THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^o. 2 - 2022, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2022.2.05

STUDIES AND RESEARCH ON ELECTROCHEMICALLY OBTAINING ZINC MATRIX COMPOSITE MATERIALS USING THE Al_2O_3 DISPERSION PHASE

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ABSTRACT

The paper presents the electrochemical production of composite zinc matrix coatings using Al_2O_3 *as dispersed phases. It was found that by correlating the working parameters with the concentration of the dispersed phase in the electrolyte, the mechanical characteristics and the corrosion resistance of the deposits could be improved.*

KEYWORDS: Zn composite coatings, electrodeposition, Al_2O_3, corrosion in saline fog

1. Introduction

Electrochemical galvanizing was initially applied to improve the corrosion resistance of ferrous materials (steels, cast iron). Following the improvement of the processes of further treatment of zinc deposits by bleaching (nitrogen neutralization), passivation, staining, coatings were included in the category of protector – decorative. In order to improve the mechanical properties of coatings, respectively to decrease internal stresses and fragilization and to increase ductility, coatings may be subject to dehydrogenation [1].

The behavior of zinc-based deposits is influenced by the climatic conditions of exploitation. They are heavily attacked in an industrial atmosphere containing sulphur dioxide, and on their surface water-soluble corrosion products were formed. In conditions of indoor atmosphere and moderate humidity these coatings have a high stability. They are resistant to corrosion by various lubricants and solvents, including chlorinated ones, of water, except for the marine ones.

Zinc-based coatings are stable in dry air, but in humid air and water with carbon dioxide, oxygen, sulphates, they are covered with carbonate, oxide, sulfate films that protect the metal against corrosion.

The thickness of the layers deposited must take into account the degree of aggressiveness of the environment, being thicker the more difficult the operating conditions are.

In addition, the zinc coating on steel in the atmosphere at normal temperature is anodic (due to the pronounced electronegative character of zinc), but, by heating over 70 °C it becomes cathodic [2].

Thus, the existence of discontinuities such as pores, cracks, exfoliations in the deposited layer leads to the formation of local galvanic elements that can influence the behavior in case of corrosion. The metal in the deposited layer, since it is more electronegative, becomes anode and corrodes, and the support (the metal of the piece) becomes cathode, thus being protected. However, over time, the appearance of deposits changes due to the coating with corrosion products [3].

Due to the anterior mentioned properties and the low-cost price, zinc-based coatings are applied for the corrosion protection of parts in the car building industry, electronics and electrotechnics industry, petroleum, consumer goods.

The use of alumina as a dispersed phase in the production of composite coatings is due to its mechanical and chemical characteristics: it is hard (hardness 9 on the Mohs scale), chemically inert (it does not dissolve in water or in mineral acids, being attacked only by alkaline hydroxides and bi-sulphates in the melt and by phosphoric acid) and has the ability to take various forms and perform various functions [4, 5].

The research carried out aims to obtain composite coatings with zinc base by electrochemical means using technical alumina particles (contains 98.5% γ - Al_2O_3 and maximum 10% - α - Al_2O_3) as dispersed phase, with dimensions of approx. 5 µm and their characterization.

2. Experimental conditions

The quality of the coating depends on the surface roughness and the working parameters: the composition of the electrolyte, the current density, the temperature of the electrolyte bath, the agitation of the solution, the pH, the movement of the electrodes.

The electrolyte used in the experimental research consisted of: $ZnSO_4$ x $7H_2O$ – 310 g/L, Na_2SO_4 x $10H_2O$ – 75 g/L, $Al_2(SO_4)_3$ x $18H_2O$ – 30 g/L, pH = 3.8-4.4.

The current density used for deposits was 3 A/dm^2, the rotation speed 1000 rpm, the deposition time 60 minutes. Alumina was used as a dispersed phase at a concentration of 10-30 g/L.

High purity zinc (99.99%) was used as an anode, and the cathode (support material) was made of steel tape (0.1 %C).

The use of Na2SO$_4$ x $10H_2O$ was done in order to increase the electrical conductivity, dispersion capacity and to decrease the electrolysis voltage.

The use of $Al_2(SO_4)_3$ x $18H_2O$ was done in order to stabilize the acidity of the electrolyte as a result of the increase in cathodic overvoltage. Deposits with lower roughness can thus be obtained.

Before submitting the samples, they have undergone preparatory operations as follows:

- Pre-degreasing - it was carried out in a mixture of benzene and acetone for the removal from the surface of the sheet of fat soluble in organic solvents; the immersion time was 5-10 minutes, and the working temperature was approx. 18-25 ^{o}C;

- Chemical degreasing - for the removal of unsaponifiable fats; the solution used consists of: sodium hydroxide 20 g/L, sodium carbonate 45 g/L, trisodium phosphate 20 g/L, surfactant 3 g/L; the working temperature was 70-75 ^{o}C, degreasing time 20-30 seconds; after degreasing the samples were washed with demineralized water at a temperature of 60-65 ^{o}C for 3-5 minutes;

- Pickling - was carried out in 20% hydrochloric acid solution, at a temperature of 18-25 ^{o}C, for 1-2 minutes; after pickling the samples were washed intensively with cold water for 3-5 minutes.

The thicknesses of the obtained layers were determined with a Phynix Pocket Surfix device, and the roughnesses with a Namicon TR 100 device.

The micro-hardenings of the layers obtained were determined using a PMT3 microdurmeter with a load of 50 g.

The obtained layers were subjected to salt mist corrosion, in accordance with ISO 9227/2012, for a period of 96 hours.

To carry out the diffractometric analysis, the diffractometer DRON 3 with copper anticatode, monochromatized diffracted beam, U = 34 kV, I = 30 mA; F1 = 2 mm; F2 = 0.5 mm; ω = 1°/min; vband = 720 mm/h, at the variation of the diffraction angle within the limits $2\theta = 20°....75°$.

3. Experimental results

The powder used in the experimental research was analysed through X-ray diffraction.

The results obtained from the diffractometric analysis are presented in Table 1 and the corresponding diffractogram in Figure 1.

Analysing Table 1 and Figure 1, it can be seen that the two forms α and γ of the technical alumina have been identified.

Pure zinc deposits were made and with different phase concentrations dispersed in the electrolyte, respectively sample P1-10 g/L, P2-20 g/L, P3-30 g/L of alumina.

Table 1. *Diffractometric analysis of alumina powder*

Phase identified	**Diffraction angle Bragg 2θ [°]**	**Muller indices (hkl)**	**Interplanar distance d/n [A]**
Al_2O_3 - α	41.09	(112)	2.55
Al_2O_3 - α	44.38	(101)	2.37
Al_2O_3 - α	50.97	(102)	2.08
Al_2O_3 - γ	55.75	(200)	1.98
Al_2O_3 - γ	60.90	(222)	1.763
Al_2O_3 - α	61.95	(202)	1.74
Al_2O_3 - α	68.52	(123)	1.59
Al_2O_3 - α	71.07	(212)	1.54
Al_2O_3 - α	72.27	(233)	1.50
Al_2O_3 - γ	79.48	(220)	1.40
Al_2O_3 - α	81.59	(112)	1.37
Al_2O_3 - α	23.09	(234)	1.23

By analysing Fig. 2, it can be found that when increasing the concentration of the dispersed phase in the electrolyte, the thickness of the deposited layer increases from 62.5 µm for the pure zinc sample to 69 µm for the sample with a concentration of the dispersed phase of 30 g/L.

Following the determination of the roughness of the deposited layers, Fig. 3, it was found that it decreased compared to the deposition of pure zinc. The presence of dispersed phase particles changes the mechanism of growth of crystals, favouring nucleation, which leads to the finishing of the structure, thus decreasing the roughness of deposits. However, when the concentration of the dispersed phase in the electrolyte is increased, the roughness is increased. The roughness of the support was 0.633 µm resulting from processing with abrasive material.

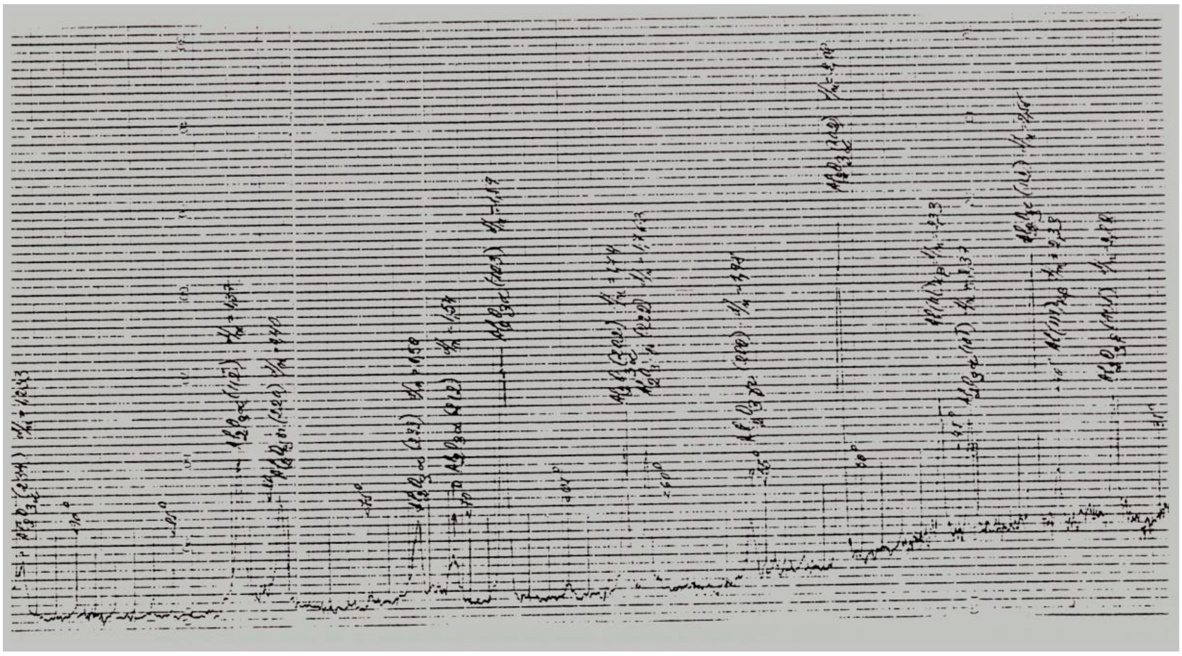

Fig. 1. *Alumina powder diffractogram* [6]

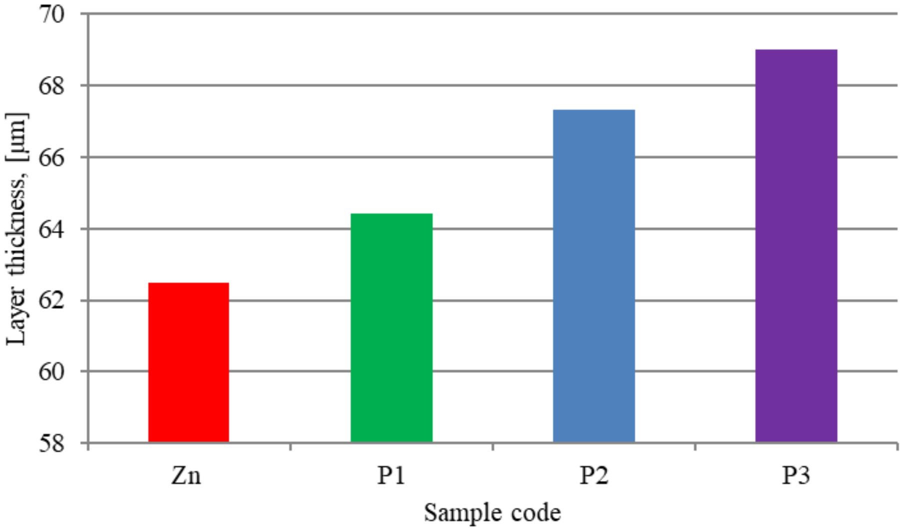

Fig. 2. *Variation of the thickness of the deposited layers with the dispersed phase concentration*

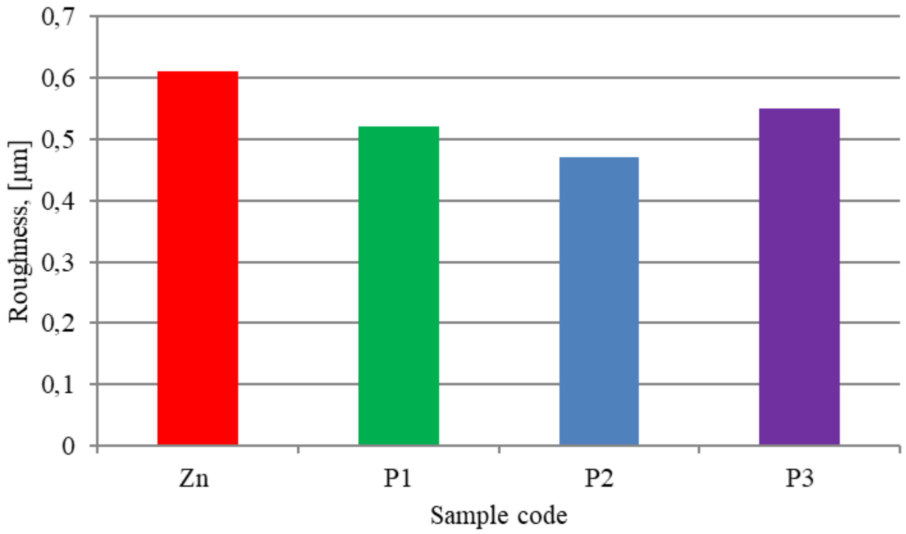

Fig. 3. *Variation of roughness of deposits with dispersed phase concentration*

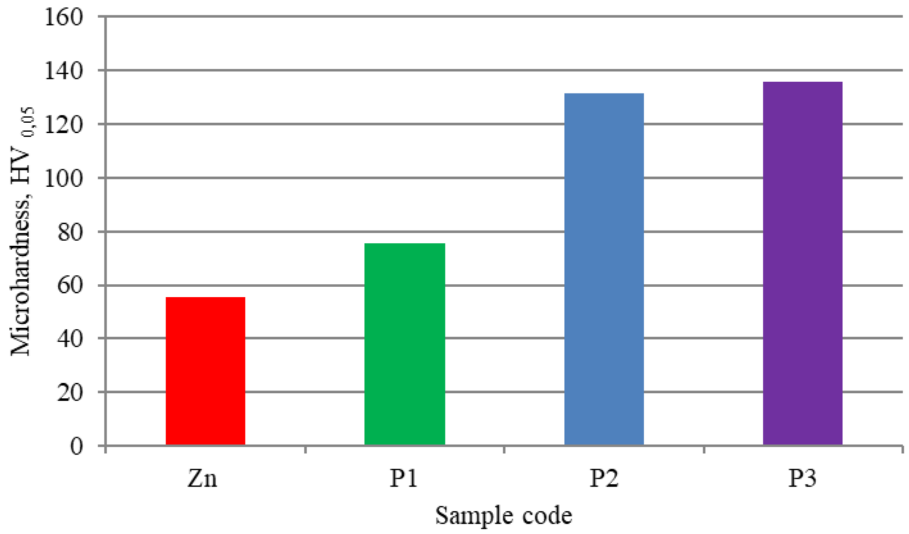

Fig. 4. *Variation of hardness of deposits with dispersed phase concentration in electrolyte*

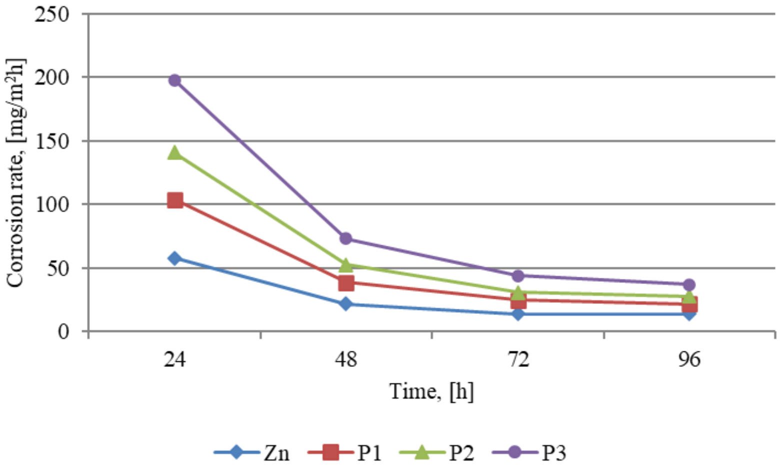

Fig. 5. *Corrosion behavior in salt mist of obtained coatings*

The salt fog corrosion behavior of the deposited layers, Fig. 5, revealed a superior resistance of composite coatings compared to the deposition of pure zinc. The best behavior was presented by sample P2 with 20 g/L dispersed phase. Thus, if for the same current density, the concentration of the dispersed phase in the electrolyte increases, the roughness increases, which favours the corrosion processes. There is a corrosion at points which evolve during the said period, depending on the passivation of the surface.

Corrosion is favoured by the presence of pore-like defects, bathroom inclusions or microcracks caused by the local increase of internal stresses. Corrosion can spread around defects, and by accumulating corrosion products in them, exfoliation of the layer can occur.

4. Conclusions

Following the experimental researches carried out, the following conclusions can be mentioned:

- Composite coatings with zinc matrix and alumina dispersed phase exhibit superior properties to pure zinc deposits. It gives hardness and thus resistance to continuous wear, resistance to corrosion, ensures a pleasant, decorative look and extends the service life of parts.
- Unlike the zinc layers obtained through other processes, those electrochemically made have more uniform thicknesses, influenced by the parameters of deposition. It was found that increasing the concentration of the dispersed phase in the electrolyte, it increased the thickness of the deposited layer from 62.5 µm for the pure zinc sample to 69 µm for the composite coating with 30 g/L dispersed phase.
- When increasing the dispersed phase concentration in the electrolyte, the roughness of the coatings was increased from 0.52 µm for 10 g/L to 0.55 µm for 30 g/L. Compared to the deposition of pure zinc (roughness 0.61 µm), there is a decrease in the size of the crystallites, which causes a decrease in the roughness.
- The composite coatings obtained have higher hardness compared to the deposition of pure zinc (55.7 daN/mm^2). They range from 75.6 daN/mm^2 for a dispersed phase concentration of 10 g/L to 135.7 daN/mm^2 for a dispersed phase concentration of 30 g/L. Hardening is due to the dispersion of alumina particles in the zinc matrix, the finishing of the grain and the increase of the deformation resistance (due to the change in the displacement of structural defects).
- Composite coatings exhibit better corrosion behavior in saline fog compared to the deposition of pure zinc. With the increase of the dispersed phase concentration in the electrolyte, due to the increase of roughness, the corrosion rate increases.

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