

EVALUATION OF THE HIGH TEMPERATURE OXIDATION AS A MEANS OF CAST IRON PREPARATION TO HOT-DIP ZINC GALVANIZING

Wojciech SKOTNICKI^a, Dariusz JĘDRZEJCZYK^a, Ilona SZŁAPA^b, Maciej HAJDUGA^a, Sylwia WĘGRZYNKIEWICZ^c

^a University of Bielsko-Biala, Poland, EU, <u>wskotnicki@ath.bielsko.pl</u>
^b BISPOL SA, Bielsko-Biala, Poland, EU
^c BELOS PLP SA, Bielsko-Biala, Poland, EU

Abstract

This paper tries to determine the possibilities of application of the high temperature oxidation of cast iron as a way of surface preparation before hot-dip zinc galvanizing and presents also results of corrosion resistance tests of zinc coatings created after high temperature oxidation of grey cast iron (with flake graphite). Research was focused on elements of overhead power lines - the jaw-chuck (screw-bow). The achieved effects were evaluated on the basis of following data: metallographic analysis, chemical analysis, measurement of the geometrical parameters of the treated surface. In order to determine the corrosion resistance the potentio-dynamic tests were performed. Experiment was made in accordance with PN-76/H-04601 in aerated solution simulating sea water - 3.5% NaCl. Based on the results of carried test it was stated that the proposed method of surface preparation ensures the correct zinc coating growth on grey cast iron surface. Corrosion tests show that zinc coating created on the surface of the elements that were previously oxidized demonstrate greater corrosion resistance then zinc coating on the crude surface or surface after traditional preparation.

Keywords: Cast iron, oxidation, surface preparation, corrosion resistance, zinc coating

1. INTRODUCTION

Zinc coatings are the most effective and economical way to protect iron alloys against corrosion. In addition to high corrosion resistance to atmospheric conditions this kind of protective layer also demonstrates the high wear resistance and hence is robust and resistant to the working conditions. FC Porter in his work [1] compared the properties of different types of coatings. The results of this study showed a clear advantage of metallic zinc coatings in relation to other types of protective systems. Author also quoted cases where the hot-dip galvanizing should be applied regardless of the economic aspect.

Although zinc coatings are used widely for many years, a lot of research works is still conduct to improve their properties [2-6]. Hot-dip zinc galvanizing of cast iron with flake graphite encounters in industrial practice difficulties caused by subsurface graphite precipitations which are a main reason of the discontinuity of zinc coatings [7-9].

The classic method of the surface preparation of parts intended for galvanizing prior to immersion in molten zinc comprises the successive operations shown in **Table 1**. After degreasing and etching, the rinsing operations is performed. Precise removal of degreasing and pickling solutions is very difficult and in the case of iron not always is successful. In practice, degreasing and pickling baths remain on the metal surface which has a negative influence on the metallization process.

The mentioned above degreasing and pickling are particularly difficult in the case of cast iron. The coating quality decrease is observed due to precipitation on the protected surface the products of reaction of applied acids and metallic matrix. For this reason the widely used technologies of steel galvanizing can be applied to gray cast iron with flake graphite after some modifications. These problems can be significantly reduced by the use of surface decarburization - high-temperature oxidation.



| In | Zing galvanizing stages | | | | |
|------|-----------------------------|---------------------------------|--|--|--|
| Lp. | Traditional process | Proposed/new process | | | |
| 1 | Abrasive-blasting | Surface oxidation 1123K/240 min | | | |
| 2 | Degreasing | Abrasive-blasting | | | |
| 3 | Water rinsing Water rinsing | | | | |
| 4 | Pickling Fluxing | | | | |
| 5 | Water rinsing | Drying | | | |
| 6 | Fluxing | Glvanizing | | | |
| 7 | Drying Water rinsing | | | | |
| 8 | Galvanizing | | | | |
| 9 | Water rinsing | | | | |
| COST | 2 PLN/kg | 1,5 PLN/kg | | | |

| Table 1 | 1 Comparison | of traditional | and galvanizin | g steps | proposed in | this paper |
|---------|--------------|----------------|----------------|---------|-------------|------------|
|---------|--------------|----------------|----------------|---------|-------------|------------|

The proposed method of surface preparation should allow to improve the quality of zinc coatings and reduce the amount of waste generated during the galvanizing process and reduce harmful emission sources. Additionally galvanizing process costs can be reduced by approximately 25%.

2. OWN RESEARCH

In the study the cast iron grade GJL-250 with flake graphite and typical chemical composition specified in PN-EN 1560:2001 was used. Test specimens were taken from the commercial parts used for the manufacture of network equipment - designed as a cover plate of passage holder for cables suspension (**Fig. 1**).



Fig. 1 Cover plate for passage holder

Cover plates are made of cast iron secured additionally by zinc coating. Traditional cover plates surface preparation results in cracked and laminated zinc coating where in places of discontinuity corrosion arise.

3. **RESEARCH METHODS**

The research material was divided into three groups and subjected to surface treatment shown in **Table 2**. Sandblasting was performed using a pneumatic cabin cleaner with a cylindrical jet made of boron carbide. The angle of inclination of the cleaning nozzle to treated surface was approximately 45° at an operating pressure of 0.4 MPa. Blasting was performed using typical A95 corundum with a grain size of 1-2 mm and a hardness of 1355 HV. The process of high-temperature oxidation was carried out in ambient air in a furnace chamber, with electronic temperature controller PSK 600/25 VEB - Lokomotivbau Elektrotechnische Werke Company.



| Series No. | Surface treatment | Method of surface preparation | | | |
|------------|----------------------------|---|--|--|--|
| I | CRUDE SURFACE | Pickling in HCl (12 %; 35gFe/dm ³) fluxing (pH = 4.80; 28°Be; 1.4gFe/dm ³) | | | |
| П | SANDBLASTING | Blasting with electro-corundum 95A Pickling in HCl (12 %; 35gFe/dm ³) Fluxing (pH = 4.80; 28°Be; 1.4gFe/dm ³) | | | |
| | HIGH TEMPERATURE OXIDATION | Pickling in HCl (12 %; 35gFe/dm³) Fluxing (pH = 4.80; 28ºBe; 1.4gFe/dm³) | | | |

Table 2 The method of surface preparation prior to galvanizing

4. TEST RESULTS

To analyze the cross-sectional structure of the created zinc coating the metallographic specimens were prepared. For metallographic observation an optical microscope Axiovert A - 100 and scanning microscope Joel - J7 were used. Results of samples of observations are shown in **Fig. 2**.



Fig. 2 The cross-section of zinc coating: a) the crude surface, b) the surface after oxidation

In the next part of the study the quality assessment of zinc layers put on elements previously decarburized was made using X-ray microanalysis. The results are shown in **Fig. 3** and **Table 3**.







| Point | Distance | Chemical composition, % | | | | | | | |
|-------|---------------------------|-------------------------|-------|-------|-------|--------|--------|--|--|
| No | from Fe-Zn surface, µm | С | 0 | Si | Mn | Fe | Zn | | |
| 1 | 80 | 1,412 | 0,000 | 0,004 | 0,000 | 0,050 | 99,095 | | |
| 2 | 60 | 1,048 | 0,000 | 0,000 | 0,018 | 4,702 | 94,070 | | |
| 3 | 40 | 1,046 | 0,000 | 0,237 | 0,003 | 7,211 | 92,397 | | |
| 4 | 20 | 2,200 | 0,718 | 0,010 | 0,000 | 10,723 | 87,014 | | |
| 5 | 10 | 1,235 | 0,000 | 0,029 | 0,000 | 16,668 | 82,580 | | |
| 6 | 5 | 1,334 | 0,000 | 0,009 | 0,000 | 17,886 | 80,899 | | |
| 7 | 5 | 0,829 | 0,000 | 1,083 | 0,027 | 97,332 | 2,246 | | |
| 8 | 10 | 0,380 | 0,000 | 1,352 | 0,042 | 97,273 | 1,059 | | |
| 9 | 20 | 0,482 | 0,433 | 1,794 | 0,271 | 97,530 | 0,859 | | |
| 10 | 30 | 0,820 | 0,062 | 0,870 | 0,135 | 96,282 | 0,645 | | |

Table 3 Distribution of selected elements in the surface layer of cast iron after galvanizing

To determine the corrosion resistance of the tested parts the potentiodynamic tests were performed in accordance with PN-76/H-04601 standard in the aerated solution simulating sea water of 3.5 % NaCl. These studies were performed with application of a potentiostat Solartron SI 1286, and the measuring cell in the three-electrode system. The device was computer-controlled and equipped with modern control software (CorrWare, ZPlot) and software to results analyze (CorrView, Yawn), allowing conducting repeatable experiments with the elimination of interference. The test results are shown in **Table 4** and **Fig. 4**. During the study the potential of anodic-cathodic transition E_{K-A} and the corrosion current i_{Kor} has been measured.

| Table 4 The results of measurements | s of | corrosion | potential | and | corrosion | current |
|-------------------------------------|------|-----------|-----------|-----|-----------|---------|
|-------------------------------------|------|-----------|-----------|-----|-----------|---------|

| Kind of surface | Е _{к-А} [mV] | i _{kor} [A/cm²] |
|-----------------|-----------------------|--------------------------|
| crude | -1317 | 2,35×10 ⁻⁷ |
| sandblasted | -605 | 8,88×10⁻ ⁸ |
| oxidized | -520 | 2,19×10 ⁻⁸ |
| bronze | -242 | 2,56×10 ⁻⁸ |



Fig. 4 Registered potentiodynamic polarization curves - hot-dip zinc galvanized GJL-250 cast iron - 1) crude surface, 2) sand-blasted surface, 3) oxidized surface, 4) bronze





5. RESULTS ANALYSIS

As a result of hot-dip zinc galvanizing process of tested samples in the described conditions a uniform and continuous coating were created - **Fig. 2**. On the basis of conducted own research and literature data it was found that the structure and metallic phases composition of coatings created on the samples after high-temperature oxidation corresponds to the coating structure after classical surface preparation. Typical coating structure consists of a clearly visible diffusive - alloy layer and the outer layer. The diffusive layer can be divided in phase Γ , ζ and δ the outer layer is formed of a η phase. In the case where the surface of cast iron was prepared traditionally the graphite penetration inside the zinc coating confirmed that the minimum thickness of about 60-65 microns was achieved on the crude casting surface. For the shot-blasted and sand-blasted surface coating thickness was 69-77 microns. For cast iron, where the high temperature oxidation was used as a way of surface preparation the coating thickness had the highest value - 85-90 microns. So, it means that the coatings thickness fulfills the requirements of PN- EN- ISO 1461.

The chemical composition analysis was the supplement to microscopic observation, which showed that the zinc coating put on the oxidized cast iron surface demonstrate structure according to the Fe-Zn system (Fig. **3a**). In the zinc layer being in contact with the cast iron base the iron contents was approximately 17 %, whereas the zinc contents was about 82 % zinc. Thus the contents of Fe and Zn corresponds to intermetallic phase Γ - Fe₃Zn₁₀. Analysis made at a distance of 20 - 40 microns from the sample surface revealed that the chemical composition corresponds to the phase δ - FeZn₁₀. The zinc and iron content was correspondingly 89 %, and 9.5 %. The next measurements at a distance of 60 microns from the surface confirmed the presence of phase ζ - FeZn₁₃. The zinc content was 94 %, whereas the iron contents was about 6 %. The highest zinc content equal to 99 % was measured in the outer coating sub-layer. The analysis of the chemical composition was also performed in the cast iron surface layer. The cast iron matrix enrichment in zinc was observed. Zn content decreases with increasing distance from the surface, and change from 2.40 % at 10 microns depth to 0.65 % at 80 microns depth. The graphite voids created by the high-temperature oxidation were subjected to linear RTG analysis (Fig. 3b), which confirmed that in the free "after graphite" spaces both zinc and silicon contents is increased and at the same time iron contents was reduced. The enrichment of the metal matrix and "after graphite" voids in zinc may be the reason of the corrosion resistance to increase of the materials previously oxidized. Therefore, in order to verify the above hypothesis the potentiometer dynamic tests were used to determine the corrosion resistance of specially treated cast iron. The results achieved in the form of polarization curves (Fig. 4) can be divided into two main parts: the area of cathodic polarization and anodic polarization. From the point of view of the conducted research the more important section is the anodic polarization area. Observing the curve course, we can determine how behaves the material placed in a corrosive environment. The most important characteristic points determined from the graph are: Ekor corrosion potential and corrosion current ikor. On the basis of measurements of potentiodynamic polarization of cast iron electrode coated with zinc the significant differences in the potential of zinc coatings were discovered. For the crude surface created directly after casting the potential was about -1317 mV. The reduction of potential about 50 % to the value of -605-664 mV was recorded for the surface after shot-blasting and sand-blasting. Further lowering of potential to -520 mV was recorded for the surface where the oxidation process was applied. Decreasing of the potential resulted in diminishing the corrosion current value of one order of magnitude (2.35 × 10⁻⁷-2.86 × 10⁻⁸ A/cm²), and decreasing the corrosion rate. With the change in coating thickness the proportions of the diffusive layer and a pure zinc layer also change. In addition, the removal of graphite from the subsurface layer of cast iron by oxidation prevents it penetration into the zinc coating.



SUMMARY AND CONCLUSIONS

On the basis of preliminary tests the following conclusions can be formulated:

- The achieved results confirm that the high temperature treatment (oxidation) of gray cast iron castings surface, allows for hot-dip zinc coatings creation with the correct structure and thickness.
- The zinc coating created on the surface after oxidation reveal the structure in accordance with Fe-Zn system.
- The enrichment of the metal matrix and "after graphite" voids in zinc may be the reason of the corrosion resistance increase of the materials previously oxidized.
- The appearance of the zinc coated surface of oxidized products meet the requirements of corresponding standards.
- The corrosion resistance of oxidized and hot-dip zinc galvanized cast iron is similar to the bronze resistance tested in the same conditions.

REFERENCES

- [1] Porter F.C. *Economics of Coatings for Steelwork Protection.* Progress in the Understand and Prevention of Corrosion 10th European Corrosion Congress. Barcelona 1993, s.687.
- [2] Sandelin R. W. *Galvanizing characteristics of different types of steel*. Wire and Wire Products 1940, 11, s.655-676.
- [3] Foct J., Perrot P., Reumont G.: Interpretation of the role of silicon on the galvanizing reaction based on kinetics, morphology and thermodynamics. Scripta Metallurgica et Materialia, 1993, 28, s.1195-1200.
- [4] Thiele M., Schulz W. Coating formation during hot-dip galvanizing between 435°C and 620°C in conventional zinc melts a general description. Proceedings Intergalva, 2006.
- [5] Gierek A., Tatarek P., Liberski P. *Badania zjawisk rozpuszczania w układzie żelazo Armco kąpiel cynkowa w warunkach stacjonarnych*, Inżynieria materiałowa, 2005, 5, s. 667-689.
- [6] Wesołowski J., Głuchowski W. Universal and cost-saving zinc coating on products made of reactive steel. Metall 2006, 60, 5, s.299-302.
- [7] Jędrzejczyk D., Skotnicki W., Węgrzynkiewicz S., Hajduga M. Influence of the surface state on hot dip Zn galvanizing effects of iron alloys. Metal 2012. 21st International Conference on Metallurgy and Materials. Brno, Česká Republika, 23-25.5.2012. - ISBN 978-80-87294-29-1. s.62
- [8] Jędrzejczyk D., Hajduga M. *Cast Iron Zinc Galvanizing Improved by High Temperature Oxidation Process.* Journal of Achievements in Materials and Manufacturinh Engineering 2010 Vol. 43. s. 418-422.
- [9] Jędrzejczyk D., Hajduga M. *Effect of the Surface Oxidation on the Hot-Dip Zinc Galvanizing of Cast Iron*. Archives of Metallurgy and Materials 2011 Vol. 56. s. 839-849.