THE ASSESSMENT OF HEAT TREATMENT IMPACT ON HOT-DIP ZINC COATING STRUCTURE AND SELECTED PROPERTIES

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Abstract

In the presented paper the subject related to the heat treatment (HT) of hot-dip zinc coating was initiated. Authors assumed that in the future widely understood optimization of coating HT will results in both mechanical as well as functional properties improvement. Investigations were focused on the hot-dip zinc coating deposited at industrial conditions (acc. PN-EN ISO 10684) on the Fe-C alloys surface (steel and cast iron). In the paper beside basic information: microhardness measurements, optical microscopic observation also examples of EDS after HT are enclosed. It was stated that although the applied HT results in coating hardness increase, the too high temperature level may cause coating cracking and delamination. As the processing temperature increases, the coating structure changes - the iron content in individual Zn phases increases. Zinc coating deposited on cast iron is more inhomogeneous.

Keywords: Hot-dip zinc coating, heat treatment, surface quality

1. INTRODUCTION

The global production of zinc was over 10 million tons in 2008, 7 years later it increased by additional 2 million tons. The mining potential of this resource is 430 million tons and is growing all the time. Over half of the world's zinc resources are used to protect steel against corrosion in form of galvanizing [1]. Part of the zinc is used for hot-dip zinc galvanizing, which consists in keeping the pre-finished products in a zinc bath (the temperature of a bath is 455 - 480 ºC; time of the immersion is mainly a few minutes [2,3]). The product of galvanizing process is a coating deposited on a metal product with a thickness adjusted to the thickness of the coated parts [4]. The zinc coating structure consists of intermetallic Fe-Zn compound layers, which have been identified as gamma (Γ, $Γ_1$), delta (δ), zeta (ζ) and eta (η) outer layer highly rich in Zn. The iron content in individual phases is shown in **Table 1** [5,6].

Table 1 The content of iron in the intermetallic phases of the hot-dip zinc coating [5, 6]

phase; formula	wt. % (Fe)
Γ; Fe_3Zn_{10}, $FeZn_3$, Fe_4Zn_9	20.40 - 27.52
$Γ_1$; Fe_5Zn_{21}, $FeZn_4$, $Fe_{11}Zn_{40}$	16.90 - 19.02
δ; $FeZn_{10}$, $FeZn_7$	7.87 - 10.87
ζ; $FeZn_{13}$	6.17
η; Zn(Fe)	0.03 - 0.04

Covering Fe-C alloys with a zinc coating is justified both due to the fact of obtaining a high corrosion resistance, as well as consider economic aspects (relatively low cost, high efficiency, simplicity and reliability). It is one of the oldest and most common methods of corrosion protection of steel or cast iron elements. From the technological point of view, the galvanizing principles have been kept unchanged, however, due to the emerging new applications (especially in the automotive and construction industries) modern galvanizing is a dynamically growing technology [2,7]. In addition to its advantages, the zinc coating has also disadvantages, including a relatively low hardness of the outer layer - the hardness of the η phase is about 50 HV [8,9]. The possibilities of increasing the hardness of the outer layer are becoming the object of further research. Seeking for new, simple and economical ways that do not require the use of advanced technology or expensive alloy additives. The HT of zinc coating is promising direction to improve its hardness. There are not many publications regarding this subject. In the publication of Szabadi László and co. [10], where the abrasive wear of the zinc coating on S235JRG2 steel was discussed, also the results of the HT of zinc coated elements are presented. The base sample zinc coating (without HT) hardness measured by Vickers method was equal to 47.1 HV in average. HT resulted in an increase of the zinc coating hardness up to 106.6 HV. In the publication is no detailed data on the values of the HT process parameters. Azadeh and co. [11] investigated the effects of HT on the coating microstructure and formability of hot dip galvanized steel DC01. Samples were heat treated at a temperature range of 500 - 540 °C for 10 - 180 s. After the HT, the samples were cooled in the water. The presented results (SEM, EDS, XRD, FLD diagrams) have shown that the proposed temperatures and treatment times are resulting in changes of the coating. It has been found that the use of higher temperatures in combination with shorter processing times improves the coating formability behavior. Whereas the publication of Fang and co. [12] shows the influence of temperature on the morphology changes of the zinc coating after the "hot forming" process. The treatment was carried out to a temperature of 910 ºC for 5 minutes.

1.1. The purpose of research

The aim of the conducted research is to supplement and systematize data concerning the influence of HT on the properties of the hot-dip zinc coating. The publication assumes that the proposed treatment will increase the hardness of the zinc coating without significant deterioration of its other properties, essential for industrial applications (such as corrosion resistance). The analysis of preliminary test results will be used to determine the range of changes of HT parameters in basic research (optimization), such as the temperature or heating time of galvanized steel and cast iron elements. The parameter values will be optimized at the end of the experiment.

2. EXPERIMENTAL

2.1. Experimental methods

The assessment of HT influence on the zinc coating properties was determined based on the results of microscopic observations (optical microscope Axiovert 100A), microhardness measurement on the cross-section of the coating (Mitutoyo Micro-Vickers HM-210A) and EDS analysis (scanning electron microscope EVO 25 MA Zeiss with the EDS attachment).

The microhardness measurements were conducted to verify the HT influence on the properties of the zinc coating. In turn, the aim of microscopic research was to provide information on the condition of the coating after HT. The EDS analysis enabled identification of individual Zn-Fe phases and provided information of the HT effect on the coating structure.

2.2. Samples preparation

The test samples were made of gray cast iron with flake graphite EN - GJL 250 and low-carbon steel DC01. For the tests steel and cast iron samples with a diameter of 25 mm and a thickness of 4 mm were prepared. The samples were subjected to a hot-dip galvanizing process at industrial conditions acc. PN-EN ISO

10684:2006 standard [13]. Technical parameters of the galvanizing process were as follows: flux treatment; immersion in the bath (Zn with Al, Bi, Ni additives, temperature: 460 °C, time: 1.5 minute); water cooling.

Next samples were subjected to the controlled HT at temperatures: 390, 430, 470, 530 ºC (where the temperature range for the entire experiment is 200 ÷ 530 ºC). This process was carried out in the electric chamber furnace. The time of treatment was 7 minutes for all samples. After HT samples were taken out of the furnace chamber and cooled in the air to ambient temperature. The sample marking method is shown in **Table 2**. Before metallographic examinations, the thickness of the coating was measured using electronic PosiTector 6000 tester (method of the magnetic induction, head with the diameter Ø = 9 mm). The thickness of the coating was in each case included in range: 45 - 50 µm.

Table 2 Samples designation

MATERIAL	SAMPLE NUMBER	HT TEMPERATURE, (ºC)
steel	1.0	base sample (without HT)
	1.1	T_1 = 390
	1.2	T_2 = 430
	1.3	T_3 = 470
	1.4	T_4 = 530
cast iron	2.0	base sample (without HT)
	2.1	T_1 = 390
	2.2	T_2 = 430
	2.3	T_3 = 470
	2.4	T_4 = 530

3. ANALYSIS OF RESULTS

3.1. Microhardness results

The microhardness measurements of the coatings were carried out using the Vickers HV0.02 method, dedicated for thin coatings. **Figure 1** presents the data aquired during measurements on steel samples.

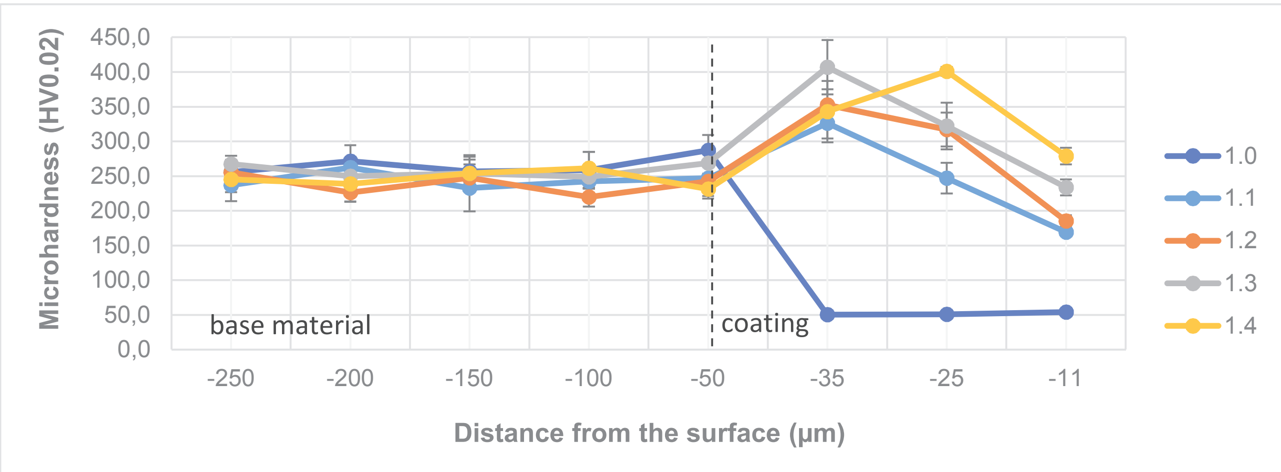
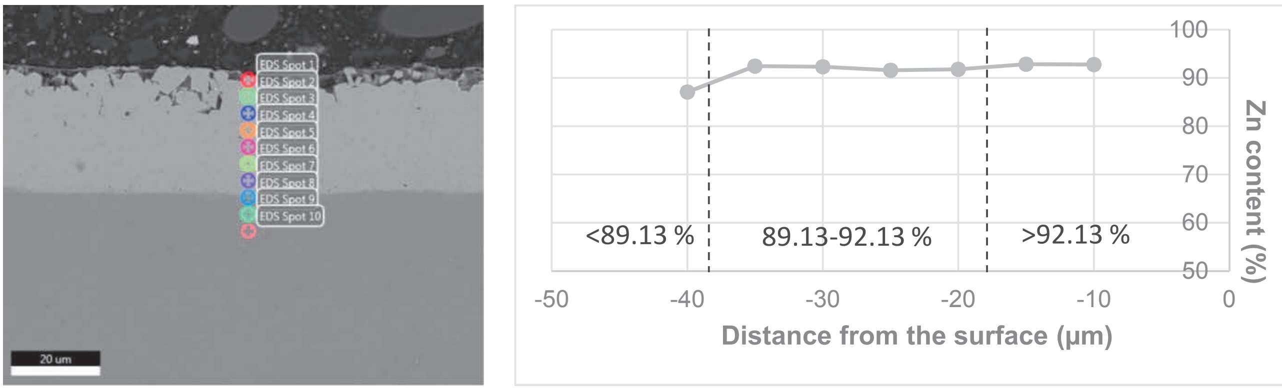


Figure 1 Average results of microhardness measurements for zinc coatings deposited on steel - Vickers method HV0.02

Changes in microhardness values are observed for each of the applied processing temperatures over the entire cross section of the coating, i.e. in the area from the outer surface of the coating to approx. 50 µm depth. For the base sample (1.0) measured values of the hardness were in line of the data given in literature and reached the value 50 HV0.02 ± 4.3. In the case of heat treated samples (1.1, 1.2, 1.3, 1.4), the hardness of the surface layers increases with the increase of the HT temperature. The results of hardness measurements for the outer layer of zinc coatings on steel were as follows: 169.4 HV0.02 ± 5.2 (sample 1.1), 185.4 HV0.02 ± 8.5 (sample 1.2), 233.5 HV0.02 ± 11.5 (sample 1.3) and 278.9 HV0.02 ± 12.1 (sample 1.4). The microhardness value level determined in the base material (steel, cast iron) is similar for all temperatures. The microhardness results at the cross-section of coatings applied to cast iron are similar steel.

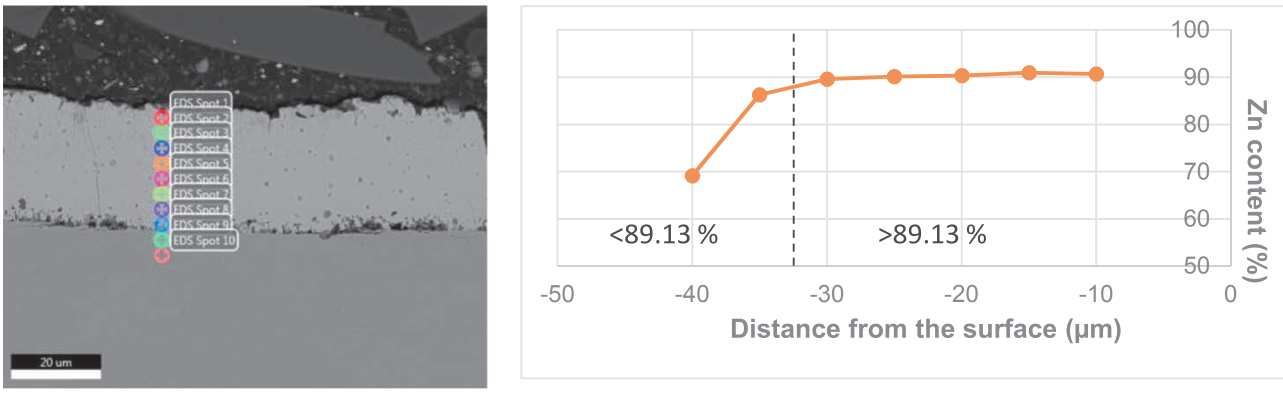
3.2. Results of EDS analysis

The EDS analysis was carried out at the cross-section of coatings at 3000x magnification. **Figures 2, 3** show a microstructure with analyse points and distribution of zinc content in coatings applied to steel. The charts were made on the basis of the first 7 out of 10 points from the EDS point analyse (found in the coating). The theoretical approximate ranges of individual Zn sublayers were marked in **Figures 2b** and **3b** by vertical dashed lines, assuming that the complement to 100 % is iron. These ranges correspond theoretically to the intermetallic phases (Γ, Γ_1, δ, ζ),



a) b)

Figure 2 Microstructure observed at the cross section of hot-dip zinc coating on steel (sample 1.1) with EDS analyse points (a), zinc content distribution at the cross section (b)



a) b)

Figure 3 Microstructure observed at the cross section of hot-dip zinc coating on steel (sample 1.4) with EDS analyse points (a), zinc content distribution at the cross section (b)

HT caused the changes in the structure of the coatings - as the HT temperature increases, the zinc content decreases. For coatings on samples 1.1, 2.1 (heat treated in T_1) the zinc ranges theoretically corresponding to the following phases: Γ/Γ_1 (<89.13 %), δ (89.13-92.13 %) and ζ (>92.13 %) were observed. For coatings subjected to HT at higher temperatures (T_2, T_3, T_4), only characteristic ranges for the gamma and delta phases were observed. In the zinc coating applied to cast iron samples the ranges characteristic for Γ, Γ_1 and δ were observed, with a similar distribution of phases at the cross-section of the coatings to this one observed on steel. In none of the heat-treated coatings the Zn content characteristic for η (99.96 - 99.97 %) were observed. This is probably due to the increase in the diffusion range of iron to the subsequent outer layers, which is activated by the HT.

3.3. Microscopic observations results

For examination of the cross-section samples were etched with 4 % HNO_3 solution. Observations of the surface were carried out at magnifications: 100 ÷ 500x. **Figure 4** presents an example of coating microstructure deposited on steel (1.4) and cast iron (2.4). During microscopic analysis, the coating thickness was verified at a magnification of 500x.

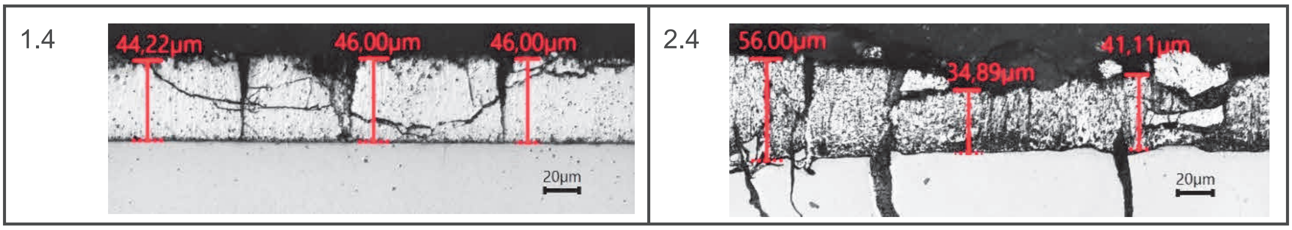


Figure 4 Microstructure observed at the samples cross-section (HT at temperature T_4)

The zinc coating after HT shows considerable variation. The coating on the steel is more uniform, while on the cast iron shows significant larger changes in thickness, which increases especially in the places of graphite penetration. Both in the case of zinc coatings on steel and on the cast iron, the occurrence of discontinuities - cracks occurring in most cases spread from the external surface of the coating perpendicular to the base surface was observed in the outer layer. For steel, the observed discontinuities - cracks sometimes cover the entire thickness of the coating, and for cast iron, it happens that they combine with graphite precipitations derived from a metal matrix.

In the case of coatings on steel samples, the outer surface is more uniform than in the case of coatings on cast iron. The thickness of the coating treated in T_4 measured under the microscope is in the range: 44.2 ÷ 46.0 μm (steel samples) and 34.9 ÷ 56.0 μm (cast iron samples). On cast iron samples, the zinc layer is non-uniform. This is due to the presence of graphite, and on the other hand to the influence of the HT.

4. CONCLUSIONS

- The achieved microhardness results confirm that applied HT essentially changes the hardness of zinc coating deposited on Fe-C alloys surface. With increasing the HT temperature also the hardness of the coating increases.
- On the basis of EDS analysis the proper zinc coating structure identification is possible. As the temperature of the HT increases, the content of Zn in the coating decreases toward outside the coating. In the structure mainly the characteristic ranges of Zn content for gamma phases were observed. Only in the coating without HT the range of zinc content for eta (η) surface layer was observed. The applied HT intensify the Fe diffusion into the subsequent outer layers, which results in higher level of coatings hardness.
- HT results also in coating discontinuities revealed during microscopic observations. In the case of steel samples, the treatment at the highest temperature from the adopted range caused only cracks in the coating, while in the coating on the cast iron, also delamination was observed. To verify if these

discontinuities may reduce corrosion resistance, it is planned to carry out appropriated tests in a salt chamber.

- The presented investigations are introduction to the main researches, where a wider range of heating time (t = 1 ÷ 10 min.) and temperatures (T = 200 ÷ 530 °C) will be applied. Ultimately, in the experiment, it is planned to determine the optimal processing parameters, and thus to obtain a higher hardness of the zinc coting applied to fasteners without significantly reducing the corrosion resistance or increasing the brittleness of the coating. This will allow a more universal application of the results of the tests. Determining the optimal conditions of HT of the zinc coating (time, temperature) from the point of view of its hardness, resistance to abrasion, corrosion resistance, etc. may contribute to increase the durability and extension of applications for hot-dip galvanizing parts.

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