



CORROSION BEHAVIOR OF ZINC ALLOY LAYERS

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ABSTRACT

The alloying of zinc with some additional elements in specific quantities could be reliably used in the hot-dip coating process. These elements conferr substantially improved performance to the end-product specially by improving corrosion resistance.

In this paper the influence of adding different percentages of aluminum and bismuth into the zinc bath was researched.

The technological conditions for obtaining zinc-bismuth-aluminium coatings with 0.27% - 0.52% bismuth and 0.11% Al are presented. The degree of micro-alloying and assimilation in the zinc bath was determined by spectrometric analysis of alloy samples, taken from the melt at different time intervals.

Corrosion resistance of the layers was assessed by two types of tests: corrosion behaviour in seawater for a period of five weeks and electrochemical tests in 3% NaCl solution. Both applied corrosion tests show an increase in corrosion resistance to bismuth content increasing and metallographic analysis of samples corroded shows a general corrosion process.

KEYWORDS: coating, bismuth, aluminium, corrosion

1. Introduction

The improvement of the corrosion resistance is the main objective in the improvement of the metallic coatings, being the defining characteristic of the protective coatings. Rate of corrosion can be modified by the addition of an alloying element. The sense of the modification will depend on the proportion of the alloying element in the base metal, its valence, the concentration and the nature of its characteristic lattice defects [1].

The corrosion behavior of the coat also depends on various factors such as: the coat chemical composition, thickness, adherence, uniformity, porosity [2-4].

To increase the corrosion resistance, adherence, limiting pollution and zinc-iron reaction, it is used more and more micro alloyed zinc melts with various elements: aluminum, nickel, titanium, tin, bismuth, etc. There is a great interest in carrying out research, which explores the influence of the alloying elements in zinc melt on coating layers characteristics and the characteristics of the melt.

In this paper the influence of adding different percentages of aluminum and bismuth into the zinc bath was researched.

In the interest of environment and health safety there is a trend in reducing or even eliminating altogether lead from zinc baths. In North America 25% of zinc coating plants have zinc baths without lead [5] and in Western Europe and Canada this percent is even higher. Lead has an important role in zinc baths [6, 7] that must be taken over by another micro-alloying element and the research in this area suggests the use of bismuth. The bismuth isn't toxic [8] like lead. The role of bismuth in zinc coating/galvanizing baths is still controversial. Most authors believe that bismuth increases zinc melt fluidity, reduces surface tension and increases zinc drainage onto the steel support [9, 10].

It may be added at a concentration of 0.1-1% below 0.5% most likely [11] bismuth influence on the protection layer is still questionable. It is believed to reduce film thickness as an effect of melt fluidity without changing the typical structure of a zinc deposition [11].

Aluminium is added to the galvanizing bath, in a continuous flow of the steel strips/plates, at a rate of 0.1-0.3% (optimal 0.14-0.17% [12]). Aluminium is added primarily to act as a brake to the reaction between zinc and steel support. Reducing the iron-zinc reactions it results a decrease in the brittle

intermetallic compound layer which has a negative impact on the layer adhesion and plasticity.

Because, compared to zinc, it has a higher affinity to iron, the aluminium present in the zinc bath will quickly form the $Fe_2Al_{5-x}Zn_x$ compound on the steel surface. This ternary compound arranged in a thin layer onto the steel support will limit the diffusion processes leading to the formation of Fe-Zn intermetallic compounds [13]. The aluminium content in the layer will be much higher than that in the zinc bath. At 0.14% Al in the bath, the entire zinc coating (including the ternary alloy layer) contains about 0.20% Al [13].

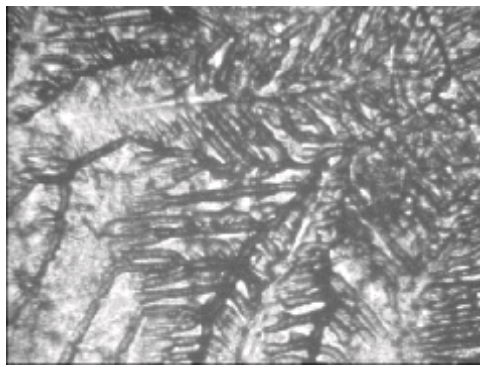
Also, the aluminium reduces the layer thickness, increases its brightness and increases the corrosion resistance. The presence of aluminium in the molten zinc leads to increased fluidity, oxidation speed reduction and decrease iron content (and consequently the amount of dross). Aluminium zinc alloying to improve zinc-coating layer can reach high percentages like galfan (5% Al) and galvalumme (55% Al).

2. Experimental research

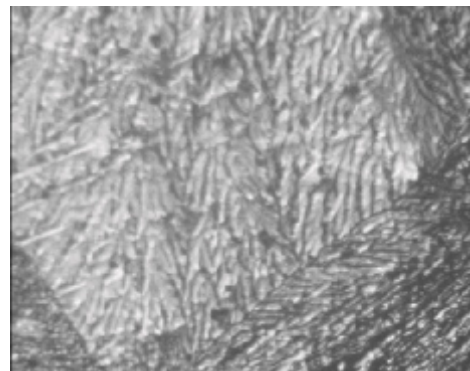
For the preparation of the galvanizing bath pure zinc was used (99.996 wt.%).

Micro alloying with bismuth was made directly, using metallic pieces, finely crushed, followed by mechanical mixing. Laboratory experiments at the micro alloying zinc melts were performed in the temperature range typical galvanizing processes, working at 450-460°C. Assimilation process of bismuth in the melt was stable, maximum efficiency is obtained. Aluminium alloying was made with Al-Zn alloy with 5% Al.

The presence of aluminium in the galvanizing bath, even at low contents (0.11% Al) leads to the formation of Al_2O_3 thin films on zinc bath surface thus preventing the formation of ash that can adhere to the coating surface causing defects. Also in the presence of aluminium coatings of very fine dendrites and metallic brilliancy [14] up to lustre are obtained (Figure 1).



Zn-Bi



Zn-Bi-Al

Fig. 1. Morphology of the surfaces (bath temperature 450 °C, immersion 7 s) x100

The determination of the chemical composition of the obtained alloy was done using an X-ray spectrometer on solidified samples (taken from the melt after homogenization and at different times).

The chemical composition of the obtained alloys is presented in Table 1.

The composition of the steel samples support is presented in Table 2.

Table 1. The chemical composition of the Zn-Bi-Al alloys

Alloy	Bi wt. [%]	Al wt. %	Zn wt [%]	Other items wt. [%]
Zn-Bi-Al 1	0.27	0.11	99.35	Bal.
Zn-Bi-Al 2	0.36	0.11	98.75	Bal.
Zn-Bi-Al 3	0.52	0.11	99.02	Bal.

Table 2. The chemical composition of the steel straps, wt. [%]

C	Si	Mn	P	S	Al	As	Ti	V	Cu	Ni	Cr	Mo
0.025	0.015	0.210	0.013	0.010	0.046	0.004	0.002	0.001	0.005	0.008	0.025	0.001

The practical cooling conditions with a cooling speed much higher than that of equilibrium conditions [15] together with the low content of bismuth in the studied alloys lead to a biphasic structure formed from polygonal grains of zinc and fine crystals of

bismuth uniformly spread in the zinc matrix (Fig. 2a). At higher bismuth content the proportion of the crystals dispersed in the zinc mass gets higher, and also their dimensions are larger, as it can be seen in Fig. 2b.

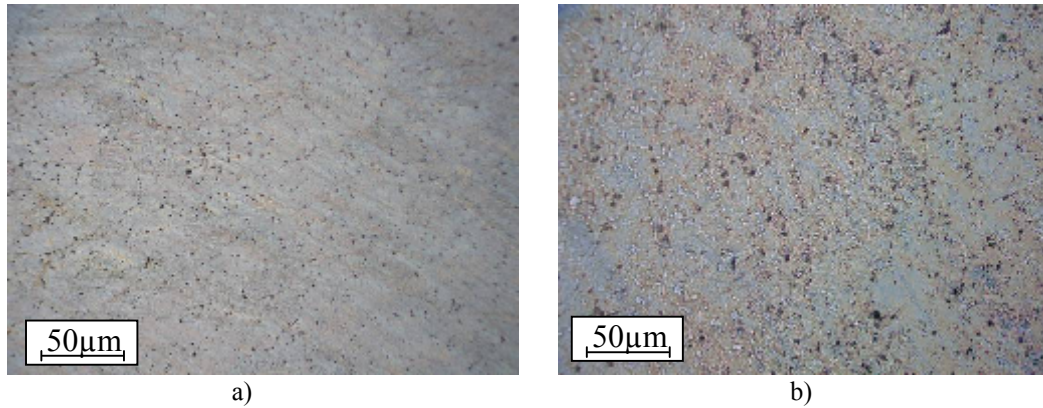


Fig. 2. Microstructure of zinc micro-alloyed with bismuth a) 0.27% Bi; b) 0.52% Bi [11]

Micro-alloying the zinc with bismuth doesn't change significantly the aspect of the microstructure of the coating layer compared to coating with pure zinc (Fig. 3 a and b).

Bismuth yet acts on the layer made of iron-zinc alloys in the sense of thinning it down by the formation of a mechanical barrier between the intermetallic compounds phase and the liquid zinc phase. For higher bismuth content a small decrease in iron-zinc reactions is observed, the layer of intermetallic compounds from the steel-coating

interface is thinner compared to its thickness when it is coated with pure zinc (Fig. 3b).

Having a higher affinity for iron than for zinc, aluminum will form at the surface of the steel support a thin microscopic film, out of Fe₂Al₅ compounds.

This layer, dense and compact, exerts a strong braked effect on the growth of the iron-zinc intermetallic compounds and microstructure of the coating layer shows a fine and uniform layer of intermetallic compounds at the interface steel/coating (Fig. 3c).

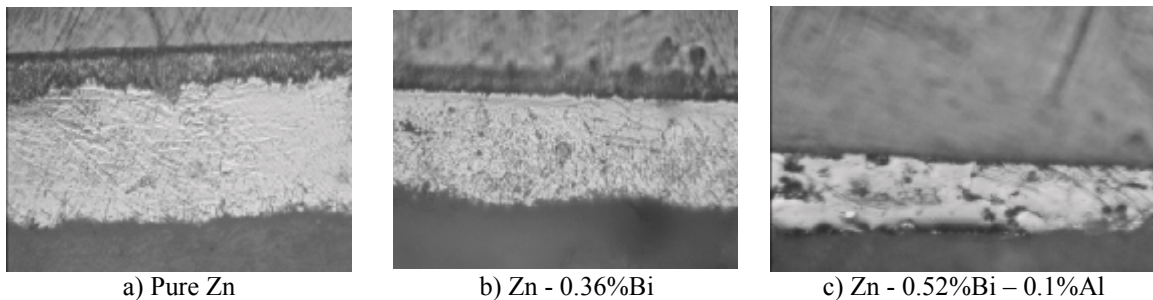


Fig. 3. Microstructure of the layers, (bath temperature 450 °C, immersion 9s) x100

Regarding the thickness of the layer (as shown in Fig. 3) bismuth and especially aluminum decrease the coating thickness. This effect is given by the increase in fluidity of the melt when bismuth and aluminum are added.

Corrosion resistance of the layers was assessed by two tests, gravimetric indices for corrosion behaviour in seawater for a period of five weeks and electrochemical tests in 3.5 wt% NaCl solution.

To determine the corrosion rate in sea water samples were sampled from every type of coating

applied on the steel strip. These samples were immersed individually in recipients containing solution that imitates sea water: NaCl – 27 g/L; MgCl₂ – 6 g/L; CaCl₂ – 1 g/L; KCl- 1g/L; pH = 6.5-7.2, at room temperature.

The following steps have been covered: surface degreasing, weighing, immersing into sea-water containers, with a similar surface exposure to the corrosive agent. After each week the samples were washed, dried and weighed to determine the mass variation.

For the calculation of corrosion rate the following relation was used:

$$V_{corr} = \frac{\Delta m}{S \cdot t} [g \cdot m^{-2} \cdot h^{-1}] \quad (1)$$

where:

Δm – the weight loss by corrosion, [g];
 S – the surface area of the corroded surface, [m²];
 t – the corrosion time, [h].

Results are presented in Figure 4. After seven days of exposure to corrosive environment the loss in weight of the samples was comparable.

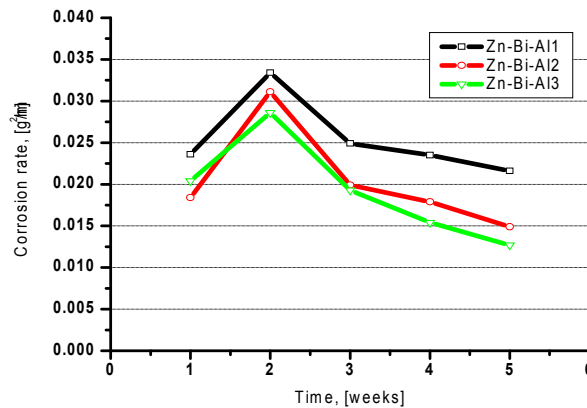


Fig. 4. The variation of the corrosion rate as a function of the exposure time to the corrosive environment

After 14 days, the corrosion speed is modified according to the occurrence of the corrosion products and to their intrinsic characteristics.

Thus the Zn-Bi-Al 1 has, in this case, the highest corrosion rate (0.0334 g/m²·h) and the best behavior is observed at the sample coated with zinc microalloyed with 0.36% Bi – 0.11% Al (0.0286 g/m²·h). In the third week the corrosion rate significantly

decreases for all samples and decreases continuously for the next two weeks. Generally, the corrosion resistance increased with bismuth content.

The microscopic analysis of the surface shows the evolution of the corrosion process in time until the generalized corrosion of the surface at the end of the testing period as it can be seen in Fig. 5.

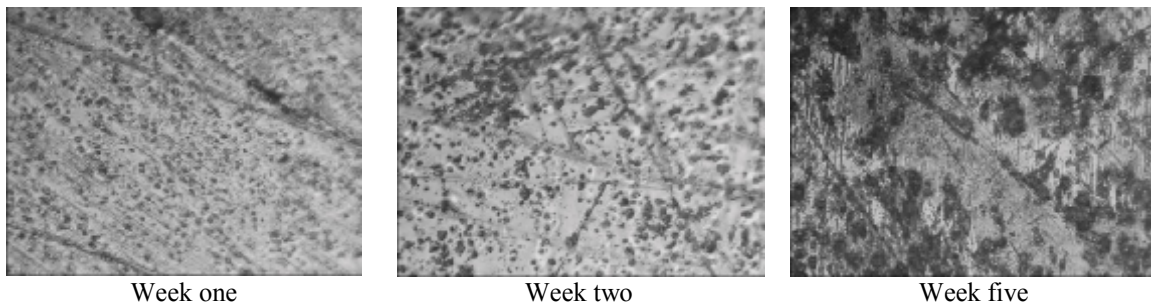


Fig. 5. The modification of the surface during the corrosion process for sample Zn-Bi-Al 1, x100

For the electrochemical tests, the corrosive environment used was a NaCl solution 30 g/L. A three-electrode cell, consisting of working electrode (Zn-Bi-Al coating samples) with an exposed area of 2 cm², an Ag/AgCl electrode as reference electrode and a platinum plate as a counter electrode, were used. Potentiodynamic polarization curves were recorded in

the potential range from -1000 mV to -100 mV, at the scan rate of 2 mV/s. All measurements were performed at room temperature.

Before experiments samples were cleaned with water and acetone. Fig. 6 shows the Tafel curves. These curves were processed and the results shown in Tab. 4.

Table 4. Electrochemical corrosion result by Tafel Method

Coating	i_{cor} [$\mu\text{A}/\text{cm}^2$]	R_p [$\Omega \text{ cm}^2$]	v_{cor} [mm/y]
Zn-Bi-Al 1	19.6300	673.46	0.208
Zn-Bi-Al 2	15.0741	918.68	0.181
Zn-Bi-Al 3	13.9972	889.23	0.166

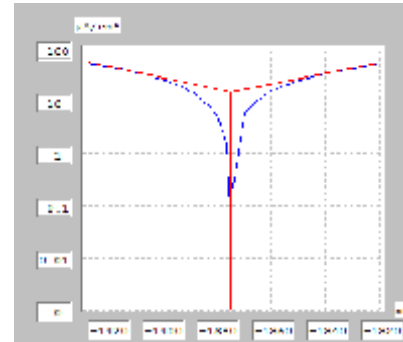
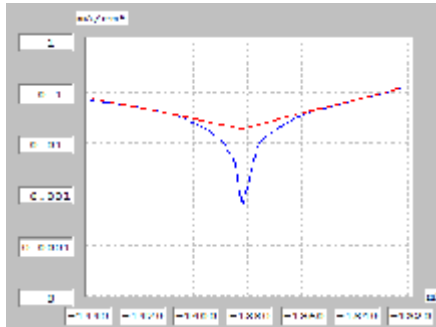


Fig. 6. a) Tafel curve for Zn-Bi-0.36%Bi coating b) Tafel curve for Zn-Bi-0.11%Al coating

Electrochemical test shows the same trend of decreasing corrosion rate when the bismuth content increases.

Increased corrosion resistance can be caused by the cumulative effects of bismuth and aluminum to the zinc melt characteristics and their products corrosion.

3. Conclusions

- Bismuth has a melting temperature lower than zinc and it is easily assimilated in galvanizing bath;
- Microstructure of alloy samples, taken from the galvanizing bath, reveals a homogeneous structure with polygonal grains of zinc and fine crystals of bismuth, uniformly spread in the zinc matrix;
- Layers microstructure shows a decrease in thickness in the presence of bismuth and aluminum especially;
- In the presence of bismuth and aluminum reactions between iron and zinc are strongly braked;
- The corrosion rate in seawater for a period of five weeks shows a similar variation for the three types of layers studied;
- The most significant corrosion rate is achieved for all the samples in the second week and then decreases continuously in the next weeks;
- Metallographic analysis of samples corroded shows a general corrosion process;
- Both applied corrosion tests show an increase in corrosion resistance to bismuth content, increasing from 0.2% to 0.52%.

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