Arch. Metall. Mater. **64** (2019), 1, 201-206

DOI: 10.24425/amm.2019.126239

D. JĘDRZEJCZYK*[#], E. SZATKOWSKA*,**

CHANGES IN PROPERTIES OF HOT-DIP ZINC COATING RESULTING FROM HEAT TREATMENT

This paper analyses the heat treatment of the hot-dip zinc coating deposited on both cast iron and steel. The aim of research is to increase coating hardness and wear resistance without decreasing its anticorrosion properties. Hot-dip zinc coating was deposited in industrial conditions (acc. PN-EN ISO 10684) on disc shape samples and bolts M12x60. The achieved results were assessed on the basis of microscopic observation (with the use of an optical and scanning microscope), EDS (point and linear) analysis and micro-hardness measurements. It was discovered that the heat treatment of zinc coating results in an increase in hardness which is caused by the corresponding changes in microstructure.

Keywords: hot-dip zinc galvanizing, heat treatment, coating hardness

1. Introduction

Although hot-dip zinc galvanizing has been used for years in industrial application, it is still the most common technology aimed at protecting Fe-C alloys against corrosion influence of aggressive environment. Zinc is invariably the most crucial element applied in anticorrosion galvanizing where over half of the world's zinc resources is used [1]. The anticorrosion properties of zinc coating play an essential role in the protection of different machine parts and are determined by the structure of the created layer which is composed of a number of sub-layers. The zinc-coating structure created on Fe-C alloys (cast iron and steel) is precisely described by corresponding Fe-Zn phase equilibrium diagram [2÷6]. The last published Fe-Zn diagram is presented in Fig. 1a. There are no essential changes with reference to the version that was regarded as the most correct for many years – Fig. 1b. There are numerous models describing the sub-layers formation with the application of stable equilibrium Fe-Zn phase diagram [7÷9] and only a few regarding stable and meta-stable solidifications [10÷13]. Generally, it was stated, that there are three phases occurring in the Fe-Zn diagram as a result of the peritectic reaction: Γ – Fe_3Zn_{10}, δ – $FeZn_7$, ζ – $FeZn_{13}$ and iron solid solution in zinc – η, which is settled on the surface during pulling out of the bath – Fig. 1a, b. Next research referred to different forms of δ – phase existing within different temperature range (δ_1, δ) and with different morphology (δ_C – compacted, δ_P – palisade). Also $\Gamma 2$ phase that is created as a result of a reaction between $\Gamma 1$ and δ phases was distinguished [14]. The model of ideal growth of Zn coating in presented in Fig. 1c [10], where the liquid solution diffuses along the channels between the cells and the sub-layers increase the thickness as a result of bulk diffusion through the cells. The application of flux determines two different δ phases growth but only the δ_P phase is visible in the coating after the flux evaporation is complete – Fig. 1d

The mechanical properties of zinc coating are the consequences of its structure. The hardness value of individual layers is as follows: Fe_3Zn_{10} (T_s = 782°C) – gamma (Γ) – not determined; $FeZn_7$ (T_s = 665°C) – delta (δ) – 270 HB; $FeZn_{13}$ (T_s = 530°C) – zeta (ζ) – 220 HB; 100% Zn (T_s = 425°C) – eta (η) – 50÷70 HB [15]. Hardness is an important parameter influencing the protective and anticorrosion coatings properties. The hardness of the most frequently-used zinc coatings differs essentially. There is a direct relation between the hardness level and the tribological properties of zinc coating. Zinc-plated coatings deposited in the galvanic technology demonstrate the hardness ab. 50 HV. It is possible to increase this hardness level up to 500 HV by introducing alloyed elements, i.e. Ni (14%) [16,17]. In the case of lamellar zinc coatings the hardness of the outer surface can reach even 500 HV which is due to the application the thermosetting surface varnish as the top layer.

The heat treatment (HT) of zinc coating is a simple and economical way that can result in an increase in hardness without any loss of anticorrosion properties. In literature only a few papers deal with this topic but the provided data are incomplete and calculated for a wide temperature range. In the publication [18], an increase of the zinc coating hardness from 47 HV up to 106 HV is reported but there is no information regarding HT parameters. Research on the influence of HT on the coating microstructure and the formability of hot dip galvanized steel DC01 [19] at the temperature range of 500÷540°C for 10÷180

---

* UNIVERSITY OF BIELSKO-BIALA, 43-309 BIELSKO-BIAŁA, 2 WILLOWA STR., POLAND
** BOSMAL AUTOMOTIVE RESEARCH AND DEVELOPMENT INSTITUTE LTD, 93 SARNI STOK STR., BIELSKO-BIALA, POLAND
[#] Corresponding author: djedrzejczyk@ath.bielsko.pl

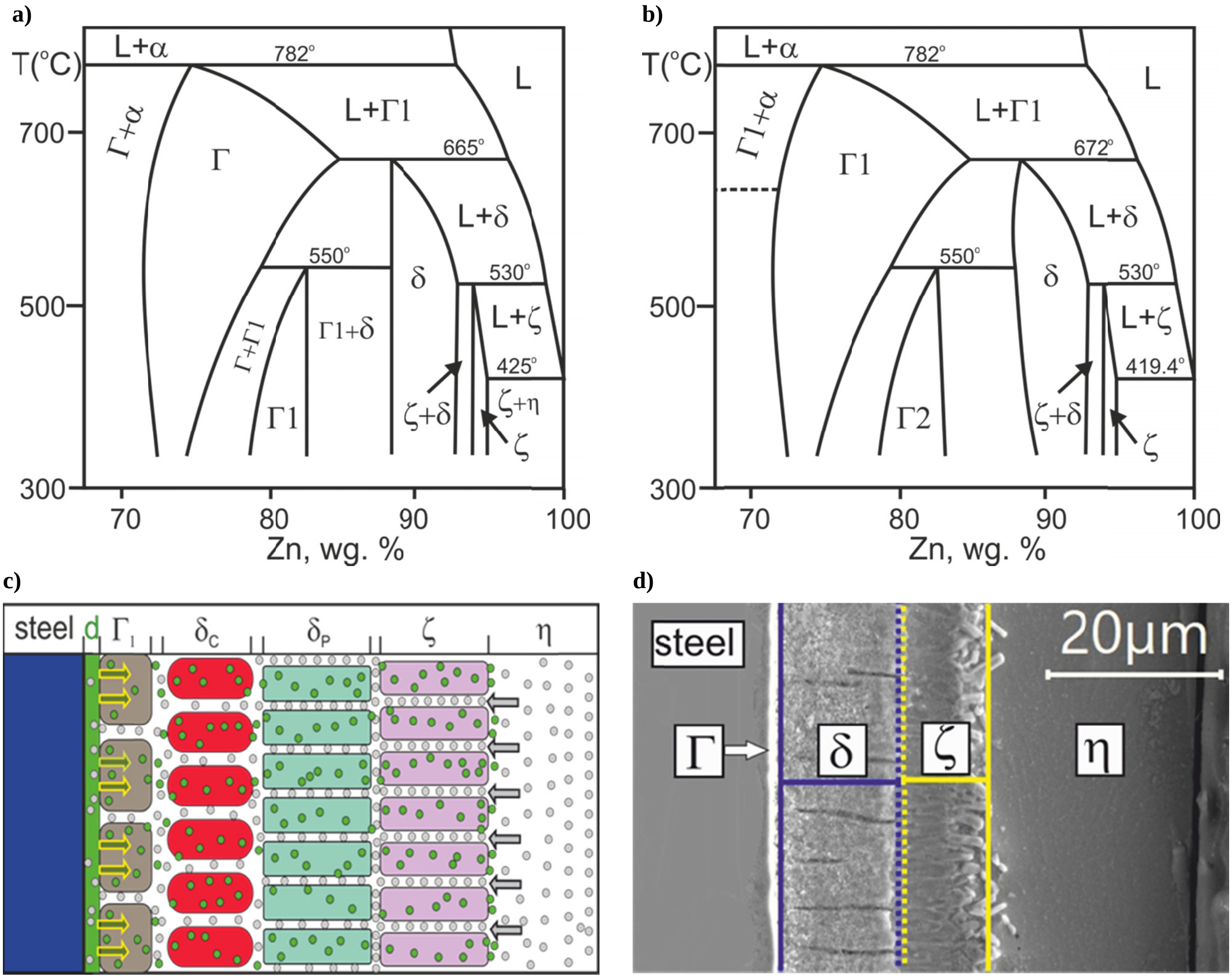

Fig. 1. Fe-Zn equilibrium diagram – a [5,6]; b – [2], model of ideal zinc layer growth during hot-dip zinc galvanizing – c [10]; real structure of zinc coating deposited on steel (own investigations) – d

secs shows that the proposed temperatures and treatment times contribute to significant changes in the coating structure. It has been found that the use of higher temperatures in combination with shorter processing times improves the coating formability. The coating structure changes during „hot forming" process in temperature of 910°C for 300 secs was also studied [20].

The aim of the planned and partially performed research is to verify if HT can be applied as the method of increase zinc coating properties such as hardness and resistance to wear without decreasing its corrosion resistance. In the bolts case it is also important to determine the influence of the suggested treatment on the steel properties (possible tempering).

2. Experimental research

2.1. Methods of investigation

The assessment of the impact of heat treatment on the zinc coating properties was determined with the use of disc shaped samples measuring 25 mm in diameter and 4 mm in thickness and made of inoculated cast iron with flake graphite EN – GJL 250 and low-carbon steel DC01 as well as 23MnB4 steel (M12-60 bolts). The chemical composition of the applied materials is presented in Table 1. During investigations the following parameters were analyzed: the microstructure of zinc coating structure and 23MnB4 steel – with the use of an optical microscope (Axiovert 100 A) and EDS analysis (scanning electron microscope EVO 25 MA Zeiss with an EDS attachment), the microhardness changes at the cross section of both: coating and subsurface layer of steel (Vicker's HV 0.02, Mitutoyo Micro-Vickers HM-210A device 810-401 D; Brinell's HBW method, Innovatest universal tester 700M).

TABLE 1

The chemical composition of materials applied in the experiment

Material	Chemical composition, %							
	C	P	S	Mn	Al	Si	Cu	Ni
DC01 steel	0.201	0.0096	0.0071	1.01	0.018	0.084	0.181	0.067
GJL – 250 cast iron	3.25	0.065	0.035	0.55	—	2.00	—	—
23MnB4 steel	0.22	0.023	0.020	1.00	—	0.20	0.23	0.005

2.2. Samples preparation

A diagram of the planned and partially conducted research is presented in Fig. 2. In the following analysis the preliminary results marked red in Fig. 2 are discussed. The samples and bolts were subjected to a hot-dip galvanizing process in industrial conditions acc. PN-EN ISO 10684:2006 standard. The 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: 90 secs); water cooling. Next samples were subjected to the HT in temperature range: 390°C÷530°C (screws were subjected to processing in temperature 300°C and 430°C). This process was carried out in an electric chamber furnace. The time of treatment was 420 secs for all samples and 660 secs for bolts. After HT samples were taken out of the furnace chamber and cooled in the air to ambient temperature.

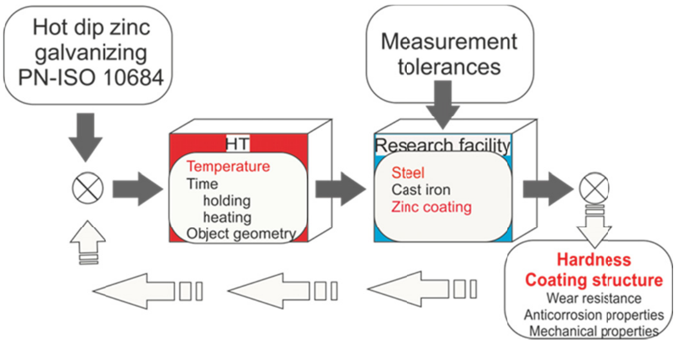

Fig. 2. Diagram of conducted research

3. Results analysis

3.1. Zinc coating deposited on disc samples

The microscopic observation covered both the cross section of zinc coating deposited on the surface of the disc shaped samples and on the zinc coating deposited on bolts head. The observations of the surface were carried out at magnifications: 100÷500×. Figure 3 presents an example of zinc coating microstructure deposited on steel (Fig. 3a÷c) and cast iron (Fig. 3d).

The HT in the applied range, i.e. 390÷530°C has a significant influence on the compactness of zinc coatings. There are visible cracks running through the whole coating thickness perpendicularly to the base surface. With increasing HT temperature, both the number and size of the cracks increase. For example the cracks thickness observed after HT in temperatures: 430°C, 460°C and 530°C reaches correspondingly: 0.5 μm; 3 μm and even 19 μm (Fig. 3). The zinc coating surface deposited on steel is more uniform (with thickness ranging from 44 to 46 μm), while the coating on cast iron surfaces shows a significant thickness diversification (35÷56 μm). The increased roughness of coating is caused additionally by graphite penetration from metallic matrix. As the result hollows with even 28 μm depth are measured on the cross section of coating on cast iron (Fig. 3d).

The changes observed in zinc coating morphology occur in accordance with the Fe-Zn equilibrium diagram [2÷6] and result in an increase coating brittleness. An increase in HT temperature results in an increase in the thickness of the iron-rich layers (Γ, δ). Fig. 4 presents as an example the changes of Zn and Fe content

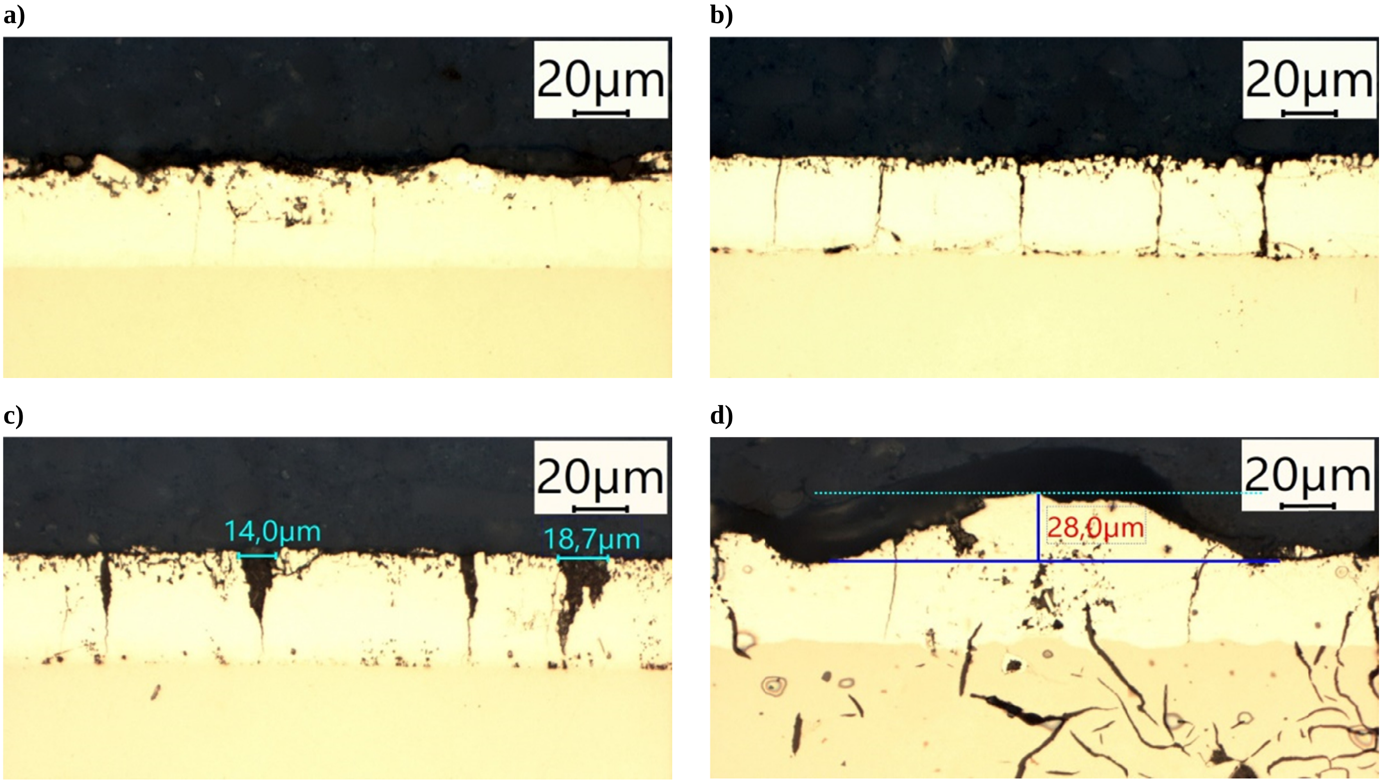

Fig. 3. The microstructure observed at the cross section of zinc coating deposited on steel after the HT – a (430°C), b (460°C), c (530°C) and cast iron – d (530°C)

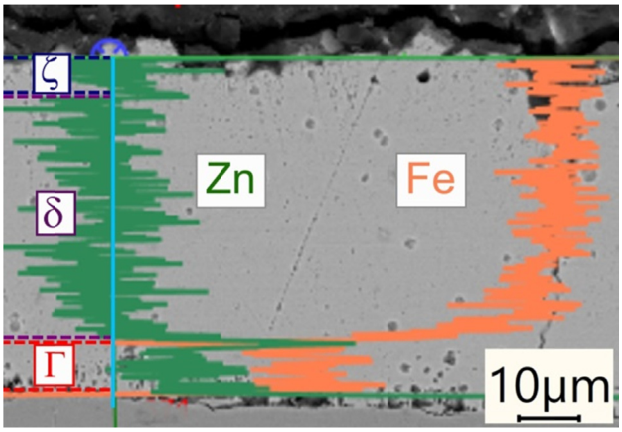

Fig. 4. The linear EDS analysis at the zinc coating cross section deposited on steel after the HT – 460°C

after HT in 460°C. On the basis of the achieved result it is clear that after the HT there is practically no η phase. The outer layer of the zinc coating has a decorative character and improves the susceptibility of covered elements to plastic processing. On the other hand the outer layer consisting of phase η corrodes more intensively than intermetallic phases of transitional layer (after the wear of outside coating layer the rate of the corrosion process reduces and stabilizes as the layers of intermetallic phases Fe-Zn are dissolve with a lower intensity), so there is a possibility that such a change of the structure will not have a significant influence on the corrosion resistance of the coating.

The EDS point analysis confirmed that the Zn content in the top 5 μm layer of coating amounts to approx. 94%, and deeper in, the zinc content drops to 92% at 45 μm, and only a thin bottom layer of approx. 7 μm above the steel surface has a zinc content of less than 76%. In addition to the EDS analysis, the presented phase structure of the coating has also been confirmed by the measurements of micro-hardness combined with the results of own research and literature data [5]. The level of microhardness was measured both on the outer zinc coating surface – HV 0.025 – Fig. 5. and the zinc coating cross section – HV 0.02 – Fig. 6. The trends of changes in the observed microhardness of cast iron and steel are similar. In both cases the measured values exceeded 300 HV 0.025. In addition the level of hardness measured after the heat processing in the highest temperature is slightly higher in steel coating (about 22 HV) which can result from the penetration of graphite to the coating applied on the cast iron. Generally the measured hardness is much higher than reported in the literature (higher than 106 HVM – [18]) and for this reason the coating stays too brittle. The microhardness measured at the coating cross section shows that the achieved values are still lower than those measured in metallic matrix. Only HT in 530°C can provide outer hardness near 300 HV 0.02. Whereas lower temperatures – 460°C and 430°C ensure hardness level equal to 150 HV 0.02. Considering that in higher temperature range strong deterioration in coating quality is observed it could be concluded that achieving coating hardness level by HT higher than 150 HV without decreasing its anticorrosion properties will be difficult.

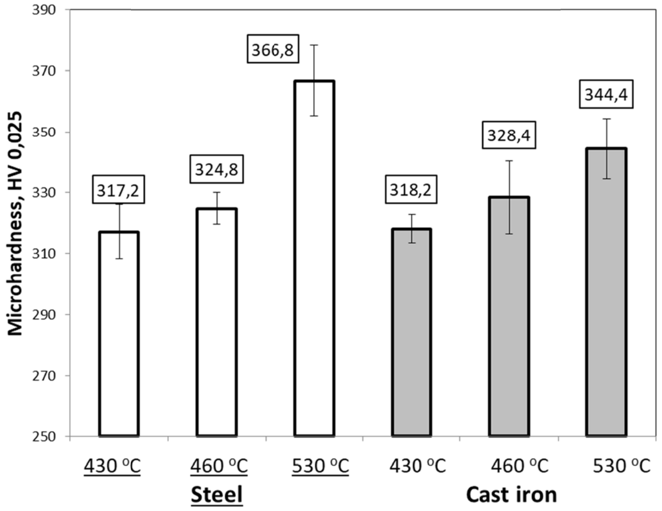

Fig. 5. The microhardness measured on the outer zinc coating surface after HT deposited on steel and cast iron

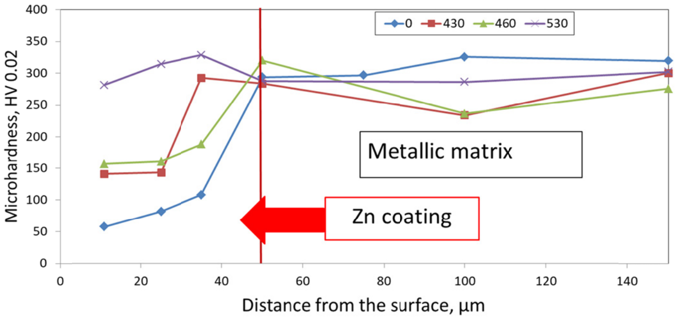

Fig. 6. Microhardness measured at the cross section of zinc coating deposited on cast iron after HT

3.2. Zinc coating deposited on bolts

Taking into account literature data [18÷20], results of experiment regarding disk shape samples and quite different dimensions, weight and shape of M12-60 bolts to the HT the following parameters were chosen: $T = 300$°C, 430°C; $t = 660$ secs. The applied lower temperature should ensure the coating layer free of cracks. Longer holding temperature results from a higher weight of the bolts and lower heating rate. Because the tested bolts were made in the 8.8 strength class where to achieve such high mechanical properties the heat treatment of steel was necessary it was also rational to verify if additional zinc coating HT will influence on the bolts steel microstructure (tempering).

The conducted HT influences the measured microhardness similarly to the disk shaped samples – Fig. 7. The outer coating hardness increases from 58 HV 0.02 (sample 0 – without treatment) to 250 HV 0.02 (sample 1 – T = 300°C) and 285 HV 0.02 (sample 2 – 430°C). The measured values are closer to the values measured inside the base bolts material. Unfortunately the hardness of the subsurface steel layer slightly decreases from 320 HV 0.02 to 300 HV 0.02 and 290 HV 0.02. The measurement of HBW hardness in depth of 2 mm confirmed hardness decrease correspondingly from 271 HBW to 255 HBW and 245 HBW. These

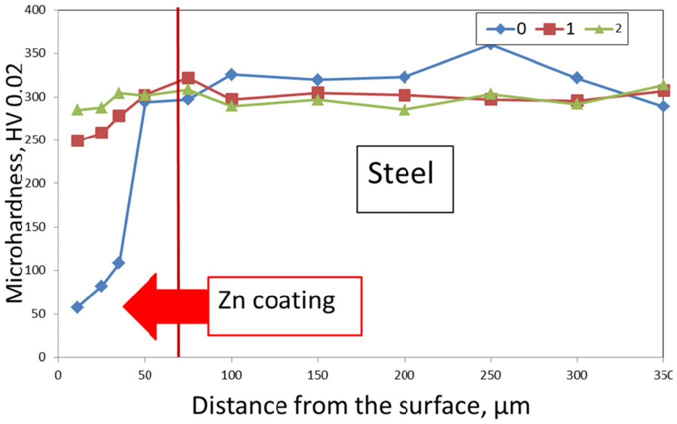

Fig. 7. Microhardness measured at the cross section of zinc coating deposited on M12-60 after HT

changes result directly from the observed steel microstructure. The structure achieved in crude bolt without heat treatment is typical feather-like, where the length of precipitations is in the range of 10÷14 µm. After heat treatment the structure admittedly is keeping its character, but the dimensions of precipitations after zinc coating HT increase. There are also visible changes in the zinc coating structure – Fig. 8. There is no delamination, cracks and surface degradation of zinc coating visible as the result of conducted heat treatment.

The coating without heat treatment shows structure composed of four phases, whereas the structure after heat treatment reveals practically three phases. The structure observed after the HT is similar to the result observed in the hot forming steel samples dipping in the zinc bath with temperature stabilized at 460°C, reheated after cooling to 500°C and cooled by rate of 10°C/s to room temperature [20]. Observed coating of about – 20 µm in thickness contains three phases: ζ, δ and Γ phase and is also in accordance with the opinion [19] regarding the influence of higher temperature on coating structure where the δ and Γ phases grow at the expense of the ζ phase. A similar statement was presented by Murder [5], i.e.: in the coating heat treated at higher temperatures δ phase growths towards the surface coating consuming ζ layer. In the next step the continuous growth of Γ phase proceeds at the expense of δ phase. Only in paper [18] quite different zinc coating structure is observed after HT. Four layers are distinguished in zinc coating of 120 um in thickness whose chemical composition (Fe, Zn contents) makes phase identification very difficult.

Considering that the target hardness level equals 100÷150 HV 0.02, the applied parameters, both temperature and time still

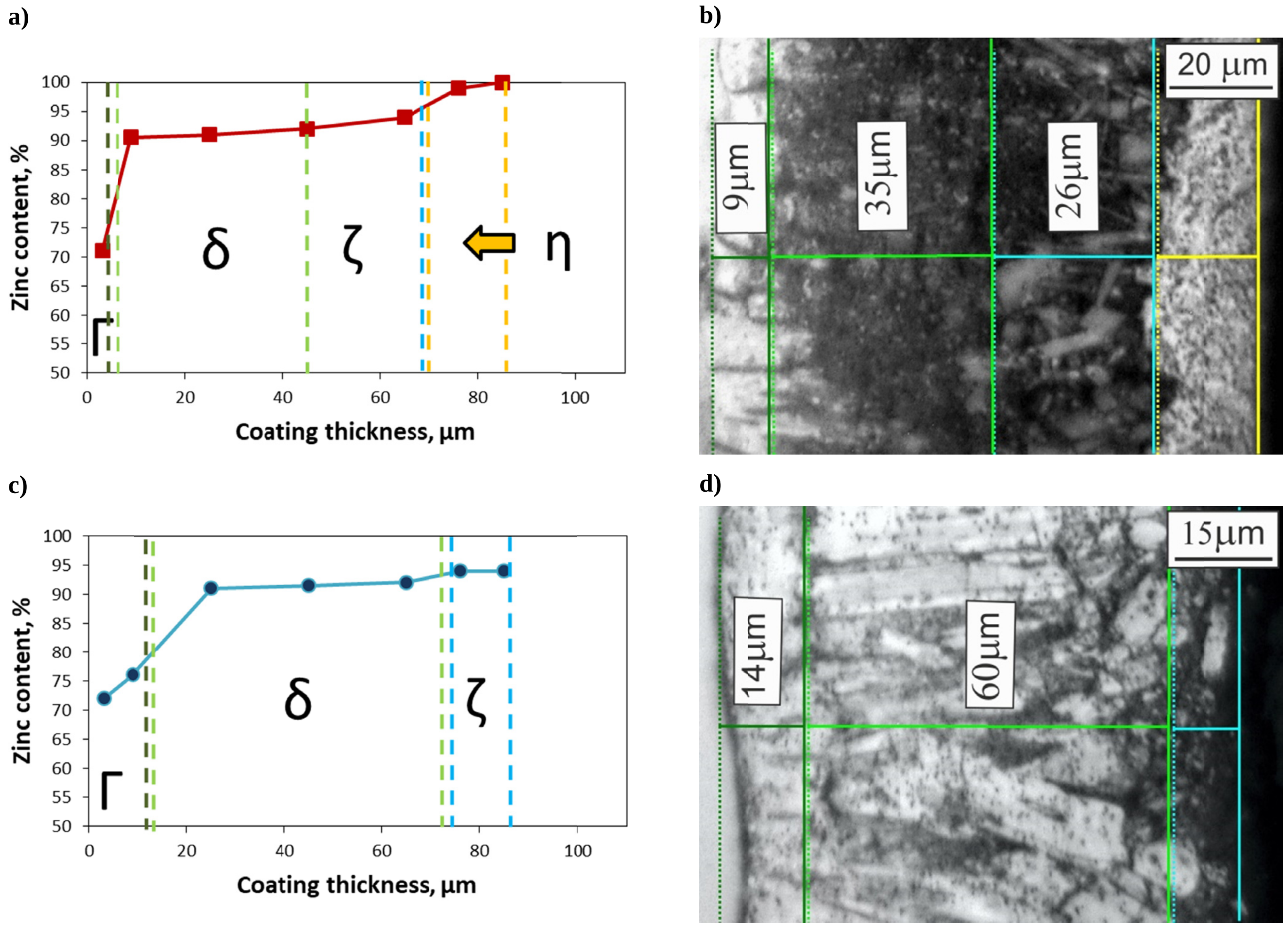

Fig. 8. The Zn distribution at the coating cross section deposited on bolt head before (a) and after HT (c) compared to coating microstructure: b – without HT; d – after HT in 430°C

appear too high. The achieved relatively high hardness level can result in increased brittleness of zinc coating. This problem will be investigated separately using typical pin-on-disk tribological tests and bolts friction coefficient measurements using Schatz Analyse M12 testing machine system.

Under normal conditions, the thickness of the individual phases of the zinc coating depends on the dissolution process (going into the liquid phase) of the growing phase at the interface with liquid zinc. This process (dissolving) affects also diffusion increase in the thickness of the remaining layers. The process will proceed until the rate of thickness growth in each of the individual zones of alloyed layers is equal to the rate of dissolving, it is until achieving the dynamic balance within the coating. In the analysed case the situation is different because the Zn amount in the coating is limited. It is quite possible that during the HT the liquid solutions diffuses along the channels between the cells (like in the model presented in Fig. 1c – [10]), but a more probable occurrence is bulk diffusion resulting in thickening of δ and ζ phases.

As a result of the applied heat treatment the structure of the Zn coating ensured a much higher level of hardness than in the case of hot-dip zinc galvanizing. Receiving such a structure only by hot-dip zinc galvanizing technology is impossible because every time a sample is removed from the bath, a layer of pure zinc settles on the outer surface.

Parameters of the heat treatment should take into account among others both geometry, as well as mass of galvanized elements. For precise determining the rate of heating of the tested samples the next investigations are planned with using the thermal imaging camera and "ANSYS Fluent" software to the simulation of the heating process.

4. Conclusions

1. As a result of applied HT of hot-dip zinc coating deposited on Fe-C alloys it is possible to essentially increase the coating hardness in a wide range of values.
2. Improperly selected parameters of the heat processing – too high temperature, too long holding time can lead to coating quality deterioration, increase in brittleness and the appearance of a lot of cracks.
3. Increase of heat treatment time of M12×60 bolts does not result in zinc coating discontinuities. It confirms that parameters of the HT should be precisely selected and dependent among others things on the geometry and mass of the treated elements.
4. Considering that in higher temperature range strong deterioration in coating quality is observed, the final quality evaluation of heat treated coating will be possible only after planned additional complex investigation, i.e. wear and anticorrosion resistance tests.
5. As a result of HT in the examined range of applied parameters the structure of zinc coating changes. The thickness of alloyed layer δ and Γ increases while η phase disappears.
6. The proposed HT, in addition to influence on the structure and properties of hot-dip zinc coating also exerts an impact on structure and properties of hardened bolt's material. This problem can be avoided by an appropriate choice of HT parameters, i.e. lower temperature treatment within longer time.

REFERENCES

[1] Data of the International Lead and Zinc Study Group, reports for: 2008, 2015.

[2] O. Kubaschewski, Iron-Binary Phase Diagrams, Springer-Verlag, Berlin (1982).

[3] P.B. Burton, P. Perrot, Phase Diagram of Binary Iron Alloys. American Society for Metals, Metal Park. OH (1993).

[4] T.B. Massalski, Binary Alloy Phase Diagrams. ASM International (1990).

[5] A.R. Marder, Prog. Mater. Sci. **45** (3), 191-271 (2000).

[6] P. Pokorný, J. Cinert, Z. Pala, Materials and technology **50** (2), 253-256 (2016).

[7] A. Bohran-Tavakoli, Zeitschrift für Metallkunde **75**, 350-355 (1984).

[8] C.E. Jordan, A.R. Marder, Metallurgical and Materials Transactions **25A**, 937-947 (1994).

[9] C.R. Xavier, U.R. Seixas, P.R. Rios, ISIJ International **36**, 1316-1317 (1996).

[10] W. Wołczyński, B. Kucharska, G. Garzeł, A. Sypień, Z. Pogoda, T. Okane, Arch. Metall. Mater. **60** (1), 199-207 (2015).

[11] W. Wołczyński, Z. Pogoda, G. Garzeł, B. Kucharska, A. Sypień, T. Okane, Arch. Metall. Mater. **59** (3), 1223-1233 (2014).

[12] W. Wołczyński, Z. Pogoda, G. Garzeł, B. Kucharska, A. Sypień, T. Okane, Arch. Metall. Mater. **59** (4), 1393-1404 (2014).

[13] P. Perrot, J.C. Tissier, J.Y. Dauphin, Zeitschrift für Metallkunde **83**, 786-790 (1992).

[14] D. Kopyciński, E. Guzik, Inżynieria Materiałowa **29** (6), 780-783 (2008).

[15] D.W. Evans, 2014 Coal Operators' Conference, Northfields Ave, Australia, 177-185 (2014).

[16] B. Sonntag, K. Thom, K., N Dambrowsky, B. Dingwerth, Galvanotechnik **7**, 1499-1513 (2009).

[17] O. Fayomi, A. Popoola, International Journal of Electrochemical Science **7**, 6555-6570 (2012).

[18] L. Szabadi, G Kalácska, L. Pék, I. Pálinkás, Sustainable Construction and Design, 82-91 (2011).

[19] M. Azadeh, M.R. Toroghinejad, ISIJ International **49** (12), 1945-1951 (2009).

[20] F. Fang, X.F. Du, Y.M. Chen, IOP Conf. Series: Materials Science and Engineering 292 Materials Science and Engineering **292**, 1-4 (2017).