CORROSION RESISTANCE OF ZINC COATING DEPENDING ON SURFACE PREPARATION OF BOLTS MADE OF STEEL GRADE 23MnB4

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Abstract

The results of the corrosion resistance of hot-dip galvanized coatings obtained on bolts made of steel grade 23MnB4 have been presented in the paper. The bolts were subjected to various treatments (heat, mechanical and chemical) before application of the zinc coating. Comparative evaluation of corrosion resistance of galvanized bolts was performed by accelerated corrosion tests in salt chamber and using electrochemical methods. The bolts were exposed to an atmosphere of neutral salt spray according to standard ISO 9227:2012 and the following methods: linear polarization and potentiodynamic cyclic voltammetry according to PN-EN ISO 10271:2012. In order to correlate corrosive environment of the tests, the 5% neutral salt solution was used at temperature 35°C. Results of the study were related to the results obtained for the bolts without zinc coating.

It was found that the tested zinc coatings on the bolts are leaky and have relatively short-term corrosion protection. The surface preparation of bolts before hot-dip galvanizing and the centrifugation of excess zinc after process affected the results of corrosion tests. Therefore, in order to improve the quality of the anti-corrosion coatings on the bolts the further research is recommended in the field of the surface preparation before hot-dip galvanizing.

Keywords: Hot-dip zinc galvanizing, corrosion resistance, accelerated corrosion test, salt chamber, electrochemical research

1. INTRODUCTION

The reliability of today construction and materials is related to their resistance to the behavior of the aggressive corrosive environment. For protection purpose safeguards are applied on the surface of steel in the form of metallic coatings. During operation of the coatings they are subject to wear which is accompanied by corrosion processes of both the coating and the base material. Metallic protective coatings are one of the better methods of corrosion protection, for example protection of steel by zinc galvanized coating takes both barrier and electrochemical protection mechanism. Electrochemical protection is typical for protecting metals with electrochemical potential lower than potential of base material in the presence of electrolyte [1].

Hot-dip galvanizing, next to the electrochemical and spraying methods, is one of the most popular methods of steel coating. The process can be carried out under conditions of low temperature (455-480ºC) and high temperature (530-560ºC) [2]. The surface preparation before galvanizing determines the quality of the zinc coatings used in different methods of surface preparation: mechanical (stream abrasive) and chemical (degreasing, etching, fluxing). In addition to the quality of the zinc coating influence of both the material and the technological process was analyzed. The durability of the coating determines the corrosion rate of the zinc film during use in a corrosion environment. Hot-dip galvanized surfaces form of three layers of iron alloy with zinc composition changing with the distance from the surface of the ground surface. Well prepared coatings are characterized by very good adhesion to the substrate and a high tightness. [2-4].

The protective effect of the zinc coating is cathodic protection of substrate. The term of protection depends on the type of coating and its thickness. In the first stage, steel is protected as a result of zinc digestion. The zinc coating is oxidized producing sealing passive film consisting of oxides and zinc hydroxides, which as a result of aging, change the structure and produce a white corrosion film. At the time when the whole zinc produced white corrosion red corrosion of steel starts to appear [3].

The results of corrosion studies of hot dip galvanized coatings on M12x40 bolts of 23MnB4 grade were presented. The objective of the study was to evaluate the influence of the surface preparation of the bolts before applying of the zinc coating on the corrosion resistance of the coating produced.

2. TESTED MATERIAL

The object of the research was hexagon bolts M12x40 class 8.8 made of steel grade 23MnB4 containing the addition of boron. The chemical composition of the tested steel included : 0.24% C, 0.9% Mn, 0.3% Si, 0.26% Cu, 0.41% Cr, 0.025% S, 0.0052% P. **Figure 1** shows the bolts tested before and after zinc galvanizing**.**

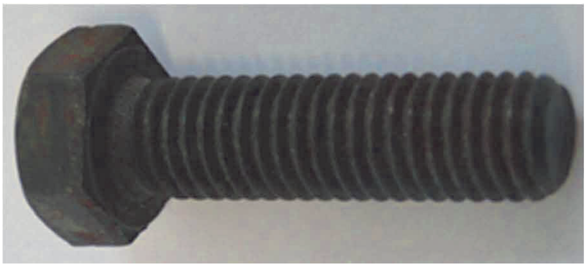
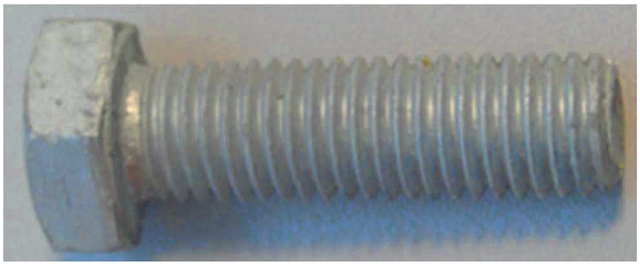
a)  b) 

Figure 1 Tested bolts a) before, b) after hot-dip galvanizing process

Before hot-dip galvanizing material has been divided into two main groups: S - bolts in the state of delivery, Z - bolts after annealing. Anneling of bolts was carried out in the steel container filled with pure quartz sand that is placed in the oven at 1050ºC for 25 minutes. Then the bolts S were subjected to the two types of processing before HDG: a multi-stage treatment (shot blasting with steel shot GL40, etching in the 14.8% HCl solution, t = 10 minutes, rinsing and fluxing in TIBFLUX60) and chemical treatment (eatching in 14.8% HCl solution, t = 30 min., rinsing and fluxing in TIBFLUX60). Such prepared research material was divided as follows: S1 (bolts in the delivery state, the treatment of multi-stage: mechanical and chemical before HDG), S2 (bolts in delivery state, chemical treatment before HDG), Z1 (bolts after annealing, multi-stage treatment: mechanical and chemical before hot HDG) and Z2 (bolts after annealing, chemical treatment before HDG). In the further process, zinc method entraining at 457ºC and time 1.5 min molten zinc bath spiked nickel, bismuth and aluminum was executed. All bolts were galvanized in one production batch. After the HDG centrifugation of excess zinc was performed. Galvanized bilts were quenched in water. This material was studied for corrosion resistance in salt spray chamber and accelerated electrochemical tests. To correlate the corrosion results with zinc coating parameters, the bolts were subject to metallographic assesment (**Figure 2**) and hardness measurement by Vickers method in accordance with PN-EN ISO 6507-4:2007 [5]. The measurements in ten points were made for samples in the delivery state (S) and annealed (Z). The average values with the standard deviation were calculated. The results present as follows: S1 315.8±*2.0 HV10,* S2 322.6±*2.8 HV10, Z1* 137.6±*4.5 HV10 and Z2* 140.0±*2.5 HV10.*

During the microscopic observation the thickness of galvanized zinc measurement at several measuring points has been calculated. Mean values and standard deviations are as follows: S1 69.7±*21.2 µm, S2 49.8±16.1 µm, Z1 83.4±24.0 µm, Z2 66.8±12.5 µm.*

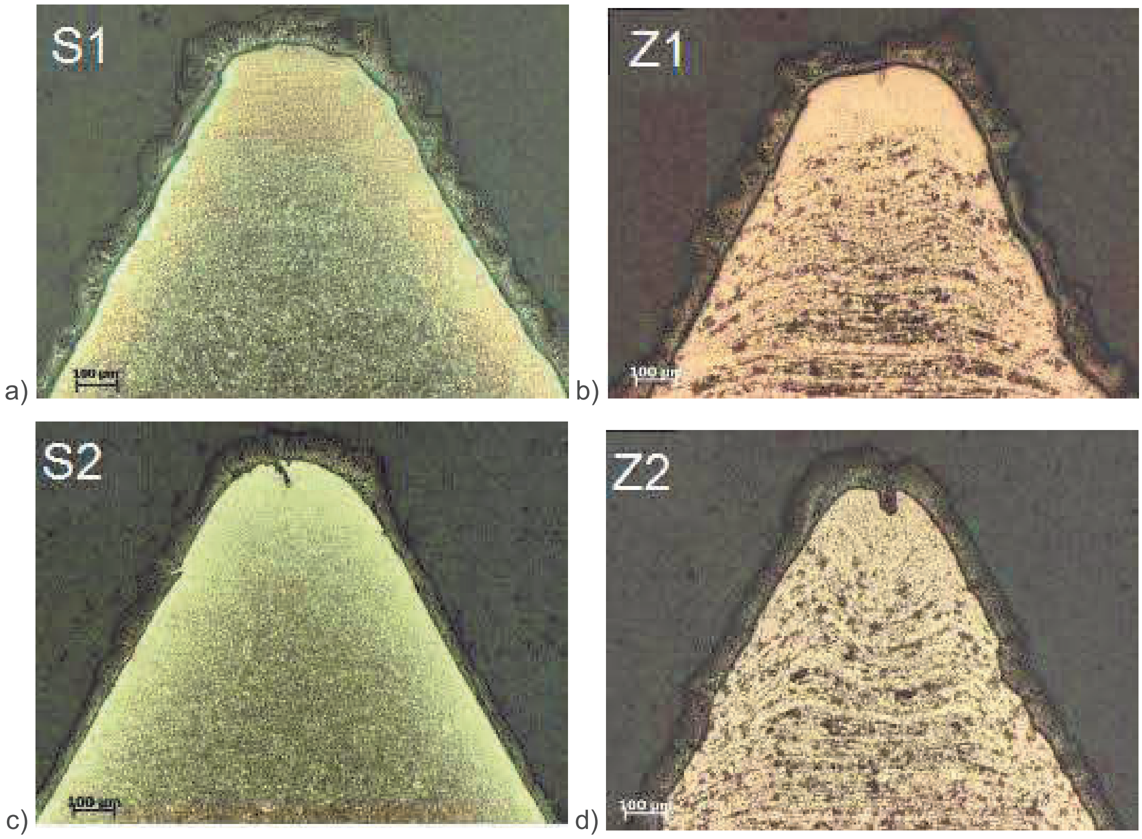


Figure 2 The structure of the zinc coating at bolts: a) state S1, b) state Z1, c) state S2, d) state Z2; magnification 100x

3. INVESTIGATION METHOD AND ANALYSIS RESULTS

3.1. Resistance to neutral salt spry test - NSS Test

Salt spray test consists of subjecting research facilities in continuous operation salt spray produced by spraying brine solution in standardized conditions. The brine of concentration 50 g/l NaCl and pH 6.9 was sprayed at a temperature 35°C and at a pressure 1 bar. Before carrying out the test the corrosiveness of the chamber on the basis of the loss of mass of steel reference plates (after 48 h of the test average weight loss of the plates is 70 ± 20 g/m^2) was checked and amounted to 75 g/m^2. The determination of the level of corrosive of the chamber is designed to check the correct operation of the chamber and the reproducibility and repeatability of test results. In addition pluviometric constant was fixed at 1.4 ml/h (the collection of salt spray for a minimum 16 h test should be in the range of 1.5 ± 0.5 ml/h). Tested bolts were suspended on flax rope and have been tested in salt chamber for 120 hours. In order to documant the corrosion process the bolts were photographed every 24 h. The interpretation of the results was visual appearance of white zinc corrosion or red metal corrosion. The time of first points of corrosion had been measured. The results of corrosive have been presented in **Table 1.**

Table 1 The results of corrosive test in salt chamber

Time of test [h]	Bolt S1	Bolt S2	Bolt Z1	Bolt Z2
0				
96	 white zinc corrosion	 points of red corrosion	 white zinc corrosion	 white zinc corrosion
120	 points of red corrosion	 red corrosion	 points of red corrosion	 points of red corrosion

3.2. Electrochemical corrosion test

The electrochemical research of corrosion resistance was based on potentiostatic and potentiodynamic method in corrosive 5% NaCl solution oxygenated as a result of free contact with air at 35ºC. The research was done by use of PGSTST302N potentiostat, no AUT83628 produced by ECO CHEMIE B.V. company. The instrument cooperates with program recording progress of study. The samples were conditioned in the examined solution for 1 hour. The research was carried out in relation to the reference electrode. It was calomel electrode of + 244 mV potential compared to NEW in T = 25ºC. The study was conducted by use of linear polarization method with potential ranging from -0.1 V to 0.1 V, with 1 mA current, scanning rate 0.001 V/s and cyclic voltammetric method in the range from -1.0 V to 1.6 V potential, scanning rate 0.1 V/s.

The results of research were calculated in Nova 1.7 software. The following parameters, as average of three measurements, were established: open circuit potential OCP, corrosion potential E_{Cor}, corrosion current density j_{Cor}, corrosion rate V_p and polarization resistance R_P. All parameters for galvanized bolts were calculated by comparing to zinc, for which the electrochemical eguivalent was 21.98 g/mol, density 7.13 g/cm^3 and tested area of surface was calculated individually for each sample. However, in case of screws without coating for the above parameters the electrochemical equivalent of 27.92 g/mol and a density of 7, 86 g/cm^3 were used. **Table 2** presents the measurement results of corrosion resistance in 5% NaCl solution both for galvanized and without zinc coated bolts. The examples of linear polarization curves in 5 % NaCl solution for all types of bolts are shown in **Figure 3.**

Table 2 The measurement results of corrosion resistance of zinc coating in 5% NaCl solution

Determined parameters	Bolt before processing	Bolt after shot blasting	Bolt S1	Bolt S2	Bolt Z1	Bolt Z2
OCP [V]	-0.40	-0.53	-0.97	-0.47	-0.99	-0.43
E_{cor} [mV]	-401	-507	-976	-474	-1008	-436
j_{cor} [μA/cm^2]	21.32	102.21	0.30	0.06	0.07	0.05
V_p [mm/rok]	0.25	1.19	15.77	0.57	0.53	0.47
R_p [Ω/cm^2]	3244	1332	120	1358	1225	1360

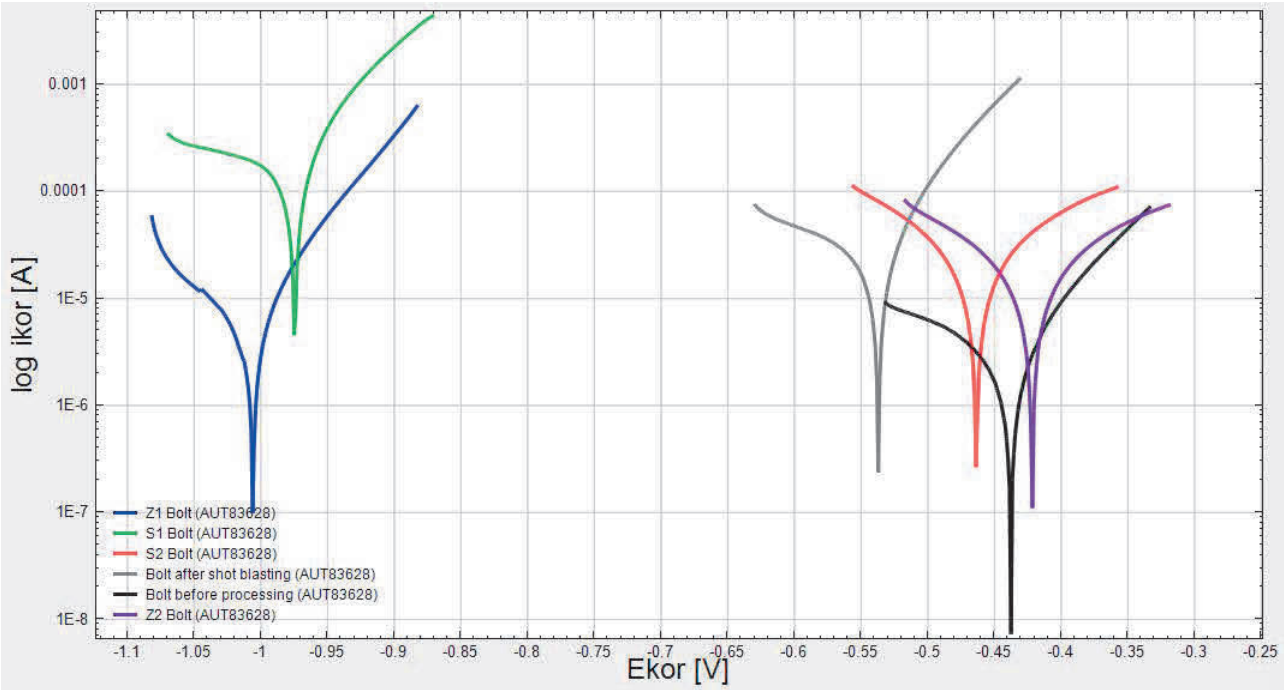


Figure 3 Examples of the polarization curves of bolts before processing, after shot blasting, S1, S2, Z1, Z2 in 5% NaCl solution

4. SUMMARY AND CONCLUSIONS

The hardness of the steel bolts was 320 HV10 and after annealing decreased to 138 HV10. The average thickness of zinc coatings ranged from 50 to 84 μm. The zinc coatings formed on the surface of bolts after annealing (Z) were higher then in galvanized screws in delivery state (S). In each case (Z and S) the coatings created on the surface after multi-stage treatment (shot blasting and etching) have higher thickness compared to coatings on surface after chemical treatment. Chemical composition of the steel used affects both the structure of zinc coatinga and hot-dip galwanizing as well as creation of the protective layer. In the structure of the coating (**Figure 2**), the extended alloy layer, discontinuities, damages on the border of coating-metal appear. The negative influence of the above mentioned defects on corrosion resistance is observed. The centrifugation of excess zinc process is an additional factor affecting protective properties.

The value of the corrosion potential E_{Cor} of bolts without coating are in the range from -401 mV to -507 mV while for screws with zinc coating, depending on the preparing process of the surface before dip-hot galvanizing, range from -436 mV to -1008 mV (**Table 2**). The smallest value of the corrosion potential characterized by bolts after multi-stage treatment has been recorded at screws marked as S1 and Z1. This testifies to good tightness of zinc coating and protection ability known as cathode protection. In case of the layer which protects steel as a result of zinc digestion in the corrosive environment, another useful parameter is layer thickness (the thicker coating the longer time of cathodic protection). Presented considerations correlate with the measurement results of the zinc coating thickness that are largest on bolts S1 and Z1.Considering all the parameters of the corrosive studies for bolts S1 and Z1 (**Table 2**) and the coating thickness created on its screw, it can be concluded that the bolts with zinc coating Z1, after mechanical and chemical treatment process, have the best properties for barrier and electrochemical protection. The best corrosion resistance of screws S1 and Z1 is confirmed by the results in the salt chamber, for example after 96 hours. Therefore, surface preparation determines the resistance to aggressive corrosive environment that is extremely important for structure connected elements.

It is a different situation when it comes to bolts S2 and Z2 after chemical treatment before creating of zinc coating. The value of the corrosion potential E_{Cor} range from -474 mV to -436 mV (**Table 2**). High value of the corrosion potential indicates a leak in zinc coating. The observation confirms the potential results of tests on uncoated screws that have value from -401 mV to -507 mV. It indicates that screws S2 and Z2 are inappropriate for cathodic and barrier protection. Another disqualifying parameter of these coatings are low thickness of the zinc layer. Summarizing, all parameters (corrosion results, low zinc thickness) concerning bolts S2 and Z2 do not meet expectations as regards protection properties of steel. The conclusion correspond to corrosion results obtained in salt chamber. Bolts S2 and Z2 had red point corrosion after 96 hours /120 hours.

To sum up it may be concluded that:

1) The thickest and the most leaky zinc coating have the bolts after multi-stage treatment before creating HDG zinc coating.
2) The best barrier and cathodic protection shows the zinc coating created on bolts surface after annealing and multi-stage treatment (mechanical and chemical).

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