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DIVERSIFICATION OF INTERMETALLIC Zn PHASES GROWTH ON STEEL DURING HOT-DIP GALVANIZING

The steel substrate formed as the result of oxy-acetylene cutting (OAB) was treated differently – using: softening annealing, grinding and electro-polishing. Investigations were focused on the influence of additional processing on the structure and corrosion resistance of the deposited zinc coating. The hot – dip Zn galvanizing process was conducted in industrial conditions. Parameters were fixed: temperature 457 °C, dipping time 150 s. The coating thickness diversification dependent on the sub-surface steel structure was analysed and compared to the previous results. The correlation between conducted treatment and coatings morphology was determined.

Keywords: hot-dip zinc galvanizing, heat affected zone, softening annealing, oxy-acetylene cutting

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. According to the PN-EN 61284 standard all parts of fittings of overhead power lines made of steel (without stainless steel) should be protected by hot-dip zinc galvanizing or in other way ensuring the similar corrosion protection [1]. Hot-dip zinc galvanizing is the most popular and probably the best available protection system of steel that offers multiple advantages in comparison to other methods – for example, since zinc is anodic to iron, a break in the coating does not lead to corrosion of the substrate. On the other hand a lot of research is still conducted regarding mainly the influence of different technological factors (bath chemical composition, bath temperature, surface state, time of operation, reaction and fluxing agent character) on the final layer quality that decides about its corrosion resistance [2-8]. Anticorrosion properties of zinc coating are determined by structure of created layer composed normally of few sub-layers: Γ - Fe_3Zn_{10}, δ- $FeZn_7$, ζ - $FeZn_{13}$ and iron solid solution in zinc - η [9-11]. The growth of Zn sub-layers is similar to structure growth proposed for Ni/Al/Ni interconnection [12-13]. The proposed mechanism suggests that also properties of steel base can influence on the kinetics of Zn coating growth.

Beside corrosion resistance equally important is also coating thickness evenness. Also in this case there are many factors that cause the zinc coating thickness variations. The heterogeneity of the coating thickness is also regarded as a defect and reduces the quality of the final product [14]. There are also divergences in literature regarding of the influence of surface condition on the structure and thickness of zinc coating. According [12], surface condition of steel do not affect essentially the structure of zinc coating but this influence is more visible in cast iron – Fig. 1. Whereas our own investigation revealed that changes in the structure of the coated steel influence fundamentally on the structure, thickness and properties of the zinc coatings created by hot-dip galvanizing. This effect is observed especially after the thermal cutting process (in comparison to cold rolled surface), where after forming both the scale layer is visible on the cut surface and the heat affected zone (HAZ) is observed in subsurface steel zone – Fig. 2.

The HAZ thickness depends above all on process temperature and beam concentration, that next influence on puncture thickness and heating rate of the forming material (1050-1380°C – OAB) [15]. Because the OAB cutting temperature is relatively high and the beam concentration rather low – it results in wide HAZ. The thermal impact of beam results in hardening of layers surrounding the cutting kerfs (even in low-carbon steel) and the quenching of the cut surface of steel with higher carbon content [16].

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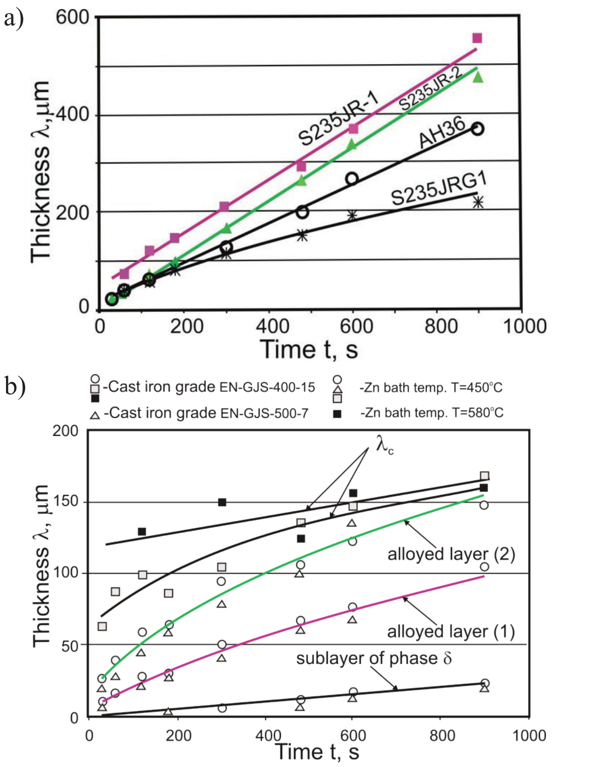

Fig. 1. The kinetic of Zn coating growth on steel S235JR surface–a (after polishing - 1; rolled+ abrasive blasting cleaned - 2); and on cast iron – b (alloyed layer created on crude surface – 1; alloyed layer created on polished surface - 2; λ – the total coating thickness)[12]

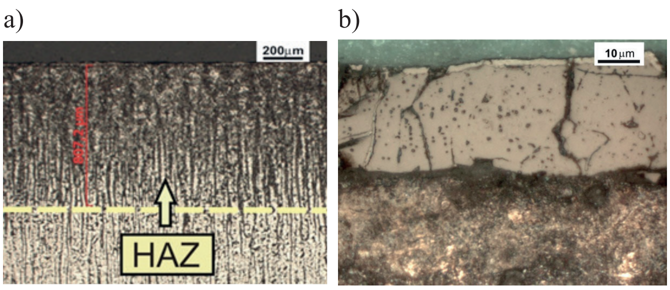

Fig. 2. Additional effects visible after OAB cutting of steel, a – HAZ (heat affected zone), b – scale layer [own investigations]

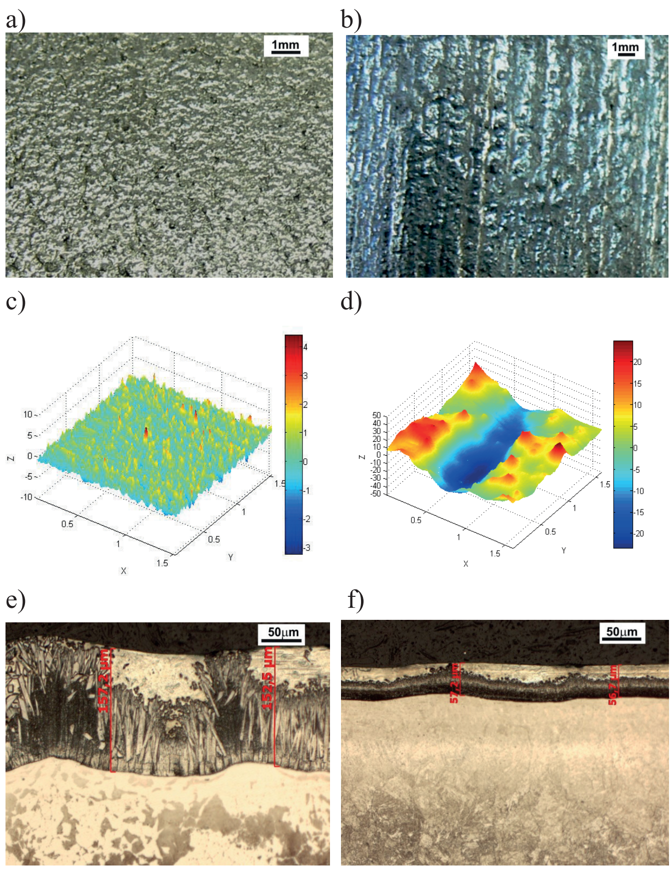

Fig. 3. The essential differences between front (a, c, e) and side (b, d, f) surface of zinc coated elements formed by OAB; a, b – surface appearance; c, d – isometric surface image; e, f - zinc coating cross section

No prescriptions either recommendations had been found for galvanizing plants in the literature, both constructional and technological which would suggest that the way of reaching the required coating quality with uniform thickness created on components, which surfaces were shaped by various methods - also by thermal cutting. Authors of a many works indicate in the general way the need to apply additional treatment after the cutting (heat treatment or the grinding).

TABLE 1

Characteristic of the tested treatment

Labelling	Kind of additional treatment after oxy-acetylene cutting	Treatment parameters
OABG	**GRINDING (G)**	Grinding, Shotblasting (steel shot GL-40), Pickling (HCl, 12 %), Fluxing (TIBFLUX 60 - pH 4,9, 0,17 g/l Fe, 292 g/l $ZnCl_2$, 189 g/l NH_4Cl)
OABEP	**ELECTROPOLISHING (EP)**	Alkaline degreasing (temp. 60 °C), Pickling (H_2SO_4 10 % and HCl 18 %), Electro-polishing (alkaline degreasing 60 °C), Fluxing (TIBFLUX 60)
OABSA	**SOFTENING ANNEALING (SA)**	Softening annealing in temp. 920 °C, Shotblasting (steel shot GL-40), Pickling (HCl, 12 %), Fluxing (TIBFLUX 60)

The reason of the research start was an essential diversification of the Zn coating thickness measured on the front surface (after cold rolling forming without cutting) and the side surface shaped by cutting with the oxyacetylene blowpipe (OAB) - links fittings for overhead power lines – a double eyes links type SLINK made of S355JR steel – Fig. 3. In the first already published part, the research was directed to elimination of the coating thickness diversification by application of other (apart from OAB) cutting method (water jet, laser) - it was stated that application of laser cut instead of OAB decreases the coating thickness difference to about 25%. The aim of current research was to check if the more thorough cleaning of the steel surface area before galvanizing (electro-polishing (EP), grinding (G)) or additional heat treatment (SA) can decrease the differences in the coating thickness and structure.

2. Experimental

2.1. The research object

The study was conducted on links commonly used as overhead power lines fittings - made of S355JR steel. Research was focused on a double eyes link type SLINK 626502006. Chemical composition of material used in experiment was as follows: 0,18 %C; 0,23 %Si; 1,5 %Mn; 0,012 %P; 0,008 %S; 0,030 %Cu. Carbon and sulphur were determined using LECO CS-125 analyzer. Other elements were analyzed on the ICP-OES spectrometer.

Preparation of material for galvanizing: links were cut from steel sheet with a thickness of 20 mm by oxy acetylene blowpipe (OAB) - CNC 500 MESSER cutter (temp. 1200 °C, υ=400 mm/min). Three series of samples were prepared – the main difference between analyzed series was a method of the additional treatment conducted after material cutting. The labeling way of materials for testing is shown in Table 1.

Hot-dip Zn galvanizing - Hot-dip Zn galvanizing process was made in industrial conditions in temperature: 457°C and dipping time t=150 s in Zn bath enriched in: nickel, bismuth and aluminum. The bath chemical composition was as follows: 99,859 %Zn, 0,0481 %Ni, 0,0417 %Bi, 0,0002 %Al, 0,037 %Fe, 0,0058 %Pb, 0,0014 %Sn, 0,0067 %Cu, 0,0006 %Cd. During the galvanizing of all elements the special attention was paid to maximum repetitiveness of technological process parameters.

3. Method of investigation and results review

3.1. Hardness measurement

The hardness measurement was carried out using Vicker's method according to PN – EN ISO 6507 – 2007 [17]. The examination was divided in two stages. In the first stage the hardness (HV10) of side link SLINK surface after cutting was measured. The measurement was made perpendicularly to cutting plane. The average values from a dozen places of the measurement were as follows: OABG - 329 HV10, OABEP - 299 HV10 and OABSA - 158 HV10. In the second stage the hardness measurement (HV0,5) was made starting from the cutting edge toward the sample core. The step of the measurement was established to 200 μm. Results are presented in Fig. 4.

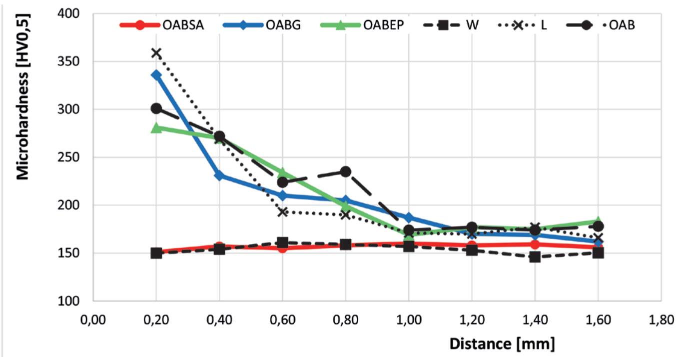

Fig. 4. Results of hardness measurement (HV0,5) on the side surface of links in direction from cutting edge to the sample core, black lines – the previous results, colour lines – the current results (W – water jet, L – laser)

3.2. Surface quality determination

During surface investigation the roughness and 3D isometric surface images were determined by application of the profile measurement gauge - Perthometer Concept (MAHR). An example of measurement results are presented in Fig. 3c, d and Fig 5.

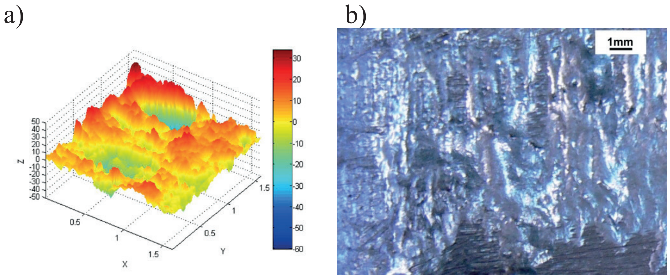

Fig. 5. The isometric image of side surface after OAB cutting - a and the view of zinc coated side surface of link - b

The front surface roughness after zinc coating expressed by Ra value was about 0,5μm. Side surface after OAB cutting was much more inhomogeneous and corrugated. Additionally the determined Ra value amounted to 2,13 μm after cutting and 1,60 after zinc coating.

3.3. Metallographic analysis

Metallographic examinations were made for all samples after cutting and hot-dip zinc galvanizing. 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: 50, 100, 200 and 1000x. Chosen results of observation - the structure of base material and Zn coatings are presented in Fig. 6. The measurement of Zn coating thickness was made for all samples after galvanizing. Results measured in several places on flat and side surfaces are put together in Table 2, where also the previous investigation data are enclosed (after normal OAB, water jet and laser cutting).

TABLE 2

Results of Zn coating thickness measurement

Labelling	Additional treatment	The average coating thickness [µm]	
		Flat surface	Side surface
OABG	GRINDING	**144**	**66(-54%)**
OABEP	ELECTROPOLISHING	**140**	**68(-51%)**
OABSA	SOFTENING ANNEALING	**146**	**134(-8%)**
OAB	WITHOUT [17]	**158**	**57(-64%)**
WATER	WITHOUT [17]	**159**	**156(-2%)**
LASER	WITHOUT [17]	**160**	**137(-14%)**

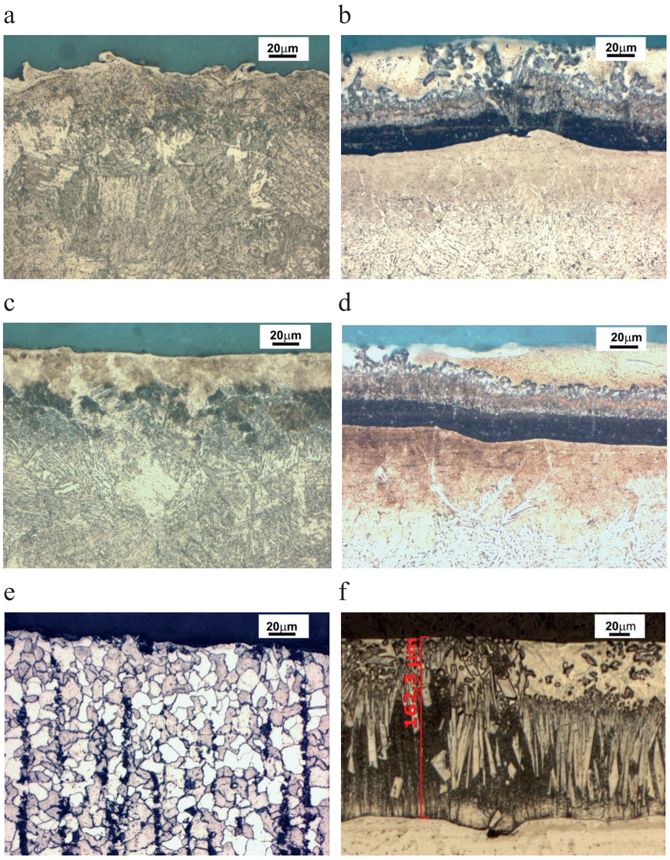

Fig. 6. The steel subsurface structure after OAB cutting and additional treatment (a, c, e) and after zinc coating (b, d, f): grinding (a, b), electro-polishing (c, d) and softening annealing (e, f)

3.4. X-ray analysis

Further examination was made with application of scanning microscope "PHILIPS XL30" equipped with X-ray analyser. Intermetallic phase's distribution that was determined at the coating cross section (the measure step was 5-10 µm) is enclosed in Fig. 7.

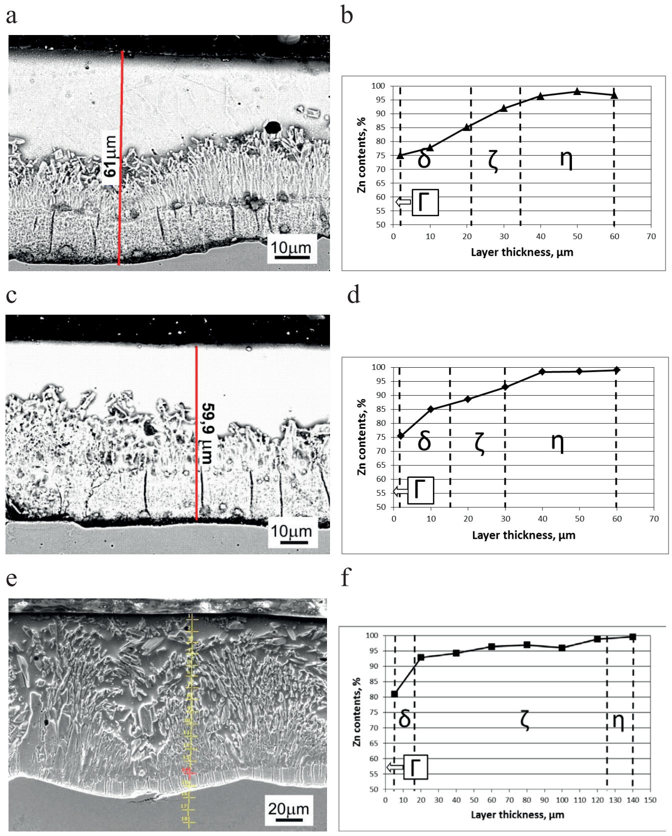

Fig. 7. The Zn coating cross section after OAB cutting and additional treatment and Zn distribution at the coating cross section after OAB cutting and additional treatment (a, b - grinding, c, d – electro-polishing, e, f - softening annealing)

3.5. Corrosion test in neutral salt fog (spray)

The corrosion tests were made in salt chamber in F.Ś. BISPOL S.A. in Bielsko - Biała. The NSS test was conducted according the requirements of PN-EN ISO 9227:2012 standard [18]. The following process parameters were applied: 5 % NaCl; pH 6,7 - 6,9; temperature 35 °C; salt fog fall 1,6 ml/h. The results of NSS test after 640 h in salt chamber were as follows: time to white corrosion appearance (time to red corrosion appearance): grinding – 24 h (312 h); electro-polishing – 24 h (264 h); softening annealing – 24 h (576 h).

4. Results discussion

Hardness comparison. It follows from conducted measurements – Fig. 4 that the surface hardness after grinding has the highest value (ab. 329 HV 10). A little bit lower hardness but very close to value measured after OAB cutting without additional treatment was determined after electro polishing (ab.299 HV 10). In both cases the hardened zone inside the tested element is up to 0,8-1mm deep (Fig. 2). After the softening annealing the surface hardness does not differ essentially from values measured in sample core (ab. 158 HV10) and is similar to values measured after water jet cutting.

Surface condition and steel microstructure. The surface created after electro-polishing is the most smooth ($R_a = 0,2\mu m$), and in narrow subsurface zone the great structure differentiation is observed (within 30 μm length). These changes results in a little bit lower hardness measured in 20 μm distance from the surface. The most porous and undulating surface was observed after softening annealing (R_a=1,6 μm), whereas the roughness after electro polishing shows intermediate values R_a (ab. 1,2μm). The steel structure after annealing is composed mainly of ferrite with small amounts of perlite, whereas the structure after electro-polishing and grinding is changed by heat influence - the needle structure appeared. HAZ existing in the material cut with OAB - changes the steel properties, and in consequence of the higher thermal stability of created phases (lower bainite) influences on diffusion rate at the steel/coating boundary and base dissolving processes accompanying of the zinc-coating growth.

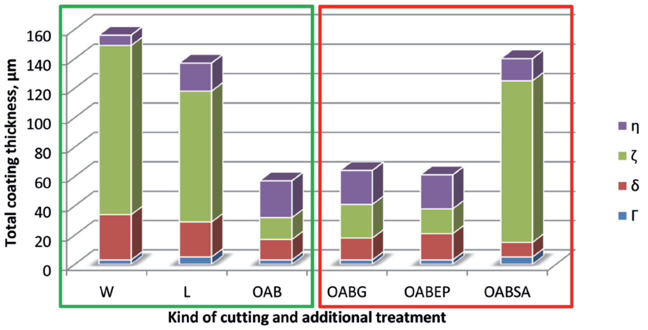

Fig. 8. The comparison of Zn coating structure achieved in the current investigation – red rectangle to the previous results achieved by application of other cutting methods (W – water jet, L – laser) – green rectangle [17]

Coating internal structure and thickness diversification. After traditional etching with 4% HNO_3 the dissimilarity of zinc coating structure created on the side wall after additional treatment – electro polishing and grinding in comparison to zinc coating after softening annealing is clearly visual – Fig. 6. At the Zn coating cross section created on the surface OABG and OABEP fundamentally three phases are visible (η, ζ, δ) - phase Γ is very thin and difficult for the identification at the measuring step equal to 5-10 μm. In both cases thickness of alloyed layer is about 60% of the total Zn coating thickness. Coating growth on the surface OABSA was realized on typical for steel S355JR the ferritic-pearlitic structure (restored to original condition by heat treatment). So, the coating in this case has greater thickness, and ζ phase is dominating in the structure (Fig. 7f and 6f). The structure diversification was additionally confirmed by RTG analysis – Fig. 7. Thickness of η phase reaches in OABG and OABEP coatings up to 30 μm, whereas in OABSA coating this phase occupies only 15 μm. The coating thickness on flat surfaces (crude – after rolling) of all tested links was stable and amounted to about 140-160 μm. Thickness measurement of the SA sample coating - on the side surface cut with OAB revealed value similar to the average measured on the flat surface. In samples G and EP, on side surfaces significant deviation of coating thickness from average value for flat/rolled surface was stated. Differences amount in this case from 72 up to 78 μm (total coating thickness is about 140 μm) (Tab. 2). The lowest zinc coating diversification was reached in OABSA case where the side wall zinc coating thickness was only 2% lower than coating thickness on front surface. This difference after OABG and OABEP cutting amounts correspondigly to 54 and 51% (64% for OAB without additional treatment). Higher zinc coating thickness differences for standard OAB cutting method can proove that also the surface cleannes, that without additional treatment is not sufficient in this case, can cause the zinc layer growth rate decrease, althought this influence is not such strong like application of thermal treatment.

Comparison to laser and water jet cutting. Comparing results achieved after investigation of the following cutting methods: OABG, OABEP, OABSA, to previous tests: laser and water jet cutting – Fig. 8, Table 2, it is clear that the best final result guarantee the water jet cutting. The zinc coating thickness diversification is here only about 2% (8% OABSA, 14% L). Although the OAB cutting is considered as the cheapest method - but if we add the additional thermal treatment cost the situation could change essentially.

Corrosion resistance. On the basis of the corrosion examinations - the NSS test, it was stated that so-called the "white corrosion/rust" appears on all samples after 24 h. White rust is an effect of corrosion attack on zinc that usually appears as a voluminous white deposit. This corrosion process can completely remove zinc in a localized area and brings to the "red corrosion/rust" that is the more important corrosion resistance parameter which means that the plating layer lost the protective properties and allowed the base metal to corrode. The more resistant the zinc plating deposit is, the longer it will take to see red corrosion products. The highest corrosion resistance (time to the appearance of the red corrosion) was measured for the Zn coating on the surface OABSA - 576 h. Time to red corrosion appearance in the case of sample OABG amounted to 312 h, and for the sample OABEP - 264 h. So, it means that zinc coating deposited on steel surface after softening annealing is almost twice more resistant to corrosion in comparison to grinding or electro-polishing effect. Moreover, despite the small differences between coating thickness deposited on electro-polished and grinded surfaces the corrosion resistance is much higher after grinding.

5. Conclusions

On the basis of above results analysis the following conclusions can be expressed:

1. Although the OAB cutting belongs to the cheapest methods of steel elements forming, in some cases, i.e. when the hot-dip zinc galvanizing is applied, this method can cause serious, difficult to avoid problems (diversification of zinc coating growth dependent on the base steel surface condition).
2. The main reason of zinc coating thickness diversification created on cold rolled and OAB cut surfaces is not the scale layer barrier generated during cutting and decreasing the iron diffusion but the heat affected zone being the effect of exerted by burner thermal impact upon the steel metallic matrix.
3. There is the direct correlation between the steel surface

hardness and zinc coating thickness diversification. The lowest difference was measured for softening annealing - 8% (158HV10), a much more greater for electro-polishing 51% (299HV10) and grinding 54% (329HV10)

4. The best way to reduce the Zn coating thickness diversification put on steel elements, where surfaces were formed with oxyacetylene blowpipe (OAB) cutting or other thermal method, is application of additional heat treatment – softening annealing that removes the heat affected zone (HAZ) created after thermal cut.
5. Results achieved after additional heat treatment are similar to this case where the steel elements were formed in low temperature process - by water jet – both coating thickness diversification as well as the zinc coating structure are almost the same.
6. The application (after OAB cutting) of additional processing: grinding or electro-polishing reduce also of Zn coating thickness diversification observed on the cut surface in comparison to cold rolled one but not in such range like thermal treatment.
7. There is direct relation between Zn coating thickness diversification and corrosion resistance of galvanized elements. Time to the appearance of the red corrosion in the environment of the 5%NaCl, on galvanized elements after the additional heat treatment is almost twice longer than on samples galvanized after the additional grinding or electro polishing.

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