



ANALYSIS OF THE ZINC LAYER ON STEEL PRODUCTS WITH VARYING SILICON CONTENT

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Abstract

This work experimentally evaluates the effects of chemical composition, particularly the amount of silicon on the quality of the applied coating technology of hot dip galvanizing. The experiment is aimed at determining the microstructure, thickness and quality of the zinc layer on the test samples of different steel grades. For the experiment there were selected structural steels S235JR and S355J2 with low silicon content. High strength steel S690QL with higher silicon content was chosen for comparison.

Results of independent measurements of coating thickness using optical microscopy and magnetic method indicate only minimal differences between steel S235JR and S355J2. Steel S690QL exhibits thick and uneven layer of the zinc. Steel S690QL should be evaluated as unsatisfactory type of steel for hot-dip galvanizing.

Keywords: Zinc Layer, GDOES, Optical Microscopy, Steel S690QL

1. INTRODUCTION

Hot galvanizing technology involves the creation of hot-dip zinc alloy coating on the surface of the steel component. This technology is a complex process of diffusion, elementary metallurgical reactions and thermodynamic changes [1].

Steel products free from grease, mill scale, rust and other impurities are immersed in galvanizing baths containing molten zinc. In the bath, the coating comprises several layers composed of the Fe-Zn phases (with an outer layer of pure zinc) on the steel surface within a few minutes. Hot dip galvanizing is one of the most common methods of coating metals for long lasting corrosion protection [2].

Steels selected for the experiment belong to the group of structural steels. Especially grades S235 and S355 are among the most widely used construction materials for welding and assembly of steel structures. Both grades belong among the steels which are not alloyed with silicon and are most often hot-dip coated. Conversely, high-strength quenched and tempered steel S690QL with increased silicon content was chosen to assess its impact on the quality of the zinc layer. This steel has recently been used for highly stressed welded structures (e.g. bridges, reservoirs, water tanks, cranes etc.) operating at normal and especially at low temperatures.

Another aim of this work was to verify the ability of the magnetic method for determining the thickness of zinc coating.

2. THEORETICAL

The precondition for achieving well galvanized layer is a complete wetting of the surface in zinc melt. Components for zinc coating are subjected to a chemical pre-treatment for achieving a clean metallic surface and for its activating. Steel is primarily degreased in the degreasing bath and then pickled in the pickling bath.



Pickling results in the removal of oxides, scale and corrosion products from the surface. The flux is applied on the surface prior to dipping into the bath. In the dry process (exploited in this work), the material is immersed in a flux bath and subsequently it is dried. After that, the batch is placed into the zinc bath [2].

Structure of hot-dip galvanized coating

Metallurgical reaction of iron and zinc are very sensitive to various influences. There is a significant influence of chemical composition (contents of Si, P, S, Mn, C, Al, Al, Sn, Ni, Pb, Bi [2]), the structure of the steel and also the technology parameters of hot dip galvanizing. Galvanized coating then forms various structures (**Figure 1**).



Figure 1 Structure of hot-dip galvanized coating [3]

The chemical composition of the substrate greatly affects the structure of the newly created surface. If the wrong type of steel which is characterized by higher contents of silicon and phosphorus is selected, there is a rapid increase of grains and so called Sandelin or Sebisty structure is created. This creates a thick and irregular layer of unsightly zinc coating, which significantly reduces its lifetime. The layer of zinc has a lower adhesion and it is uneven.

Robert W. Sandelin studied silicon content in hot-dip galvanized steel, and the result of his work was that for steel with silicon content higher than 0.03 wt. % there is a sharp increase in the zinc coating thickness [4]. Further research of John J. Sebisty developed theories regarding the exceedance of Sandelin area (i.e. 0.03 to 0.12 wt. % Si), when the coating thickness decreases temporarily with increasing silicon content. The coating thickness increases again with silicon content increasing above 0.25 wt. % (**Figure 2**) [5].



Figure 2 Sandelin diagram



(1)

Phosphorus has similar effects as silicon. Effect of phosphorus on the hot-dip galvanizing is apparent in steels with silicon content up to 0.03 %. In order to prevent negative effects of Si and P and thus create high-quality hot dip zinc coating, it is necessary to satisfy the basic condition [1]:

Si + 2.5 P < 0.09

- where: *Si* silicon content (wt. %)
 - *P* phosphorus content (wt. %).

3. EXPERIMENTAL

3.1. Experimental materials

Three types of steel were selected for the experiment: S235 a S355 a S690QL. Their chemical composition was determined by GDOES (see **Table 1**). Samples with 100 x 75 x 15 mm dimensions were galvanized together under the same galvanizing parameters. The samples were hung on the same crane, dipped in the same baths with the same dive time. The samples underwent standard dry galvanizing process including degreasing, pickling and rinsing. Then the samples were dipped in a flux solution, placed in a drying oven and subsequently they were immersed into the zinc bath for 300 seconds. Afterwards the air cooling was carried out, wherein the zinc coatings have matured 48 hours.

	C (%)	Mn (%)	Si (%)	P (%)	S (%)	Cr (%)	Ni (%)	Mo (%)	Cu (%)
S235JR	0.109	0.994	0.015	0.013	0.008	0.033	0.014	<0.001	0.025
S355J2	0.138	1.75	0.018	0.010	0.005	0.031	0.013	<0.001	0.013
S690QL	0.099	1.45	0.347	0.012	<0.001	0.081	0.038	0.117	0.040
	Ti (%)	Co (%)	B (%)	Pb (%)	V (%)	W (%)	Zr (%)	AI (%)	
S235JR	<0.001	0.005	<0.001	0.002	<0.001	<0.001	0.002	0.053	
S355J2	0.017	0.017	<0.001	<0.001	0.003	<0.001	0.003	0.055	
S690QL	0.001	0.007	<0.001	0.002	<0.001	<0.001	0.002	0.074	

Table 1 The chemical composition of the samples determined by GDOES

3.2. Calculation of steel applicability galvanizing factors according to EN ISO 1461

Based on the chemical composition of the sample material (see **Table 1**) the so-called steel applicability galvanizing factors (see **Table 2**) were calculated using formula 1. On the basis of chemical composition, structural steel S235 and S355 can be considered very suitable for hot dip galvanizing. Conversely, the S690QL steel is inappropriate.

Table 2 Estimated ap	plicability of steels fo	r hot dip galvanizing
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Steel	Factor <i>Si</i> + 2.5 <i>P</i>	Evaluation
S235JR	0.0475	The steel is suitable for hot dip galvanizing
S355J2	0.0430	The steel is suitable for hot dip galvanizing
S690QL	0.3770	The steel is not suitable for hot dip galvanizing



3.3. Experimental methods

Glow discharge optical emission spectrometry (GDOES)

The average chemical composition of the base material sample was determined by "bulk" analysis on glow discharge optical emission spectrometer Spectruma Analytik GmbH (Model GDA 750) under the excitation conditions of 700 V and 35 mA.

Magnetic method

Measurements of zinc coating were performed using a thickness gauge QUANIX 4200. All of the measurements of the samples were carried out 10 times, at least 10 mm from the burnt edge. Tested samples could not therefore be affected due to high temperatures used during oxy-fuel cutting.

Optical microscopy

Optical microscope Neophot 21 (operated at the Faculty of Mechanical Engineering) was used to determine the thickness of the zinc layer. The samples were embedded in resin and exposed to a standard grinding and polishing. Subsequently, they were analyzed in cross sections.

4. RESULTS

4.1. Results of magnetic method

Measurements showed clear differences in both the thickness of the zinc coating layer and the scattering in the measured values. S235JR and S355J2 steels have uniform zinc coating layer relative to the measured area of the sample. In the case of S690QL steel, there is a significant unevenness of coating thickness.

The thickness of the zinc layer on the S235JR steel was measured in the range from 66 to 72 microns; the average value was 69 microns. Measured thickness of the zinc layer on the S355J2 steel was in the range from 73 to 82 microns; the average value was 78 microns. Mean thickness of the zinc layer was about 9 microns larger compared to S235JR steel. A small increase in zinc coating can be attributed to higher levels of silicon in S355J2 steel.

However, the measurement results of S235 and S355 steels are insignificant compared to the measurement results of S690QL steel. On this steel, coating thickness in the range from 245 to 284 microns was measured; average value 260 microns. From these results, the increase in the zinc layer of about 200 microns compared to steels with low silicon content is evident.

	The thickness of the zinc layer (µm)										
	1	2	3	4	5	6	7	8	9	10	average
S235JR	68	69	66	68	70	69	71	70	68	72	69
S355J2	77	80	82	79	78	80	79	81	73	75	78
S690QL	245	256	259	260	252	267	262	254	258	284	260

Table 3	Observed	thickness	of the	zinc	coating	on	steel	samr	les	usina	magne	tic	met	hod
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4.2. Results of optical microscopy

Measurement of metallographic cross section of common structural steel S235JR (**Figure 3**) was performed in ten spots, zinc layer thickness ranged from 59 to 67 microns. Zinc coating reached a thickness of 63 microns on average.



The results of metallographic measurement of S355J2 steel (**Figure 4**) show the layer thickness in the range from 73 to 81 microns; 76 microns in average. The figure shows the increase of η phase compared with S235JR steel.

Thickness of the zinc coating on the S690QL steel (**Figure 5**) ranged from 238 to 267 microns. The average value of all measurements was 255 microns. In this sample, a very uneven ζ phase, forming a layer of consistent crystals, can also be observed.



Figure 3 Metallographic cross section of S235JR steel, including the measurement of the zinc layer



Figure 4 Metallographic cross section of S355J2 steel, including the measurement of the zinc layer



Figure 5 Metallographic cross section of S690QL steel, including the measurement of the zinc layer



4. DISCUSSION

Table 4 shows the average values of the measured thicknesses of the zinc layer of all three samples from the records of the two methods. The table shows that the magnetic method produces similar results as optical microscopy.

Table 4 Thickness of the zinc layer of	observed on the steel samples
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	Thickness of the zinc layer (μm)							
Used steel	Magnetic method	Optical microscopy						
S235JR	69	63						
S355J2	78	76						
S690QL	260	255						

Regarding the quality of the zinc coating, the prerequisites resulting from Sandelin principle have been met. For steels with silicon content below 0.02 %, a coating less than 100 microns thick was formed during hot dip galvanizing, which is fully satisfactory. Conversely, on the sample with the Si content of 0.347 wt. %, a much larger and therefore inconvenient Zn coating layer was formed.

5. CONCLUSION

S235JR and S355J2 steels which are not alloyed with silicon showed satisfactory thickness and structure of the zinc coating. Sandelin principle was confirmed for S690QL steel. This steel is not appropriate for hot dip galvanizing.

Magnetic method showed similar results as optical microscopy, but with a wider scattering of the measured values. This measurement can be recommended to determine the thickness of the zinc layer on hot dip galvanized metal sheets in the galvanizing plant.

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