ZINC COATINGS ON STEEL SUBSTRATE ATTAINED BY DIFFERENT ELEMENTS ADDED

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Abstract: The purpose of this work was to identify the influence of different process variables, such as bath temperature, immersion time and bath alloy additions, on the morphology and coating thickness attained using innovative alloys systems containing different percentages of Ni, Pb, Sn and Bi. Steel samples were galvanized by the hot-dip method in micro alloyed zinc baths at different temps and temperatures Experiments were aimed to obtain zinc coatings with increased resistance to corrosion, which adheres very well to steel support, not conducive Fe-Zn reactions, not have negative environmental impacts and presents uniformly dispersed phase structure in zinc matrix. Layers obtained in micro alloyed zinc with nickel, bismuth, tin, lead are analyzed.

Keywords: *galvanizing, Ni, Pb, Sn, Bi, thick layer, corrosion.*

1. Introduction

Hot dip galvanised coatings are widely used in industry for corrosion protection of steels. The steel is protected by the Zn coating through a barrier effect and a galvanic effect, in which Zn acts as the sacrificial anode while steel acts as the cathode. Although Zn has high corrosion resistance in most non-aggressive atmospheric environments, corrosion problems of Zn coatings have been often found in aggressive atmospheric environments where salt and sulphur dioxide are present. To overcome this problem, new types of Zn coatings with higher corrosion resistance are needed.

To increase the resistance to corrosion, adherence, limiting pollution and zinc-iron reaction, its use more and more alloyed zinc melts. Alloyed zinc melts in galvanising is ollso important in the case of Sandelin steel galvanising. It is characterized by the formation of thick layers and which can be hot - dip galvanised only in micro alloyed zinc melts. There is a great interest in carrying out research which explores the influence of the alloying elements in zinc melts on coating layers characteristics and the characteristics of the melts [1, 2, 3, and 4].

The paper aims to analyse the effect of small quantities of nickel, tin, bismuth and lead on the zinc melts.

Lead has an important role in zinc baths [2] that must be taken over by another micro-alloying element and the research in this area suggest the use of bismuth. Bismuth isn't toxic [3] and like lead it has the same fluidization effect on the melt also decreasing the superficial force [4; 5].

There is a great interest in carrying out research [1], which explores the influence of the alloying elements in zinc melts on coating layers characteristics and the characteristics of the melts. Thick layer of hot dip galvanizing process varies with temperature and immersion time and depends on the chemical composition of melt. Elements of micro alloying change the fluidity and surface tension of zinc melt and consequently drainage of zinc when support is extract from the melt [2, 3]. Immersion temperature affects both quality and quantity of zinc deposit on the surface of bands and produce ash, slag and dross. The usual working temperature in galvanizing process is chosen between 450-460^{o}C. At lower temperatures is more difficult adhesion between zinc and steel and at higher temperatures (over 470^{o}C) when the layer thickness starts to decrease, Fe-Zn alloys begin to break passing interface in the melt and form a large amount of dross. Time of immersion is determined by the thickness of steel sheet and desired thickness of the layer. For a given temperature, a given composition to melt and the same work speed, increasing the duration of immersion leads to a corresponding increase in deposit weight. The optimal duration is determined by technology. Times too small leading to defective adhesion and uniformity, and too large leading a strong attack, large layer of alloy Zn-Fe and the emergence of such compounds in the melt (matt, ash), [5].

2. Experimental research

In the framework of the research were analyzed four different zinc melts micro alloyed with nickel, tin, bismuth, lead whose chemical composition is presented in Table 1.

It has galvanized steel sheet to chemical composition according to Table 2.

Table 1. The chemical composition of micro alloyed Zn melts

Alloy	Ni [%]	Bi [%]	Sn [%]	Pb [%]	Zn [%]
Zn-Ni-Bi-Sn	0.16	0.71	2.95	-	96.18
Zn-Ni-Pb-Sn	0.16	-	2.88	0.72	96.24
Zn-Ni-Pb-Bi-Sn	0.16	0.41	3.49	0.43	95.51

Table 2. The chemical composition of steel support, in %

C	S	Mn	P	S
0,030	0,030	0.300	0,015	0,010
Al	Ti	V	Ni	Cr
0.046	0.002	0.001	0.008	0.025

For the preparation of the zinc bath, pure zinc (SHG) was used.

Micro alloying with nickel, bismuth, tin, and lead was made directly, using metallic elements, 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^{0}C.

Experimental immersion times were 3, 5, 8, 15 seconds. In the experiments did not apply any control and uniformity process, coating thickness resulting in free flow of zinc from the sample.

According to Zn-Ni phase diagram (Fig.1), nickel and zinc forms intermetallic compounds and solid solutions based compounds. Nickel is insoluble in zinc and at the 418^{o}C and 94.8% Zn forms the (σ + Zn) eutectic.

Alloying with Ni was made directly through the use of finely crushed Ni, (fine pieces < 1mm) and mechanical stirring. Micro alloyed process is longer, being at least one hour at the temperature of 700^{0}C.

Assimilation efficiency is low because nickel was lost in slag and dross (Table 3 and Table 4).

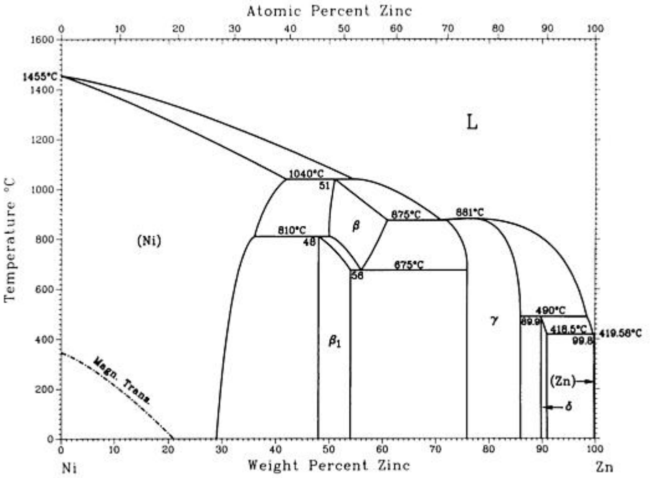


Figure 1: *The Zn - Ni phase diagram [6]*

Table 3. The chemical composition of dross

seample	**1**	**2**	**3**	**4**	**5**
Ni, %	0,024	0,021	0,034	0,022	0,018
Fe, %	0,024	0,024	0,021	0,025	0,024
Zn,%	diff.	diff.	diff.	diff.	diff.

Table 4. The chemical composition of slag

seample	**1**	**2**	**3**	**4**	**5**
Ni, %	0,019	0,021	0,024	0,016	0,018
Fe, %	0,016	0,020	0,021	0,020	0,020
Zn,%	diff.	diff.	diff.	diff.	diff.

Assimilation efficiency of the direct alloying experiments was found in 77%, measured three hours after the introduction of nickel (to calculate a concentration of 0.21% Ni and 0.16% Ni was obtained). In the literature it is recommended both directly alloying with metallic nickel and the use of alloys with a maximum of 5% nickel [5].

In the equilibrium diagrams of Zn-Bi (Fig.2), there is an insolubility of the two metals who forms a eutectic at 97.3% Bi and 254.5 ^{0}C. Given the low melting temperature of bismuth (271^{0}C) micro alloying was made with metallic bismuth, grinding and mixing in the melt by mechanical stirring.

Assimilation process of bismuth in the melt was stable, maximum efficiency is obtained. Bismuth is a micro alloying element used to replace lead, the same effect of melt fluidity and reduction of surface tension without being toxic.

Micro alloying the melt with 0.1% Bi, influences surface tension and fluidity similarly using a Pb content of ~ 1% [5,7]. Although bismuth is more expensive, the quantity needed for alloying bath is much lower, costs are compensated. Bismuth is also very stable in the melt and requires replenishment just proportional added zinc.

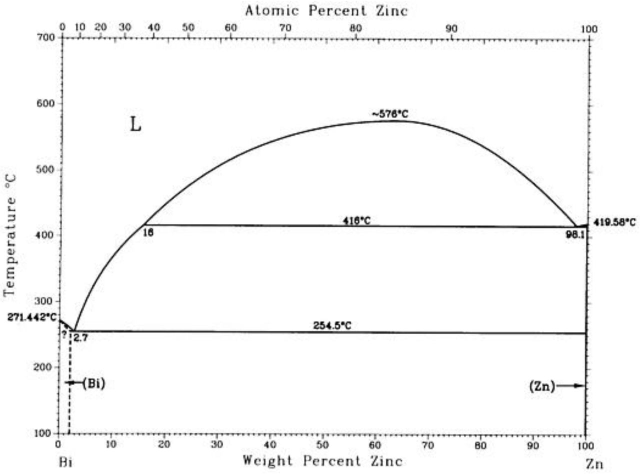


Figure 2: *The Zn - Bi phase diagram [6]*

In the experiments, micro alloying with tin was made with metallic tin. Sn-Zn equilibrium diagram (Fig.3) shows a total insolubility of this element in zinc with the formation of a eutectic at 198.5 ^{0}C and 91.2% Sn. Tin, like most analyzed elements form intermetallic compounds with nickel.

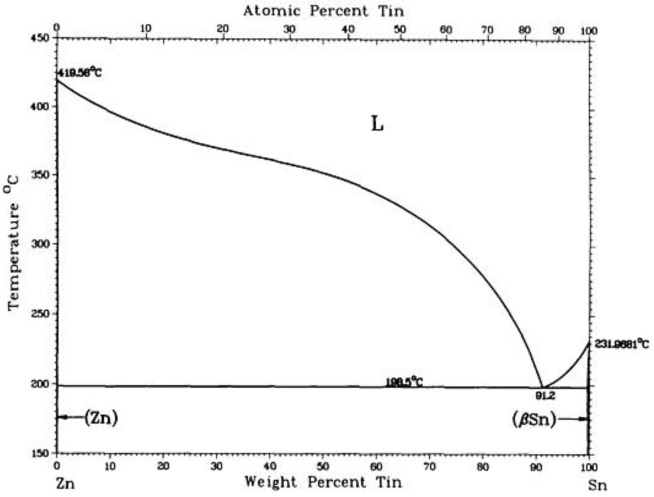
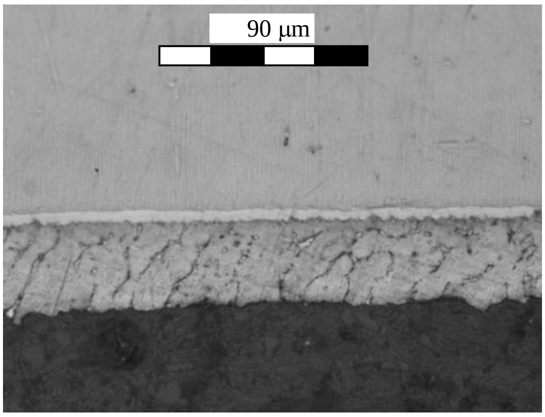
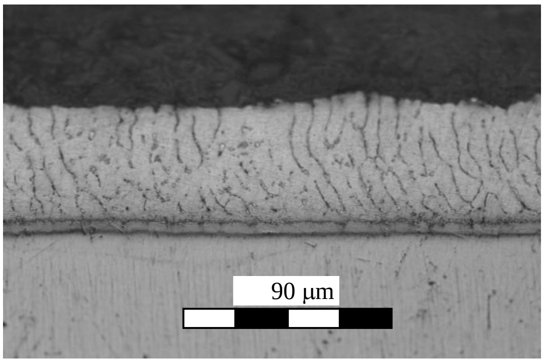


Figure 3: *The Zn – Sn phase diagram [6]*

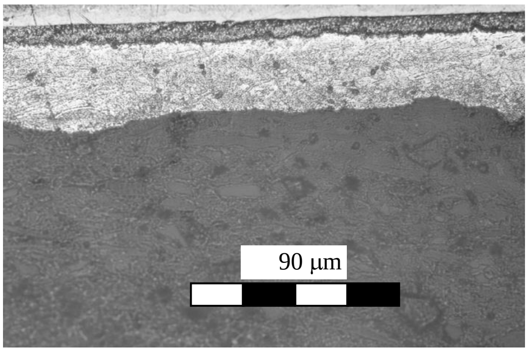
Microstructure of coatings obtained is presented in Fig. 4. It shows a thin layer of intermetallic compounds Zn-Fe and metallic layer consisting of intermetallic compounds (Zn-Ni, Zn-Ni-Sn, Ni-Sn, Ni-Bi) finely dispersed in zinc matrix.



a) Ni-Sn- Bi



b) Ni-Sn- Pb



c) Ni-Sn- Pb-Bi

Figure 4: *Microstructure of coatings obtained in zinc alloyed*

Analysing changes in layer thickness of coatings obtained from micro alloying with nickel (and elements for improving fluidity and structure) shown in Figs 5, 6 and 7. At 450^{0}C, is observed poor uniformity and high values of thickness, compared with 460^{0}C operating temperature of melt. After the trials for these types of coatings is proposed technological temperature of 460^0C and maintenance period of 3-5 seconds. The elements of micro alloying used can enhance the surface quality of the zincked steel by: uniformity, texture, and luminosity. This surface layer is dependent on the melting fluidity, its superficial tension and the solidification characteristics.

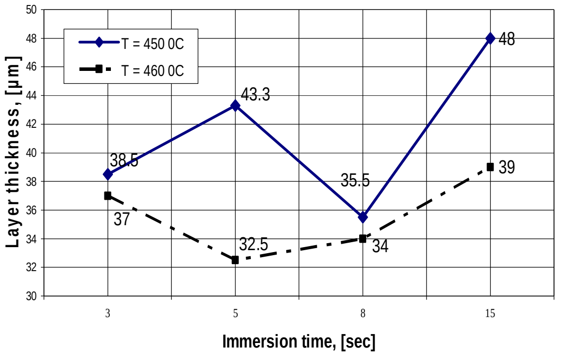


Figure 5: *Layer thickness variation depending on temperature and duration of immersion, (alloyed Zn with Ni-Bi-Sn)*

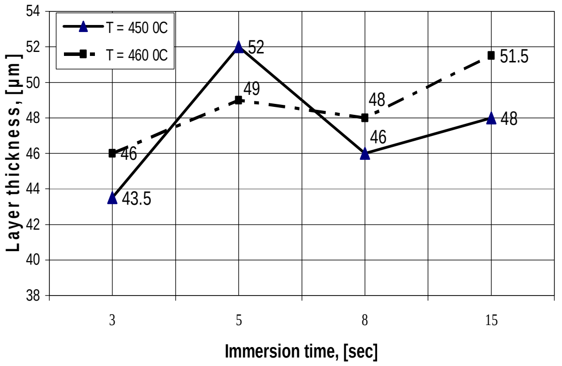


Figure 6: *Layer thickness variation depending on temperature and duration of immersion, (alloyed Zn with Ni-Pb-Sn)*

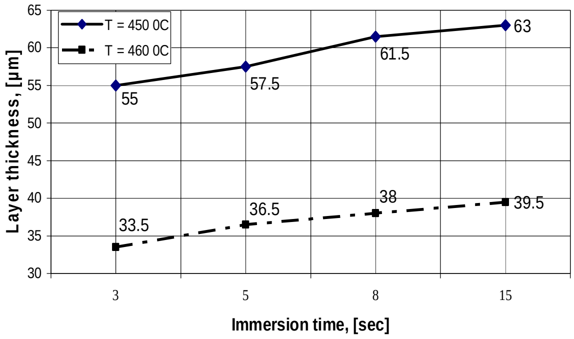


Figure 7: *Layer thickness variation depending on temperature and duration of immersion, (alloyed Zn with Ni-Pb-Bi-Sn)*

According to the combination of the micro alloying elements the surface can have different types of metallic layer which can have an important effect on the coating aspect.

One can notice the changing of the surfaces' morphology according to the micro alloying elements as compared to surface morphology resulted at the coating with pure zinc; thus, at micro alloying with Ni-Sn-Pb, the surface morphology reveals the forming of some big crystals with a fan aspect (Fig. 8). If a part of Pb is changed to Bi the crystals are significantly getting finished (Fig. 9).

Figure 8: *The coating morphology with Zn-Ni-Sn -Pb, x50*

Figure 9: *The coating morphology with Zn-Ni-Sn-Pb-Bi, x50*

For measuring the corrosion 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 corrosive environment used for electrochemical tests was a solution of 3% NaCl at room temperature.

The samples were prepared for analysis by being degreased with acetone, washed and dried [5].

From the experimental data obtained from measurements we chose representations in the form of Tafel, lg. I_{cor} - f(E_{cor}) polarization curves. The analysis of the graphical representations (Figs. 10-12) made it possible to determine the characteristic quantities of corrosion: corrosion current intensity I_{cor}, corrosion potential E_{cor}, corrosion current density i_{cor}, corrosion speed v_{cor} and penetration index p is show in Table 5. Corrosion behavior in seawater appreciated by electrochemical tests show a lower resistance to corrosion coating with Zn-Ni-Pb-Bi-Sn. Comparing the chemical composition of the threetypes of coatings is a big difference in content of tin (more than 3% in sample no.3).

Table 5. Values of the corrosion process

Tip of coating	i_{cor} [A/m^2]	v_{cor} [g/m^{2}h]	p [mm/an]
1. Zn- Ni-Bi-Sn-Cd	8.6230	0.0253	0.0012
2. Zn- Ni-Pb-Sn	9.2242	0.0271	0.0013
3. Zn- Ni- Pb-Bi-Sn	13.8614	0.0405	0.0020

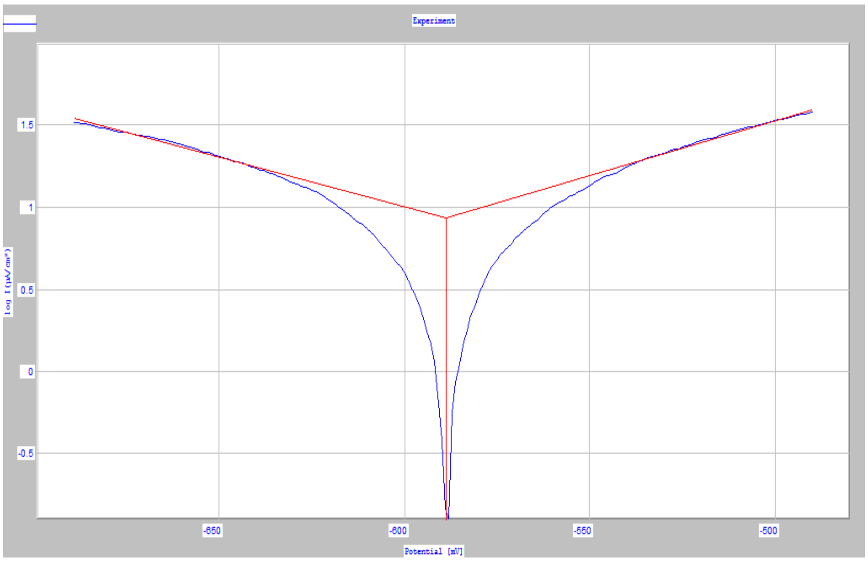


Figure 10: *Tafel curve for Zn-Ni-Bi-Sn*

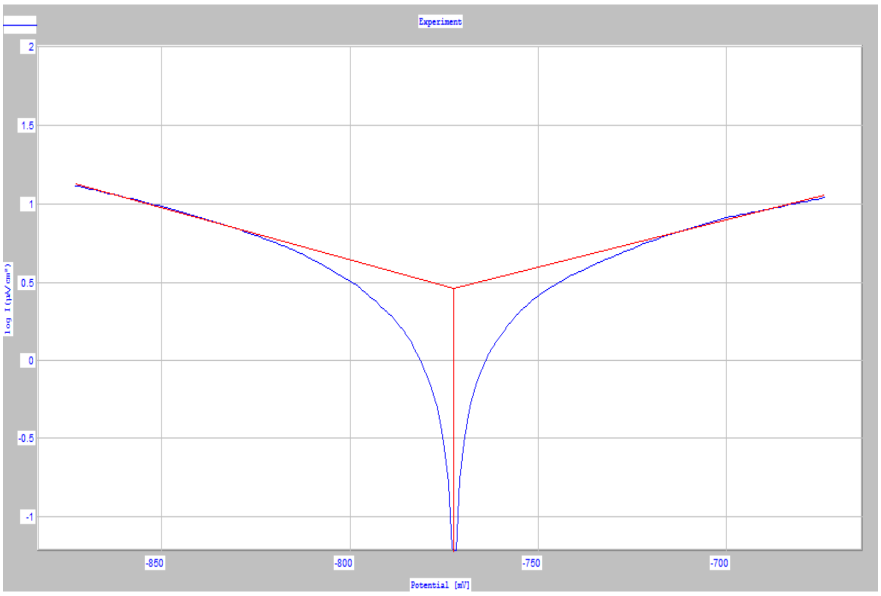


Figure 11: *Tafel curve for Zn-Ni-Pb-Sn*

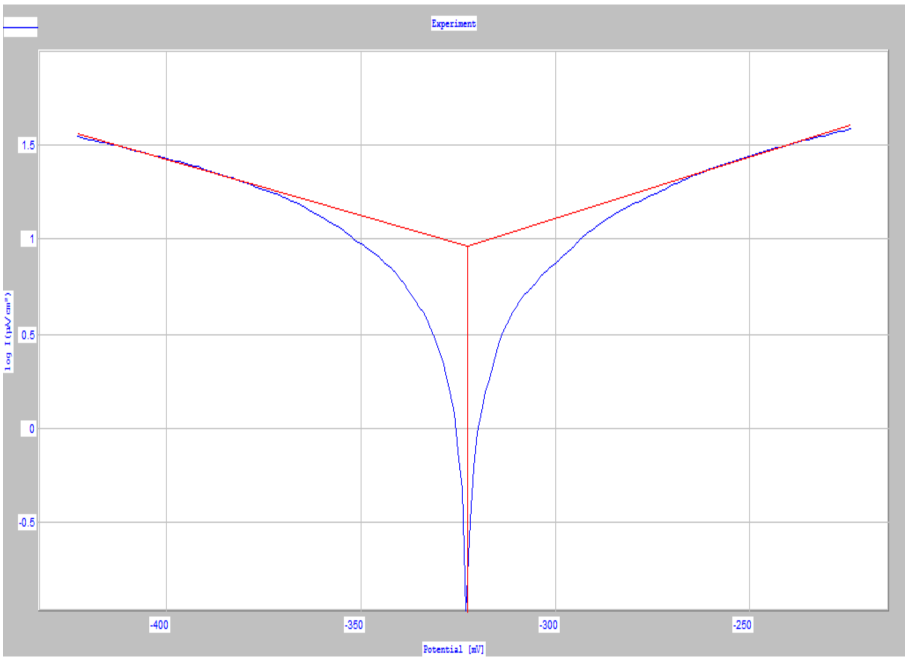


Figure 12: *Tafel curve for Zn-Ni-Pb-Bi-Sn*

Conclusions

- coating thickness is less at the same time adding lead or lead and bismuth show a higher fluidity for zinc melt.

- Microstructure shows a thin layer of intermetallic compounds Zn-Fe and metallic layer consisting of intermetallic compounds (Zn-Ni, Zn-Ni-Sn, Ni-Sn, Ni-Bi) finely dispersed in zinc matrix.

- At alloying with Ni-Sn-Pb surface morphology reveals the forming of some big crystals with a fan aspect. If a part of Pb is changed to Bi the crystals are significantly getting finished.

- Corrosion behavior in seawater appreciated by electrochemical tests show a lower resistance to corrosion coating with Zn- Ni- Pb-Bi-Sn.

References

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