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THE EFFECT ON SOME CONTROLLING FACTORS OF QUALITY OF HOT-DIP GALVANIZED COATINGS

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Abstract: *This article presents a study related to hot-dip galvanizing as a method to protect the steel surface. Two types of alloys were studied: Zn-Al and Zn-Al-Ti-B, each in 5 different concentrations. Besides the composition of the deposited alloys as variable parameters the immersion time of the steel samples in the galvanizing bath and the bath temperature were also taken into consideration. In this study, it was observed the effect of these parameters on the thickness of galvanized layers, the aspects related to the structure and the adhesion of deposited layers onto steel substrates. Thermal analysis studies were made to highlight the effect of Zn alloy composition and galvanizing temperature on the structural transformation in deposited layer.*

Key words: *hot-dip galvanizing, chemical composition, galvanizing temperature, immersion time, DSC analysis.*

1. Introduction

Steel remains the material most widely used both in domestic and industrial applications due to its excellent properties. But one of its weaknesses is low resistance to corrosion and wear. Due to this disadvantage various protection methods have been developed to improve the life of steel against corrosion and wear [3].

One of the most efficient methods for protecting ferrous materials against oxidation and corrosion is the hot-dip galvanizing. This technique consists of applying a deposit by immersing the parts in a molten zinc bath, at temperatures between 440 ºC and 460 ºC, for a certain amount of time and their subsequent cooling in air [2], [6], [1]. To have an adequate protecting role, the deposited layer must have certain dimensional and structural characteristics. Under certain conditions, the reaction between the steel substrate and the liquid zinc bath leads to the formation of a very thick layer, with intermetallic compounds, mechanical properties and to subsequent processability of the inadequate coating [4], [10], [5], [9].

The quality of the galvanized steel products is influenced by the following main parameters: the chemical composition of the steel substrate, the chemical composition of

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the zinc alloy, the galvanization temperature and the period of the steel immersion in the galvanizing bath [2], [1], [7], [8].

In the deposited layer, as long as it is liquid, there is an active process of iron diffusion and other ferrous alloy elements. This in turn depends on all the parameters involved in the galvanization and it eventually decisively determines the structure and properties of the coating [2], [4].

2. Experimental Procedure

In the research two groups of alloys for galvanizing have been used: Zn-Al and Zn-Al-Ti-B with the compositions shown in Table 1 and Table 2.

The chemical composition of Zn-Al alloys Table 1

Alloy Set 1	**Chemical composition [%]**							
	Pb	Mg	Al	Cd	Fe	Sn	Cu	Zn
1.1	0.0008	0.001	0.868	0.000	0.007	0.0014	0.069	99.053
1.2	0.0006	0.001	0.713	0.000	0.005	0.0021	0.065	99.213
1.3	0.0007	0.001	3.790	0.000	0.011	0.0018	0.056	96.139
1.4	0.0008	0.001	3.994	0.000	0.012	0.0016	0.045	95.946
1.5	0.007	0.001	5.276	0.001	0.015	0.0020	0.038	94.668

The chemical composition of Zn-Al-Ti-B alloys Table 2

Alloy Set 2	**Chemical composition [%]**									
	Pb	Mg	Al	Cd	Fe	Ti	B	Sn	Cu	Zn
2.1	0.0139	0.001	1.107	0.003	0.003	0.055	0.011	0.0014	0.026	98.820
2.2	0.0120	0.001	2.137	0.003	0.005	0.430	0.080	0.0008	0.014	97.319
2.3	0.0221	0.001	2.198	0.003	0.005	0.430	0.080	0.0035	0.034	97.223
2.4	0.0181	0.001	2.518	0.003	0.003	0.500	0.100	0.0017	0.027	96.828
2.5	0.0103	0.001	2.559	0.003	0.003	0.510	0.100	0.0005	0.013	96.802

The experimental research program was carried out according to the scheme shown in Figure 1, where it is observed that during the coating process the variable parameters

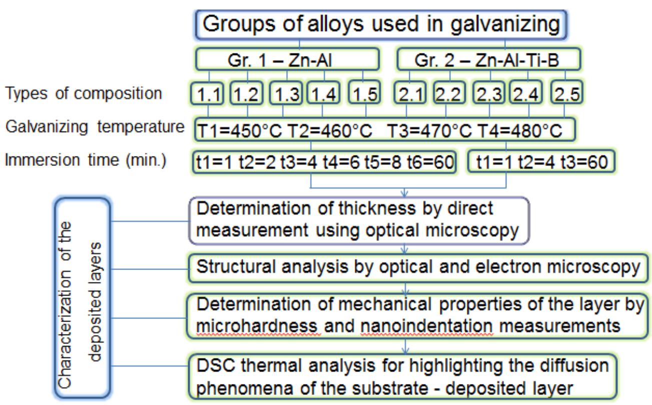


Fig. 1. *The experimental research program*

were: composition of the galvanizing bath (each 5 composition of each group of alloys), immersion temperature and dipping time of the steel samples into the molten zinc alloys bath.

The quality of the deposits by the hot-dip galvanizing process was estimated by the thickness of the obtained layer and the structure. For the assessment of the elements diffused from the steel substrate in the galvanized layer was carried out by a separate study, thermal analysis using the DSC (Differential Scanning Calorimetry) method.

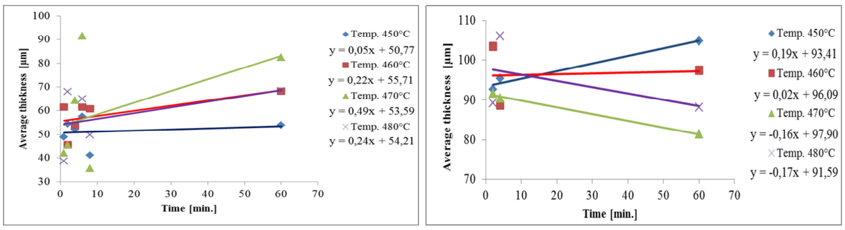
3. Results and Discussions

The coatings by hot-dip galvanizing have been carried out on steel sheet with a thickness of 3 mm and 1 mm. The characterization of the deposited layer was performed in multiple steps, the final results being arithmetic means for thickness, some representative areas for the structures, and other types of analysis.

3.1. Evolution of the Deposited Thickness Depending on the Working Parameters

The thickness of the deposited layer were examined in cross-sections of the samples, the measurements being performed by optical microscopy. In each case the final result was the average of at least 20 measurements. The obtained values were plotted according to the variable parameters during the experimental research.

The thicknesses of the coatings were between 35-112 µm for alloy group 1 and between 74-114 µm for alloy group 2. The graphical representation of the dependencies between the thickness of the deposited layer and the variable parameters in the study were performed so that in the same graph is displayed the dependencies between the thickness and two parameters: once according to time and temperature, once depending on the composition of the galvanizing alloy (%Al) and time and another time depending on temperature and composition. Such dependencies are shown in Figures 2, 3 and 4.



a) b)

Fig. 2. *The dependence of the deposited thickness on the immersion time: a) alloy 1.2; b) alloy 2.4*

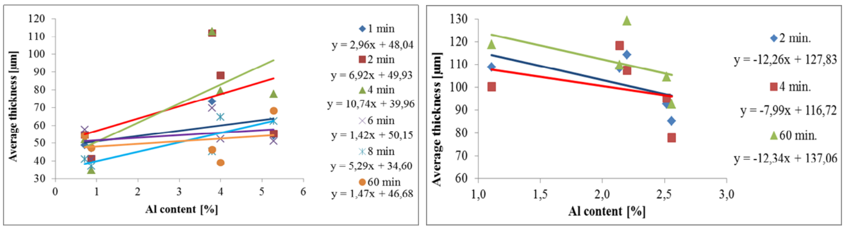


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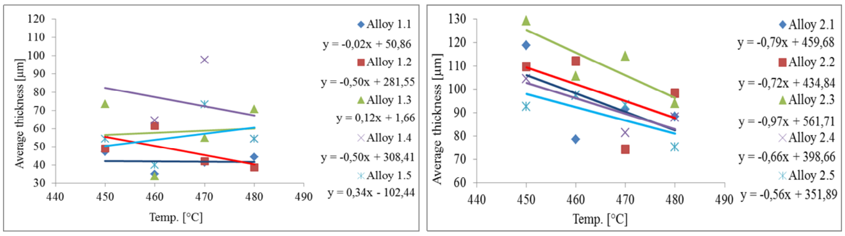
Fig. 3. *The dependency of the deposited thickness on the alloy composition for a galvanizing temperature of 450°C: a) alloy group 1; b) alloy group 2*



a) b)

Fig. 4. *The dependency of the deposited thickness on the galvanizing temperature: a) alloys 1 for an immersion time of 1 min.; b) alloys 2 for an immersion time of 60 min.*

From the analysis showed partially above it was observed that the dependency of the deposited thickness on the galvanizing temperature is correlated with the composition of the bath, but especially with the period of immersion in the bath. Following detailed research, it was found that for low immersion times of samples in the galvanizing bath, the lower temperatures may determine relatively high thicknesses of the deposited layer, but with inadequate structural and adhesion characteristics (Figure 4a). This is due to the fact that the galvanizing alloy cools rapidly in contact with steel samples, solidifying without other important interactions. Yet, as the temperature increases, the galvanizing bath maintains better fluidity in contact with samples, the layer becomes more uniform, with slightly smaller thicknesses and better characteristics (Figure 4b).

Differences of behaviour were observed between the two groups of alloys as shown in Figure 3. For alloys group 2, the thickness decreases with increasing the Al content compared to an existing growth trend to alloys group 1.

3.2. Structure Analysis

The structure obtained in the deposited layers was analysed by optical microscope (Nikon MA100) and electron microscopy (SEM, Hitachi, S3400N, using high vacuum).

According to previous studies the morphology of a galvanization layer obtained in a bath of pure molten zinc includes the following phases (Figure 5): the first phase formed on the steel substrate is a thin gamma (Γ) layer presenting a flat interface between the steel substrate and the delta layer, followed by the gamma1 (Γ1) layer. The second phase is the delta (δ) phase consisting of two layers showing the same physical characteristics but different metallographic structures. The delta (δ) phase has a columnar structure leading to a preferentially perpendicular growth on the interface with a microfracture appearance. The third phase is zeta (ζ), iron-repleted, growing with a columnar morphology. It can represent up to 50% of the deposit. And, finally, although not shown

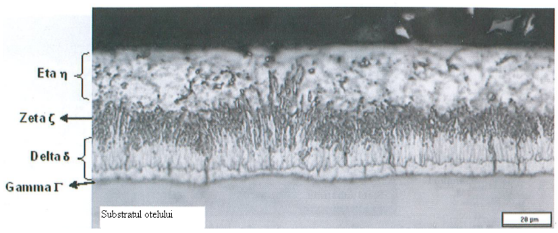
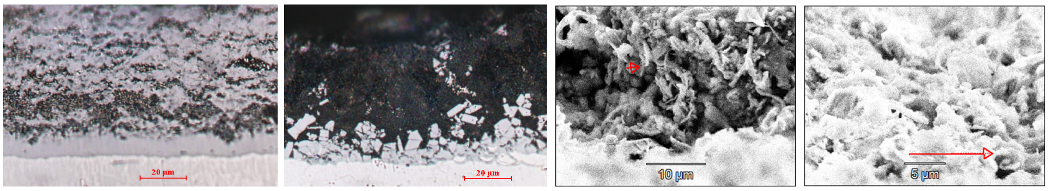


Fig. 5. *The microstructure of a hot dip galvanizing layer on a steel pipe* [2]

on the Fe-Zn equilibrium diagram, the eta (η) phase containing almost pure zinc which is in reality a solid solution of iron in zinc. In general, the gamma, delta and zeta layers are tougher than the steel substrate resulting in an exceptional protection against abrasion. As the eta layer is more ductile, it also improves impact resistance [2], [8].

There were found certain differences in the size and delimitation of areas, described in Figure 5, in the layers deposited in this study. This is clearly due to the presence of alloying elements in the galvanizing bath (Figure 6a). Furthermore, it was observed the existence of several compounds having typically polyhedral shape preferentially distributed near the steel substrate of sizes correlated mainly with the time and temperature of the immersion in the galvanization bath (Figure 6b).



a) b) c) d)

Fig. 6. *The microstructure of the deposited layers by optical microscopy: a) alloy 1.5 sample at a temperature of 450ºC immersed in the bath for 60 min.; b) alloy 1.1 sample at a temperature of 450ºC immersed in the bath for 60 min.; c and d) alloy 1.5 sample at a temperature of 480ºC immersed in the bath for 60 min. by electron microscopy*

The general structural observations showed that the presence of the polyhedral shaped compounds increases quantitatively with higher galvanizing temperatures and bath immersion times. The presence of these compounds influences decisively the mechanical properties of the layers, mainly their homogeneity in terms of these properties.

3.3. Thermal Analysis

For the thermal analyses there were sampled small pieces of ~80 mg, containing both a layer portion and a substrate one. They were subjected to the differential calorimetry study to determine the critical temperatures in the melting-solidification processes, also monitoring the possible transformations in solid state in the layer. These data provide information on changing the composition of the deposited layer from that of the galvanizing baths used, as a result of the diffusion processes between the substrate steel and the galvanizing layer.

There were plotted the variation curves of thermal effects with the temperature (DSC analyzes), at a temperature variation range of 5 °C/min. Critical data from these curves (eutectic temperatures, liquidus and solidus temperatures) were centralized and graphically processed according to the variable parameters established in the experimental research, similarly to the graphical representation of the dependencies for the thickness of the deposited layer.

In Figure 7 are shown the thermal analysis curves by DSC for the group alloys 1 at a given deposition temperature and an immersion time of 60 min.

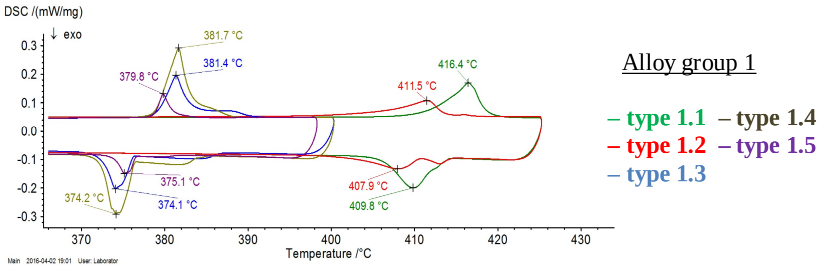
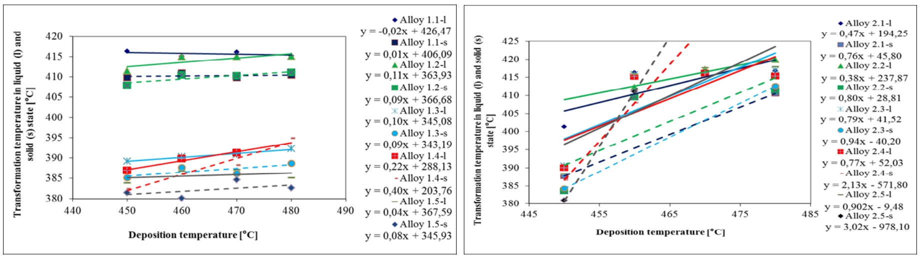


Fig. 7. *The dependence between the chemical composition of the alloy and the critical transformation temperatures at a galvanizing temperature of 450 °C*

The dependencies of the thermodynamic data extracted from the thermal analysis curves by the variable parameters in the experimental research were represented in the graphs as in Figure 8.

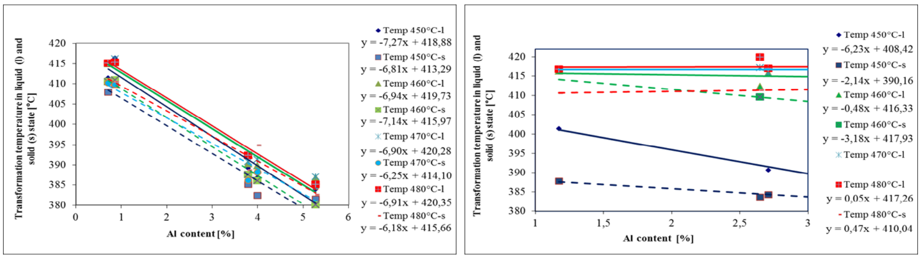


a) b)

Fig. 8. *The dependence between the melting (l) and solidification (s) temperatures of the alloy from the deposited layer by the galvanization bath temperature for: a) Zn-Al group alloys (Table 1) and b) Zn-Al-Ti-B group alloys (Table 2). Bath immersion time = 60 min.*

Figures 8a and 8b show that in all cases the increase in temperature of the galvanizing bath exacerbates the diffusion of elements from the steel substrate into the deposited layer. Given that Fe is the predominant element in this process of diffusion, the result is an increase in the melting and solidification temperatures of the alloy deposited in the layer. A higher intensity of this process is visible for Zn-Al-Ti-B alloys group, as compared to the Zn-Al alloys (the lines in Figure 8b have much higher slopes than those in Figure 8a). This difference can be attributed to the differences in the composition of the steel substrates, but to a greater extent to the presence of Ti and B in the second group of alloys used in galvanization.

The effect of the chemical composition of the galvanizing bath should be analysed in correlation with the appearance of the equilibrium diagram of the Zn-Al system. The studied compositions are on the right side of the diagram and the higher the concentration of Al (i.e. the Al-Ti-B sum), the lower the liquidus and solidus temperatures of the alloy deposited in the layer (Figures 9a and 9b). From this point of view there are significant differences between the two groups of the alloys. Thus, for Zn-Al group alloys (Figure 9a) it is observed that the effect of the chemical composition of the studied cases is the same (the slopes of the lines are the same, they are practically parallel). This indicates that the melting and solidification temperature changes are determined mainly by the action of other factors changed in the process (the immersion temperature and time in the galvanization bath). In relation to the phasic equilibrium diagram of the Zn-Al system, it can be translated by the upward movement of the liquidus and solidus curves (temperature rise) due to the Fe diffusion from the substrate into the deposited alloy.



a) b)

Fig. 9. *The dependence between the melting (l) and solidification (s) temperatures of the alloy from the layer deposited by the galvanization bath composition at different bath temperatures for: a) Zn-Al alloys; b) Zn-Al-Ti-B alloys. Bath immersion time = 60 min.*

For the Zn-Al-Ti-B alloys, there are important differences compared to that of the Zn-Al alloys (Figure 9a). As the temperature of the galvanizing bath increases, the lesser the impact of the chemical composition of the bath on the iron diffusion from the substrate into the layer. However the iron diffusion in the case of Zn-Al-Ti-B alloys is more active than in the case of the Zn-Al system alloys (correlation between Figures 8b and 9b).

4. Conclusions

The thickness of the layer deposited during galvanizing is a crucial quality parameter, the length of the anti-corrosion protection being approximately proportional to it. The study shows that the factors modified during the process (the composition of the galvanizing bath, the temperature and the immersion time) have an interrelated and complex influence on the thickness of the deposit. For deposits by hot-dip galvanizing of Zn-Al alloy layers, sufficiently good information for selecting working conditions is offered by the thermal equilibrium diagram of this binary system. Increasing working parameters such as bath temperature and immersion time determines in relation to the Zn-Al diagram an upward movement of the liquidus and solidus curves concurrently with the extension of the solidification range, as a result of the increased diffusion of Fe from the steel substrate in the deposited layer. The higher the solidification range of the deposited alloy, the more pregnant is the downward trend of the layer thickness. At the same time, the exacerbation of the Fe diffusion is associated with the increase of the amount of intermetallic compounds in the structure. They can have complex effects, such as, on the one hand, the improvement of the mechanical properties of the layer, but it could also create some inconvenience in terms of corrosion resistance.

The additions of elements such as Ti, B to the galvanization alloy cause significant changes in its behavior, becomes much more active in relation to the substrate, resulting in an exacerbation of the diffusion from the substrate into the layer. As a result increases the influence of the factors that influence the diffusion, respectively the galvanizing temperature and immersion time. Thus, in the case of the use of complex alloys for hot-dip galvanizing, a more rigorous control of the variation interval of the working parameters is required to obtain layers with thicknesses and structures corresponding to the requirements.

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