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ECOLOGICAL CHEMICAL METHOD FOR PREPARATION OF A ZINCATE ELECTROLYTE FOR ELECTRODEPOSITION OF LOW-ALLOYED Zn-Fe ALLOYS

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ABSTRACT

An ecological chemical method was developed to obtain a non-toxic zincate electrolyte for the electrodeposition of low-alloy Zn-Fe (< 1 wt. % Fe) alloys. The self-dissolution parameters of zinc in 120 g L^{-1} *NaOH from alternative sources - self-dissolution rate (V) and full removal time (*t_{frc}*), were compared for three zinc sources: hot-dip galvanized steel (A-Zn), galvanic industry waste (B-Zn), and battery waste (C-Zn). Optimal conditions for the dissolution of zinc from A-Zn were selected: concentration of the activating additive hydrogen peroxide (50 mL* L^{-1} *50 %* H_2O_2*), temperature (50 - 55°C), and solution saturation time (10 - 15 min). A procedure is proposed for the preparation of the final alkaline zincate electrolyte for deposition of low-alloy Zn-Fe (< 1 wt. % Fe) alloys, including preparation of basic solutions of the primary ions-zinc from chemical dissolution of A-Zn and an alkaline iron concentrate derived from spent hydrochloric pickling solutions for carbon steel, containing two Fe-complexing ligands. By controlling the solution composition and the reflectivity of the Zn-Fe coatings, a design for an alkaline zincate electrolyte has been proposed, enabling the production of high-quality alloys.*

Keywords: Zn-Fe alloy, ecological method, zincate electrolyte, chronopotentiometry.

INTRODUCTION

In recent years, there has been growing interest in alternatives to the toxic cadmium coatings used for decades to protect steel products from corrosion in many industrial applications. Various studies have shown that alloying zinc with metals from the iron group (Fe, Ni, Co) enhances their corrosion resistance [1 - 3]. Concerns about the toxicity of nickel and cobalt salts have prompted scientists to develop electrolytes to produce more environmentally friendly Zn-Fe coatings. They are preferred in several areas where corrosion resistance or properties such as ductility, heat resistance, and a good decorative appearance are of priority [4, 5]. The iron content in Zn-Fe coatings, as well as their corrosion resistance, varies depending on the type of electrolyte, the Zn/Fe ionic ratio in the bath, the deposition regime [6], and especially, the cathodic current density, which strongly influences their structure and morphology [7]. Depending on the type and composition of the electrolytes used for deposition, the iron content in Zn-Fe alloys can vary significantly, ranging from 0 to 100 wt. %. There is evidence that high corrosion resistance is achieved when using lower iron-doped alloys, ranging from 0.3 wt. % [8] to approximately 15 - 20 wt. % [9]. In the automotive industry, Zn-Fe alloys with up to 1 wt. % iron are most commonly used [10]. Apart from the most frequently recommended application area - the automotive industry [11], low-alloy Zn-Fe coatings can also be applied in several other areas, such as the military industry, optics, in solar collectors due to their black colour, in mechanical engineering, and also as a material for implants [12, 13].

Electrolytes for the electrodeposition of zinc-iron alloys can generally be divided into acidic - sulfate, chloride [14 - 16], alkaline - cyanide and non-cyanide zincate electrolytes [17 - 19]. Zincate non-cyanide electrolytes are non-toxic and environmentally friendly, with a simple composition that facilitates easy maintenance when working with soluble zinc anodes [20 - 23]. They offer a wide range of cathodic current densities for the deposition of high-quality coatings, along with a high deposition rate [24 - 26]. Another advantage is that they are not aggressive to the equipment and are suitable for both suspension and drum deposition. It is known that zincate electrolytes require stabilising additives to prevent the deposition of spongy coatings or powders. The most commonly used additives include ascorbic acid, triethanolamine, sorbitol, which also serves as a complexing agent for ferric ions (Fe^{3+}), as well as glycine, among others [27 - 30]. It is also important to note that the macrodispersive ability of zincate electrolytes is high and is second only to that of cyanide zinc electrolytes [6]. It should be noted that this indicator strongly depends on zinc concentration, and the relief of the products must be considered when selecting the composition. To achieve the specified high indicators for these electrolytes, it is necessary to observe the ratio as accurately as possible $C_{Zn2+} : C_{NaOH\ free} = 1:10$ [7]. This is mandatory, because in these electrolytes, sodium hydroxide not only contributes to the high values of electrical conductivity, but also serves as an easily accessible and inexpensive ligand for binding free zinc ions into non-toxic oxycomplexes (zincates) by the reaction Eq. (1):

$$Zn^{2+} + 4OH^{-} \leftrightarrow Zn(OH)_4 - 2H_2O \leftrightarrow ZnO_2^{2-} \quad (1)$$

The presence of a free sodium base shifts equilibrium (1) to the right, increasing the stability of zincate anions.

Some sources indicate that a non-cyanide zinc electrolyte for low-alloy Zn-Fe coatings can be obtained by dissolving zinc oxide in a concentrated sodium hydroxide solution using bath-stabilising organic additives (triethanolamine or gelatin), as well as receiving an iron concentrate as a source of iron ions to control the Zn/Fe ratio in the alloy [31, 32].

One possibility for obtaining a non-cyanide zinc electrolyte for low-alloy Zn-Fe coatings, which is at the same time economically efficient and environmentally friendly, is to apply a chemical method of dissolving zinc from recycled hot-dip galvanised steel products or from waste from the production of chemical power sources, for which there is a lack of data in the literature. During hot-dip galvanising of steel, layers with varying mechanical properties, thicknesses, and morphologies are formed, depending on the specific process parameters [33]. The structure of zinc coatings on hot-dip galvanized steel is usually a multilayer composite that includes layers of iron-zinc intermetallic compounds to pure zinc on the steel substrate in the following order (Fig. 1): steel, γ-ZnFe with up to 75 % Zn - 25 % Fe, δ-ZnFe with up to 90 % Zn - 10 % Fe, ξ-ZnFe with up to 94 % Zn - 6 % Fe and 100 % Zn.

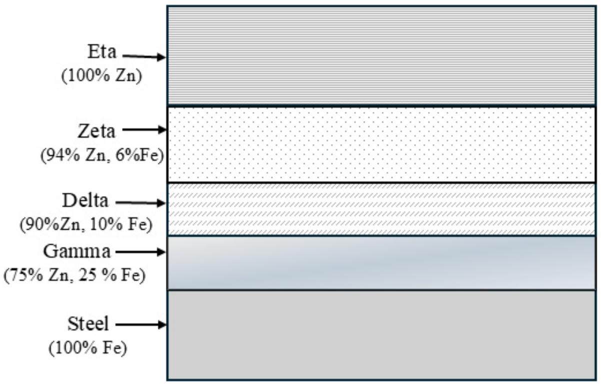

Fig. 1 Hot-dipped galvanised coating (~120 microns thick) showing underlying alloy layers and outer layers of pure zinc [33].

The present study aims to develop an environmentally friendly chemical method for preparation of alkaline zincate electrolyte for electrodeposition of low-alloy Zn-Fe alloy coatings (Fe up to 1 wt. %) by recycling zinc waste from various industries and using spent carbon steel pickling solution as a source of Fe^{2+}.

EXPERIMENTAL

Zinc self-dissolution parameters - self-dissolution rate (V) and time to complete removal of the coating (t_{frc})

The rate of self-dissolution of zinc in concentrated NaOH (120 g L^{-1}) was evaluated using a weighing method. The following relationship was used, (Eq. 2):

$$V = (m_1 - m_2) / S\, t_{frc}, \ (g\ dm^{-2}\ h^{-1}) \quad (2)$$

where t_{frc} is the time for complete removal of the zinc coating, h; m_1 - the initial weight of the sample, the selected source of Zn, g; m_2 - the weight of the sample after complete removal of Zn, g, S - the surface area of the sample, dm^2.

The time to complete zinc removal (t_{frc}) was evaluated by two independent methods. The first method involves comparing the appearance of the zinc source after chemical treatment in concentrated solution of NaOH with that of reference samples (Fig. 2): hot-dip galvanized steel, HGS (Fig. 2a), HGS with completely removed zinc coating (Fig. 2b) and clean steel sheet, pickled in hydrochloric acid (Fig. 2c).

As a second independent method for estimating the time to complete zinc removal (t_{frc}) and the rate of zinc self-dissolution, the stationary electrode potential of samples with varying residence times in 120 g L^{-1} NaOH was measured. The recording of the E-t dependences under different dissolution conditions was carried out using a potentiostat type OH-405 (HUNGARY) and an X-Y recorder. The criterion for evaluating the time required for complete Zn removal (t_{tcr}) was a sharp jump in the potential in the positive direction. Purposefully, after the sharp jump in the potential in the positive direction, the sample was left in the solution for additional 5 - 10 min. It was found that the final measured mass m_2 remains unchanged, indicating that the substrate is not further attacked after the removal of the zinc. The concentration of the selected optimal organic additive, the temperature from 200°C to 600°C, and the residence time in concentrated NaOH were varied.

A Sartorius A 200 S analytical balance was used to measure the mass. To further control coating thickness, a Dermitron D-3000 magnetic thickness gauge for metal coatings was also used.

The tests were conducted by immersing the samples in the solution twice, each for 1 hour, to demonstrate the reproducibility of the results.

Principles of preparation of alkaline zinc electrolyte for electrodeposition of Zn-Fe (< 1 % Fe) alloy

The alkaline zincate electrolyte for electrodeposition of low-alloy Zn-Fe alloys was prepared from a zinc ion solution containing the zincate anions and free NaOH, obtained by chemical dissolution of zinc from a secondary zinc source. As a source of ferroions (Fe^{2+}), a spent hydrochloric acid pickling solution for carbon steel was used. The solution needed to contain stabilizing additives as complexing agents for ferroions. The complexing agent for Zn^{2+} is NaOH, and for ferroions, Fe^{2+}, the introduced complexing agents are of two types: L_1 - a carbon-containing oxygen compound and L_2 - an amino compound of unsaturated hydrocarbons, with which they form a biligand complex $[Fe(L_1.L_2)]$. L_2 also has the property of a surfactant, which means that in addition to being a complexing agent, it is also a structure-determining additive.

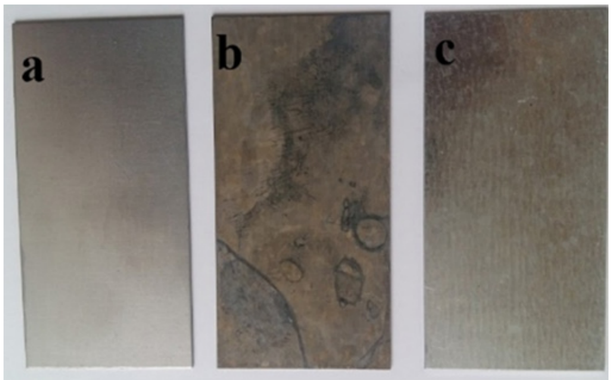

Fig. 2. External view of the different stages of zinc removal on hot-dip galvanized steel, HGS, with which the samples were compared: (a) - HGS hot-dip galvanized steel; (b) - HGS after complete removal of the zinc coating and (c) - steel sheet pickled in hydrochloric acid.

Control of the composition of the electrolyte and the quality of the coatings

The prepared electrolyte was analyzed for all components present in the solution. A precise digital pH meter type H183141 was used to assess acidity.

The concentration of ferroions, Fe^{2+}, was estimated by an analytical method based on direct titration of the solution with complexone III in the presence of salicylic acid at pH = 4 ÷ 5 [34]. Hydrogen peroxide (3 %) was previously added to the solution to oxidise the ferrous ions, Fe^{2+}, to ferric ions, Fe^{3+}. Titration with complexone III resulted in the decolourisation of the violet-colored solution.

The concentration of zinc ions, Zn^{2+}, was also determined by an analytical method based on the complexometric titration of zinc in the presence of the indicator eriochrome black T after separation of iron by the procedure described above. The oxidation of ferrous ions, Fe^{2+}, to ferric ions, Fe^{3+} occurs by the addition of hydrogen peroxide (3 %), and their subsequent precipitation by the addition of ammonia [34].

There is evidence that, over time, the concentrations of the ligands L_1 and L_2 in solution gradually decrease as they are incorporated into the coating. Their control is critical to the properties of Zn-Fe coatings. The basis of the method by which we determined the concentration of L_1 is the fact that in a weakly acidic medium, L_1 is oxidized by $KMnO_4$ in the presence of a $MnSO_4$ catalyst. The excess of $KMnO_4$ is determined by adding a precise amount of oxalic acid, $H_2C_2O_4$ [34]. The colour change indicates this excess, and hence the exact amount for oxidised ligand L_1.

The concentration of ligand L_2 was assessed by qualitatively determining the change in gloss of the coatings resulting from the deposition rate, respectively, from the current density through the Hull cell [35]. The deterioration in coating quality, as indicated by a decrease in gloss, served as a criterion for assessing a reduction in the ligand L_2 content in the electrolyte below the critical value. Fig. 3 illustrates a diagram of the Hull cell, along with its corresponding parameters.

The purity of the resulting zinc and iron concentrate stock solutions and the final zinc electrolyte was assessed by applying ICP (Inductively Coupled Plasma) analysis. This method enables the detection and quantification of elements in a sample by utilising high-temperature plasma to excite atoms. The process involves preparing the sample, evaporating it in an argon plasma, and then recording the spectrum emitted by the resulting ions (ICP-MS).

The reflectivity of ZnFe coatings was tested using a KSJ MG6-SM Metal Gloss Meter according to the silver mirror standard. The numerical expression of the coating's reflectivity is the current strength in mA, as measured in the circuit. A strict constancy of the supply voltage, on the order of 6 V, was maintained.

RESULTS AND DISCUSSION

Self-dissolution rate of zinc in a solution of sodium hydroxide by the gravimetric method.

To optimise the conditions for zinc dissolution, the self-dissolution rates of three types of zinc sources were initially studied using a gravimetric method. Samples with dimensions of 2 x 2 dm^2 were prepared from hot-dip galvanized steel, which we designated as A-Zn, anode monolithic waste from galvanic production (B-Zn) and waste from battery production (C-Zn). The mass of the samples was measured before and after successive immersion for 1 hour in 120 g L^{-1} NaOH at room temperature (20°C) without stirring.

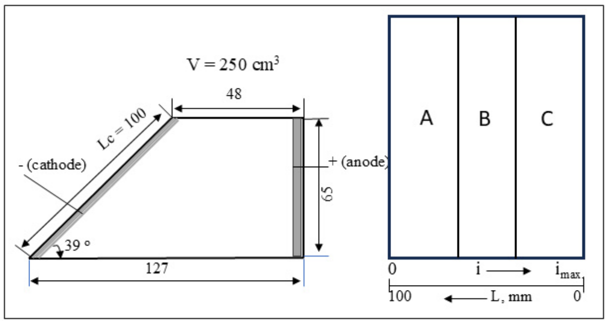

Fig. 3. Hull cell and a way to describe the characteristic zones in terms of the coating structure depending on the current density [35].

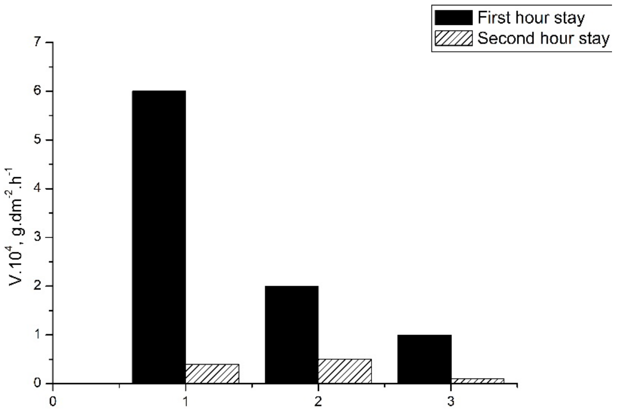

Fig. 4. Comparison of the self-dissolution rate of three types of zinc sources: (1) Zn from anode monolithic waste from electroplating plants (B-Zn); (2) Zn from hot-dip galvanized steel (A-Zn), and (3) Zn from batteries (C-Zn) in 120 g L^{-1} NaOH at a temperature of 20°C without stirring.

The results obtained are shown in Fig. 4.

It is evident from Fig. 4 that after the first hour of immersion, the zinc dissolution rate becomes negligible, likely due to surface passivation. This tendency to passivation decreases in the order C-Zn → B-Zn → A-Zn. The differences in the self-dissolution rate for the three types of zinc sources and between the first and second immersion can be explained by the varying composition and structure of the zinc coatings at depth.

Fig. 4 also shows that the rate of zinc self-dissolution is very low for all three zinc sources. Although it does not exceed 6.10^{-4} g cm^{-2} h^{-1}, the rate of self-dissolution is highest for samples of anode monolithic waste from electroplating industries (B-Zn). To increase the rate of chemical self-dissolution of zinc, gravimetric measurements were carried out when zinc samples were left in 120 g L^{-1} NaOH at a temperature of 20°C in the presence of three different activating additives: 30 g L^{-1} original organic additive (AD - 1) [36], 30 g L^{-1} sodium persulfate, $Na_2S_2O_8$ (AD - 2) and 50 mL L^{-1} of 50 % hydrogen peroxide, H_2O_2 (AD - 3). To eliminate the limitations resulting from the thickness of the zinc coating on the scrap hot-dip galvanized sheet, these studies were conducted with B-Zn at a volumetric loading of 4 dm^2 L^{-1} and a test time of 1 h. The results obtained are presented in Fig. 5.

Fig. 5 shows that the rate of self-dissolution of zinc in the presence of additives AD - 1 and AD - 2 is the same, but it is significantly lower, almost 7 times, compared to that in the presence of AD - 3. For this reason, for further research, we selected the additive AD - 3 and the easily accessible, inexpensive hydrogen peroxide (H_2O_2) at a concentration of 50 mL L^{-1}. From the comparison of the results in Fig. 4 and 5, it is evident that in its presence, the dissolution rate of A-Zn increases by almost 3000 times.

As a method for assessing the rate of self-dissolution of zinc, the method for measuring the stationary potential of the samples from the residence time in the solution under various conditions, namely the chronopotentiometric method, was used. The concentration of the activating additive, the solution temperature, and the time during which the solution was operated, respectively, were varied to saturate the solution with zincate anions.

The time to complete zinc removal (t_{frc}) was measured now of the sharp shift in potential to the positive direction. After this time, the samples were left in the solution for an additional 5 - 10 min to demonstrate that, during this time, the substrate was not further attacked by sodium hydroxide due to surface passivation.

In addition, to the chronopotentiometric dependences (Fig. 6 - 8a), the same figures also present data derived from the E - t dependences (Fig. 6 - 8b) on the time for complete removal of the zinc coating (t_{frc}) under different conditions. From their course, one can more clearly judge the change in the rate of the ongoing process.

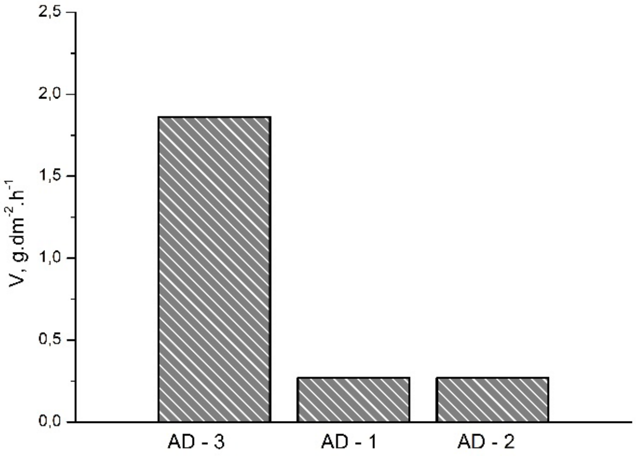

Fig. 5. Self-dissolution rate of B-Zn in 120 g L^{-1} NaOH at a temperature of 20°C in the presence of different activating additives AD: AD - 1 (30 g L^{-1} patented additive [36]); AD - 2 (30 g L^{-1} $Na_2S_2O_8$ and AD - 3 (50 mL L^{-1} 50 % H_2O_2).

From the analysis of the data obtained in Fig. 6a, b it follows that the rate of chemical dissolution of the zinc coating of hot-dip galvanized steel is strongly influenced by the increase in the concentration of the additive AD - 3. With an increase in the concentration of the additive from 5 - 50 mL L^{-1}, the self-dissolution time of zinc decreases almost 8 times (Fig. 6b). From Fig. 7b, it is seen that increasing the solution temperature from 20°C to 40 - 44°C results in a twofold decrease in the dissolution time. The observed effect may be because, in addition to being an oxidizer, hydrogen peroxide is unstable and decomposes rapidly, especially at elevated temperatures. The subsequent increase in temperature to 60°C does not significantly alter the process rate. From these data, it can be concluded that for the practical use of the method of chemical dissolution of hot-dip galvanized sheet metal, it is advisable to apply temperatures no higher than 40 - 50°C.

From the course of the curve in Fig. 8b it is seen that it is expedient to carry out chemical dissolution in solutions with the shortest possible operating time - up to about 15 min, up to which time the dissolution rate is relatively constant. With increasing time for which the solution has been operated and therefore saturated with zinc ions, the self-dissolution rate decreases sharply. This is judged by the rapid increase in the self-dissolution

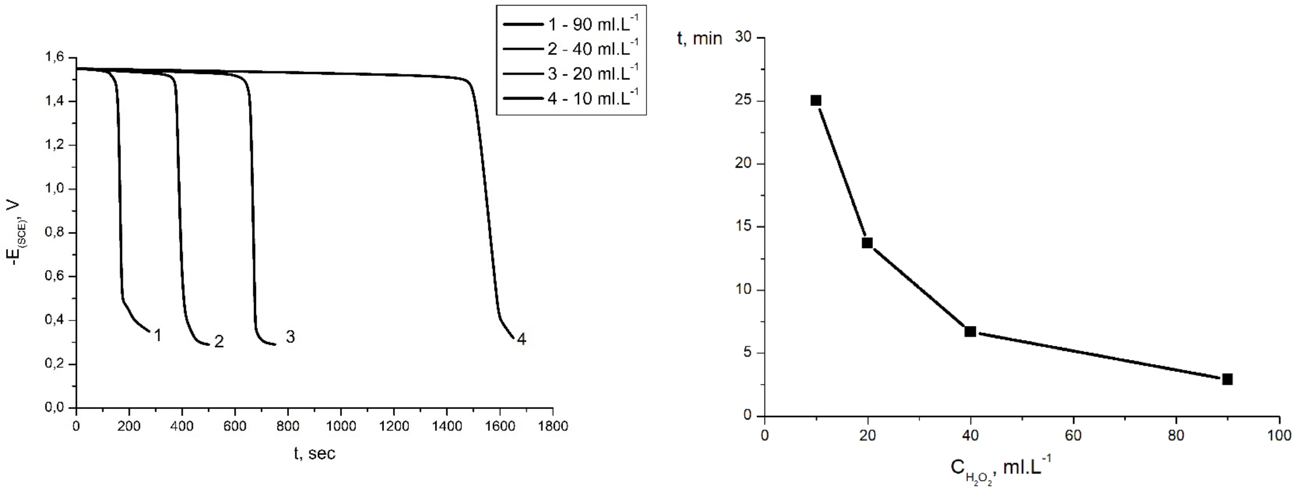

Fig. 6. (a) Chronopotentiometric dependences of the dissolution of A-Zn in 120 g L^{-1} NaOH (t = 60°C) at various concentrations of the activating additive AD - 3 (50 % H_2O_2): 1 - 90 mL L^{-1}; 2 - 40 mL L^{-1}; 3 - 20 mL L^{-1}; 4 - 10 mL L^{-1}; (b) a derivative dependence from the data in (a) for the time of complete removal of the coating depending on the concentrations of the activating additive AD - 3.

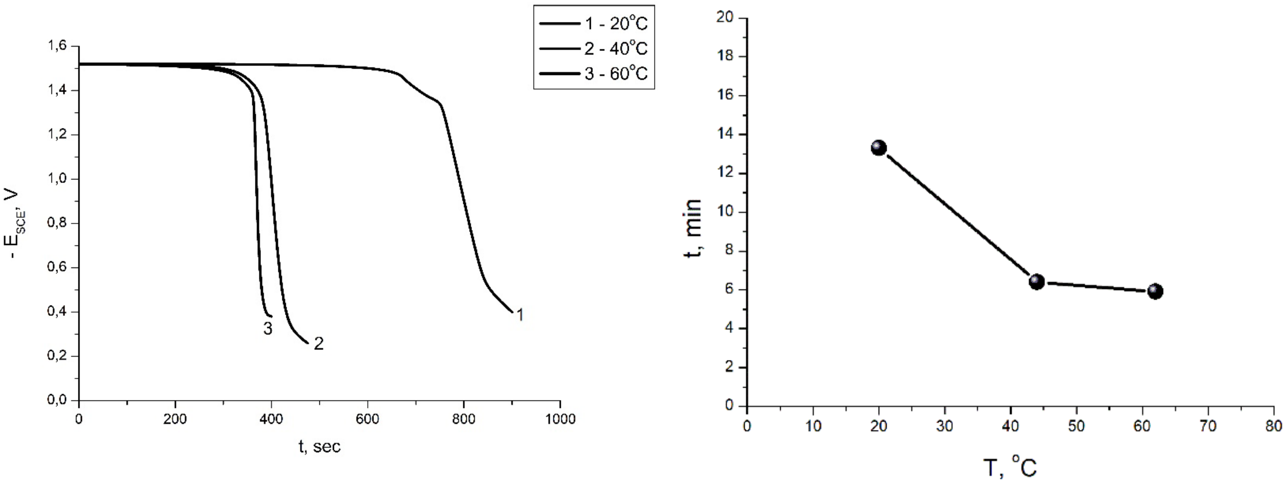

Fig. 7. (a) Chronopotentiometric dependences of the dissolution of A-Zn in 120 g L^{-1} NaOH and 50 mL L^{-1} of additive AD - 3 at various temperatures: 1 - 20°C; 2 - 40°C; 3 - 60°C; (b) Derivative dependence from the data in (a) for the time of complete removal of the coating as a function of the solution temperature.

time (Fig. 8b). From these data and from additional ones obtained in a zincate electrolyte with high saturation (10 g L^{-1} Zn, 100 g L^{-1} NaOH) it can be concluded that saturation does not positively affect the rate of zinc dissolution. The general conclusion that must be drawn is that of all the listed factors, the concentration of the additive AD - 3 has a decisive importance for the rate of self-dissolution of zinc from HGS.

Thickness of the removed coating

The average thickness of the stripped zinc coating was measured with a Dermitron calliper using the two independent methods described above to determine the time required for complete stripping of the zinc coating. The first method is to remove the zinc coating and visually compare its appearance with reference samples (Fig. 2). This method yields an average value

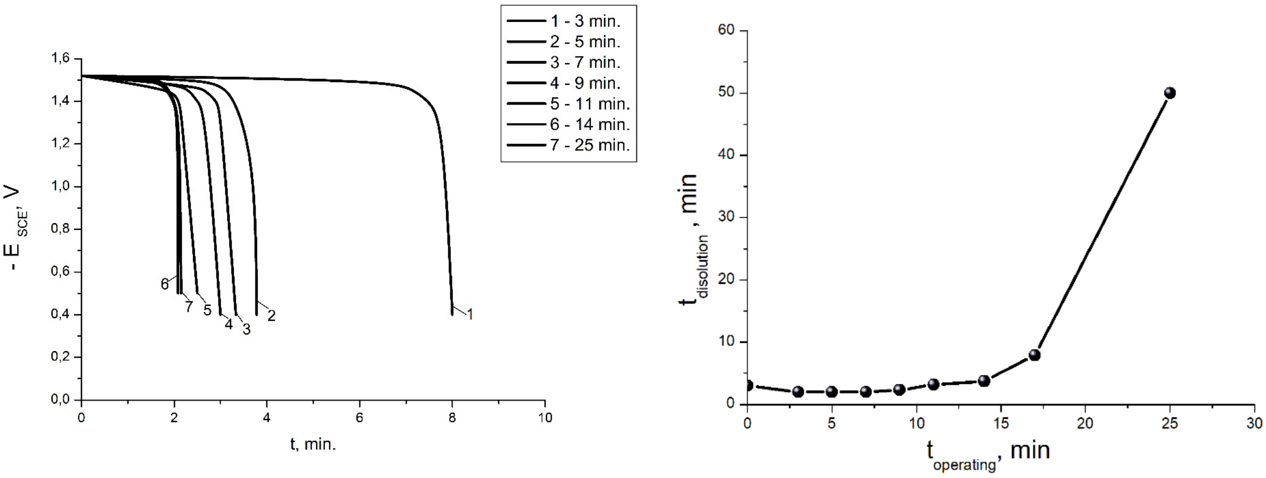

Fig. 8. (a) Chronopotentiometric dependences of the dissolution of A-Zn in 120 g L^{-1} NaOH and 50 mL L^{-1} of additive AD - 3, t = 60°C, depending on the solution operation time: (1) - 3 min.; (2) - 5 min.; (3) - 7 min.; (4) - 9 min.; (5) - 11 min.; (6) - 14 min.; (7) - 25 min.; (b) Derivative dependence from the data in (a) for the time of complete removal of the coating, depending on the solution operation time.

of about 5 μm.

The second method was by measuring the thickness at the moment corresponding to the complete removal of zinc from chronopotentiometric data (t_{frc}) - that is, the time taken for the sharp deviation of the potential in the positive direction. By this method, the measured average thickness of the removed zinc was about 8 μm. The difference in the thicknesses of the removed zinc coating by the two methods can be explained by the inhomogeneity of the zinc coatings on the hot-dip galvanized steel (Fig. 1). When calculating t_{frc} from chronopotentiometric data, the removal of both pure zinc in the coating and the layers of intermetallic compounds of zinc and iron is included. In the removal method and in the visual comparison of the surface appearance of HGS with coating, HGS without coating, and pure pickled steel, it was evident that layers corresponding to intermetallic compounds of zinc and iron remain undissolved. Therefore, the obtained thickness of the removed coating is lower (5 μm compared to 8 μm for the second method).

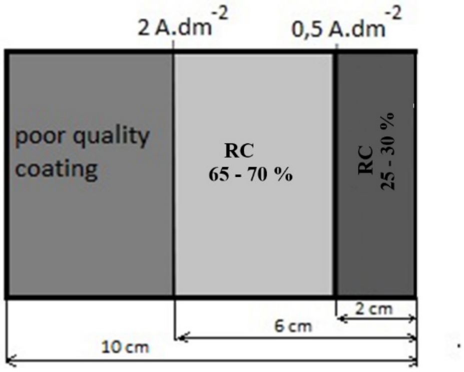

Fig. 9. Relationship between the reflectivity of Zn-Fe alloys in % and the change in current density on the surface of a sample in the Hull cell (from Fig. 2) with a total volume of 250 mL when applying a direct current of 1A and a deposition time of 10 min.

Preparation of zincate electrolyte for Zn-Fe (~1 wt. % Fe) alloy

Preparation and control of basic solutions of metal ions

Based on the above-obtained data on the dissolution rate of hot-dip galvanised steel sheet as a source of zinc (A-Zn), we proceeded to the procedure for preparing the alkaline zincate electrolyte (AZE) for the deposition of low-alloy Zn-Fe (~1 % Fe) alloys.

The first stage is the chemical dissolution of A-Zn to obtain a basic zincate solution containing zincate anions ZnO_2^{2-} and free NaOH. The solution is obtained by a single rapid chemical dissolution of zinc from a sample of hot-dip galvanized steel sheet, HGS (A-Zn). The sample subjected to dissolution had a total surface area of 25 dm^2, a mass of zinc coating of 10 g and corresponded to a volumetric loading of 25 $dm^2 L^{-1}$. The solution contained 120 g L^{-1} NaOH with the addition of 50 mL L^{-1} 50 % H_2O_2, and its temperature was 55°C. The saturation time was set to 10 min, based on our preliminary data showing that, after zinc removal, the base is no longer attacked by sodium hydroxide due to passivation. As a result, the samples' residence time for a more extended period is not fatal to the results obtained for the measured concentrations.

The second stage is the preparation of an alkaline complex iron concentrate containing biligand complexes of ferroions $[Fe(L_1.L_2)]$ with a concentration of 5 g L^{-1}. The procedure involves the preparation of a highly alkaline solution (pH not lower than 13 - 13.5) of NaOH with an approximate volume of 2/3 of the final one. In it, directly while stirring, the required amount of ligand L_1 is first added to obtain its final concentration of 300 g L^{-1}. Then, again directly, while stirring, ligand L_2 is added in an amount to achieve its final concentration in the concentrate of 5 g L^{-1}, in which case it is necessary to consider that the density of the starting solution is ρ = 1.12 g cm^{-3}. Then, to the obtained alkaline solution of NaOH and both complexing agents, a corresponding amount of the acidic pickling solution containing Fe^{2+} is added, and the mixture is topped up with water to the required working volume. The pH of the solution is adjusted to 13.

The exact concentrations of the primary metal ions in the zinc and iron stock solutions were determined by analytical methods. The concentration of the free ligand L_1 was determined analytically [34].

To control the concentration of ligand L_2, the direct relationship between its decrease due to inclusion in the Zn-Fe alloy and the deterioration of the quality of the latter was considered, and subsequently, a decrease in the reflective capacity (RC) of the coating, measured relative to the RC of a silver mirror, that is, in %. For this purpose, in addition to a glossometer, the Hill cell shown in Fig. 2 was used. In galvanostatic mode, due to a change in the distance between the two electrodes, a change in the current density on the cathode surface was observed. In this case, zones of the coating with different RC, measured with a glossometer, are clearly distinguished on the surface of the samples (Fig. 9). Critically low RC is that outside 65 - 70 %, which is established at current densities lower than 0.5 A dm^{-2} and higher than 2.0 A dm^{-2}.

ICP analysis provided data on the presence of possible heavy-metal ion impurities, as presented in Table 1.

Preparation of the final alkaline zincate electrolyte

An electrolyte for electrodeposition of a Zn-Fe (up to 1 % Fe) alloy with the following initial composition was prepared from the basic solutions of metal ions: 10.0 g L^{-1} Zn^{2+}, 0.12 g L^{-1} Fe^{2+}, 12 g L^{-1} ligand L_1, 5 g L^{-1} ligand L_2, and 120 g L^{-1} NaOH, 50 ml L^{-1} with the addition of 50 % H_2O_2. The pH was controlled with a pH meter and must not be lower than 13.

To the basic zincate solution obtained by chemical dissolution of A-Zn, with constant stirring, the required amount of the basic iron solution was added until a ferroion concentration of Fe^{2+}. 0.1 g L^{-1} was achieved.

Table 2 lists both the basic composition of the newly developed electrolyte for Zn-Fe coating deposition and the recommended concentration ranges for its components, within which high-quality alloys can be deposited. To optimize the composition and deposition conditions, it is necessary to conduct additional, more extensive studies on the relationship between coating properties and deposition conditions.

CONCLUSIONS

The following important conclusions can be drawn from the conducted research: (i) An ecological chemical method was developed for the preparation of a non-

Table 1. ICP results for the presence of heavy metal ion impurities for the alkaline zincate electrolyte obtained by rapid chemical dissolution of zinc from hot-dip galvanized steel sheet.

Contents, g L^{-1}							
Al	Si	Pb	Sn	Co	Ni	As	Sb
0.026	0.008	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Table 2. Recommended basic composition of the electrolyte and range of variation of the concentration of its components for deposition of low-alloyed Zn-Fe alloy. Basic composition and range of variation of the components of the alkaline electrolyte for deposition of Zn-Fe alloy.

Components	Main composition, g L^{-1}	Interval, g L^{-1}
Zn^{2+}	10.0	8 - 12
Fe^{2+}	0.12	0.08 - 0.16
L_1	12	10 -15
L_2	5	4 - 6
$NaO_{Hfre}e$	100	80 -120
Na_2CO_3	30	20 - 40
pH > 13		

toxic zincate electrolyte for electrodeposition of low-alloyed Zn-Fe (< 1 wt. % Fe) alloys by self-dissolution of zinc in NaOH 120 g L^{-1} from an alternative source of secondary zinc - hot-dip galvanized steel. (ii) The optimal conditions for dissolution of zinc from the A-Zn source were selected, namely, concentration of activating additive of hydrogen peroxide (50 mL L^{-1} 50 % H_2O_2), a temperature of 50 - 55°C, and solution saturation time (10 - 15 min.) (iii) The procedure for preparing the final alkaline zincate electrolyte for the deposition of low-alloy Zn-Fe (< 1 wt. % Fe) alloy was indicated, including the provisional preparation of an iron alkaline concentrate from spent hydrochloric acid pickling solutions for carbon steel, containing two complexing ligands for ferroions. (iv). By controlling the composition of the solution and the reflectivity of the low-alloy Zn-Fe coatings, a preliminary composition of the alkaline zincate electrolyte is proposed, which allows the production of alloys of excellent quality.

Authors' contributions

D. L.: literature research, experiments, data processing and analysis.

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