THE SYNERGISTIC EFFECT OF THE OPTIMAL AlNi ADDITION TO THE ZINC BATH AS AN ALTERNATIVE TO THE BATHS CONTAINING Pb, Bi AND Sn

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Abstract

The existing knowledge on the use of alloying additives in the zinc bath was analyzed. The appropriate content of alloying additives in the bath affects the quality of the coatings and also optimizes the consumption of zinc. Al and Ni are currently used as standard bath alloying additives. Zinc baths also contain Pb, Bi and Sn, interchangeably used, as standard. These metals improve the fluidity of liquid zinc, which results in a beneficial reduction of zinc consumption and improves the appearance of the coating. However, the presence of Pb in the bath should be limited due to its toxicity, while Bi and Sn increase the risk of liquid metal embrittlement (LME). These metals can also contribute to lowering the corrosion resistance of coatings. An alternative to the currently used baths containing Pb, Bi or Sn can be a bath containing only the addition of AlNi. The article specifies the optimal concentration of Al and Ni addition for the bath. The synergistic effect of AlNi addition on the kinetics of coatings growth in the temperature range of 440-460 °C was determined. The microstructure was disclosed and the chemical composition in the micro-areas of the coatings on low-silicon steel and on steel from the Sandelin range was determined. It was found that the synergistic effect of the optimal AlNi additive content allows to obtain coatings with the correct appearance and thickness meeting the requirements of EN ISO 1461. The AlNi content effectively reduces the reactivity of Sandelin's steel. The coatings obtained in the bath containing only the AlNi additive have a similar structure and thickness to the coatings obtained in the alternative baths containing Pb, Bi or Sn.

Keywords: Hot-dip galvanizing, zinc coatings, alloying additives

1.   INTRODUCTION

The hot-dip galvanizing technology is currently one of the basic methods of protecting steel against corrosion. Its development is focused on the search for possibilities of improving the quality of the coating and reducing the consumption of zinc. This goal is achieved by the appropriate selection of alloying additives for the galvanizing bath, the synergistic effect of which allows to reduce the amount of zinc ashes, the reactivity of steel and improve the processability of the bath. The standard bath contains Al, Ni and a group of metals that improve the fluidity of the zinc bath: Pb, Bi and Sn [1]. The addition of Al protects the surface of the zinc bath against excessive oxidation, which significantly reduces the amount of zinc ashes. Already at the content of 0.005 wt% Al, a barrier layer of Al_2O_3 is formed on the surface of the bath, which protects it against further oxidation [2]. Currently, the addition of Al is used as a standard, which contributes to the reduction of zinc consumption. The addition of Ni allows to limit the reactivity of the steel caused by the Si content in the Sandelin range. Nickel effective interaction in the bath is achieved by keeping its content from 0.04 up to 0.06 wt% [3]. Lead, bismuth and tin are a third group of alloying additives that are used interchangeably to improve the fluidity of liquid zinc. Lead lowers the surface tension of liquid zinc and improves the fluidity of the bath. The zinc bath has the best fluidity with the Pb content in the range of 0.4-0.5 wt% [4]. Addition of 0.1 wt% Bi gives a similar intensity of liquid zinc flowing from the surface as approx. 1 wt% Pb [5], which means that its required content in the bath is almost 10 times lower. Often a supplement to bismuth is the addition of Sn, which also

improves the castability of zinc [6]. Additions of Pb, Bi and Sn, in addition to having a beneficial effect on the course of the galvanizing process, also have an unfavorable effect. Lead is harmful to both human health and the environment. In the EU and the USA, its use as an alloying additive in a zinc bath is in many cases limited [7]. An alternative to the addition of lead is bismuth and tin which are not harmful to the environment. It was found, however, that Bi [8] and Sn [9] may contribute to cracking of the structure during galvanization as a result of the phenomenon of liquid metal embrittlement (LME). The German Directive DASt-Richtlinie 022 [10], which is applied in many countries, limits the content of Bi and Sn in the bath when galvanizing responsible building structures. Recent studies also show that the presence of Pb, Bi and Sn in the bath can reduce the corrosion resistance of coatings [11-13]. The article presents the results of research on the growth kinetics and structure of coatings obtained on low-silicon steel and Sandelin's steel in a bath with optimal Al and Ni content without the addition of the traditionally used Pb, Bi and Sn additives. A zinc bath containing only Al and Ni additives, although it is not used on an industrial scale, is currently an alternative to eliminate the undesirable effects of Pb, Bi and Sn additives.

2. MATERIALS AND METHODOLOGY

Steels with a content of 0.01 wt% Si (low-silicon) and 0.04 wt% Si (Sandelin) were the substrate materials for the tests. The content of P in this steel did not exceed 0.02 wt% which minimizes the influence of this element on the course of the reaction between Fe and Zn. The chemical composition of the steels and galvanizing bath is presented in **Table 1**. The galvanizing bath was prepared from electrolytic zinc (99.99%). Al and Ni were introduced in the form of ZnAl4 and ZnNi0.5 mortars. The content of Al and Ni was maintained during the research at the level considered to be optimal. Before starting the tests, Fe was dissolved in the bath until it was saturated. The steel samples were galvanized at temperature: 440, 450 and 460 °C with the immersion time of 60, 150, 300 and 600 s. Before immersion in the zinc bath, samples were degreasing, etching and fluxing. After removal from the bath, samples were cooled in air. In order to determine the structure of the coatings, metallographic tests were carried out on the GX51 light microscope (Olympus) together with the analySIS software allowing for image recording. The thicknesses of the coatings were determined using a DeFelsko PosiTector 6000 inductive-magnetic meter. To determine the chemical composition of the coatings, the EDS X-ray spectral analysis was performed. The tests were carried out on a Hitachi S-4200 scanning electron microscope with a microanalyzer, using the Voyager 3100 software from Noram Instruments.

Table 1 Chemical composition of steel and bath for galvanizing

| Steel grade	Content (wt%)					
	C	Si	Mn	S	P	Fe and other
Low-silicon	0.018	0.012	0.366	0.009	0.007	residue
Sandelin	0.072	0.043	0.639	0.014	0.011	residue
Bath for galvanizing	**Al**	**Fe**	**Ni**	**Pb**	**Sn**	**Bi**	**Zn and other**
	0.007	0.031	0.051	0.0011	0.0007	0.0001	residue

3. RESULTS OF RESEARCH

The average total thickness of the Zn-AlNi coatings depending on the immersion time is shown in **Figure 1**. Analyzing the influence of the immersion time on the thickness of the coatings obtained in the temperature range of 440-460 °C (**Figure 1a**), it can be concluded that on low-silicon steel with the extension of the immersion time in the bath, the increase in the thickness of the coating is slower and slower. The same coating growth can be observed on steel from the Sandelin range (**Figure 1b**). It can also be observed that an increase in temperature contributes to an increase in the thickness of the coating. However, the nature of the growth curve, the course of which is parabolic, does not change. Obtaining such a course of the growth curve is particularly important for Sandelin's steel, where the coating growth is very rapid and has a linear course [14]. In the tested Zn-AlNi bath, the addition of Ni [15] to the bath made it possible to eliminate the Sandelin effect.

On low-silicon steel, the obtained coating thicknesses are comparable to the thickness of the coatings obtained in alternative baths containing Pb, Bi and Sn. In the tested Zn-AlNi bath at the temperature of 450 °C and immersion time of 150 s, a coating of 51.01-1.79 µm on low-silicon steel and 48.20-1.82 µm on Sandelin's steel was obtained. For comparison, at the same temperature and immersion time of 180 s the average thickness of the coatings on low-silicon steel was 53.69 µm in the Zn-AlNiPb bath [11], 51.09 µm in the Zn-AlNiBi bath [12] and 54.45 µm in Zn-AlNiBiSn bath [13]. In the tested Zn-AlNi bath, it is possible to obtain coatings with a thickness meeting the requirements of EN ISO 1461 on low-silicon steel and Sandelin's steel. The cross-sectional appearance of the coating obtained at 440 °C on low silicon steel is typical. The coating shows a layered system of phases, from the steel substrate of the δ_1 phase layer with a compact structure and the ζ layer with characteristic crystallites entering the outer layer of the coating and the solution of iron in zinc - η (**Figure 2**). The outer layer is a zinc alloy layer containing dissolved iron. Along with the extension of the immersion time, a clear increase in the thickness of the δ_1 phase layer is observed. On the other hand, the increase in the bath temperature causes a marked decrease in the thickness of the ζ phase layer and the increase in the thickness of the δ_1 phase layer. The ζ phase layer is in direct contact with the liquid zinc. Under such conditions, its growth is determined by the reactive diffusion of iron and zinc, but also by dissolution in liquid zinc [16]. The decrease in the thickness of the ζ phase layer may therefore indicate an increase in the speed of dissolution processes at higher temperatures and their dominance over the processes of diffusive growth of this phase.

a)   b)
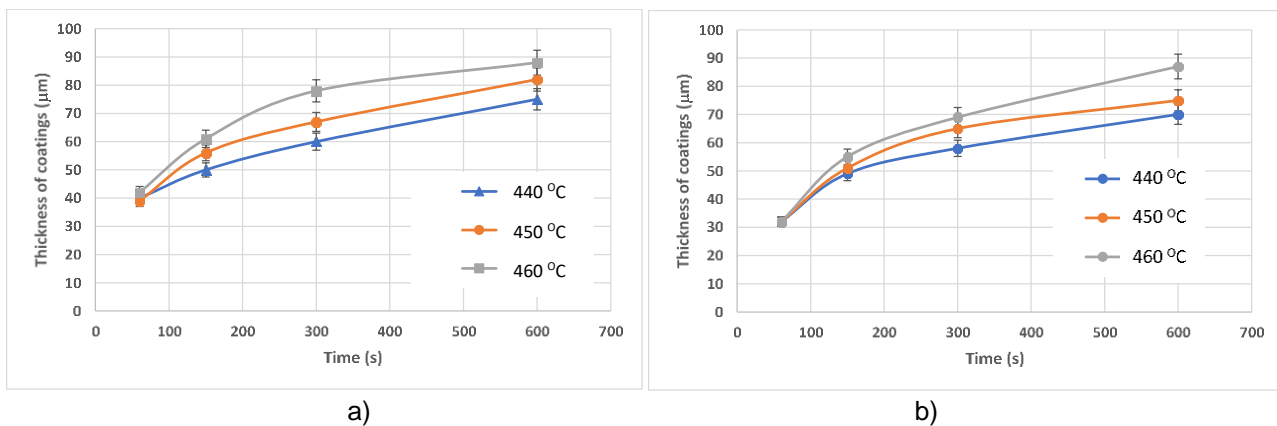
Figure 1 Kinetics of coatings growth obtained on: a) low-silicon and b) Sandelin's steel (Zn-AlNi bath)
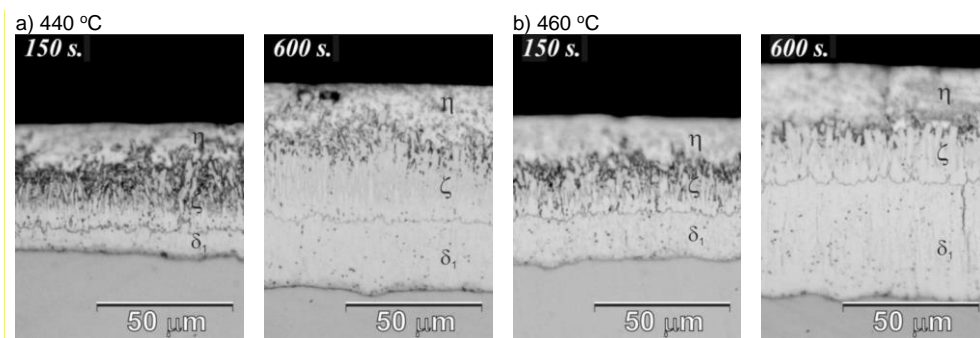
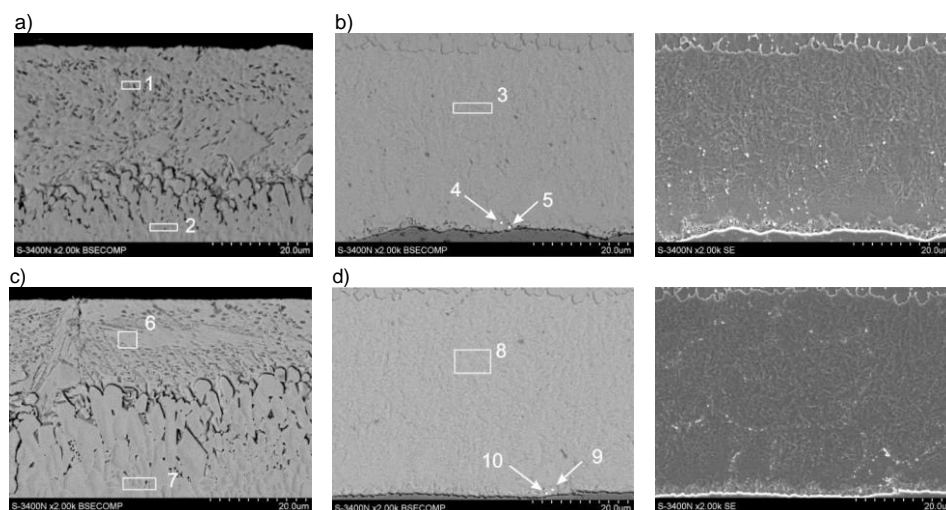**Figure 2** Structure of coatings obtained in Zn-AlNi bath on low-silicon steel

A similar layer structure is demonstrated by coating obtained in the Zn-AlNi bath on Sandelin's steel (**Figure 3**). The structure of the coating obtained on Sandelin's steel is not the typical structure that is formed on steels with silicon content corresponding to the Sandelin range. In this range of silicon concentration, it should be expected a coating with a significantly expanded diffusion layer. As a result of the intensifying influence of Si, the ζ phase increases with a simultaneous decrease in the thickness of the δ_1 phase [6]. Analyzing the structure

of the obtained coating, it can be concluded that the growth of Fe-Zn intermetallic phases in the diffusion layer is identical to that of low-silicon steel. However, the ζ phase layer on Sandelin's steel shows a different morphology compared to the coating on low silicon steel. Its structure is more columnar and, especially at higher temperature and longer immersion time, it lacks a compact zone, and the oblong crystals are located directly on the δ_1 phase layer (see **Figure 3b**, 600s).
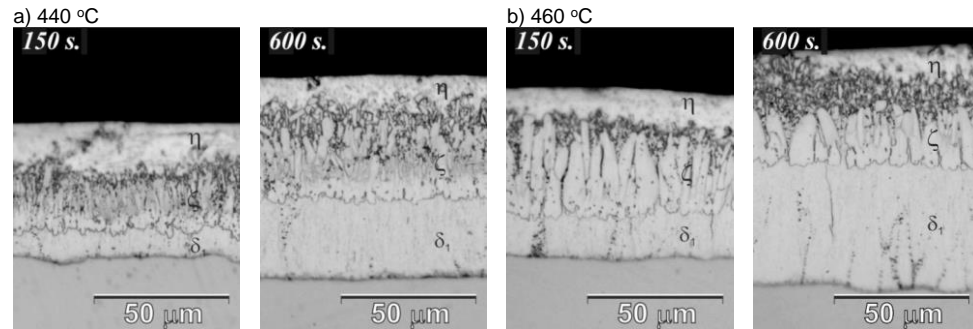
Figure 3 The structure of the coatings obtained in the Zn-AlNi bath on Sandelin's steel

Chemical composition tests were carried out in the characteristic micro-areas of the obtained coatings. The image of the coating obtained on low-silicon steel is shown in **Figures 4a, b**. The percentages of the analyzed elements in these areas are given in **Table 2**. EDS analysis showed that the composition of coating outer layer mainly contains Zn (point 1). A small amount of iron was found in the outer layer. A zinc bath always contains dissolved iron, the content of which can reach a saturation level of 0.03 wt% at 450 °C [17]. The outer layer is thus a solid solution of Fe in Zn η [16]. The analysis of chemical composition in selected areas of the diffusion layer indicates the presence of more iron in it. The chemical composition of point 2 may correspond to phase ζ and point 3 to phase δ_1. At the border with the substrate, a thin, uneven layer with a high Fe content can be observed. Two areas with different Fe content can be distinguished in this zone. The chemical composition of the light area (point 4) may correspond to Γ_1 phase, and the dark area (point 5) to Γ phase. The microstructure of coating obtained on the Sandelin's steel is shown in **Figures 4c, d**. EDS analysis shows that the outer layer of the coating contains mainly Zn as well as approx. 0.1 wt% Fe (**Table 2**, point 6). This confirms the presence of a solid solution of Fe in Zn η in this region. The remaining points of the analysis are similar to the analysis obtained on low-silicon steel. On Sandelin's steel, the presence of areas at the border with the ground was also found, the chemical composition of which may correspond to the phases Γ_1 (point 9) and Γ (point 10).

Figure 4 Microstructure of the Zn-AlNi coating on low-silicon steel: a) outer layer, b) diffusion layer; on Sandelin's steel: c) outer layer, d) diffusion layer; temperature 450 °C, immersion time 600 s

The coatings obtained in the Zn-AlNi bath show a typical layered structure formed by phases of Fe-Zn system. No components containing Al and Ni, which are alloying additives to the zinc bath, were found in the coating. Coatings of a similar structure are obtained in the case of the Pb, Bi and Sn, additives commonly used in the zinc bath. However, all these metals show limited solubility both in Zn and in the intermetallic phases of Fe-Zn system. According to Zn-Pb equilibrium system [18], lead is not soluble in solid zinc. Also, Bi-Zn equilibrium system [19,20] indicates the lack of solubility of Bi in Zn and Zn in Bi, and the Sn-Zn equilibrium system [21,22] shows the lack of solubility of Sn in Zn. The effect of such behavior is the formation of Pb [11], Bi [12] and Sn [23] precipitates, mainly in the coating outer layer and on the coating surface. Especially when bath contains the combined addition of Bi and Sn, intense precipitation of these metals is observed on the coating surface [13]. The precipitates have a two-phase structure of the SnBi alloy as the solubility of Bi in Sn is limited to 1.7 wt% [24], while tin does not form a solution with Bi in the solid state at all [25]. The available literature does not clearly confirm the lack of solubility of Pb, Bi and Sn in the intermetallic phases of Fe-Zn system. However, the studies conducted so far have not shown the presence of these metals in the intermetallic phases of Fe-Zn system [11-13]. These metals are released mainly in the area of the intermetallic phase ζ, which shows the greatest heterogeneity in structure. The presence of Pb, Bi, Sn and BiSn precipitates does not affect the coating layered structure; the morphology and phase composition are similar to those obtained in Zn-AlNi bath tested. However, the presence of Pb, Bi, Sn or BiSn alloy precipitates changes the electrochemical system between the structural components of the coating. This is of great importance for the corrosive action as Pb, Bi as well as Sn are more cathodic to Zn (Zn $E°(Pb^{2+}/Pb)$=-0.1262 V, $E°(Bi^{3+}/Bi)$=0,308 V, $E°(Bi^+/Bi)$=0,5 V, $E°(Sn^{+2}/Sn)$=-0.1375 V, $E°(Zn^{2+}/Zn)$=-0,7618 V; vs. SHE [26]).This leads to the formation of corrosion cells in which Zn is the anode and dissolves, while the precipitates containing Pb, Bi and BiSn, being a cathode, are in a rather passive state [27]. Consequently, Zn is used to protect the precipitates rather than to protect the steel substrate. Corrosion resistance tests in accelerated corrosion tests of coatings confirmed the reduction of corrosion resistance of coatings obtained in baths containing Pb, Bi and Sn. Also, these coatings showed higher values of corrosion current density (i_{corr}) compared to coatings obtained in baths without the addition of these metals [11,12,13]. Tests carried out in Zn-AlNi bath show that removing the Pb, Bi and Sn additives from the bath does not significantly affect the coating thickness and structure. The lack of structural components containing these metals in the coating may, however, improve the corrosion resistance.

Table 2 Chemical composition in selected micro-areas of the coating obtained on low-silicon (point 1-5) and Sandelin (point 6-10) steel in a Zn-AlNi bath (analyses points as shown in **Figure 4**).

Point of measurements - low-silicon steel	Content of elements				Point of measurement – Sandelin's steel	Content of elements			
	Fe-K		Zn-K			Fe-K		Zn-K	
	(wt%)	(at%)	(wt%)	(at%)		(wt%)	(at%)	(wt%)	(at%)
point 1	0.2	0.2	99.8	99.8	point 6	0.1	0.1	0.1	0.1
point 2	6.2	7.2	93.8	92.8	point 7	7.1	8.2	7.1	8.2
point 3	9.0	11.4	90.1	88.6	point 8	11.2	12.9	11.2	12.9
point 4	18.9	21.4	81.1	78.6	point 9	19.4	22.0	19.4	22.0
point 5	32.6	36.2	67.4	63.8	point 10	35.1	38.8	35.1	38.8

4.   CONCLUSION

The conducted tests provided the basis for determining the synergistic effect of the AlNi additive in the bath on the coating formation on steels with different silicon content. When analyzing the structure of coatings on the tested steels, it should be stated that it is correct. No influence of alloying elements in the bath on the coatings formation on steels below the Sandelin range is observed. On the other hand, the limiting effect of AlNi additives on the coating formation on steel from the Sandelin range is clearly visible. In the tested bath, the rapid increase in the coating thickness, characteristic of Sandelin's steel, is stopped. The conducted tests allow to conclude that the coatings obtained in the Zn-AlNi bath on Sandelin's steel have a structure typical for

steels with low silicon contents. The nature of the changes in the thickness of the coatings with the extension of the immersion time is also similar. Summarizing the test results, it should be stated that the proposed chemical composition of the bath guarantees obtaining zinc coatings with the correct structure and allows to limit the thickness of the coatings on steels in which the silicon content is considered critical for the galvanizing process. The Zn-AlNi bath is an alternative to applications where Pb, Bi and Sn additions are undesirable.

ACKNOWLEDGEMENTS

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