THERMAL DIFFUSION AS THE ALTERNATIVE OF HOT-DIP ZINC COATING FOR FASTENERS

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Abstract

During the investigation a quality of the thermal diffusion coating dedicated for anticorrosion protection of fasteners was assessed. Because of similarity of parameters and structures, properties of the inspected coating (thermal diffusion) were compared with effects get as a result of hot-dip galvanizing. Coatings were deposited in industrial conditions on flat samples and screws made of 23MnB4 steel. The corrosion resistance of coatings was measured by neutral salt test - NSS. The kinetics of the corrosion on flat samples was additionally determined basing on the computer image analysis. Microscopic examinations concerned the thickness, the structure and the state of the surface (roughness) of assessed coatings. Conducted EDS analysis allowed for comparing the structure of coatings with the theoretical model. It was stated that the thermal diffusion coating was admittedly less resistant to corrosion in the examined environment, but as a result of the further optimization of process parameters (duplex method) and the method of surface preparation the significant improvement in anticorrosion properties is expected.

Keywords: Zinc coatings, thermal diffusion, hot-dip galvanizing, fasteners

1. INTRODUCTION

Fasteners are very important part of constructions that influence on its final lifetime. There are a lot of parameters affecting on screw joint quality: initial material (wire rod) properties, cold processing conditions, heat treatment effects, anticorrosion coating deposition quality, hydrogen saturation and other [1]. Beside the mentioned factors also anticorrosion properties matters greatly the construction stability. In order to lower the threat from corrosion screws are made of different materials starting from the carbon steel, through the alloyed steel, aluminium alloys or also titanium alloys. For example for screw connections in road tunnels, or in interiors of pools 1.4529 steel is recommended [2]. Despite the screw connections made of the carbon steel after hot-dip galvanizing demonstrate the lower corrosion resistance than the stainless steel [3], fasteners working in less aggressive environments, are most often made of the carbon steel which is usually protected by putting of the zinc coating. The most often applied methods of zinc plating are as follows: galvanizing, lamellar, hot-dip and sherardizing [4]. With reference to screw connections all of mentioned methods are applied. Hot-dip mechanism of zinc coating creation is very similar to thermal diffusion process. In both cases the diffusion coating layer is created: 100 % Zn; $FeZn_{13}$, $FeZn_7$, Fe_3Zn_{10} after hot-dip zinc galvanizing and $FeZn_7$, $Fe_{11}Zn_{40}$, 50% Fe after thermal diffusion [5]. The hardness of zinc layer achieved after thermal diffusion is even higher than after hot-dip galvanizing ($FeZn_7$ - 300-350HB; pure zinc - 70HB). Amongst advantages of thermal diffusion galvanizing apart from the greater coating hardness also the higher adhesion to the base (diffusion coating), the possibility of using to high-strength steels galvanizing, the evenness of the coating put on the thread, the greater deformability and the reduced tendency to sparking during friction are mentioned [4]. Unfortunately there are a lot of differences in literature data regarding the corrosion resistance of thermal diffusion coating in comparison to other zinc coatings [5-9]. On the one hand the accelerated comparative investigations of thermal diffusion and hot-dip coatings conducted in the environment of the neutral salt spray [5, 7] demonstrated lower corrosion in case of the thermal diffusion coating (1000 hours to the iron corrosion; for the hot-dip coating - 250 hours to the iron corrosion). Similar examinations concerning fasteners applied in roof connections showed the similar corrosion resistance of the hot-dip and thermal diffusion coatings [8], in addition in case of the TD coating a smaller weight decrease was stated - **Figure 1** [9]. Next in examinations [10] it was stated, that protected by thermal diffusion galvanizing steel sheet is less resistance against corrosion than sheet after hot-dip galvanizing.

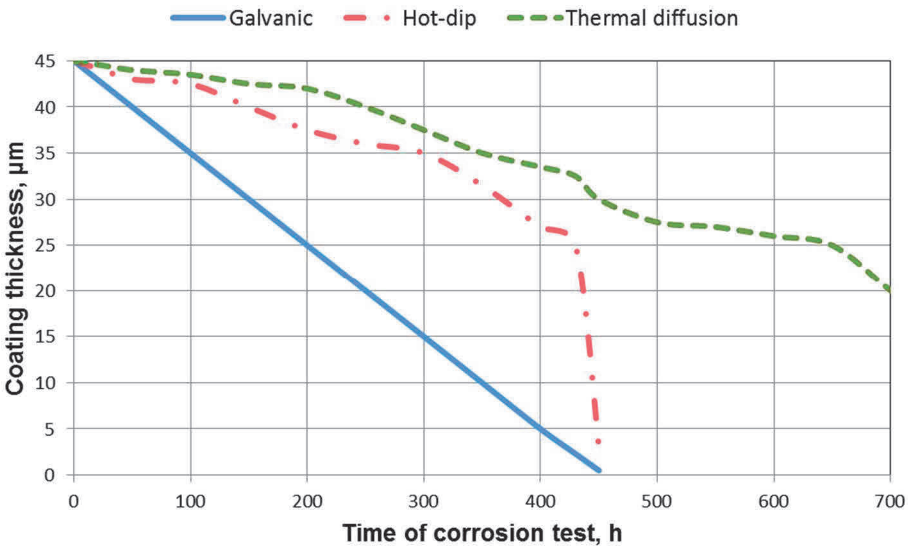

Figure 1 Comparison of different coatings resistance in neutral salt spray (NSS) [9]

Considering differences existing in literature authors decided to make an attempt to explain the reason of such data discrepancy with reference to both flat samples as well as fasteners protected by zinc coating deposited by hot-dip and thermal diffusion methods.

2. EXPERIMENTAL

2.1. Corrosion test methodology

Corrosion examinations - NSS tests, were conducted in a salt chamber - MARWO, MS 600 type, in the company laboratory of S.F. BISPOL S.A., according to the ISO EN 9227 standard. The duration of experiment amounted to 1000 h. Parameters of corrosion environment were as follows: environment - fog of the 5% of water NaCl solution, pH - 6.7 ÷ 6.9, temperature - 35 °C, the rate of the salt fog fall - 1.6 ml/h. Samples were treated in industrial conditions: thermal diffusion according to PN-EN ISO 17668:2016-04 [11] in the mixture of zinc powder with activator and the filler in rotation chambers, turning with speed of 5-10 turns/min, in temperature 400 °C, within the time of the 4 h; hot-dip galvanizing according to PN-EN ISO 10684 [12] - etching in 12% HC, fluxing, dipping in Zn bath with Al, Bi, Ni; in temp. 460 °C, within time 1.5 min, cooling in water. During the experiment M10 screws and flat samples made of steel 23MnB4 and dimensions 25x25x3 mm, made in the 8.8 strength class were used.

2.2. Microscopic analysis

After corrosion tests the surface roughness of flat samples were evaluated using Phase View ZeeScan optical assembly for 3D surface scanning. Further the coated samples with the thermal diffusion coating was analysed using the metallographic examinations with application of the scanning microscope (SEM) EVO 25 MA Zeiss with the EDS attachment that enables both qualitative and quantitative analysis of the chemical composition. Results of microscopic observations were compared to the theoretical model of the coating structure and to analogous inspections of the hot-dip coating which is very close in terms of the structure to the thermal diffusion coating. Additionally a computer image analysis was used to the evaluation of the surface state after corrosion tests, for this purpose the "ImageJ" software was applied.

3. ANALYSIS OF RESULTS

3.1. Corrosion kinetics

In **Figure 2** an appearance of samples after thermal diffusion galvanizing and corrosion test is presented with reference to the initial state of the sample surface. According to the ISO EN 9227 standard the surface of the samples should be assessed macroscopically in 24 h intervals. Basing on conducted experiment it was stated, that corrosion of iron - so-called "red" corrosion appeared on samples already after 24 h (**Figure 3** - sample no. 2). The analogous effect was achieved in case of inspected screw, where the considerable part of the screw was covered with the red corrosion already after 24 h. As a result of further holding in a salt chamber the part of surface covered by product of iron oxidation slightly increased.

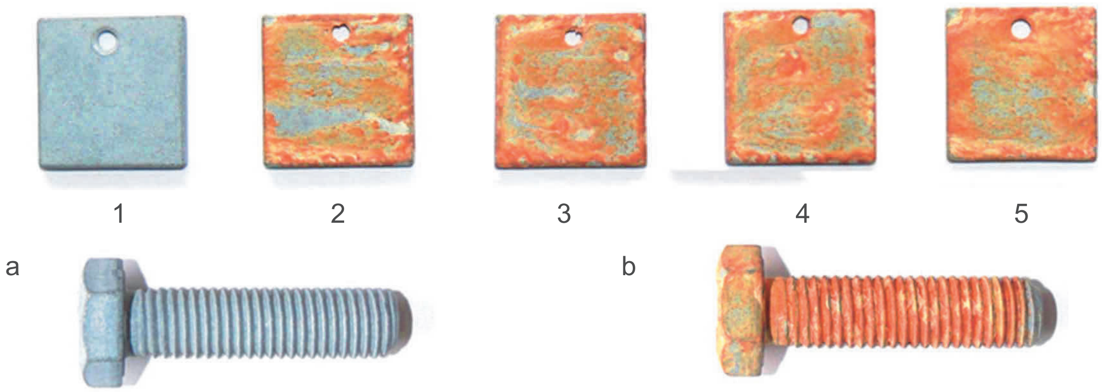

Figure 2 An appearance of samples investigated in corrosion test: 1 - initial sample, 2 - sample after 24 h, 3 - sample after 48 h, 4 - sample after 72h, 5 - sample after 96 h together with screw M10 before test - a and after 96 h in salt chamber - b.

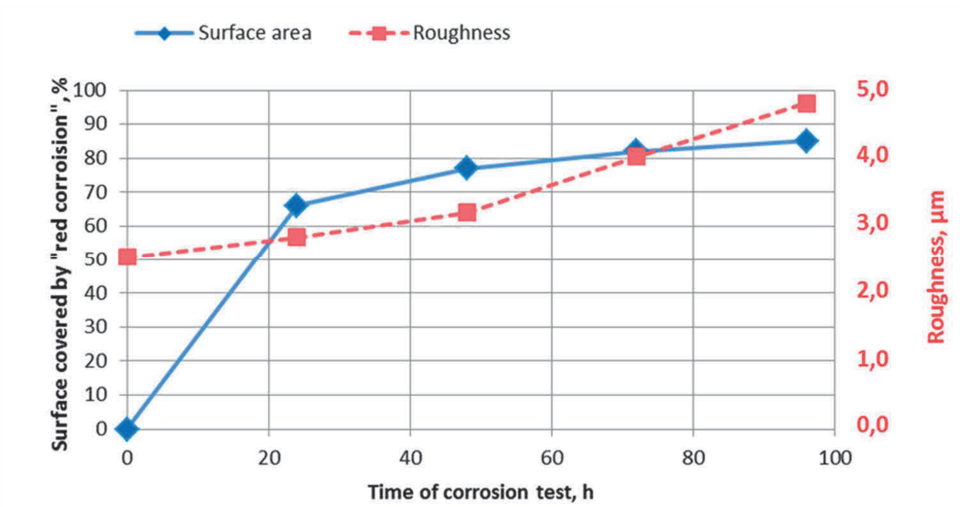

Figure 3 Kinetics of the corrosion of flat samples after thermal diffusion galvanizing expressed in the percent of the surface occupied by "red corrosion" and roughness changes

a) b)

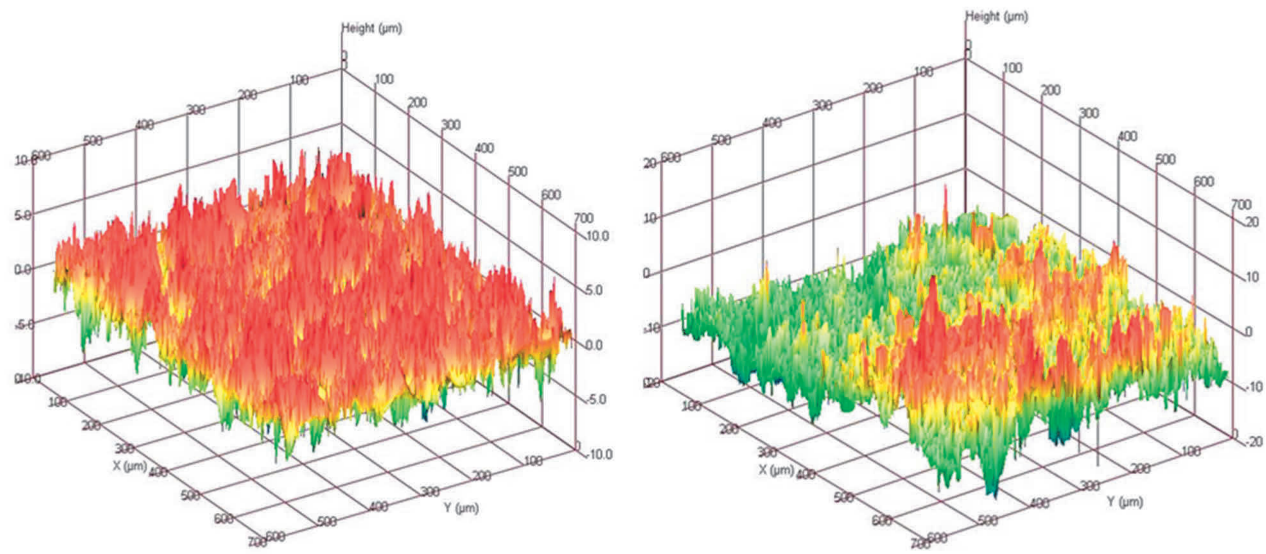

Figure 4 The comparison of isometric surface image of thermal diffusion coated flat samples before corrosion test - a and after 24 h in salt chamber - b

The conducted computer image analysis enabled quantitative determination of surface part covered by "red corrosion" - **Figure 3**. The corrosion rate, which correspond to the inclination angle of straight line from **Figure 3** is the highest in the initial stage of the corrosion, i.e. up to 24 h (2.75%/h). On the expire this time, the corrosion rate systematically decrease and in the range of 48-96 h achieves the value of 0.17%/h. It explicitly follows from the above analysis that beside traditional methods such as the measurement of the mass change, also the computer image analysis can be used to more precise determination of corrosion rate than it is taking place in case of the macroscopic evaluation, according to PN, or by comparison to standards. In case of analogous inspections of hot-dip zinc coatings [1] the red corrosion appeared after 816 h. With increasing of corrosion time also the surface roughness expressed by S_a parameter systematically increase from 2.54 µm (surface after coating) to 4.81 µm after 96 h of corrosion test - **Figure 3**. The isometric surface images presented in **Figure 4** confirmed that more and more part of surface covered with corrosion product results in its non-uniformity. The achieved results confirms very low corrosion resistance of thermal diffusion coating with reference to the hot-dip zinc coating. It is as unexpected, that in literature data considerable divergences are ruling in this area, and steel screws are protected by this method also in Poland. Moreover, in some publications it is possible to find information about the superiority of this method above among others the hot-dip and galvanic coatings [5].

3.2. Microstructure analysis

The aim of microscopic examinations and EDS analysis was to verify the compliance of the coating structure with the theoretical model - **Figure 5** and the verification its quality considering layer thickness and appearance of the prospective discontinuities - cracks, porosity, delamination which could influence the reduction of the corrosion resistance. EDS examinations were being conducted both on the exterior surface of the coating, and on its cross section. Findings are presented in **Figure 5** and compared additionally to this ones which was get as a result of analogous inspections of the hot-dip zinc coating - **Figure 6**, where the corrosion resistance was much greater.

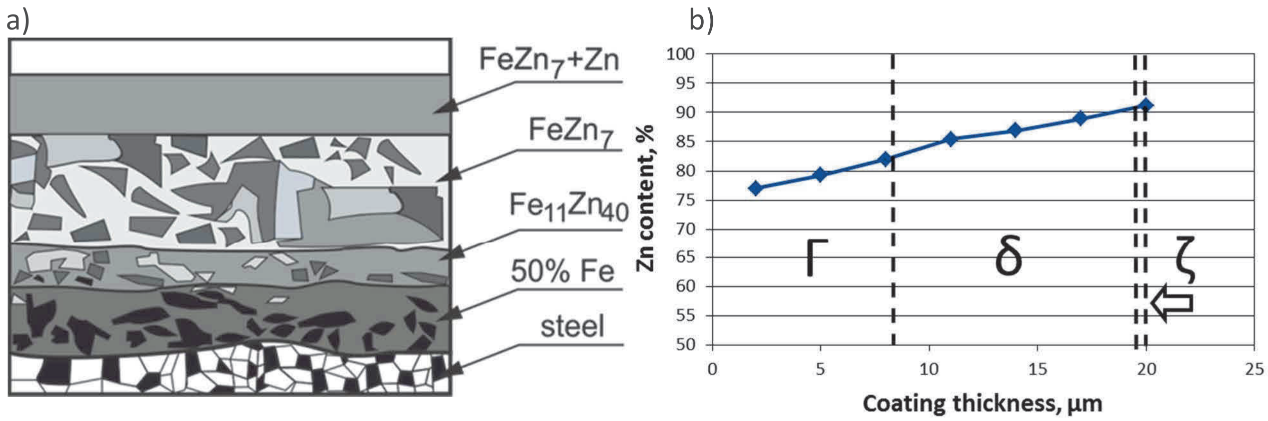

Figure 5 Theoretical structure observed at the cross section of thermal diffusion coating - a [5] together with zinc distribution at the investigated coating cross section - b

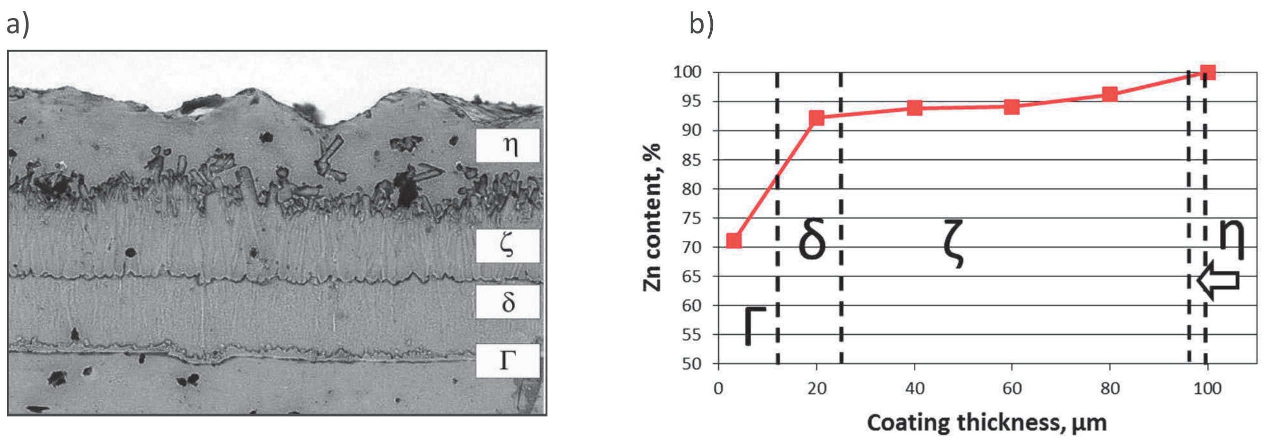

Figure 6 Theoretical structure observed at the cross section of hot-dip zinc coating - a together with zinc distribution at the investigated coating cross section - b

Conducted analysis - demonstrates, that outside surface of the thermal-diffusion coating is very inhomogeneus in terms of the chemical composition. Areas existing on the samples surface differ essentially in terms of the zinc content - from 9.61 ÷ 41.2%. Individual areas differ also in colouring and the morphology. The surface with the increased content of zinc is demonstrating the needle structure. Increased content of zinc (to ab. 91%) is appearing in brighter places. Additionally the put coating is relatively thin. Its thickness amounts to ab. 21 µm - **Figure 5**. The thickness of the thermal diffusion coating is usually included in the range 20 ÷ 120 µm [5], so the thickness of the analysed coating is close to the lower limit of the applied range. Also ranges of individual metallic phases appearing are a bit untypical. In **Figures 5** and **6** the theoretical approximate ranges of Zn content in which individual intermetallic Fe-Zn phases (Γ,δ, ζ,η) [13] appears are separated by vertical broken lines at the assumption that iron is the rest to 100%. In the inspected coating biggest part is occupied by delta phase (ab. 12 µm), with lower zinc content, the range of zeta phase appearing is very narrow (ab. 2 µm). Comparing the structure of the thermal diffusion coating to the hot-dip coating being a point of reference - **Figure 6**, the last one apart from that is 5 times thicker (ab. 100 µm) also demonstrates the correct structure, completely in accordance with the theoretical model, where on the coating cross section the high-zinc phase is dominating (zeta). Apart from mentioned remarks, on the thermal diffusion coating cross section delaminations and cracks are observed which don't exist in the hot-dip coating, and which can indeed reduce the corrosion resistance of this coating.

4. CONCLUSIONS

The conducted examinations enabled to express the following conclusions:

- Unexpectedly, the corrosion resistance of the inspected thermal diffusion zinc coating was much smaller than hot dip coating. Similar results were achieved irrespective of the shape of tested samples. Both on flat samples, as well as fasteners the corrosion of iron was observed already after 24 h.
- The roughness measurements as well as the computer analysis of corroded samples surface can be applied successfully to determination of the flat samples corrosion kinetics. Unfortunately in case of elements with more complicated geometry as fasteners application of this type method is very difficult.
- Both, discrepancies in literature data, as well as determined very low corrosion resistance of the thermal diffusion coating can result from diversification of the structure existing on the coating cross section: inhomogeneities of its outside surface in terms of the chemical composition, morphology and the too small thickness.
- Considering the imperfections of thermal diffusion surface structure the aim of the next investigations should be increase the fasteners corrosion resistance protected by this method through the optimization of the following galvanization parameters: the kind and physicochemical properties of zinc powder, temperature and time of the process duration, with reference to the structure and the thickness of deposited coating and application of duplex method.

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