RESEARCH ON THE CORROSION BEHAVIOR OF ZINC COATING BY MEASUREMENT OF POLARIZATION RESISTANCE

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Abstract: Measurement of polarization resistance of micro-alloyed zinc layers followed corrosion products characterization and corrosion behavior of the default layers analyzed. We have studied micro-alloyed zinc coatings with different percentages of nickel, tin, bismuth, lead, cadmium, exposed to a corrosive environment with 3% NaCl at room temperature. For experimental determinations was applied electrochemical method. A calomel saturated electrode was used as reference electrode and a platinum wire electrode as an auxiliary one. Analyzing the variation of polarization resistance for each sample, we can observe how initially the sample surface becomes active, which causes a decrease in polarization resistance followed in time by the formation of a layer of corrosion products which will cause a variation of polarization resistance.

1. Working method and apparatus used

In most atmospheric environments, Zn corrodes much less than steel, due to the formation of a protective layer consisting of a mixture of Zn oxide, Zn hydroxide and various basic Zn salts depending on the nature of the environment. Thus the protection of steel by a Zn coating is mainly through the barrier effect. However, at the places where the Zn coating is damaged and the steel underneath is exposed, such as at cuts or at scratches, the galvanic action between steel and Zn can protect the exposed steel from corrosion.

The measured values of polarization potential include the voltage drop (ohmic loss) due to the electrolyte and reaction products film on the metal surface. The value of this voltage drop is the polarization resistance [1; 2]. Ohmic resistance drops sharply with loss of power, unlike electrochemical polarization which decreases with a slower rate [3]. By measuring the polarization resistance, for alloyed zinc coatings, it is intended to assess the corrosion products film characteristics and corrosion behaviour of the default layers.

Measurements were performed on samples of steel sheet coated with zinc compositions corresponding Table 1, using as a saline environment corrosion 3% Na Cl at room temperature [4]. Layers of protection were obtained by hot dip galvanized, with the classical preparation of the sample surface.

Since nickel has a much higher melting temperature than zinc micro alloyed a zinc-nickel alloy, with 2% nickel, was made. Bismuth, cadmium, tin and lead are easily assimilated into molten zinc and micro alloying was achieved by introducing these elements, finely chopped directly into zinc bath. Bismuth is a novelty element for micro alloying zinc melts, used to replace lead, having the same effect on melt fluidity and reduction of surface tension without being toxic.

In all cases it was applied to the melt homogenize the mechanical mixing.

For measuring the polarization resistance, it was used a potentiostate PGP type 201. A calomel saturated electrode was used as reference electrode and a platinum wire electrode as an auxiliary one. The samples were prepared for analysis by being degreased with acetone, washed and dried [5]. After connecting the cable conductor, the delimitation of the working surface (equal for all samples) was made by insulating with resin. Measurement of polarization resistance at micro-alloyed zinc layers was made for corrosion products and corrosion behavior of the default layers analyzed. The variation curves of the polarization resistance (R_p) were experimentally determined as a function of time for galvanized samples and samples coated with alloy.

2. Experimental results

Results of the electrochemical analysis consist in the curve of the polarization resistance function of time. Analyzing the variation of polarization resistance for each sample(table 1), we can observe how initially the sample surface becomes active, which causes a decrease in polarization resistance followed in time by the formation of a layer of corrosion products which will cause a variation of polarization resistance.

Knowing the R_p, the value of I_{cor} per surface unit can be calculated using the Stern and Geary formula (1)

$$I_{cor.}\left(\frac{\mu A}{cm^2}\right) = \frac{B(mV)}{Rp(k\Omega)\cdot S \cdot (cm^2)} \qquad (1)$$

The value used for the B coefficient was of 26mV.

Surface, S, for each sample was 1 cm^2.

Table 1. Chemical composition of coatings tested

Code	Type of coating	Chemical composition, [wt%]						
		Ni	Bi	Sn	Cd	Pb	Al	Zn
0	Zn	0	0	0,0005	0,0004	0,0014	0,0005	diff.
I	Zn- Ni-Bi-Sn	0,16	0,71	2,95	0,26	0	0	diff.
II	Zn- Ni-Pb-Sn	0,16	0	2,88	0	0,72	0	diff.
III	Zn- Ni- Pb-Bi-Sn	0,16	0,41	3,49	0	0,43	0	diff.
IV	Zn-Bi I	0	0,27	0	0	0	0	diff.
V	Zn-Bi II	0	0,36	0	0	0	0	diff.
VI	Zn-Bi III	0	0,52	0	0	0	0	diff.

In the case of hot dip galvanized samples, without addition of other metals corrosion product formation leads to an increased polarization resistance to a 1 kΩcm^2 and because it did not reached zero polarization resistance during the analysis result shows that the corrosion products layer has a slow process of compaction (Fig. 1).
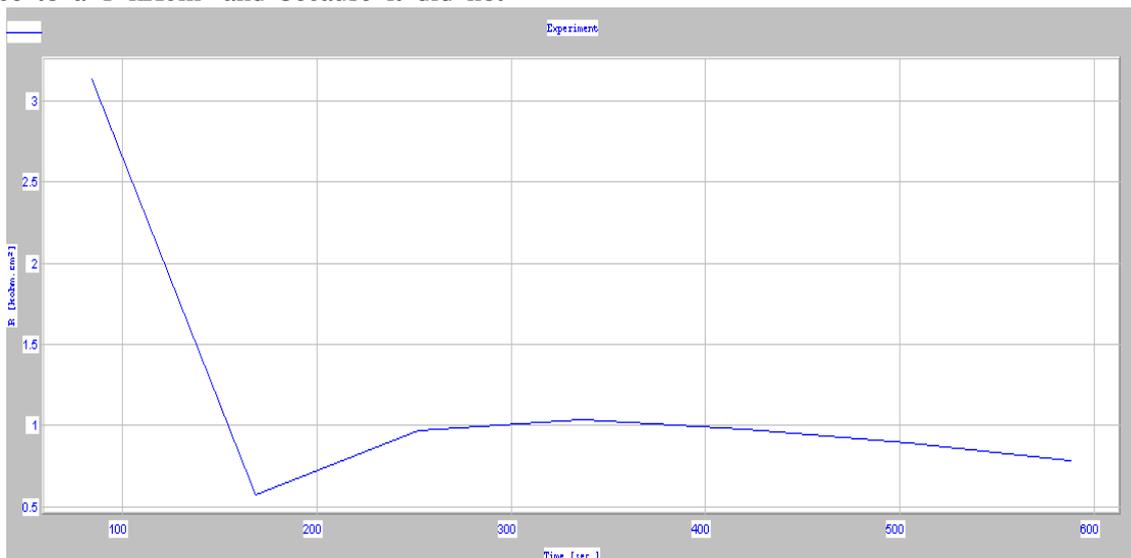

Figure 1: *Polarization resistance function of time for the sample coated with zinc*

Sample I, zinc-coated complex micro alloyed with nickel, bismuth, tin, cadmium, forming a film of corrosion products with a polarization resistance of 90 kΩcm^2 very stable and dense. Value of 0 Ω/cm^2 (circuit interruption) was reached after about five minutes (Fig. 2)

Sample II, coated with zinc and nickel, tin, lead, forming a film of corrosion products with a 45 kΩcm^2 polarization resistance and respectively 27.5 kΩcm^2, has a similar evolution in time as the galvanized sheet (figure 3)

The sample III, coated with zinc and nickel, tin, lead, bismuth, forms a film of corrosion products with a very low polarization resistance of 0.38 kΩcm^2 which did not provide surface passivity during the analysis (Fig.. 4.).
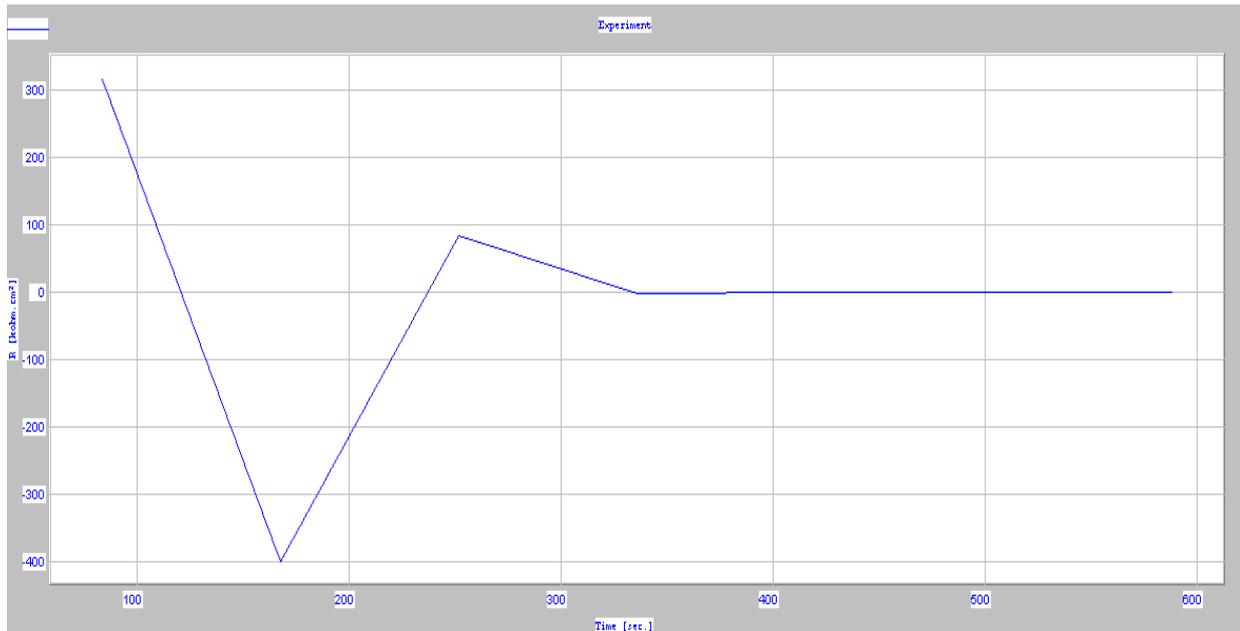

Figure 2: *Polarization resistance function of time for the sample coated with Zn- Ni-Bi-Sn*
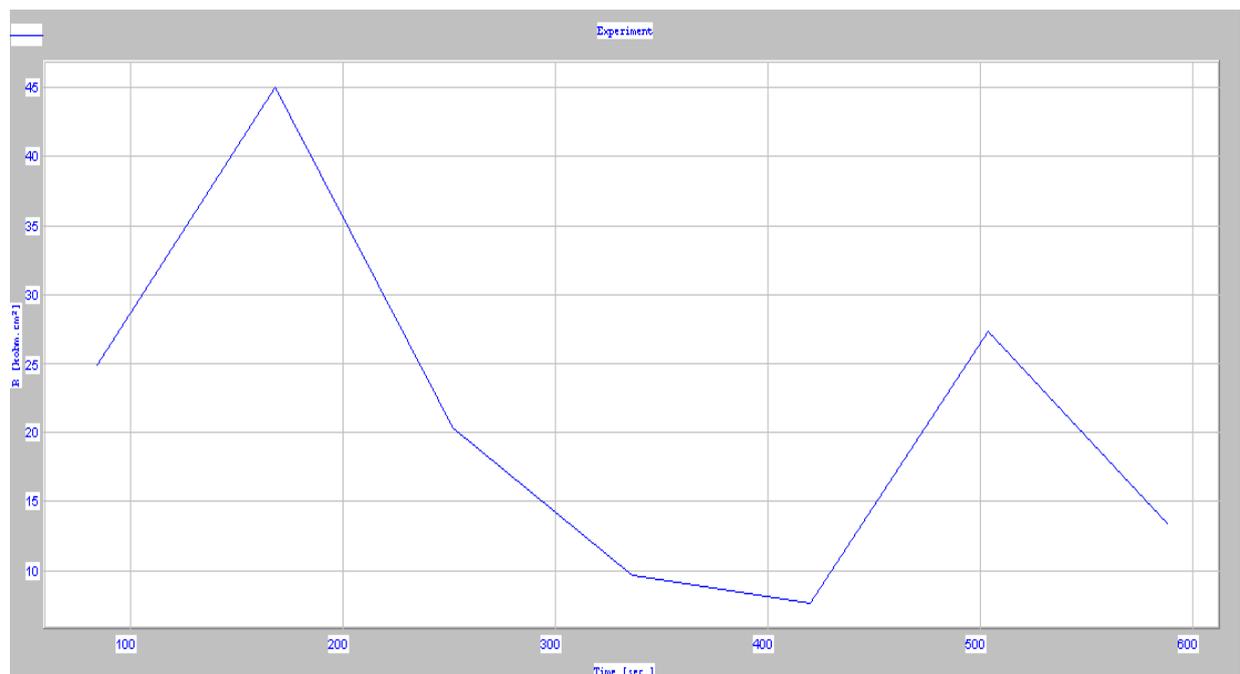

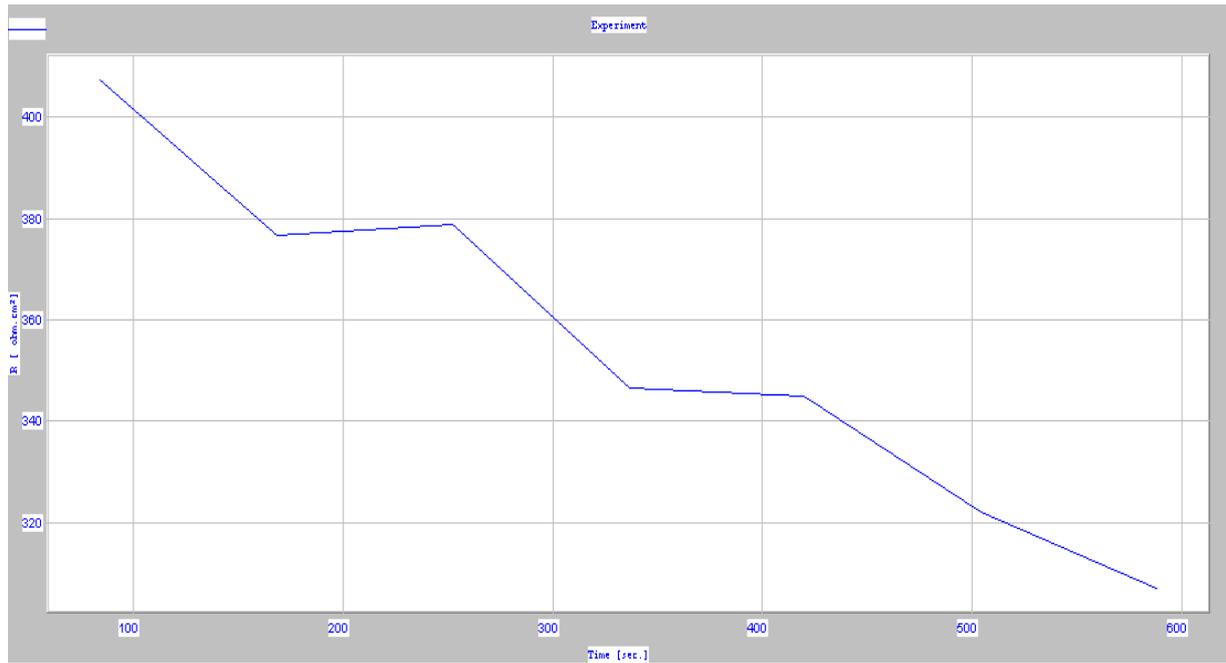**Figure 3:** *Polarization resistance function of time for the sample coated with Zn- Ni-Pb-Sn*

Figure 4: *Polarization resistance function of time for the sample coated with Zn- Ni- Pb-Bi-Sn*

Sample IV, coated with zinc and 0.27% bismuth, shows a variation of polarization resistance, very similar to the pure zinc coated sample , polarization resistance is 1.23 kΩcm^2 (Fig. 5)

Sample V, coated with zinc and 0.36% bismuth shows low polarization resistance (0.4 kΩcm^2) for corrosion products formed (Fig. 6).

Figure 5: *Polarization resistance function of time for the sample coated with Zn-Bi I*
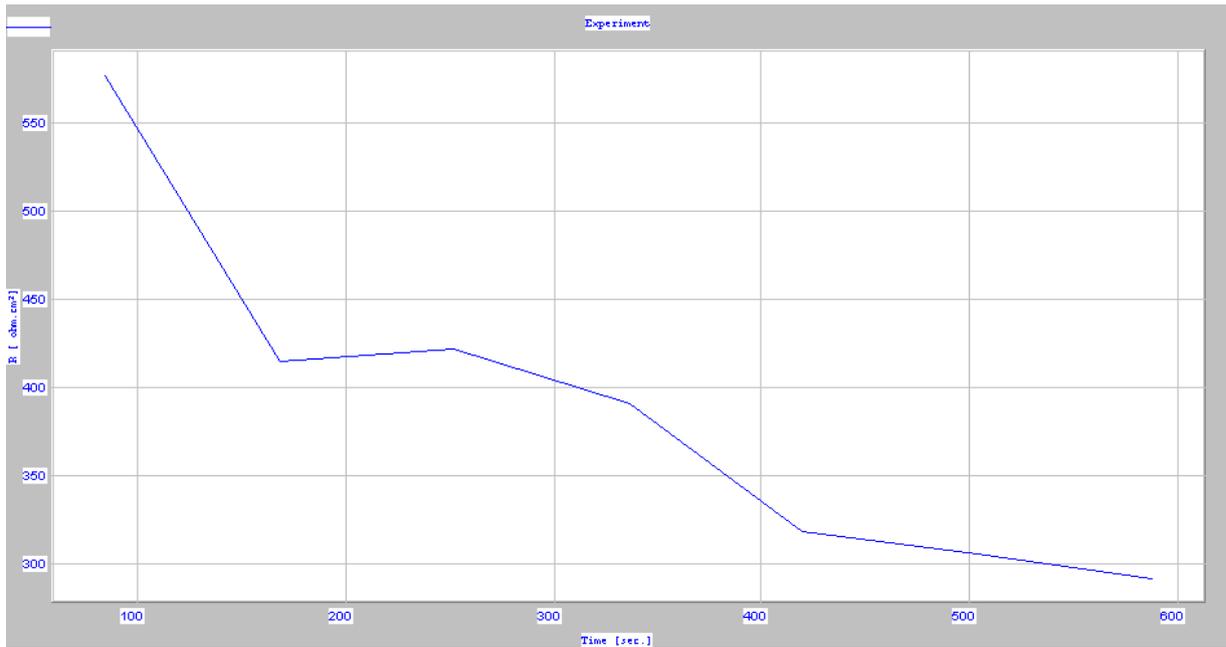
Figure 6: *Polarization resistance function of time for the sample coated with Zn-Bi II*

Sample VI, coated with zinc and 0.52% bismuth shows a variation of polarization resistance similar to the previous zinc with 0, 36% bismuth coated samples (Fig.7).
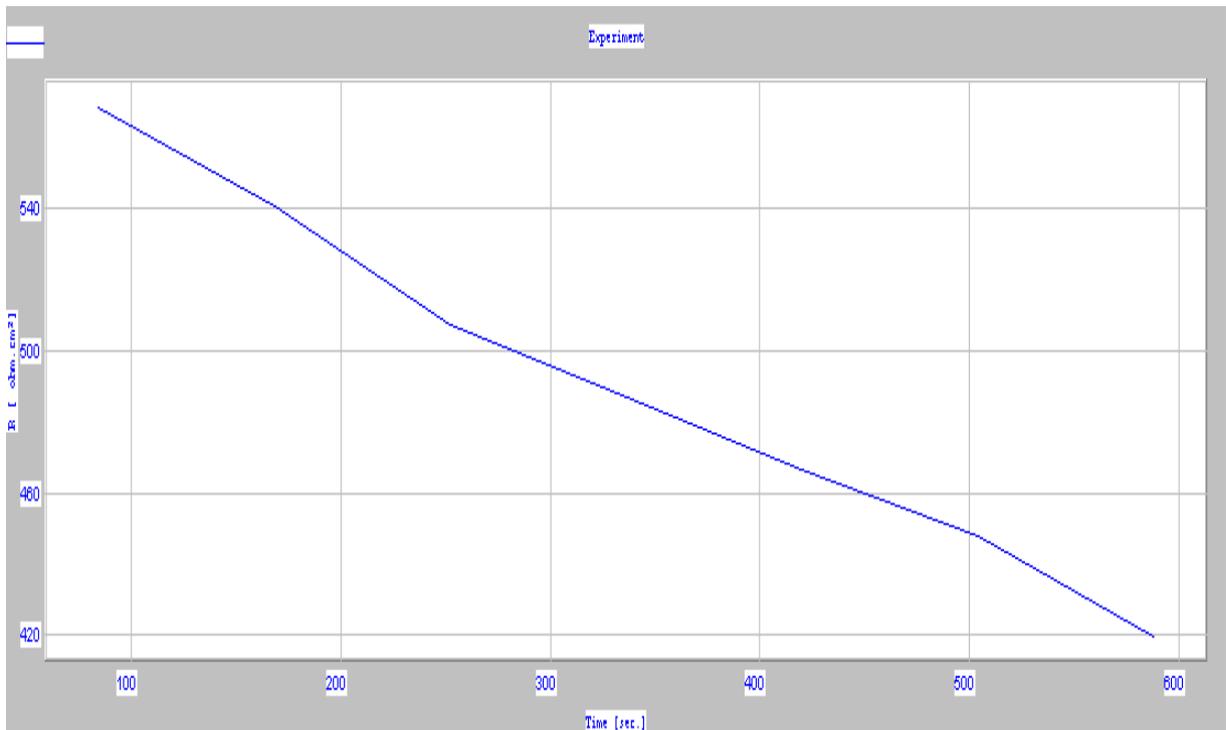

Figure 7: *Polarization resistance function of time for the sample coated with zinc Zn-Bi III*

Comparing the polarization resistance of samples coated, with different layers of zinc micro alloyed, with the polarization resistance of the zinc coated sample, we can observe:

- Rp$_I$ □ Rp$_{II}$ □ Rp$_{IV}$ □ Rp$_{Zn}$ □ Rp$_{VI}$ □ Rp$_V$ and I$_{corI}$ □ I$_{corII}$ □ I$_{corIV}$ □ I$_{corZn}$, result a higher corrosion resistance of samples coated with zinc-nickel-tin-bismuth-cadmium (code I);

255

Coatings with zinc-tin-bismuth have a corrosion resistance similar to zinc coated or lower:

$$I_{corZn} \leq I_{corIV} \square \ I_{corVI} \square \ I_{corV.}$$

Conclusions

- Analyzing the variation of polarization resistance for each sample, we can observe how initially the sample surface becomes active, which causes a decrease in polarization resistance followed in time by the formation of a layer of corrosion products which will cause a variation of polarization resistance.

- The sample coated with zinc-nickel-bismuth-tin, has form a layer of corrosion products with a polarization resistance of 90 $k\Omega cm^2$ very stable and dense, presenting a very good corrosion behavior compared with unalloyed zinc coating.

-Samples with layers alloyed with nickel shows a bigger corrosion resistance compared with unalloyed zinc coating: $I_{corI} \square \ I_{corII} \square \ I_{corIV} \square \ I_{corZn.}$

- Coatings with zinc-tin-bismuth have a corrosion resistance similar to zinc coated or lower.

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