EVALUATION OF THE RESISTANCE TO CORROSION AND WEAR OF ZINC COATINGS CREATED ON CAST IRON

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Abstract

The paper contains the second part of the research which compares corrosion and mechanical properties of different zinc coatings. The following methods of zinc coating were applied: galvanic (PN-EN ISO 4042), hot-dip (PN-EN ISO 10684) and lamellar (PN-EN ISO 10683). The first stage of the experiment covered metallographic research: roughness coefficient measurement, morphological structure evaluation with the use of scanning and optical microscope, zinc layer thickness measurement, and corrosion research in salt chambers using the following tests: in the salt chamber with neutral NaCl (PN-EN ISO 9227), climatic chamber (VDA 621-415) and KESTERNICH (DIN 50018/2,0 SO₂) chamber. The second stage of the experiment, presented in the following paper, refers to: tribological laboratory research, metallographic analysis of zinc coating microstructure in damaged areas, with the use of optical microscope, and the evaluation of the decrease in corrosion resistance as the result of destruction the continuousness of zinc layer. The corrosion research was conducted with the salt chamber with neutral NaCl (PN-EN ISO 9227).

Having analyzed the results, it was stated that the lamellar coating is the most resistant to mechanical damage and therefore its corrosion resistance didn’t change essentially after the friction test. Galvanic and hot – dip coatings are less resistant to mechanical damage, and destruction the continuousness of protection layer structure affects their corrosion resistance significantly.

Key words: lamellar zinc coating, hot – dip zinc coating, galvanic zinc coating, corrosion test, salt chamber

1. INTRODUCTION

Problems that regard the durability of materials in natural and artificial environments are extremely important in the designing of iron alloys structures intended for different metal parts. Destruction of corrosion is one of the main sources of material losses and contributes to environmental pollution [1]. The most commonly metal used for corrosion protection of steel and cast iron is zinc. This metal gained the popularity thanks to the ability to “spontaneous” healing of leakiness of the coating created on the surface of protected steel. The described phenomenon is characteristic of a so-called cathodic protection, where the coating of less noble metal is acting as the anode - the corrosion protector. The hot-dip zinc galvanizing is the oldest from methods applied at present. During this metallurgical process iron alloys elements are immersed into the bath with liquid zinc with alloyed additions: nickel (Ni), bismuth (Bi), aluminium (Al). In the temperature range 450-580 °C. the diffusive Zn-Fe layers are created, which influence of protective properties. The outside layer, composed of pure zinc creates during emerging of detail/elements from the bath with liquid metal. This technology is usually applied to protect large constructions exposed to influence of atmosphere and mechanical damage [2]. Zinc galvanizing is a most often applied technology. In this process we are dealing with electrochemical reactions, the electrolyte except Zn²⁺ includes substances like: they are Cl⁻ (baths weakly acidic) or NH⁴⁺ (baths alkaline) that support maintain a constant current density, and organic glow creative additives and reinforcing bath’s throwing agents. Fast development of this type application during the last years contributed to the coming into existence of new baths compositions and passivation colours.
[3]. So, because of that, new elaborated coatings can in some cases replace the more expensive decorative Cu-Ni-Cr covers especially when a long fastness of the sheen is required, although applying the polymer-silicate sealing after the chromate treatment eliminates also this problem. There is a large range of solutions existing in the galvanic technology regarding both aesthetic (silver, yellow, olive or black coatings colours) as well as durability aspects (coatings chromated with Cr$^{3+}$ and Co$^{2+}$ are characterized by considerable higher corrosion resistance). The latest technology employing zinc to steel protection is so-called lamellar technique [4]. This process consists in plunging the steel details in solution of zinc paint with the addition of aluminium and heating such a coating up in the furnace in temperature range 180 – 220 °C., where drying and hardening of zinc layer take place. This technique is being dedicated mainly for the automotive industry and enables material finishing in any colour and achieving the additional properties - greater wear ability that is essential for screw assembled automatically products [5]. The elimination of the hydrogen embrittlement phenomenon is an important advantage of this solution that is a key importance in case of fastener elements with increased mechanical properties – $R_m>1000$MPa [6]. Because in the available literature there is no information comparing the mechanical properties of zinc coatings, resistance to wear and corrosion, created by: hot dip, galvanic, and lamellar methods in the same conditions [7], the aim of presented study was to determine such data summary with reference to the protection of cast iron with flake graphite.

2. THE OWN RESEARCH

2.1 Tested materials and investigation methodology

The experiment was focused on samples made of gray cast iron grade EN-GJL-250 with dimensions $\varnothing$ 25 x 5. Farther, samples were divided in three groups and directed to the galvanizing process (thick chromate coating was used), hot dip and lamellar. Data concerning the way of surface preparation are enclosed in the Table 1. Zinc plated samples were subjected to the following investigations: roughness measurement - the topography after tribological test; microscopic observations – thickness and structure of coated layer and corrosion resistance measurement – the salt chamber test.

<table>
<thead>
<tr>
<th>No</th>
<th>Kind of process</th>
<th>Surface preparation</th>
</tr>
</thead>
</table>
| 1  | Electro-galvanizing acc. PN-EN ISO 4042 [8] | • chemical degreasing, temp. 60 °C  
• etching in 18% HCl and 10% $H_2SO_4$ with inhibitors  
• degreasing and electro-polishing, temp. 60 °C, 1000 A  
• galvanization in the weak acid chlorine Zn bath, temp. 35 °C, pH 5,1  
• Passivation - jons Cr$^{3+}$, Co $^{2+}$, NO$^3-$ temp. 45 °C, pH 1,9 |
| 2  | Hot-dip acc. PN-EN ISO 10684 [9] | • etching in 12% HCl  
• fluxing  
• galvanizing in the bath: Zn with additions Al, Bi, Ni; temp. 460°C, time 1.5 min  
• cooling in water |
| 3  | Lamellar acc. PN-EN ISO 10683 [10] | • shotblasting 0.4 mm  
• triple painting (95% Zn, 5% Al)  
• temperature holding in 120 °C  
• cooling to temp. 25 °C – air jet |

2.2 INVESTIGATION METHODOLOGY – EQUIPMENT

2.2.1 The salt chamber

Fig. 1 depicts the salt chamber located in the F.S BISPOL S.A laboratory, made by MARWO Company, MS 600 type, 600 liter capacity, in which the NSS test was carried out. There is one type of corrosion research designated for each chamber because of atmosphere cleanliness maintenance. The chambers in which the climatic tests are carried out, have automatic parameter control: humidity (0 – 100%), temperature (-20°C - 70°C), ...
+70°C and fog descend volume. The elements tested are arranged inside in such a way that the surface exposed is as large as possible and set at the 30° angle to the bottom of the chamber.

![Fig. 1 The climatic chamber for NSS test](image1)

![Fig. 2 The appearance of the device for tribological test](image2)

2.2.2. Tribological test

The tribological test consisted in applying mechanical friction to every kind of coating and calculation of the friction coefficient. To perform that, surfaces of the tested samples were subjected to friction with a ø 4 steel rod with constant pressure of 0.5 kg, which was making circles on the surface of the samples with the speed of 45 sales/min for 30 minutes. During the test the friction coefficient was measured every 0.2 s.

2.3. RESULTS ANALYSIS

2.3.1. Topography and coefficient of friction of tested samples

During surface investigation the 3D topography was determined by application of the profile measurement gauge - Perthometer Concept (MAHR). Measurement results are presented in Table 2 and Fig. 2.
Table 2 The surface friction and thickness of layer of investigated samples

<table>
<thead>
<tr>
<th>Group No.</th>
<th>Kind of process</th>
<th>Layer thickness [µm]</th>
<th>Rv [µm]</th>
<th>Friction coefficient, µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Galvanic</td>
<td>20,2</td>
<td>20,2</td>
<td>0,212</td>
</tr>
<tr>
<td>2</td>
<td>Hot-dip</td>
<td>82,1</td>
<td>16,2</td>
<td>0,285</td>
</tr>
<tr>
<td>3</td>
<td>Lamellar</td>
<td>9,8</td>
<td>4,5</td>
<td>0,131</td>
</tr>
</tbody>
</table>

2.3.2 Metallographic coatings investigations

Metallographic investigation was conducted for all samples with zinc coating. Metallographic specimens were prepared in classic way. The observation was realized using optical – LM microscope. Results are presented in Fig. 3. During observation also Zn coating thickness was measured.
Fig. 3 The cross section of cast iron surface layer with Zn coating (optical microscope LM): a) galvanic, b) hot-dip, c) lamellar

2.3.3 Evaluation of corrosion resistance by NSS test in neutral salt spray

The corrosion examination in a salt chamber according to the ISO EN 9227 standard [11] was made in F.Ś. BISPOL S.A. in Bielsko-Biała. Parameters of the corrosion environment were as follows: 5% NaCl, pH - 6.7-6.9, temperature – 35°C, the rate of the salt fog (spray) fall - 1.6 ml/h. Two types of sample were included into the chamber: no. 1 – after tribological test and no. 2 - before the test. Research findings are presented in Fig. 4 and Table 3.

Table 3 Comparison of NSS test results in neutral salt fog

<table>
<thead>
<tr>
<th>Kind of process</th>
<th>Sample state</th>
<th>Time to white corrosion [h]</th>
<th>Time to red corrosion [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanic</td>
<td>after friction</td>
<td>24 h - 5% area</td>
<td>168 h - 2% area</td>
</tr>
<tr>
<td></td>
<td>no friction</td>
<td>72 h - 5% area</td>
<td>224 h - 5% area</td>
</tr>
<tr>
<td>Hot - dip</td>
<td>after friction</td>
<td>24 h – 100% area</td>
<td>192 h - 5% area</td>
</tr>
<tr>
<td></td>
<td>no friction</td>
<td>24 h – 100% area</td>
<td>224 h - 5% area</td>
</tr>
<tr>
<td>Lamellar</td>
<td>after friction</td>
<td>without</td>
<td>120 h - 5% area</td>
</tr>
<tr>
<td></td>
<td>no friction</td>
<td>without</td>
<td>224 h - 2% area</td>
</tr>
</tbody>
</table>

Fig. 4 Results of NSS test in neutral salt fog (spray) after 224 h: a) galvanic b) hot-dip c) lamellar, 1 – after tribological test, 2 – before tribological test

3. RESULTS DISCUSSION

The summary enclosed below presents investigation results, which aim was: identification and interpretation the factors influencing the variety of zinc coating structures created by application of the three most popular techniques and evaluation of the coating resistance both to corrosion and mechanical wear. It results from the tribological research analysis that the lamellar zinc coating is the most resistant to mechanical damage/wear, two other coatings (hot-dip, galvanic) show much lower properties and behave similarly – Fig. 2. The surface profile presented in Fig. 2c (lamellar coating) is regular without greater unevenness – Rv reaches here the lowest value – 4,5 μm [12]. Surface profiles in Fig.2a and b have the same character, i.e.: in the place of friction that was in contact with steel rod a deep furrow/U shape groove was created which depth is equal to galvanic coating thickness but in the case of hot-dip zinc coating reaches 16,2 μm. Microscopic observation of the hot – dip coating cross section - Fig. 3, confirmed the high level of abrasion
wear. Although there was no coating delamination almost the whole outside sublayer was removed (phase η and partially ζ). On the other hand the exerted influence did not damage the coating entirely and the internal layers (the rest of ζ, phase δ and Γ) could still protect the cast iron against corrosion.

The cross section of the lamellar coating revealed significant displacement and delamination of zinc flakes from the protected base. The flakes deformation/displacement is probably the main reason of corrosion resistance decrease observed during the salt chamber test. The microscopic observations revealed the separation of zinc layer from the protected base within the damage area length which occurred during the tribological test of the galvanic coating. Practically, the whole zinc layer was removed. Moreover, the layers sectors close to the damaged area are delaminated from the cast iron surface and character of zinc coating cracking direction (perpendicularly to cast iron/zinc coating surface) proves rather chipping than grinding mechanism of the wear. Although the galvanic coating was partially removed from the cast iron surface and there was an open access to the protected alloy base after the tribological test, time to red corrosion product creation in the salt chamber was longer than in case of lamellar coating where the surface looked to be less damaged by friction forces. The hot – dip zinc coating demonstrates the greatest thickness of zinc layer, nevertheless the coating stability in the salt chamber, considering the time to red corrosion appearance, is similar to the galvanic zinc coating. The salt chamber test revealed that the lamellar coating not have the properties typical of zinc coating. There is practically no cathodic base protection. High corrosion resistance is guaranteed only when the coating is fully hermetic. White corrosion did not occur on the lamellar coating sample during the whole inspection time of the NNS test. The corrosion resistance (expressed in time to red corrosion appearance) of sample with lamellar zinc after tribological test decreased by almost 50% (sample no. 1 - 120h to red corrosion, sample no. 2 – 224h to red corrosion). Samples with galvanic and hot - dip zinc coating have similar corrosion resistance (time to red corrosion) both after and before tribological test.

4. CONCLUSION

On the basis of conducted preliminary examinations it is possible to express the following conclusions:

- thickness of inspected zinc coatings - galvanic and hot-dip isn't a parameter deciding on the corrosion resistance;
- lamellar zinc coating does not demonstrate cathodic protection, unlike the other two coatings, and behaves similarly to powder coating, where breaking the protective layer continuousness leads to quick occurrence of corrosion point;
- according to the tribological test, the lamellar zinc coating has the highest friction resistance, and hence results also its highest resistance to mechanical damage;
- as far as the importance of ecological activities and minimizing the amount of noxious metals released to the atmosphere is appreciated, the lamellar coatings should be preferred as environment friendly because there is no zinc oxide on their surface during exploitation.

LITERATURE

[9] PN-EN ISO 10683 Polska Norma, Części złączne, Nieelektrolityczne płatkowe powłoki cynkowe
[10] PN-EN ISO 10684 Polska Norma, Części złączne, Powłoki cynkowe nanoszone metodą zanurzeniową