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# CHANGE OF MECHANICAL PROPERTIES OF ZINC COATINGS AFTER HEAT TREATMENT

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Hot-dip galvanized coatings represent a protection based on passivation of the single zinc layer. It is one of the most commonly used surface treatments of steel. However, pure zinc forms merely an insignificant upper layer. Coating crosscut is formed by intermetallic phases that can cause decrease in the level of anticorrosion protection. This results from an iron diffusion from the base material. Goal of this paper is to analyse the changes in the mechanical properties of these phases in relation to zinc coating heat treatment. For the experiment, annealing temperatures of 200 °C and 300 °C were used, and the staying time was set at 1, 3 and 5 hours. Furthermore, samples without any heat treatment were subjected to comparison as well. Moreover, following tests were conducted: bending test in compliance with the ČSN EN ISO 1519 standard, and tearing test (in accordance with the ČSN EN ISO 4624 standard). On the basis of performed tests, the changes in mechanical properties of the zinc coating after heat treatment could be analysed.

**Keywords:** annealing; structure; mechanical degradation; hot-dip galvanizing

Use of anticorrosion protection requires the knowledge of the basic principles of corrosion processes and the mechanics of individual corrosion types, as well as anticorrosion protection. Chemical reaction with the elements from the corrosive environment turns metal into a solution identical or similar to the one it was originally produced from. For this reason, anticorrosion protection is indispensable (Trethewey and Chamberlain, 1995; Tulka, 2005).

General emphasis aimed at corrosion prevention has been constantly rising. Such a trend can be seen especially in surface treatments of steelworks in civil engineering, agriculture and machinery industry. Zinc coating of individual steelworks has a long tradition. These steelworks are assembled together; therefore, the zinc coating forms the only corrosion prevention of the entire assembly. In order to improve the corrosion prevention, paint can be used (Čičo et al., 2011; Votava and Kumbár, 2017). A properly used paint system does not only improve the corrosion prevention, but also modifies the visual appearance of the entire assembly. Drawback of such surface measures is that the upper layer can crack and peel because of bad paint fixation to the zinc coating.

Cracks in the paint system hold in air humidity which condensates on the zinc coating surface, which results in a chemical reaction generating $ZnCO_3$. Duplex corrosion protection of welded joints is thus highly relevant for this. In case of corrosion protection failure, the weld is always a potential place for initiation of a corrosion macrosegment (Čičo et al., 2006; Poláková and Dostál, 2019).

Zinc coatings may become subjects of mechanical degradation during and after their heat treatment. One of the reasons for inclusion of heat treatment to the production process lies in elimination of H2 from the base material. Hydrogen comes to the base material by diffusion in the process of preliminary treatment, such as staining, degreasing. Therefore, heat treatment prevents hydrogen brittleness. The dominant layer in the anchoring profile is formed by phases Gamma and Gamma-1, which are both very hard and fragile at the same time, which can cause the occurrence of coating delamination even under a low mechanical stress.

Individual intermetallic phases grow into a whole coating profile not only during the targeted heat treatment of zinc anticorrosion coating but also during everyday service heat stress. As a result, the ratio of the pure zinc decreases at the expense of massive growth of Zeta phases, thereby mechanical and anticorrosion properties of the whole coating may be reduced. However, the base material to which the zinc coating is applied also plays a significant role (Votava et al., 2018).

The anticorrosion capacity of the whole system may be harmed due to heat treatment of anticorrosion zinc coatings. The reason for heat treatment is the possibility of "dehydrogenation" of the base material (Fiala et al., 2003; Machek, 2013), which results in elimination of potential cracks originating in subsurface layers of the steel part.

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## Material and methods

The experiment was executed on specimens made of steel sheet of the quality S235JRG1; the sheet size was 160 × 65 mm and the sheet thickness was 1 mm. Before the zinc dipping, the samples were degreased and steeped.

Tested samples were hot-dip galvanised under the laboratory zinc plating conditions. Degreasing of samples was performed in aqueous solution of HCl, the bath temperature was 50 ±2 °C and samples were dipped for 120 s. The zinc coating was composed of $ZnCl_2$ and $NH_4Cl$. The temperature of the galvanising bath was 450 ±5 °C. In order to improve foundering performance, the galvanising zinc bath was alloyed by 2% of pure aluminium. Such aluminium ratio is considered to improve the coating anticorrosion properties (Votava, 2014). Pure zinc formed 98% of the bath. The galvanizing bath was made of graphite.

After removing from the galvanising bath, samples were gradually cooled in air. The thickness of the zinc coating substrate is highly dependent on the time during which the component remained in the zinc bath. According to the experimental measurements, the period of 120 s results in coating thickness of approx. 65 µm.

Subsequently, the specimens were heat treated in a muffle furnace MP-05 at the temperatures of 200 and 300 °C for 1, 3 and 5 hours; the speed of run-up temperature was lower than 30 minutes. There were always six samples in each group. These samples were subjected to metallographic analysis and the changes of intermetallic phases were observed.

Tests were processed in compliance with the following standards:

– ČSN EN ISO 1519 Bend test (cylindrical mandrel);
– ČSN EN ISO 4624 Pull-off test for adhesion.

## Results and discussion

### Measuring the zinc-coat thickness

The zinc coat layer thickness was measured non-destructively by means of Permascope device, operating on the principle of contacting measurement; the thickness of the upper deposited layer on the original material was determined digitally. Average values of zinc coat thickness are listed in Table 1. The measurement accuracy of the metallographic specimen was checked using the computer programme analysis, metallographic microscope with 500 times magnification. Metallographic specimen is shown in Fig. 1.

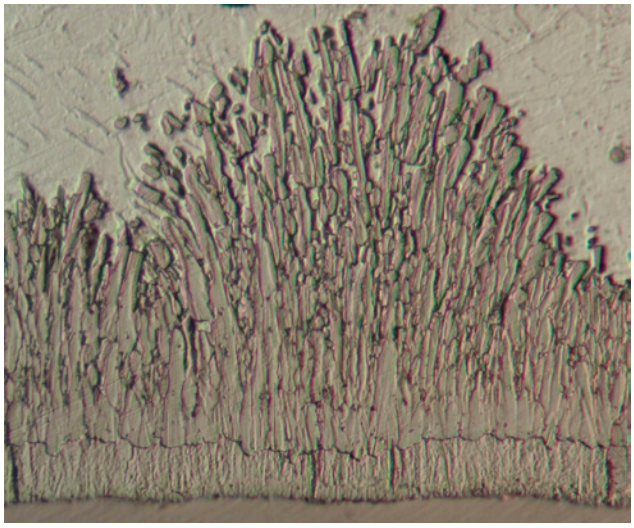


**Fig. 1** Cross-section of the zinc layer with marked measured values

On the basis of metallographic observations, it can be concluded that the upper layer is formed by pure zinc. However, the zinc layer is uneven, yet the connections of intermetallic phases with the surface are just isolated.

As it is apparent from Fig. 1, pure zinc forms c. 10 µm of the upper layer of the anticorrosion coating. The Fig. 1 also nicely shows the phase Zeta ($FeZn_{13}$), for which long monoclinic crystals are typical. These crystals are visible after a slight etch of the surface.

### Measuring the microhardness of intermetallic phases of the zinc coat

Using the HV method, the microhardness was measured by means of Hanneman's microhardness tester, with the connection with Neophot 21 microscope. The indentor with top angle of 136° was pressed to the material at the pressure of 0.1 N (Skálová et al., 1995). There were tested not only the heat-treated specimens but also those with no heat treatment (Fig. 2) for the purposes of comparison of potential differences. From among the heat-treated samples for both temperatures, three samples with 5-hour heat exposition (maximal phases growth) were analysed. Measured values are listed in Table 2.

On the basis of measurement results, it can be concluded that the bigger and/or longer the heat treatment, the higher the microhardness (Table 3). Changes in mechanical properties can be caused by diffusion of ferrum from the base material to the zinc coating (Zmrzlý et al., 2005). However, the disadvantage of this process lies in lowering of the anticorrosion protection of the inorganic coating. Under

**Table 1** Average thickness values of zinc coatings (µm)

| Group of specimens | Annealing time | | | Average zinc-coat thickness (µm) |
|---|---|---|---|---|
| Annealing temperature | 1 hour | 3 hours | 5 hours | |
| 200 °C | 54.25 | 53.16 | 54.24 | 53.88 |
| 300 °C | 55.18 | 55.45 | 54.29 | 54.97 |
| Samples without heat treatment were measured in three sets | | | | 53.15 |

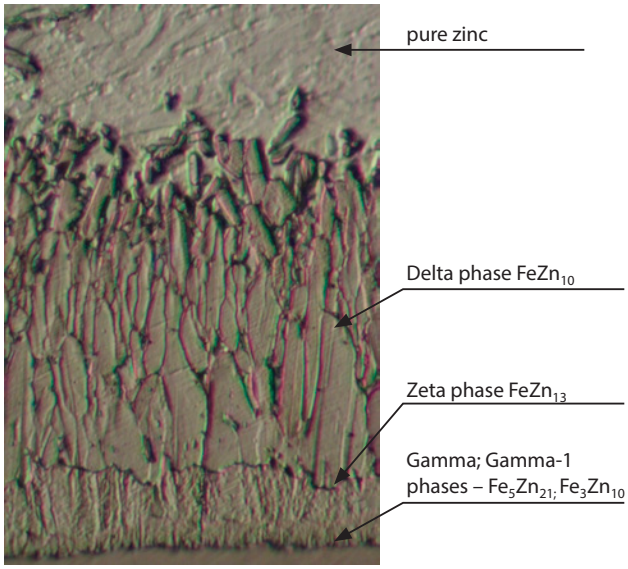


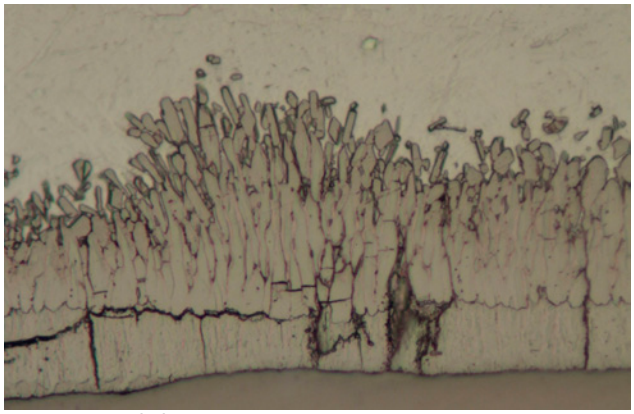

**Fig. 2** Intermetallic phases in a zinc coating

corrosion stress, one can assume that zinc ions will be drawn faster, resulting in more rapid occurrence of red corrosion (Popov, 2015).

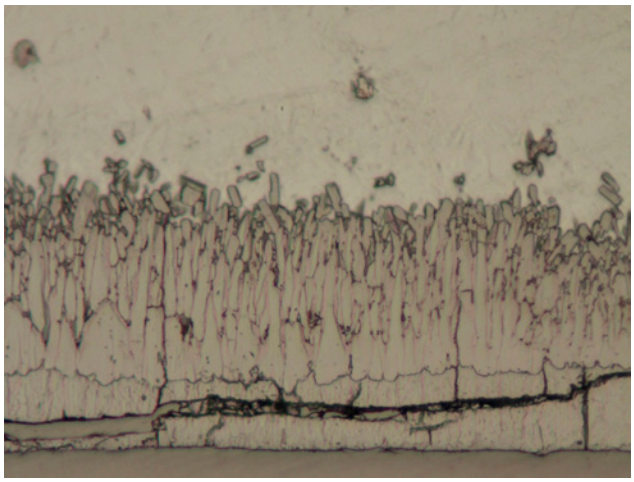
### Bending test

Bending experiment was conducted in compliance with the ČSN EN ISO 1519 standard and carried out utilizing the Elcometer 1506 cylindrical mandrel bend tester. There were taken two mandrels; the first had 10 mm in diameter and represented a severe bending load. The second bending pin had 32 mm in diameter and simulated a low bending load. The results presented in Table 4 are after 5-hour heat treatment.

According to Kuklík and Kudláček (2014), it is possible to identify cracks and further delamination of zinc coating in the phases Gamma and Gamma-1. Considering the tests performed, this hypothesis can be also stated that the massive crack growth can be seen after a 3-hour heat treatment. Such a short time is sufficient for initiation of the diffusion process. According to Adelmann et



200 °C, mandrel 32 mm



300 °C, mandrel 32 mm

**Fig. 3** Cracks in the zinc coating originating from the bending test according to ČSN EN ISO 8401

**Table 2** Microhardness of intermetallic phases of the zinc coat (HV) without heat treatment

| | 1 | 2 | 3 | Average ($HV_{0.1}$) | Standard deviation ($HV_{0.1}$) | Variation coefficient (%) |
|---|---|---|---|---|---|---|
| **Gamma** | * | * | * | * | * | * |
| **Delta** | 364 | 378 | 397 | 379.67 | 13.52 | 3.56 |
| **Zeta** | 222 | 201 | 236 | 219.67 | 14.38 | 6.55 |
| **Zinc** | 67 | 60 | 61 | 62.67 | 3.09 | 4.93 |

* By using this kind of measuring method, it was impossible to measure the microhardness for the Gamma and Gamma-1 phases. These phases can only be measured by a nanoindentor and using electron microscopy. It can be concluded that these phases showed higher microhardness than the Delta-phases

**Table 3** Change in microhardness of phases Delta and Zeta depending on heat treatment

| Heat treatment (°C) | Phase | 1 | 2 | 3 | Average ($HV_{0.1}$) | Standard deviation ($HV_{0.1}$) | Variation coefficient (%) |
|---|---|---|---|---|---|---|---|
| **200** | Delta | 376 | 357 | 381 | 371.33 | 10.34 | 2.78 |
| | Zeta | 222 | 201 | 241 | 221.33 | 16.34 | 7.38 |
| **300** | Delta | 440 | 455 | 450 | 448.33 | 6.24 | 1.39 |
| | Zeta | 265 | 270 | 294 | 276.33 | 12.66 | 4.58 |

**Table 4** Results of bending experiment

| Heat treatment | Mandrel diameter 10 mm | Mandrel diameter 32 mm |
|---|---|---|
| **Zero heat treatment** | – the samples showed cracks of an average width of 18 µm | – there were no cracks caused by the bending test |
| **200 °C** | – the average width of cracks was 23 µm | – small cracks of approx. 5 µm were shown |
| **300 °C** | – specimens annealed at temperature exceeding 200 °C showed significant changes in mechanical properties, there were severe defects. The average width of cracks was 45 µm | – there were shown microcracks of 10–15 µm (see Fig. 3) in the coating due to the minimal mechanical stress (mandrel 32 mm) |

**Table 5** Pull-off test according to ČSN EN ISO 4624 standard

| Heat treatment | Time (hour) | Measurement | | | Average (MPa) | Standard deviation (MPa) | Variation coefficient (%) |
|---|---|---|---|---|---|---|---|
| | | no. 1 (MPa) | no. 2 (MPa) | no. 3 (MPa) | | | |
| **200 °C** | 1 | 12.9 | 12.8 | 12.7 | 12.80 | 0.082 | 0.64 |
| | 3 | 12.5 | 12.9 | 12.4 | 12.60 | 0.216 | 1.71 |
| | 5 | 12.4 | 12.9 | 12.1 | 12.47 | 0.330 | 2.65 |
| **300 °C** | 1 | 13.5 | 13.6 | 13.6 | 13.57 | 0.047 | 0.35 |
| | 3 | 13.4 | 13.7 | 13.4 | 13.50 | 0.141 | 1.05 |
| | 5 | 14.2 | 14.1 | 14.5 | 14.27 | 0.170 | 1.19 |
| **Zero heat treatment laboratory temperature** | | 12.5 | 13.4 | 13.8 | 13.23 | 0.544 | 4.12 |

al. (2010), the zinc coating may be peeled off. However, this was not proven true. The test implies that the limit border temperature is 200 °C.

As it is apparent from Fig. 3, the cracks may expand both in vertical and horizontal levels. Even though the anticorrosion coating belongs to cathodic protection of base metals, microcracks in the coating significantly lower its service life. Microcracks due to higher heat treatment can be eliminated by specific chemical composition of the zinc bath (Körber et al., 2012).

## Pull-off test

The ability of the anticorrosion system to withstand dynamic and static stress is one of the criteria for the quality evaluation of protective coatings. In this respect, one of the most important characteristics is the adhesion between the anchoring profile of the base material and the coating substrate (Votava et al., 2016).

Anticorrosion system adhesion was determined according to the ČSN EN ISO 4624 standard. This standard establishes the procedure for pull-off testing in single-layered and multi-layered coating systems. Test result is determined by the tension in pulling required to damage the weakest boundary (adhesive failure) or the weakest component (cohesive failure) of the tested object. Adhesion analysis of individual anticorrosion systems was preformed immediately after complete drying of the anticorrosion coating. The delay was set at 48 hours. Test results are shown in Table 5.

On the basis of pull-off test results (Table 5), higher firmness of the coating after heat treatment was confirmed. The highest firmness values were reached by samples annealed at the temperature of 300 °C for 5 hours. Despite the higher material firmness thanks to the higher temperature of the heat treatment, there can occur microcracks, which lead to degradation of the coating as shown in the bending test.

## Conclusion

The objective of this article was an assessment of deterioration of mechanical characteristics depending on heat-treating process of the upper zinc layer. Temperatures of 200 and 300 °C and annealing times of 1, 3 and 5 hours were observed in this experiment in terms of changes in microhardness of the phases in regards to both exposure time and temperature.

Emphasis should be given to the fact that fragile Gamma-phase grew in samples with 3- and 5-hour annealing time (Gamma-phase as such is the origin of cracks caused by mechanical stress). This proposition was confirmed during the bending test according to the ČSN EN ISO 1519. Furthermore, on the basis of results of the other tests, it can be stated that heat treatment of zinc coatings results in higher firmness, yet in lower tenacity at the same time as well.

The Gamma-phase detachment from the original surface can be easily seen during the metallographic observations. The Gamma and Gamma-1 phases always occur during the heat treatment; therefore, it is necessary to focus on their elimination. According to the scientific literature, the elimination of fragile phases is quite difficult. The basis is the chemical composition of galvanized steel. Heat treatment of hot-dip galvanized zinc coatings can be recommended for machine parts, in which it is necessary to dehydrogenize the base material. Dehydrogenization is a process eliminating hydrogen brittleness and the origin of cracks in the base

material. However, the annealing temperature should not exceed 200 °C. Exceeding this temperature increases the risk of horizontal and vertical cracks in the anticorrosion coating. Due to this, the individual parts should not be subjected to increased dynamic stress. On the other hand, it is not recommended for parts which could be subject to temperature exceeding 200 °C.

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