Sherardizing and Other Zinc Diffusion Coatings*, Technicopy Limited, Gloucestershire, 1972, 261 (Translated from Russian by D.E. Hayler Stonehouse).

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20. A.I. Biryukov, R.G. Galin, D.A. Zakharyevich, A.V. Wassilkowska and T.V. Batmanova, The effect of the chemical composition of intermetallic phases on the corrosion of thermal diffusion zinc coatings, *Surf. Coat. Technol.*, 2019, **372**, 166–172. doi: [10.1016/j.surfcoat.2019.05.029](https://doi.org/10.1016/j.surfcoat.2019.05.029)
 21. W.J. Ooij and A. Sabata, Under-Vehicle Corrosion Testing of Primed Zinc and Zinc Alloy-Coated Steels, *Corrosion*, 1990, **46**, no. 2, 162–171. doi: doi.org/10.5006/1.3585083
 22. E. Almeida and M. Morcillo, Lap-joint corrosion of automotive coated materials in chloride media. Part 3 – Electrogalvanized steel/galvanneal interface, *Surf. Coat. Technol.*, 2000, **124**, no. 1, 44–52. doi: [10.1016/S0257-8972\(99\)00625-8](https://doi.org/10.1016/S0257-8972(99)00625-8)
 23. A.I. Biryukov, R.G. Galin, D.A. Zakharyevich, A.V. Wassilkowska, A.V. Kolesnikov and T.V. Batmanova, A Layer-by-Layer Analysis of the Corrosion Properties of Diffusion Zinc Coatings, *Arch. Metall. Mater.*, 2020, **65**, 99–102. doi: [10.24425/amm.2019.131101](https://doi.org/10.24425/amm.2019.131101)
 24. C. Xu, R. Wang, Y. Zhang and Y. Ding, A general corrosion route to nanostructured metal oxides, *Nanoscale*, 2010, **2**, no. 6, 906–909. doi: [10.1039/b9nr00351g](https://doi.org/10.1039/b9nr00351g)
 25. S. Jia, T. Song, B. Zhao, Q. Zhai and Y. Gao, Regular Fe₃O₄ octahedrons with excellent soft magnetic properties prepared by dealloying technique, *J. Alloys Compd.*, 2014, **585**, 580–586. doi: [10.1016/j.jallcom.2013.10.017](https://doi.org/10.1016/j.jallcom.2013.10.017)
 26. S. Tanaka, N. Hirose, T. Tanaki and Y.H. Ogata, Effect of NiAl precursor alloy on the catalytic activity for a raney Ni cathode, *J. Electrochem. Soc.*, 2000, **147**, no. 6, 2242. doi: [10.1149/1.1393514](https://doi.org/10.1149/1.1393514)
 27. M.A. Rahman, X. Zhu and C. Wen, Fabrication of nanoporous Ni by chemical dealloying Al from Ni–Al alloys for lithium-ion batteries, *Int. J. Electrochem. Sci.*, 2015, **10**, 3767–3783. doi: [10.0000/electrochemsci.org/vol10/100503767](https://doi.org/10.0000/electrochemsci.org/vol10/100503767)
 28. A.J. Smith, L.O. Garciano, T. Tran and M.S. Wainwright, Structure and kinetics of leaching for the formation of skeletal (raney) cobalt catalysts, *Ind. Eng. Chem. Res.*, 2008, **47**, no. 5, 1409–1415. doi: [10.1021/ie070801b](https://doi.org/10.1021/ie070801b)
 29. C. Xu, Y. Liu, C. Zhou, L. Wang, H. Geng and Y. Ding, An In Situ Dealloying and Oxidation Route to Co₃O₄ Nanosheets and their Ambient–Temperature CO Oxidation Activity, *ChemCatChem*, 2011, **3**, no. 2, 399–407. doi: [10.1002/cctc.201000275](https://doi.org/10.1002/cctc.201000275)
 30. R.G. Galin, Modified zinc powder, Russian Patent, 2170643, B22F1/02, C23C10/28, 2001.
 31. R.G. Galin, D.A. Zakharyevich and S.V. Rushchits, Formation and structure of diffusional zinc coatings formed in nanocrystallized zinc powders, *Mater. Sci. Forum*, 2016, **870**, 404–408. doi: [10.4028/www.scientific.net/MSF.870.404](https://doi.org/10.4028/www.scientific.net/MSF.870.404)
 32. K.R. Baldwin, M.J. Robinson and C.J.E. Smith, Corrosion rate measurements of electrodeposited zinc-nickel alloy coatings, *Corros. Sci.*, 1994, **36**, no. 7, 1115–1131. doi: [10.1016/0010-938X\(94\)90137-6](https://doi.org/10.1016/0010-938X(94)90137-6)

-
33. R. Ramanauskas, P. Quintana, L. Maldonado, R. Pomés and M.A. Pech-Canul, Corrosion resistance and microstructure of electrodeposited Zn and Zn alloy coatings, *Surf. Coat. Technol.*, 1997, **92**, no. 1–2, 16–21. doi: [10.1016/S0257-8972\(96\)03125-8](https://doi.org/10.1016/S0257-8972(96)03125-8)
 34. Y. Li, Corrosion behaviour of hot dip zinc and zinc-aluminium coatings on steel in seawater, *Bull. Mater. Sci.*, 2001, **24**, no. 4, 355–360. doi: [10.1007/BF02708631](https://doi.org/10.1007/BF02708631)
 35. A.B. Darwin and J.D. Scantlebury, Retarding of corrosion processes on reinforcement bar in concrete with an FBE coating, *Cem. Concr. Compos.*, 2002, **24**, no. 1, 73–78 doi: [10.1016/S0958-9465\(01\)00028-2](https://doi.org/10.1016/S0958-9465(01)00028-2)
 36. M. Sagiya, A. Hiraya and T. Watanabe, Electrochemical behavior of electrodeposited zinc-iron alloys in 5% NaCl solution, *Tetsu to Hagane*, 1991, **77**, no. 2, 244–250. doi: [10.2355/tetsutohagane1955.77.2_244](https://doi.org/10.2355/tetsutohagane1955.77.2_244)
 37. I. Suzuki and M. Enjuzi, The development of the corrosion resistance of an Fe-Zn alloy coating on the basis of the behaviour of the corrosion product, *Corros. Sci.*, 1986, **26**, no. 5, 349–355. doi: [10.1016/0010-938X\(86\)90010-7](https://doi.org/10.1016/0010-938X(86)90010-7)
 38. J. Giridhar and W.J. Van Ooij, Study of Zn-Ni and Zn-Co alloy coatings electrodeposited on steel strips II: Corrosion, dezincification and sulfidation of the alloy coatings, *Surf. Coat. Technol.*, 1992, **53**, no. 1, 35–47. doi: [10.1016/0257-8972\(92\)90101-F](https://doi.org/10.1016/0257-8972(92)90101-F)
 39. E. Beltowska-Lehman, P. Ozga, Z. Swiatek and C. Lupi, Influence of structural factor on corrosion rate of functional Zn–Ni coatings, *Cryst. Eng.*, 2002, **5**, no. 3–4, 335–345. doi: [10.1016/S1463-0184\(02\)00045-X](https://doi.org/10.1016/S1463-0184(02)00045-X)
 40. F.M. Queiroz and I. Costa, Electrochemical, chemical and morphological characterization of galvanized steel coating, *Surf. Coat. Technol.*, 2007, **201**, no. 16–17, 7024–7035. doi: [10.1016/j.surfcoat.2007.01.005](https://doi.org/10.1016/j.surfcoat.2007.01.005)
 41. H. Kaiser, De-alloying and dissolution induced cracking of the Zinc-iron δ -phase, *Mater. Corros.*, 1996, **47**, no. 1, 34–41. doi: [10.1002/maco.19960470106](https://doi.org/10.1002/maco.19960470106)
 42. A.I. Biryukov, O.A. Kozaderov, R.G. Galin, D.A. Zakharyevich and V.E. Zhivlin, Details of the mechanism of dissolution of iron–zinc coatings based on the δ -phase in acidic media, *Int. J. Corros. Scale Inhib.*, 2020, **9**, no. 4, 1477–1489. doi: [10.17675/2305-6894-2020-9-4-18](https://doi.org/10.17675/2305-6894-2020-9-4-18)
 43. A. Wassilkowska, R. Galin, Study of zinc oxide nanopores structure on powder medium for TDG, Proc. V International Conference on Electron Microscopy EM 2014: programme and abstracts, Kraków, Wydawnictwo Naukowe Akapit, 2014, 240–241.
 44. R. Galin, I. Atanasova and S. Fiskuchev, Equipment for thermodiffusion zinc coating. Capasite and prospects, *Machine, Technologies, Materials*, 2007, no. 2–3, 146–148.