The corrosion resistance of zinc coatings in the presence of boron-doped detonation nanodiamonds (DND)

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Abstract: The effect of detonation nanodiamonds, doped with boron (boron-DND) in detonation synthesis on the process of zinc electrochemical deposition from zincate electrolyte is investigated. It is shown that the scattering power (coating uniformity) increases 2-4 times (depending on the concentration of DND-boron electrolyte conductivity does not change, the corrosion resistance of Zn-DND-boron coating increases 2.6 times in 3% NaCl solution (corrosion currents) and 3 times in the climatic chamber.

Keywords: detonation nanodiamonds, boron, zinc, zincate electrolytes, corrosion resistance.

Introduction
During the last years, a growing number of industries are using zincate electrolytes, which completely replace cyanide. A detailed mechanism study of the additives effect in the zincate electrolytes are still not available. The electrolyte can be operated only in the presence of the polymeric surface-active agents (surfactants) additives.

Zinc coatings on their functional properties are mainly for protection against corrosion of ferrous metals as they have more negative potential (-0,76V) than steel (-0,3V). This property of zinc coatings making it one of the most used among all the metals used in the electroplating industry. Zinc coatings are important, because 60-70\% of the iron produced in the world, in fact, spent on corrosion. Zinc protects the steel from corrosion while being degraded itself.

The work [1] describes a process for the electrochemical deposition of zinc from zincate electrolyte with standard detonation nanodiamonds (DNDst) and surfactant-PEPA (polyethylene polyamine). The electrolyte composition (g / l): ZnO - 6-12, NaOH - 75-120, PEPA - 1-4 DNDst - 1-10. It has been found corrosion currents decrease using DNDst of any concentration in the investigated range. The corrosion resistance of the coating is increased 1.5-2.0 times (resulting coating is not subjected to additional chromatation or phosphotation in tests).

Recommended composition (g / l): Zn - 12, NaOH - -120, Peppo - 2 DNDst - 10.

Purpose of the present work is to obtain electrochemical zinc coating high corrosion resistance.

The objective is to study the influence of the additive of boron modified DND during detonation synthesis and polymer additive A1DM [2] on the deposition of zincate zinc electrolyte.

This work presents results of coating the zincate electrolyte containing DND modified with boron at detonation synthesis and polymer additives A1DM developed by Lithuanian researchers [2]. From an environmental point of view, PEPA is biologically hard substance (does not decompose in the environment) and A1DM - biologically soft (decomposes in the environment by present the soil and water bacteria).
Selection of DND-boron is due to the positive experience of the use of boron compounds in the process of the galvanizing, its properties are described in the papers [3-5].

Experimental procedure
DND-boron obtained by detonation of charges TNT-RDX (50/50) in an aqueous solution of boric acid (H₃BO₃) 5 wt. % concentration. The ratio: the charge weight: the amount of aqueous solution of 1:10. The process was carried out in explosion chamber "Alfa-2M" volume of 2.14 m³. The concentration of boron in the DND is 0.45 wt.%

Zinc deposition is carried out on the steel samples. When recording cathodic polarization curves, potentiostat IPC ProMF were used, as the working electrode were used a steel sample (St20) and a steel sample of pre-coated with zinc under cathodic current density of 3 A / dm² and the temperature of 20°C. The cathodic polarization curves obtained in potentiodynamic mode in the potential range from E to E currentless = -2100 mV.

When recording the curves of hydrogen release a steel sample coated with galvanized zinc were used as a working electrode (the thickness of the zinc coating is not less than 10 microns). The curves were recorded in the potentiodynamic mode over currentless potential to E = -2100 mV.

The platinum electrodes were as auxiliary electrodes. The electrode potential is measured with respect to the saturated silver-chloride reference electrode with a potential equal to 0.202 V.

Obtaining hydrogen curves was carried out in a solution of 3% sodium chloride in potentiodynamic mode (1 mV / sec) relatively to silver chloride reference electrode. Anode curves were recorded in the range of -1790 mV to -1720 mV. Polarization curves were obtained on freshly zinc coating is not less than 3 times, after which the average value of corrosion currents were determined for each potential.

The dependence has been constructed according to the experimental data: i = f (-E) and Lg i = f (-E). Corrosion potential determined in dependence i = f (-E) by extrapolating the straight sections of cathodic and anodic curves.

The authors used the classical zincate electrolyte composition (g / l); NaOH-100-130, ZnO -10-14; A1DM additive ("Chimeta" company production) -8-12 ml / L, DND-boron-0.5-7.

Results and Discussion

The deposition process kinetics of the zinc-diamond coatings in the zincate electrolyte
The preliminary study the impact of supplements A1DM on the cathodic and anodic polarization of zinc in the zincate electrolyte showed its strong influence. Curve shifts towards negative potentials reaches ~ 100 mV. This additive is adsorbed at the cathode and the anode, and does not change the mechanism of the zinc discharge. The angle of Tafel curves is ~ 120 mV, which corresponds to the difficulty of attaching the first electron, and this is consistent with the literature data [6].

Against the background of A1DM was considered the impact of nanodiamond additives DND-boron on the galvanizing process kinetics in the zincate electrolyte.

It was found a good correspondence with the polarization curves of zinc electrolyte stirring or not. Tafel plots inclination angle is within the same range, about 120 mV, i.e. zinc discharge mechanism in the presence of DND-boron remains unchanged - slow stage is the attaching of the first electron. DND-boron supplement does not affect on the potentials plateau of limiting currents, they remain in the same range of potentials: the first ~ 1850mV, the second - in 1950 mV. The limiting current plateau in the curves obtained without stirring, it remains at the same current density approximately 12 A / dm², as in curves without DND-boron additives. The second current limit curve plateau, obtained with mixing is reduced to 2 A / dm², compared with no nanodiamond additive curve. This may indicate the more trapping of DND-boron supplements with stirring; its large concentration was created in the electrode region and a partial desorption A1DM additives. DND-boron adsorption reduces the current limit. With increasing the concentration of the DND additive in the stirred-boron electrolyte the second current limit decreases of 18 A / dm² to 16 A / dm² at the concentration of additive - 5 g / l. DND-boron additive has no effect on the first current limit with stirring. This suggests that the plateau of the first current limit is occupied with A1DM additive and DND-boron.
additive is not able to be absorbed and influence on the polarization, further, the shift of the cathode potential in the negative region leads to partial desorption of A1DM additive and there is a possibility of observed nanodiamond additives action.

Follows from the obtained data the addition of boron-DND in comparison with the one A1DM additive significantly impedes zinc ionization process, which means denser layer, which is created in the presence of DND-boron additive. Moreover, with stirring the DND-boron additive effect amplifies two times in comparison with the zinc precipitation from the electrolyte without stirring.

Investigation of zinc anodic polarization in the zincate electrolyte with additives shows good reproducibility of the experiment. Electrolyte’s stirring naturally facilitates the ionization of zinc, slightly changing the angle of the Tafel dependence.

As a polarization studies result, scattering ability of zincate electrolyte was defined in the presence of additives studied by electrochemical similarity. The data are shown in Tables 1 and 2.

Table 1. The zincate electrolyte conductivity

| without DND-boron, with 2 g/l A1DM | with 0.5 g/l DND-boron + 2 g/l A1DM | with 1 g/l DND-boron + 2 g/l A1DM | with 2 g/l DND-boron + 2 g/l A1DM | with 5 g/l DND-boron + 2 g/l A1DM |
|-----------------------------------|-------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 275                               | 274                                 | 272                               | 275                               | 265,8                             |

Table 2 - The zincate electrolyte scattering power in the presence of additives

| The concentration of DND-boron, g/l | The change of the current density, ΔI mA/cm² | The potential change, ΔE, mV | The first derivative of the current potential, ΔE/ΔI, Ohm | Electrical conductivity, σ S/cm | The scattering power, ΔE/ΔI* σ | without stirring | stirring |
|-----------------------------------|-----------------------------------------------|-----------------------------|--------------------------------------------------------|-------------------------------|---------------------------------|------------------|---------|
| Only with 2 g/l A1DM             | 2                                             | 8,3                        | 4,15                                                   | 275                           | 1,14                            | 1,14             | 1,22    |
| 0.5                               | 2                                             | 33,9                       | 18,6                                                   | 16,95                         | 9,3                             | 274                           | 4,64               | 2,55         |
| 1                                 | 2                                             | 27,2                       | 19,8                                                   | 13,6                          | 9,9                             | 272                           | 3,7                | 2,7          |
| 2                                 | 2                                             | 31,2                       | 21,3                                                   | 15,6                          | 10,6                            | 275                           | 4,29               | 2,92         |
| 5                                 | 2                                             | 15,8                       | 20,5                                                   | 7,9                           | 10,25                           | 265,8                         | 2,1                | 2,72         |

The conductivity of the zincate electrolyte in the presence of DND-boron additive is slightly reduced, except the 2 g/l concentration, at which the electrical conductivity and polarizability take the maximum value, probably at this concentration redistribution of two A1DM and DND-boron additives appears because of competitive adsorption. It is noted that the scattering power of the electrolyte increases in the presence of DND-boron additive in the electrolyte without stirring ~ 4 times as compared with the electrolyte with the A1DM additive only. The zincate electrolyte scattering power in the presence of DND-boron additive is increased by 2 - 2.5 times, even with stirring, which is a very important factor in the use of nanodiamond additives.
Addition of DND-boron in the electrolyte contributes to obtaining fine-grained structure with the creation of a composite matrix, which should improve the corrosion resistance of the coatings. Corrosion currents are calculated from the polarization curves of hydrogen (anode and cathode) recorded in 3% NaCl solution on zinc coatings obtained with the test zincate electrolyte additives, such as: A1DM and DND-boron nanodiamonds. All investigated coatings were obtained with the same current density - 3 A/dm² of zincate electrolyte (Figure 1, 2).

**Figure 1.** Cathodic polarization curves of hydrogen evolution at the zinc obtained from the electrolyte without additives (7), but with 10 g/l A1DM (1) and 0.5 (2), 1(3), 2(4), 5(5), 7 (6) / l DND-boron + 10 g / l A1DM

**Figure 2.** Anodic polarization curves of zinc dissolution obtained in the electrolyte without additives, but with 10 g / l A1DM (1) and 0.5 (2), 1(3), 2 (4), 5 (5), 7 (6) g / l DND-5-B + 10 g / l A1DM
On the cathode curves the current rise observed in 1600-1700 mV potential, possibly due to the change of the layer structure obtained in the presence of A1DM additive. Processing these curves in the semilogarithmic dependence uses to determine corrosion current (current density equal to 0.0076 mA / cm²).

Analysis of hydrogen curves data showed that in the potential range of 1600-1700 mV on the curves recorded on the coatings obtained in the presence of additives like A1DM and nanodiamonds, there is a maximum, the value of which is reduced, when added to A1DM nanodiamond additive, which may indicate the inclusion of DND-boron in the coating. This is also evidenced by zinc ionization curves in 3% NaCl solution (Fig. 2), it is observed facilitating ionization on coating obtained with nanodiamonds, when compared with coatings obtained with one A1DM additive only. All this may indicate that nanodiamond additives, including into the coating during electrodeposition of zinc, improves the structure and increases its corrosion resistance.

Data provided in Table 3, confirm the previous conclusions. Corrosion currents in 3% NaCl solution reduces practically to 3.6 times on the zinc coatings obtained in the presence of DND-boron. The fact that these additives affect the coating structure and consequently on the physico-chemical properties microhardness data presented in Table 4 shows. The addition of even small quantities of additives (0.5 g / l) increases the microhardness of the coating up to 20%, other values slightly above the level of the coatings obtained without DND-boron.

**Table 3.** Corrosion current value in 3% NaCl for coatings obtained at various DND-boron additive concentrations from zincate electrolyte with 10 ml A1DM (precipitation of samples was performed at 3 A / dm²).

| The content of DND-boron in the electrolyte, g / l | Corrosion current density, i_{corr, i_{electrolysis}} mA/cm² |
|-----------------------------------------------|---------------------------------------------------------|
| -                                            | 0.0076                                                  |
| +0.5                                         | 0.0071                                                  |
| +1                                           | 0.0067                                                  |
| +2                                           | 0.0054                                                  |
| +5                                           | 0.0040                                                  |
| +7                                           | 0.0029                                                  |

**Table 4.** Zinc coatings microhardness obtained with different concentrations of additive DND-boron in the zincate electrolyte with 10 g of / l A1DM (at 3 A / dm²).

| The content of DND-boron in the electrolyte, g / l | Microhardness H_p, kgf / mm² |
|-----------------------------------------------|-----------------------------|
| -                                            | 111                         |
| 0.5                                          | 134                         |
| 1                                            | 122                         |
| 2                                            | 121                         |
| 5                                            | 116                         |
| 7                                            | 114                         |

The data of zinc coatings corrosion testing obtained with various concentrations of DND-boron in salt fog chamber are shown in Table 5. From the analysis of the data table 5 the better results were obtained for samples deposited from the electrolyte with DND-boron additive at the concentration of 5 and 7 g / l (corrosion decreased by 3.1-3.4 times), which agrees well with corrosion currents.
Table 5. Data of zinc coatings corrosion testing obtained with the electrolyte DND-boron nanodiamond additive. (Zinc deposition temperature of 25°C, the density of zinc deposition current 3 A / dm², the time of the corrosion tests - 24 hours), salt fog chamber.

| Number of the sample | 1     | 2     | 3     | 4     | 5     | 6     |
|----------------------|-------|-------|-------|-------|-------|-------|
| Additive concentration, g / l | 10 g/l A1DM | 0,5 g/l DND-boron | 1 g/l DND-boron | 2 g/l DND-boron | 5 g/l DND-boron | 7 g/l DND-boron |
| Weight after coating, g | 29.8074 | 29.9324 | 30.0020 | 30.2000 | 30.4026 | 30.1128 |
| Weight after corrosion tests, g | 29.7833 | 29.9096 | 29.9818 | 30.1875 | 30.3948 | 30.1057 |
| Weight loss during corrosion tests, g | 0.0241 | 0.0228 | 0.0202 | 0.0125 | 0.0078 | 0.0071 |
| Appearance before the corrosion test | A smooth, uniform, shiny coating |
| Appearance after corrosion tests | All samples were covered with white corrosion |

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Conclusions
1. Sharing of A1DM and DND-boron additives in the zincate electrolyte composition g / l: ZnO - 10; NaOH - 100; A1DM - 6-10; DND-Boron - 5-7 allowed
   - to increase the electrolyte scattering ability (uniformity of coating) in 2.5-4.0 times;
   - corrosion resistance of Zn- DND-boron coating increased 2.5-3.0 times;
   - microhardness increased by 10%.
2. Recommended composition of the electrolyte and the deposition conditions:
   ZnO-10;
   NaOH-100;
   A1 DM-6;
   DND-boron – 5-7 g / l;
   $i = 3 A/dm^2$;
   $t = 25°C$.

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