THE INFLUENCE OF SURFACE PREPARATION STEEL 41C4 ON THE NATURE AND CORROSION RESISTANCE OF THE HOT-DIP ZINC COATING

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Abstract

The influence of surface preparation of steel 41Cr4 on the structure and corrosion resistance of the zinc coating has been presented in the paper. The aim of the study was to determine the method of surface preparation fittings for overhead power lines made of steel 41Cr4 guaranteed to obtain zinc coating of a required thickness and high corrosion resistance.

The prepared materials were subjected to an abrasive blasting - steel shot GL40 and chemical treatment - pickling (hydrochloric acid) and fluxing (TIBFLUX60). The hot - dip zinc galvanizing process was conducted in industrial conditions in 457 °C. The (Zn) - coating morphologies and sub-layer thicknesses were evaluated on the basis of metallographic analysis. The correlation between the results of corrosion test and coatings morphology was determined.

Keywords: Surface preparation, abrasive blasting, chemical treatment, hot-dip zinc galvanizing, corrosion resistance

1. INTRODUCTION

Corrosion still causes serious problems to the safe and economic operation of a wide variety of industrial installations. This problem regards also the overhead power lines. It has been proved that metallic coatings pose one of the best methods of corrosion protection. One of the most effective, permanent and efficient solution is zinc coating usage. Generally, it was proved, that the zinc coating has a complex structure: Γ1 (Fe_3Zn), δ ($FeZn_7$), ζ ($FeZn_{13}$) and additionally η (Zn). The Fe-Zn phases reduce the corrosion rate and its intensity during the process progress. This is one of the most important advantages of the hot dip zinc coatings in corrosive environments [1-4]. In accordance with the requirements of EN 61284, fittings for overhead power lines made of steel (except stainless steel) should be protected by hot-dip galvanizing (HDG) or other method that guarantees similar protection against corrosion [5]. Overhead power lines are carried out by a vast area, they are subject to various factors: climatic, environmental and topographical features. In connection to this, it is an extremely important issue to ensure the sustainability of elements of fittings. Destruction of fittings lowers the stability of the whole product. The lack of resistance due to the progressive corrosion can cause such damage to the structure by pin fall out and off line. This results in very high costs and delays due to interruptions in energy supply [6, 7].

Proper surface preparation before HDG is a necessary and complex process. Surface preparation process can be done as follows: mechanically - abrasive blasting (shot- or sandblasting) or grinding and chemically - degreasing, pickling, rinsing and fluxing. The above-mentioned methods can be carried out in various ways. A combination of abrasive blasting method and chemical treatment (multistage treatment) is often used. The choice of the method depends on some factors, such as the state of the surface before cleaning, the nature of impurities present on the surface, kind of cutting method, kind of steel or the size and shape of the object [3, 7-10]. Surface preparation is very important in the production of structural elements shaped by higher-strength steel. In the production of network equipment 41Cr4 steel is used. For the steels with yield strength higher than 460 MPa it is recommended to use shorter pickling time or to eliminate the acid pickling process in order to avoid the hydrogen embrittlement (HE) [11,12].

In standard way fittings made of steel grade 41Cr4 after thread rolling and heat treatment, are shot-blasted. Mechanical treatment is necessary to remove mill scale and to reduce the pickling time. In chemical treatment an hydrochloric acid of 10 to 14 % concentration, the inhibitor is used [3, 4]. This procedure appears to comply fully with the requirements of the above e.g. German industry guidelines for acid etching of Grade 10.9 fasteners. This practice of surface preparation is according to well proven norms for the fastener industry to avoid HE from pickling. However, customers formulate stricter requirements- pickling should be eliminated. Though, this is not always possible, e.g. removing a HDG coating from steel and then adding a new one as a results non-compliance and corrective action procedure.

The aim of this study is the evaluation the structure and corrosion resistance of the zinc coating created on the surface prepared different methods on the steel 41Cr4.

2. TESTED MATERIAL

The study was conducted on a special bolts commonly used to connected fittings and the superstructure of electric power lines. The research was focused on a shoulder eye bolt (**Figure 1**) made of 41Cr4 steel.

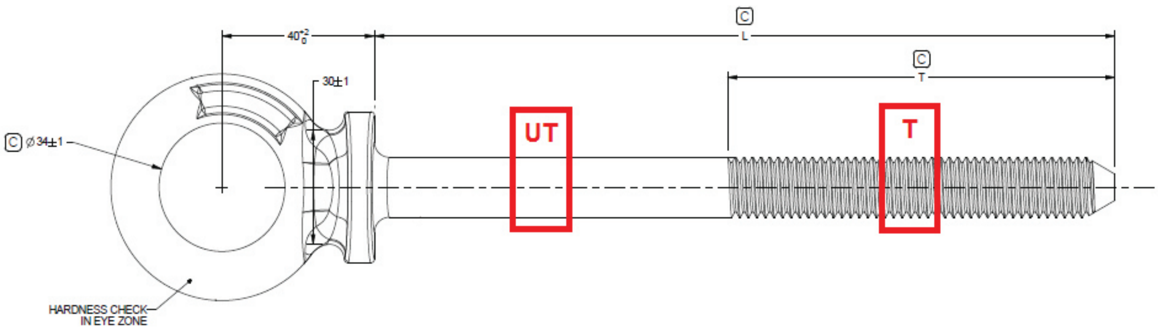


Figure 1 Tested materials - a shoulder eye bolt; UT, T- place of cut samples

Chemical composition of materials used in experiment is 0.40 %C, 0.22 %Si, 0.74 %Mn, 0.011 %P, 0.011 %S, 0.95 %Cr, 0.08 %Ni, 0.16 %Cu, 0.015 %Mo, 0.014 %Al, 0.003 %V, 0.003 %Ti (acc. EN 10083-3: 2006 for 41Cr4). Carbon and sulphur were determined using LECO CS-125 analyzer. Other elements were analyzed on the ICP-OES spectrometer.

2.1. Preparation of material for galvanizing

Technological operations. In order to perform research the samples are prepared. Cold drawn round bars diameter of 17.9 mm were cut into a length of 250 mm. In the next step, M20 thread was rolled (the cold forming). Then, the samples were quenched from 850 °C into oil and tempered of 670 °C to 250 HB.

Samples were divided into three groups. Three main series of samples were prepared (S, SP, RE) to HDG. The main difference between analyzed series was the kind of surface preparation. The labeling way of materials for testing is shown in **Table 1**.

HDG process was made in industrial conditions in temperature: 457 °C and time t = 150 s in Zn bath enriched in: nickel, bismuth and aluminum. The bath chemical composition was as follows: 99.868 %Zn, 0.0439 %Ni, 0.0444 %Bi, 0.0339 %Fe, 0.0022 %Pb, 0.0006 %Sn, 0.0053 %Cu, 0.0022 %Al. Centrifugation was performed after HDG. During the coating of all elements the special attention was paid to maximum repetitiveness of technological parameters of galvanizing process.

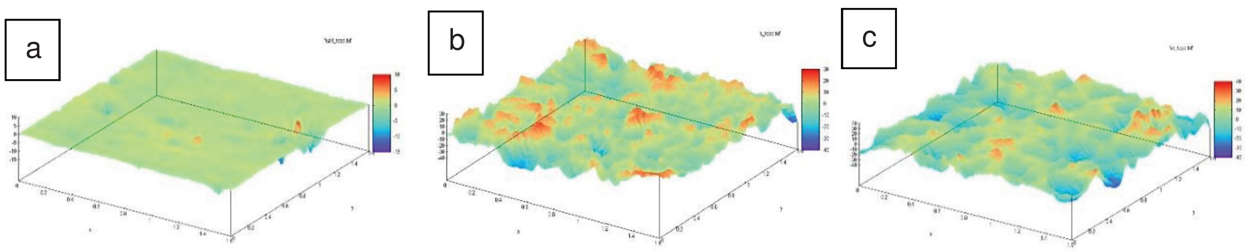
Table 1 Characteristic of the tested material

Group	Kind of surface preparation before hot-dip zinc galvanizing		Treatment parameters
S	Shotblasting + Fluxing	According to requirements of customer	- Steel shot GL40, t = 20 min. - TIBFLUX 60, pH 4.65, t = 2 min.
SP	Shotblasting + Pickling + Fluxing	According to standard procedures	- Steel shot GL40, t = 20 min. - r-r HCl 14 % with inhibitor CHP ADDITIVE 103, t = 10 min. - TIBFLUX 60, pH 4.65, t = 2 min.
RE	(Shotblasting + Pickling + Fluxing + HDG + Removing zinc coating) x 2 + Shotblasting + Pickling + Fluxing	Intensive chemical treatments „stripping and re-dipping“	- Steel shot GL40, t = 20 min. - r-r HCl 14% with inhibitor CHP ADDITIVE 103, t = 10 min. - TIBFLUX 60, pH 4.65, t = 2 min. - r-r HCl 6% (removing Zn coating), t = 3 godz.

3. METHOD OF INVESTIGATION AND RESULTS ANALYSIS

3.1. Roughness and surface topography

Perthometer Concept (MAHR), with 3D equipment and software, was used to measure surface roughness and topography. The surface roughness was described according to EN ISO 4287 and EN ISO 13565-2 standards [13, 14]. The surface roughness measurement was made on samples before HDG. The results of surface topography with value of Ra (it is an arithmetic mean of profile ordinates) are shown in **Figure 2**.



Ra = 0.33 µm **Ra = 8.19 µm** **Ra = 8.12 µm**

Figure 2 Evaluation of the surface quality before galvanizing for samples: a - crude, b - shotblasted, c - shotblasted and pickled

3.2. Metallographic analysis

Metallographic examinations for samples in the initial state, before and after HDG were carried out. Metallographic specimens were prepared in classic way. The surface was etched with 4 % HNO_3. To microscopic observation the microscope AxioImager M1m Carl Zeiss was used with magnification: 100, 200, 500 and 1000 x. The results of selected observation are presented in **Figure 3 and 4**.

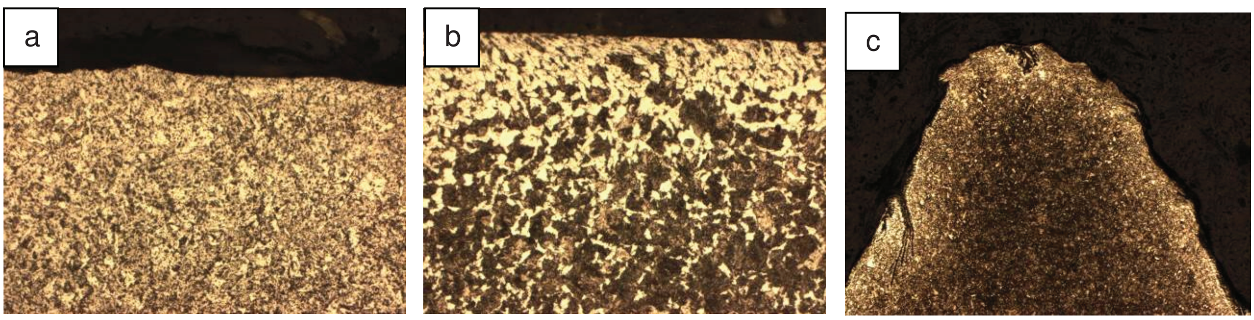


Figure 3 Cross section of the 41Cr4 steel structure: a - in the initial state, b - after heat treatment; magnification of 500 x, c - damage of the thread (cold rolling), magnification of 100 x

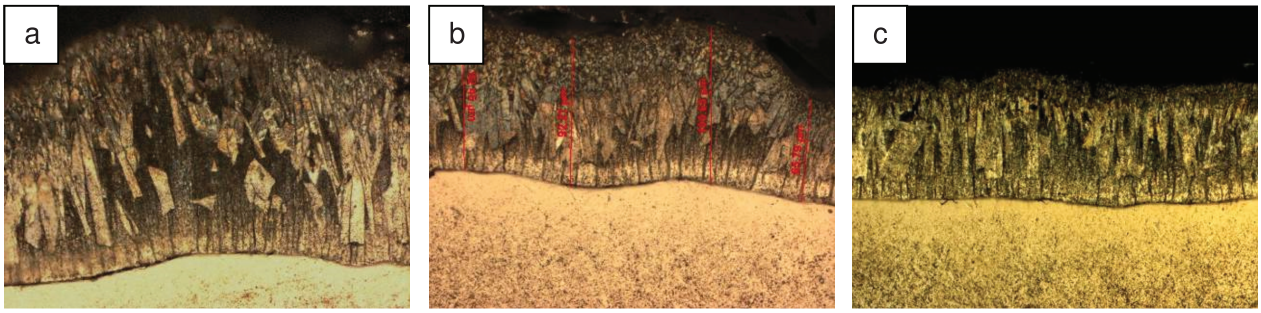


Figure 4 The zinc coating structure for samples: a - S, b - SP, c - RE, magnification of 500 x

The microscopic measurements of zinc coating thickness were made. Results measured in several places on the threaded and unthreaded surfaces are put together in **Table 2**.

Table 2 The results of zinc coating thickness measurement (ā - average)

Measurement place	S	SP	RE
	ā [μm]	ā [μm]	ā [μm]
Unthreaded	119.8	82.7	72.5
Threated	100.9	81.9	70.9

3.3. X-ray analysis

X-ray analysis was made with application of scanning microscope with X-ray analyzer in micro areas EDS (tungsten cathode). X-ray analysis was executed in order to determine chemical composition of zinc coatings. Research of chemical composition was carried out in selected cross sections of samples with zinc coatings that were stated as representative samples. The measure step was 10 μm. Intermetallic phases distribution was determined at the coating cross section. The cross section of the zinc coating structure together Zn distribution at the cross section of the coating are shown in **Figure 5**.

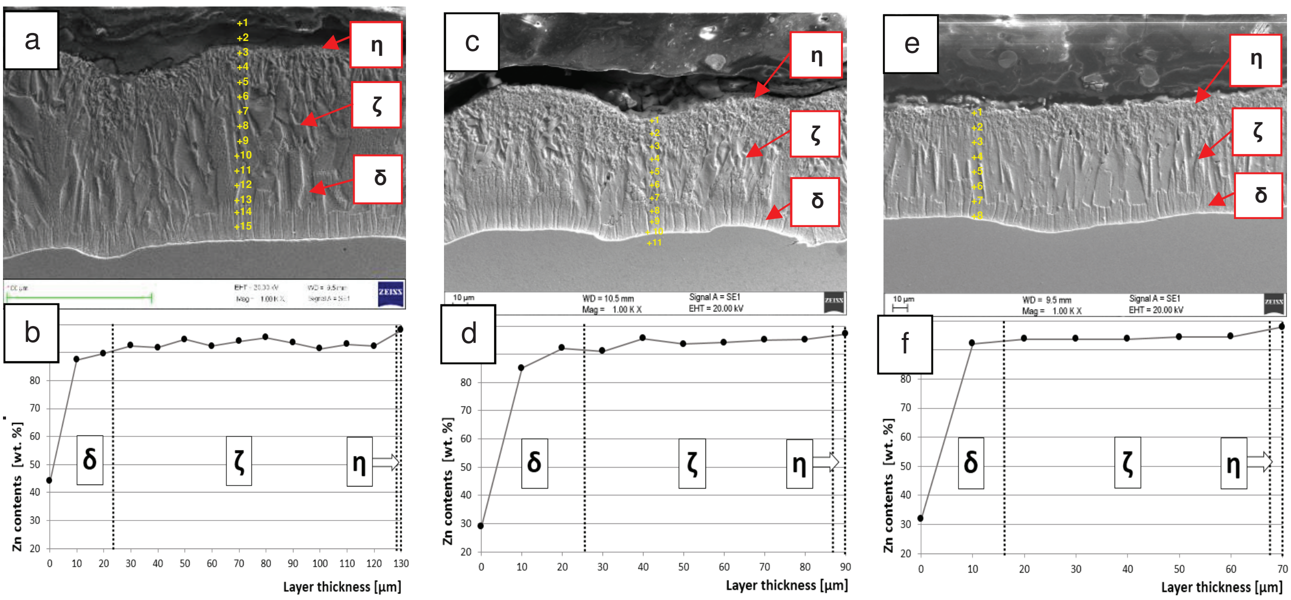


Figure 5 The microstructure of the coating created on the surface: a, b - S, c, d - SP, e, f - RE; a, c, e - cross section of the zinc coating structure and the places of examinations, b, d, f- intermetallic phases distribution

3.4. Potentiostatic polarization test

The electrochemical research of corrosion resistance was based on potentiostatic method in 5 % NaCl (was selected on purpose), pH 6.8, temperature 37 °C. The research was conducted by use of a measurement system consisting in the Autolab PGSTAT302N potentiostat produced by ECO CHEMIE B.V. company, which cooperates with the Nowa 1.7 software, by Metrohm Autolab B.V. The research was conducted by use of linear polarization method with potentials ranging from -0.1 V do 0.1 V with the scanning rate 0.001 V/s. The reference electrode was fulfilled by calomel electrode (NEK, Hg / Hg_2Cl_2(s) / KCl(nas.)) of the +244 mV potential compared to NEW with Haber-Ługgin's capillary at the end. The results of potentiostatic tests for samples S, SP and RE which were the average of seven measurements, are compared in **Table 3**.

Table 3 The potentiostatic test results of zinc coating (ā - average)

Corrosion parameters	S	SP	RE
	ā	ā	ā
OCP	-0.516	-0.497	-0.529
Ecorr. [mV]	-517.0	-506.4	-534.5
jcorr [µA/cm^2]	106.0	159.8	129.9
Corrosion rate [mm/year]	1.1	1.6	1.3
Polarization resistance [Ω/cm^2]	1457.4	1269.8	780.4

4. RESULTS DISCUSSION AND CONCLUSIONS

The structure of the material in the initial state was ferritic with pearlite (**Figure 1a**). The heat treated microstructure of the steel is clearly one of a quenched and tempered steel with tempered martensite with fine carbides (**Figure 1b**).

The surface preparation methods affect surface quality, express by the Ra parameter (**Figure 2**). The lowest surface roughness appeared the material in the initial state. In production process after thermal treatment it is necessary to use mechanical abrasive treatment in order to remove scale, which has an influence on the surface roughness. The values measured on the surface after shotblasting, and shotblasting and pickling are the same level.

The metallographic analysis confirmed that surface preparation results in the difference of the zinc coating thickness. Measurement of the zinc coating thickness reveals thicknesses that range from 70 to 120 µm (**Table 2**) by an dipping time 150 s. Zinc coating thickness on sample S is the highest. The coating observed on the samples surface SP and RE are characterized by a thickness lower about 70 - 80 µm. Diversification the zinc coating thickness is observed for the coating on sufrace S and SP. Zinc coating on surface RE is characterized uniform thickness. The manufacturing specification requires a minimum thickness of 65 µm. The additional requirement is an over-tapped nut can easily be installed.

Chemical composition of the steel influences the thickness and structure of Zn coating. The equivalent (Si+2,5P) is 0.25%. At the Zn coating cross section, created on the all samples, fundamentally Fe-Zn phases are visible (δ and ζ) (**Figure 5**). Γ-phase is difficult for the identification at the measuring step equal to 10 µm.

The thickness of δ-phase is ab. 22-25 µm. The cause of cracks is different coefficients of thermal expansion of steel and the phase δ. Therefore, during the cooling after galvanizing are being created in the local tensile stresses and cracks in the end.

Long crystals ζ-phase located between the mass of zinc are observed for all samples (**Figure 5**). In the upper part of the zinc coating they are changed to the smaller separation- especially for samples SP and E (**Figure 6**).

It was determined on the basis of chemical composition area: ζ-phase. η-phase is very thin and identified between separation of crystals ζ-phase.

The thickness and structure of the zinc coating are factors determining corrosion resistance. Comparing the parameters values, i.e. current density j_{corr}, polarization resistance R_p, corrosion potential E_{corr} and corrosion rate in mm/year zinc coatings created on the surface after multistage treatment (SP and RE) are proved higher corrosion protection than zinc coating on the shot blasted surface (S). However, due to the similar value of the corrosion parameters for it may be assumed that all samples are characterized good corrosion resistance.

On the basis of the investigation results and its discussion, the following conclusions can be formulated:

1. The surface preparation has a crucial influence on the zinc coating thickness and its corrosion resistance. Zinc coating, formulated on the surface after shotblasting present the higher thickness.
2. Using multi-stage processing before HDG ensures better results than using only mechanical treatment.
3. The process of removing zinc coating and the application of a new one, do not lowers the quality of the coatings and their corrosion resistance.

In the next stage the following research will be realized:

1. The evaluation of the zinc coating structure on the tread of eye bolts.
2. The evaluation of corrosion resistance - corrosion test acc. to EN-ISO 9227.
3. The evaluation risk of HE - hydrogen content in the tested samples.

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