

## INFLUENCE OF ALLOYING ELEMENTS IN ZINC MELTS ON THE STRUCTURE OF LAYERS OBTAINED BY GALVANIZING

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### ABSTRACT

*Zinc melts has been alloyed, in various proportions and combinations, with Bi, Sn, Ni, Pb. Depending on the characteristics of the alloying elements, the alloying technology of the zinc bath was established. To determine the degree of homogenization of the melt, samples were taken for metallographic analyses and chemical composition. In zinc alloyed melts were coated steel strips with low carbon. The layers obtained were analyzed in cross-section to determine the influence of the alloying elements on the Zn-Fe alloys from the support/zinc interface and on the thickness and structure of the phase  $\eta$  (zinc). The chemical composition was determined by X-ray fluorescence and microstructure analysis by optical microscopy.*

KEYWORDS: coating layer, optical microscopy, X-ray fluorescence, Zn-Sn-Pb-Bi-Ni alloy, galvanizing

### 1. Introduction

Hot dip galvanizing technology is widely applied for the corrosion protection of steel parts so that half of the world's zinc production is used for this purpose [1]. Classical hot dip galvanizing has seen many improvements over time. Most of them aimed at increasing the corrosion resistance of the layer, changes in the melt characteristics (fluidity, superficial tension, etc.) and reducing the amount of dross. In order to achieve these objectives, a modification of the composition of the zinc bath by alloying with various elements was applied in various combinations, namely: Al [2, 3], Sn [4], Mg [5], Bi [6, 7], Ni [8-10]. Aluminum is the most widely used and studied alloying element of zinc melt having favorable effects both on the characteristics of the layer and on the zinc melt [11]. At present, galvanizing in alloys Zn-Mg-Al is being investigated

with significant improvements in technology and product [12-14].

Bismuth is an expensive metal but can replace lead in galvanizing baths with the same effect in increasing fluidity and reducing surface tension to much lower contents and is not toxic.

Tin increases corrosion resistance of zinc layers and nickel increases melt fluidity and corrosion resistance [4, 9]. The paper analyses the influence of some of these alloying elements on the structure of the obtained layers. Several types of zinc alloys and alloying elements Bi, Ni, Sn, Pb have been studied in various combinations and concentrations.

### 2. Experimental conditions

In the pure zinc melt (Table 1) alloys were introduced in different combinations, Bi, Sn, Ni and Pb. The chemical composition of the zinc coatings studied is presented in Table 2.

*Table 1. Chemical composition of zinc used in experiments, in %*

Zn	Pb	Cu	Fe	Sn	Al	Cd
99.996	0.0014	0.0004	0.0005	0.0005	0.0005	0.0004

The alloying elements were gradually introduced into the zinc bath taking account their

physical characteristics (Table 3). As can be seen from Table 3, Bi, Sn and Pb have physical

characteristics close to that of zinc and were introduced into the galvanizing bath at 450 °C in the form of a pure metal crushed and preheated at 200 °C. Nickel has a much higher melting temperature than zinc, and Zn-Ni pre-alloyed with 2% Ni, finely ground and preheated at 200 °C, was used to alloy the

zinc bath. It was introduced into zinc bath at 600 °C. In all cases, mechanical homogenization was applied. After homogenization, samples were taken which were analyzed with an X-ray spectrometer type Invov-X System.

**Table 2.** Chemical composition of alloys used in experiments

Alloy	Alloying elements, [%]				
	Pb	Bi	Sn	Ni	Zn
Zn-Bi	0	0.36	0	0	rest
Zn-Bi-Sn	0	0.35	3.50	0	rest
Zn-Bi-Sn- Ni	0	0.41	3.49	0.17	rest
Zn-Pb- Bi-Sn-Ni	0.72	0.41	3.88	0.16	rest

**Table 3.** Physical characteristics of zinc and alloying elements used

Element	Physical characteristics			
	Density [kg/dm <sup>3</sup> x10 <sup>-3</sup> ] at 20 °C	Melting point °C	Boiling point °C	Latent heat [Cal/g]
Zn	7.13	419.5	907	27.3
Bi	9.8	271	1440	-
Sn	7.3	232	2590	13.96
Ni	8.9	1455	3000	73
Pb	11.34	327.4	1750	5.75

**Table 4.** Chemical composition of strip steel (support) in [%]

C	Si	Mn	P	S	Al	Cu	Ni	Cr
0.040	0.023	0.210	0.010	0.012	0.039	0.015	0.020	0.020

The chemical composition, of covered steel strip is shown in Table 4.

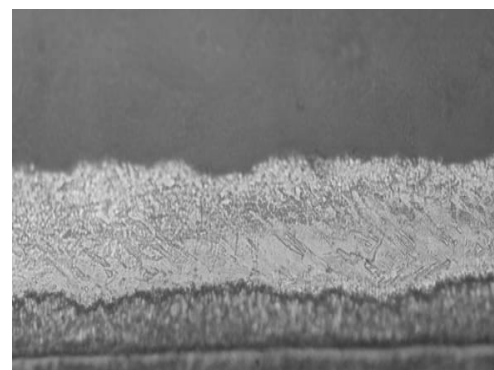
The galvanizing was done at a temperature of 450 °C with a 10 second immersion time. The obtained layers were analyzed in cross-section by optical microscopy on an Olympus-type microscope.

The two areas are distinct both on attacked and un-attacked samples. On the attacked sample (Fig. 1), the layer of Zn-Fe alloys (formed of phases  $\Gamma$ ,  $\delta$ ,  $\zeta$ ) appears darker than the zinc sheet in the layer surface (phase  $\eta$ ). On non-attack samples the intermetallic compounds white bright are observed.

### 3. Results and discussions

The metallographic analysis of the microstructure of the coating layer, obtained in alloyed zinc, shows significant changes compared to the microstructure of pure zinc layers (Fig. 1).

The influence of the alloying elements is manifested both in the structure and size of the alloy layer, which is formed at the interface with the support steel, following the reactions between iron and zinc, as well as in the structure of the resulting zone by the entrainment of the bath melt and located over the Zn-Fe alloys layer.

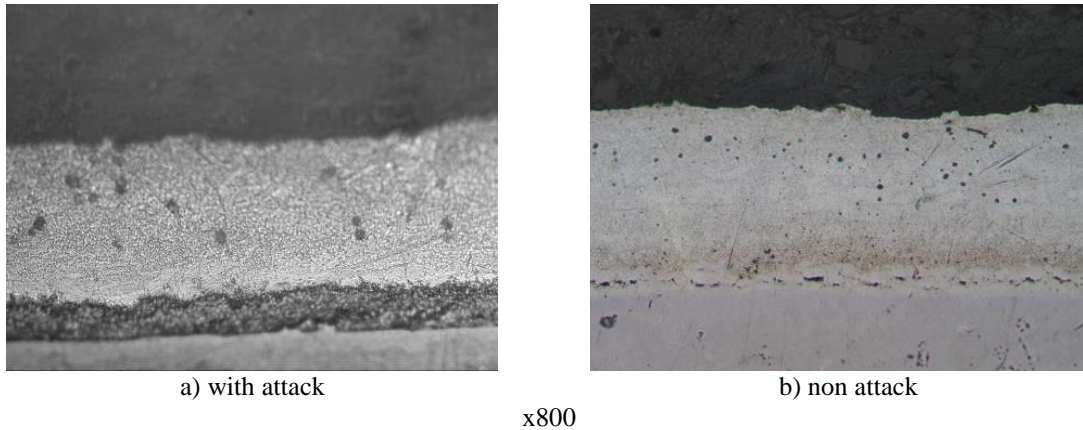


**Fig. 1.** The layer microstructure obtained in pure zinc, x200

Alloying of the zinc with 0.36% Bi. Bismuth is added to the zinc bath to increase the melt fluidity and it can replace the lead, considered toxic to the environment. Microstructural analysis of the layer obtained in this alloy (Figures 2a and b) shows a decrease in the phase layer  $\eta$  due to the increase in melt fluidity. The Zn-Fe alloy layer does not change significantly from pure zinc coating. However, there is a diminution of this when bismuth particles

mechanically block Zn-Fe layer growth (Fig. 3). Since bismuth and zinc are insoluble in the solid phase, separation of bismuth crystals is observed in the  $\eta$  phase (zinc) layer. On rapid cooling they are dispersed homogeneously (Fig. 2b) and during slow cooling they clump to the surface (Fig. 3).

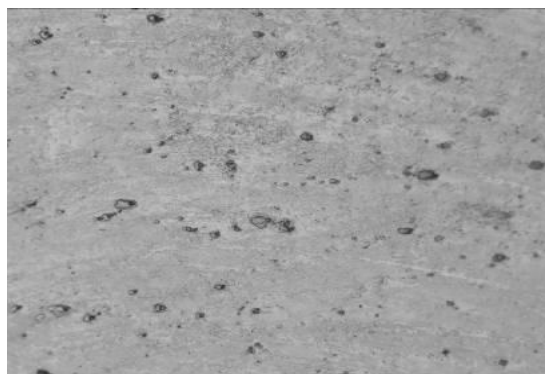
Separation of bismuth crystals in the zinc matrix was also revealed in the microstructural analysis of samples taken from the bath with Zn-Bi alloy (Fig. 4).



**Fig. 2.** Microstructure of coating layer obtained by micro alloying with 0.36% Bi



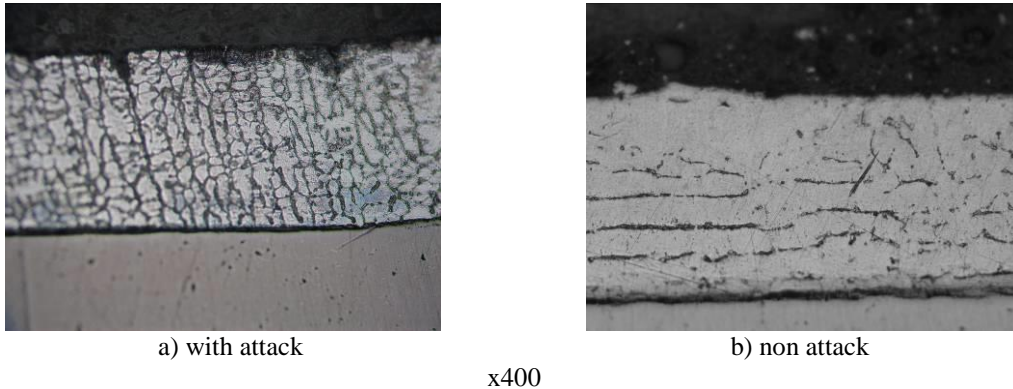
**Fig. 3.** Agglomeration of the bismuth crystals at the growth front of Zn-Fe phase, x400, non-attack



**Fig. 4.** Microstructure of Zn-Bi alloy, x400

Microstructure of Zn-Sn-Bi layers. The Tin is added to the zinc bath in order to increase the corrosion resistance of the layer. Alloying with tin increases the corrosion resistance of the coating but, at the same time, leads to an increase in layer thickness (Fig. 5 a and b). For this reason, tin is not

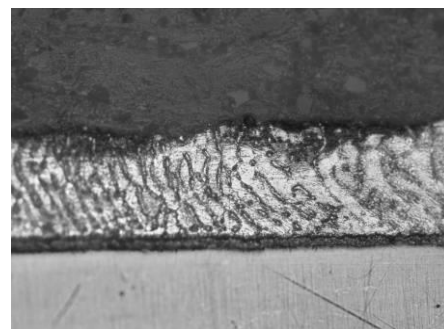
added alone to the zinc bath and it is accompanied by a melt fluidity enhancing element such as lead or bismuth. Tin, in a concentration of over 2.5%, acts on the layer of Zn-Fe alloys to reduce it by forming a mechanical barrier between the intermetallic and zinc phase (Fig. 5b).



**Fig. 5.** The microstructure of the coating layer obtained in Zn-Bi-Sn alloy

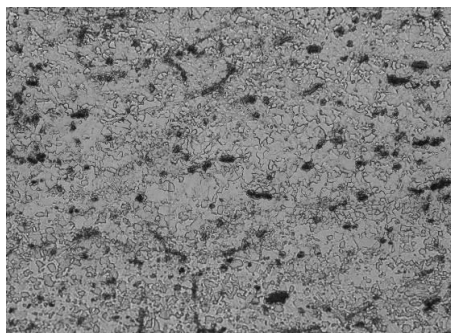
Fig. 6 shows the microscopic appearance of the Zn-Sn-Bi alloy. Tin and bismuth are elements insoluble in zinc and they separate as crystals in the zinc mass or at grain boundary.

Melt alloying with Ni. Nickel increases the fluidity of the zinc melt and increases the corrosion resistance of the coating. In the structure of the protective layers obtained in alloyed baths simultaneously with nickel-tin-bismuth (Fig. 7), it is observed the effect on the iron-zinc alloy layer, which is drastically reduced. The effect is cumulative of nickel and tin, the bismuth acting on the thickness of the layer, in the sense of reducing it, by increasing the melt fluidity and decreasing the superficial tension.



x400, with attack

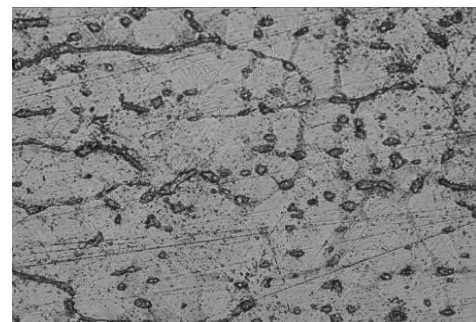
**Fig. 7.** The microstructure of the coating layer obtained in Zn-Sn-Bi-Ni alloy



x400, with attack

**Fig. 6.** Microstructure of the Zn-Sn-Bi alloy

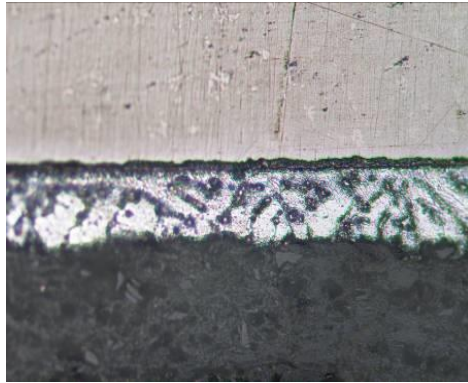
The formation of many compounds between nickel and zinc and between nickel and the other micro alloying elements (Sn and Bi) leads to the obtaining of a composite structure for Zn-Ni-Sn-Bi alloy with intermetallic compounds dispersed in the zinc matrix (Fig. 8).



**Fig. 8.** Microstructure of the Zn-Sn-Bi-Ni alloy, x400, with attack

At the simultaneous alloying with lead and bismuth we obtain finer and uniform layers with the same aspect of the microstructure (Fig. 9 a and b) as the layer obtained in Zn-Sn-Bi-Ni alloy. The presence near bismuth of an important percentage of lead

increases significantly the fluidity of the melt, and the amount of zinc (phase  $\eta$ ) entrained on the sheet is smaller. Thus, a large amount of precipitates is formed in the zinc matrix and coalescing phenomena are manifested.



a) x400 with attack



b) x400, non-attack

**Fig. 9.** The microstructure of the coating layer obtained in Zn-Sn-Pb-Bi-Ni alloy (intermetallic compounds and lead crystals in dendrite zinc matrix)

#### 4. Conclusions

Microstructural analysis of the layer obtained in Zn-Bi alloy, with 0.36% Bi, shows a decrease in the phase layer  $\eta$  due to the increase in melt fluidity in presence of Bi. The Zn-Fe alloy layer does not change significantly from pure zinc coating.

Tin leads to an increase in layer thickness of the coating and for this reason, tin is not added alone to the zinc bath and it is accompanied by a melt fluidity enhancing element such as lead or bismuth. In a concentration of over 2.5% tin acts on the layer of

Zn-Fe alloys to reduce it by forming a mechanical barrier between the intermetallic and zinc phase

In the structure of the protective layers obtained in Zn-Sn-Bi-Ni alloy is observed the effect on the iron-zinc alloy layer, which is drastically reduced. The effect is cumulative of nickel and tin, the bismuth acting on the thickness of the layer, in the sense of reducing it.

At the simultaneous alloying with lead and bismuth we obtain finer and uniform layers with the same aspect of the microstructure (Fig. 9 a and b) as the layer obtained in Zn-Sn-Bi-Ni alloy but the amount of zinc (phase  $\eta$ ) entrained on the sheet is smaller because the presence simultaneous of bismuth and lead increases significantly the fluidity of the melt.

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