Electrodeposition of zinc plating from zincate electrolyte using galvanostatic mode of pulse electrolysis

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Abstract. The process of electrodeposition of zinc plating in the galvanostatic mode of pulse electrolysis is studied. Having analyzed periodical and reference literature, we selected zincate electrolyte containing ECOMET C1 brightening additive as the research object. Based on the analysis of experimental data, we have revealed dependences of cathode current efficiency of zinc and the deposition rate of coatings on the values of current density in pulse, frequency and duty cycle of a pulse current, temperature, and the concentration of sodium hydroxide and zinc ions in solution. Using the galvanostatic mode of pulse electrolysis made it possible to increase the current density by 25%, and to reduce the concentration of brightening additives with a constant coating quality, in comparison with the stationary mode. Based on the conducted research, the modes of forming high-quality zinc plating at a speed of up to 40 μm/h are recommended.

1. Introduction

Zinc is one of the most important metals in modern industry. At the end of 2019, its global production amounted to about 13.5 million tons. The planned production volume for 2020 is 14 million tons. More than 80% of the zinc produced is spent on the manufacture of rolled metal and galvanizing of metal structures [1].

Coatings with zinc and its alloys are widely used in modern engineering to protect steel from corrosion [2]. Hot-dip and electrolytic galvanizing are the most common methods.

In hot-dip galvanizing, in accordance with GOST 9.307-89, the coating thickness is 40...200 μm, which limits the application of this method for processing complex shaped parts with small diameter holes and threaded surfaces.

With electrolytic galvanizing, the thickness of the coatings is much smaller and often ranges from 6 to 35 μm. Along with high corrosion resistance, these coatings also have a decorative function, especially after chromate treatment. The thickness of the layer can be quite accurately controlled by the amount of electricity spent on the process. The properties of zinc plating, as well as the uniform metal distribution over the surface, largely depend both on the composition of the electrolyte and on the electrolysis mode [3-6].

At present, a sufficiently large number of galvanizing electrolytes has been developed. They differ in the reaction of the medium, the state of zinc ions (hydrated metal ions in “simple” electrolytes and complex ions with various ligands), the presence of additives, etc. [5-15].
Alkaline zincate electrolytes are simple in composition and consist of two main components: zinc oxide and alkali. An electrolyte containing 10 g/L zinc, 100 g/L alkali and a brightener can be considered as a “classic” one [4]. Since the middle of the 20th century, various modes of pulse electrolysis have been applied for electrodeposition of coatings with metals and alloys, which made it possible to control the process of forming a galvanic coating with a metal or an alloy more finely and efficiently [10, 12, 16, 17].

The aim of the work is to study the influence of the main parameters of galvanostatic pulse electrolysis on the cathode current efficiency and the quality of zinc coatings formed from zincate electrolyte.

2. Experimental technique
The effect of pulse electrolysis on the cathode current efficiency and the quality of zinc coatings was studied in a rectangular, electrochemical cell with a capacity of 0.2 L. Copper (M00) plates of 0.04 dm² area were used as the cathode, and graphite plates of 0.1 dm² operating area were used as anodes. The cathode was pretreated in accordance with the requirements of GOST 9.305–84.

To polarize the electrodes, a G5-60 pulse generator was used as a source of rectangular galvanostatic pulses. The electrochemical cell was connected to the generator sequentially with a resistor having a resistance of 50 Ohm [18]. A C1-55 oscilloscope was used to record the instantaneous values of the current strength in the circuit.

In the experiments, reagents of the “hch” and “chda” brands and distilled water were used. The electrolyte was prepared as follows: alkali was dissolved in water with constant stirring, and zinc oxide was added to the resulting solution in small portions. After filtering, brightening additives were introduced [19]. To stir the solution, an MS-400 LT magnetic stirrer with a speed control from 100 to 1500 min⁻¹ was used.

The cathode current efficiency of zinc was determined gravimetrically using an AND HR-200 analytical balance. Mass determination of the samples was carried out with an accuracy of 0.0001 g. The amount of electricity \( Q \) passed through the system was calculated by the formula [20]:

\[
Q = \frac{I_p \cdot \tau_p \cdot \tau_e}{T} = \frac{I_p \cdot \tau_e}{S}
\]

where \( I_p \) is current pulse amplitude, A; \( \tau_p \) is current pulse duration, s; \( T \) is period duration, s; \( \tau_e \) is electrolysis process time, s; \( S \) is pulse current duty cycle.

The quality of the coatings was determined visually.

3. Experimental results and their discussion
To determine the effect of the main parameters of electrolysis on the current efficiency and coating quality, an electrolyte of the following composition was used: 12 g/L zinc oxide (in terms of metal), 120 g/L sodium hydroxide, 2 ml/L ECOMET C1 brightener.

With an increase in the pulse frequency from 1 to 1000 Hz, with a duty cycle of 2, the current efficiency (CE) of zinc increases from 86% to 93% (figure 1). In the frequency range from 1 to 100 Hz, bright coatings are obtained, and a further increase in frequency to 1000 Hz leads to a slight deterioration in the quality of the coatings.

The dependence of the cathode CE of zinc on the duty cycle of the pulse current was studied at a pulse duration of 5 ms and a current density in the pulse of 2 A/dm². With an increase in duty cycle from 1.2 to 4, an increase in CE of zinc occurs from 86% to 97%. A further increase in duty cycle to 10 leads to a slight decrease in zinc CE to 94% (figure 2). The best coating quality is observed at duty cycle values from 1.2 to 2.
Figure 1. Dependence of the cathode current efficiency of zinc on the frequency of pulse current at an amplitude value of current density in a pulse of 2 A/dm² and current duty cycle of 2.

Figure 2. Dependence of the cathode current efficiency of zinc on the duty cycle (S) of pulse current at the current density of 2 A/dm² and pulse duration of 5 ms.

An increase in the cathode current density from 2.5 to 10 A/dm² contributes to a decrease in the current efficiency of zinc from 88 (figure 3). Bright coatings well adhered to the base are obtained at cathode pulse current density of 2.5 to 4 A/dm². This dependence of the cathode current efficiency of the metal on the current density contributes to an increase in the covering power of the electrolyte.

Figure 3. Dependence of the cathode current efficiency of zinc on the current density in a pulse at duty cycles of 2 (curve 1), 1.5 (curve 2) and 1.2 (curve 3).

Further studies were carried out with pulse duration of 5 ms, duty cycle of 2 and an amplitude value of the pulse current density of 2.0 A/dm². An increase in the concentration of zinc ions in the electrolyte from 6 to 15 g/L leads to an increase in the cathode current efficiency of the metal from 44 to 97% (figure 4a), and an increase in the rate of the process (figure 4b).

The obtained dependences are quite accurate described (the correlation coefficient is 0.94-0.99) by the following equations:

\[ \upsilon_{\text{dep}} = 12.17 + 0.3117 \cdot C(\text{Zn}^{2+}) \] (curve 4),
\[ \upsilon_{\text{dep}} = 12.48 + 0.8696 \cdot C(\text{Zn}^{2+}) \] (curve 3),
\[ \upsilon_{\text{dep}} = 11.19 + 1.433 \cdot C(\text{Zn}^{2+}) \] (curve 2),
\[ \upsilon_{\text{dep}} = 8.780 + 2.040 \cdot C(\text{Zn}^{2+}) \] (curve 1)
This dependence of zinc deposition rate on the concentration of ions of this metal in the electrolyte and the pulse current density indirectly confirms the diffusion nature of the process. With increasing concentration of zinc, the quality of the coatings improves. A decrease in zinc concentration of less than 6 g/L leads to a decrease in current efficiency, process speed, and the quality of the coatings deteriorates.

The concentration of zinc ions in the electrolyte above 15…20 g/L is impractical for environmental reasons.

An increase in the concentration of sodium hydroxide in the solution leads to a decrease in the cathode current efficiency of the metal from 92 to 40% (figure 5). The best coating quality is observed at a concentration ratio of 1:10 g/L, which is confirmed by the research results of other authors [4, 19].
A change in electrolyte temperature has a noticeable effect on the cathode current efficiency. As the temperature rises from 10 to 55°C, the cathode current efficiency increases from 53 to 93% (figure 6). The best coating quality is obtained in the temperature range of 10°C…25°C.

4. Conclusion
Based on the research performed for the electrolytic deposition of zinc coatings from zincate electrolyte, the following galvanostatic pulse electrolysis mode can be recommended: pulse duration of 5 ms; duty cycle of 2; the amplitude value of pulse current density of 2...5 A/dm²; temperature range from 10°C to 25°C. In this mode, fine-crystalline, bright uniform coatings are obtained with a current efficiency of 44 to 97% and deposition rate of 15...40 μm/h.

The galvanostatic mode of pulse electrolysis, in comparison with the stationary mode, allows the process of forming high-quality zinc coatings at higher pulse current densities and at a lower content of brightening additives in the electrolyte.

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