CHARACTERIZATION OF GALVANIZED COATING USING RF-GDOES

Jiřina VONTOROVÁ [1], Petr MOHYLA [1], Zuzana TRAWINSKÁ [1]

VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU
jirina.vontorova@vsb.cz

Abstract

Galvanizing is an application of a zinc coating on the steel base material by electrolytic deposition. Zn coating protects anodically the base material (typically unalloyed or low-alloy steel) against corrosion. In the final phase of the galvanic process the final finishing employing chromate coating (yellow or blue) is often used. The treatment causes the non-conductivity of the surface coating of the material.

Glow Discharge Optical Emission Spectroscopy (GDOES) measures correctly, accurately and with good repeatability the thickness and composition of the zinc coating without the non-conductive surface treatment (chromate). This paper aims to verify the possibilities of the optical emission spectrometry for the analysis of non-conducting surfaces. Optical microscopy is taken as the reference method for the measurement of layer thickness, because this method is generally accepted as an accurate and correct.

Keywords: GDOES, galvanizing, zinc coating, chromate, optical microscopy

1. INTRODUCTION

Surface treatment is important area of mechanical engineering. Its task is to provide corrosion protection and modify the external appearance [1]. Thus surface finish changes functional properties of modified basic materials.

The most commonly used type of metal surface treatment is galvanizing [2]. Zinc protects the surface of the material mechanically and chemically as well. In a humid environment zinc creates a galvanic cell with Iron; therefore zinc coating provides anodic protection against corrosion of the base material. In practice, both basic galvanizing types are used - electrolytic and hot dip galvanizing [3].

The thickness of the zinc coating can be accurately determined by optical microscopy. This method is destructive, time-consuming, and economically demanding. Therefore, for its determination glow discharge optical emission spectroscopy is used. Element profile obtained using GDOES is used for characterization of various surfaces [4], e.g. brake discs [5], organic substances [6] and carburized layers [7].

For non-conductive surfaces, it is not possible to use the classic GDOES, but it is necessary to use the radio-frequency glow discharge optical emission spectroscopy (RF-GDOES) [8]. This work aims to verify the possibilities of GDOES for the analysis of zinc coating with the final layer - yellow or blue chromate. This treatment causes the non-conductivity of the surface layer of the final material.

2. EXPERIMENTAL MATERIAL

Steel plate with electrolytic zinc coating as a base material was used within this work. Dimensions of the plate were 50 x 30 x 0.5 mm. For the determination of the composition of the base material the so called "Bulk" analysis by Glow Discharge Optical Emission Spectroscopy (GDOES) was used. The results are listed in **Table 1**.

Table 1 The chemical composition of the samples determined by GDOES

	wt.%		wt.%		wt.%		wt.%
C	0.034	S	0.006	Cu	0.034	Pb	<0.0001
Mn	0.449	Cr	0.014	Ti	<0.0001	V	0.014
Si	0.011	Ni	0.047	Co	<0.0001	W	<0.001
P	0.016	Mo	0.013	B	0.002	Al	0.054

Samples were prepared by galvanizing of the surface of the substrate by zinc. Before plating, the samples were placed on the hanger (see **Figure 1**). Galvanizing is composed of several successive repetitive operations: chemical and electrochemical degreasing, rinsing, pickling, galvanizing, chromating and drying (see **Figure 2**).

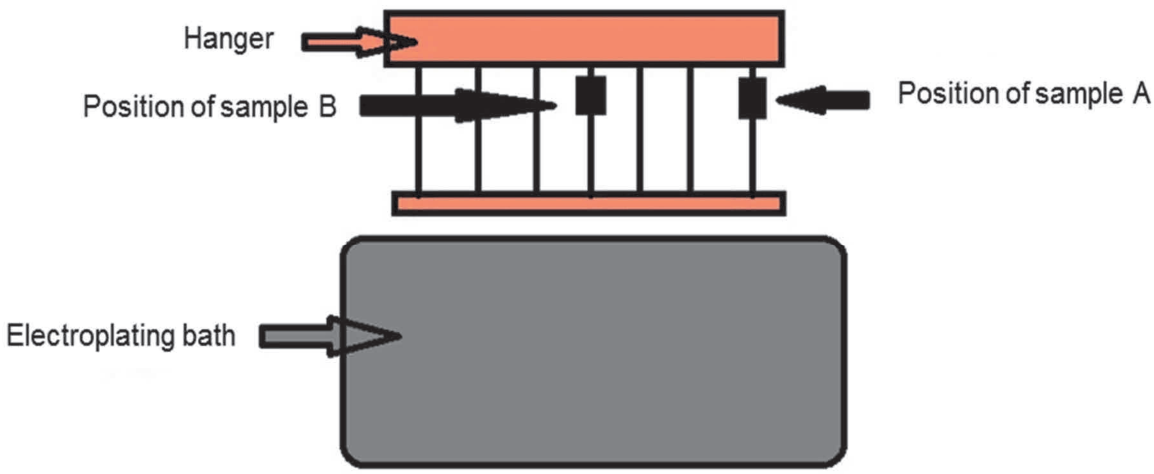

Figure 1 Location of specimens on the hanger

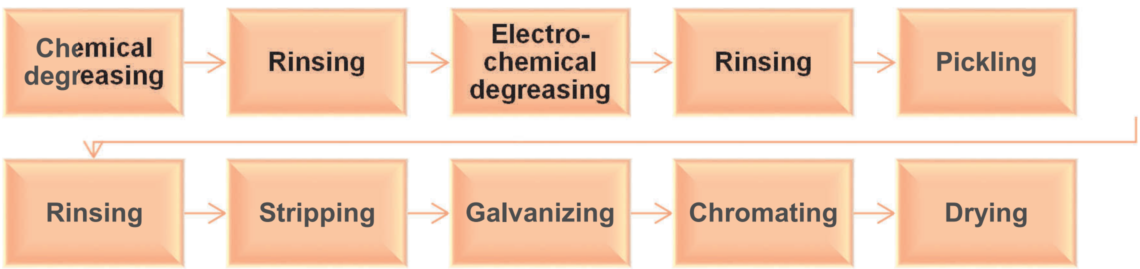

Figure 2 The basic scheme of the galvanizing process

The galvanic process was the same for all of the samples, the samples differed only by placing on a hanger (see **Figure 1**), the amount of other products on the hinge (the experiment was performed in normal operation) and the final surface treatment (see **Figure 2**). The zinc plating produced a surface with a matt gray color (see **Figure 3a**). Atmospheric corrosion let to formation of the zinc corrosion products, which are known as “White corrosion”. This prevents e. g. passivation (chromating of zinc coating). Protective layer (hydroxy compounds of trivalent chromium and zinc) is formed during passivation, this protective layer increases the corrosion resistance of the coating. The resulting passivation layer is formed as an amorphous shell. **Figure 3** shows yellow (**b**), and light blue (**c**) chromate layer.

a b c

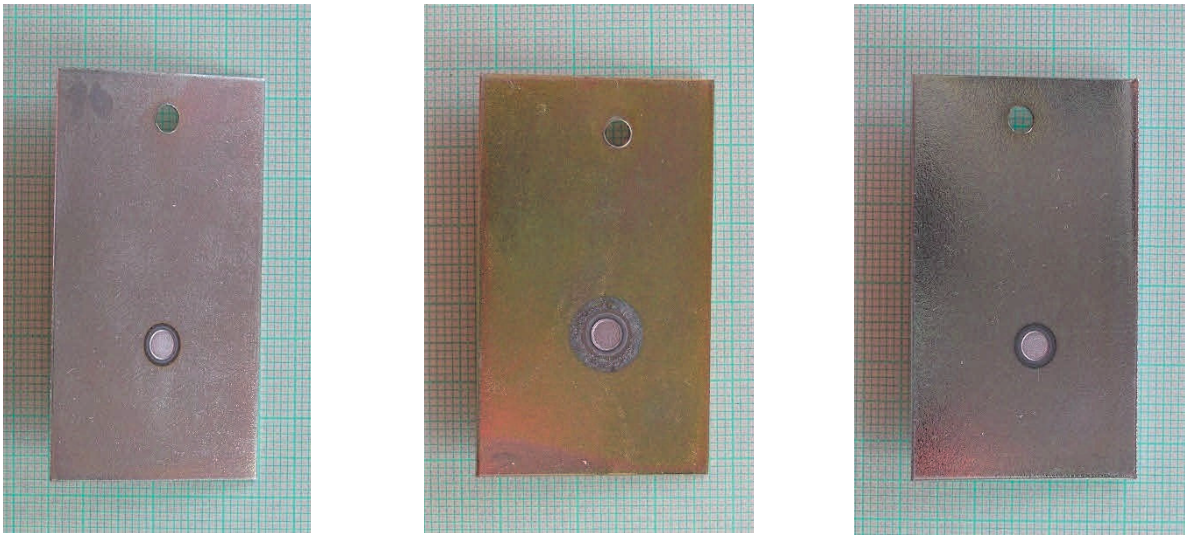

Figure 3 Samples coated with Zn (**a** - pure Zn, **b** - Zn + yellow chromate, **c** - Zn + blue chromate)

3. EXPERIMENTAL METHODS

3.1. Glow discharge optical emission spectroscopy (GDOES)

GDOES analysis was carried out using optical emission spectrometry with glow discharge Spectruma Analytic GMBH (model GDA 750 A). 'Bulk' analysis revealed the average chemical composition of the base material of the specimens as well as the chemical composition of the zinc coating after grinding off. The analysis was performed under 700 V and 35 mA excitation conditions. The profile analysis (RF-GDOES-QDP), by which alloy layers thicknesses and their chemical composition were determined, was carried out under the excitation conditions of 800 V and 2 hPa.

3.2. Optical microscopy

Optical microscopy is a destructive method, universal for all types of coatings, except soft coatings (waxes, vaseline). In the present work there is optical microscopy taken as a reference method for its precision and accuracy. Zinc and chromate layer thickness measurements on the samples were performed on an optical microscope Olympus IX70 at a magnification of 200 x. the results were analyzed using Image Pro Micro G software.

Samples were cut on Struers devices and were embedded by two-part sealing compound Durocit Kit (Struers) into forms.

4. RESULTS AND DISCUSSION

Examples of RF-GDOES-QDP spectra of galvanized sheet samples are shown in the following figures. The spectrum of sample 1A (without the chromate layer) is shown on **Figure 4**, sample 2A (with a yellow chromate layer) on **Figure 5** and sample 3A (with a blue chromate layer) on **Figure 6**. The y-axis scales of chromium, manganese and carbon have been altered in the figures. This was due to their low concentration and with the aim to make these curves mutually recognizable. Therefore, mass concentrations of chromium and carbon taken from the spectra should be divided by 200 and manganese by 20. The sputtering craters after GDOES analyzes are shown in **Figure 3**.

For example, one metallographic image of sample 3A is shown in **Figure 7**.

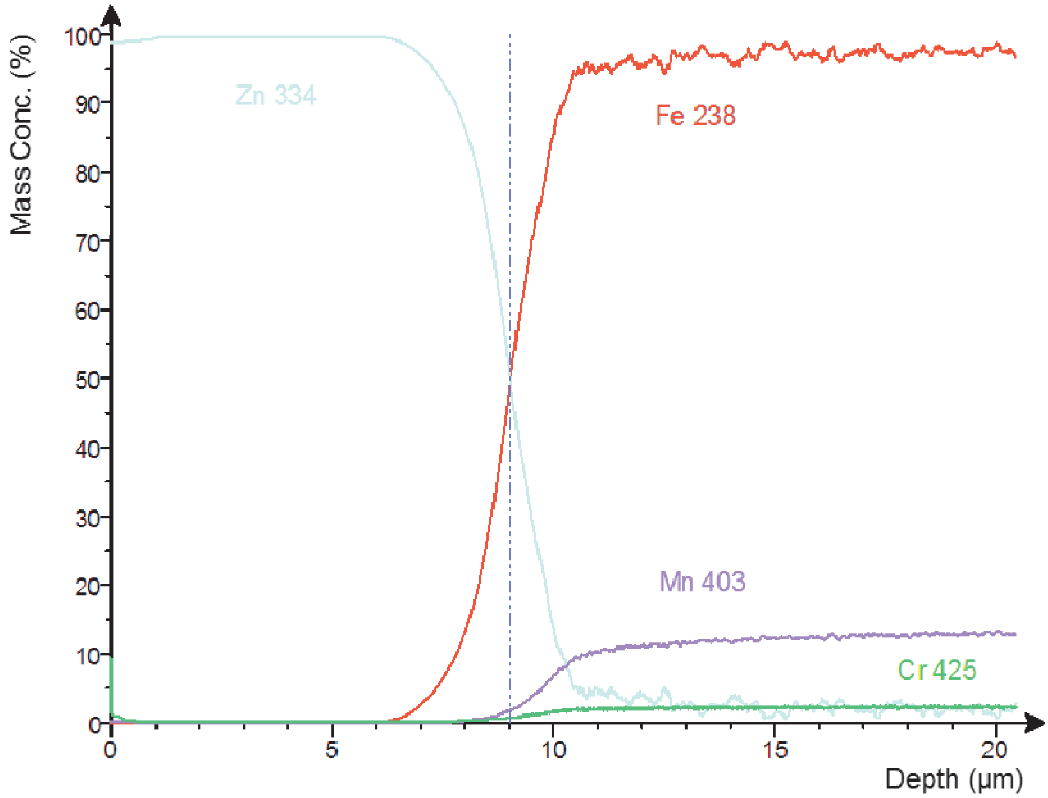

Figure 4 RF-GDOES spectrum of sample 1A (pure Zn coating)

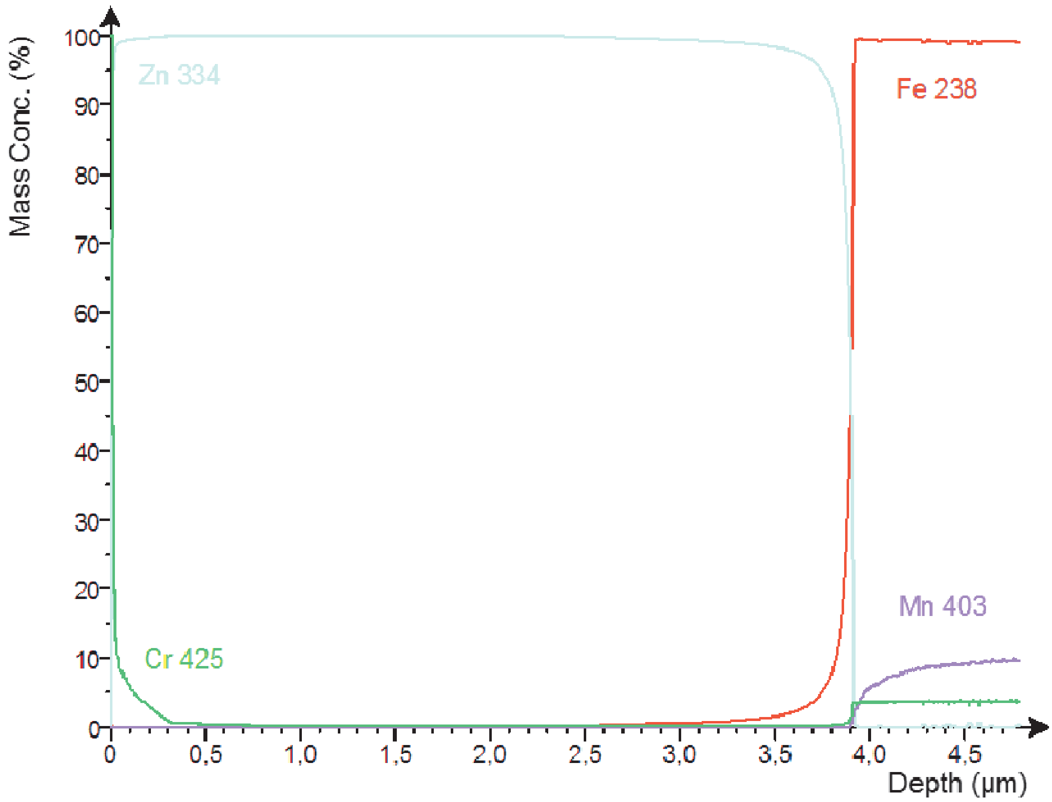

Figure 5 RF-GDOES spectrum of sample 2A (Zn coating + yellow chromate)

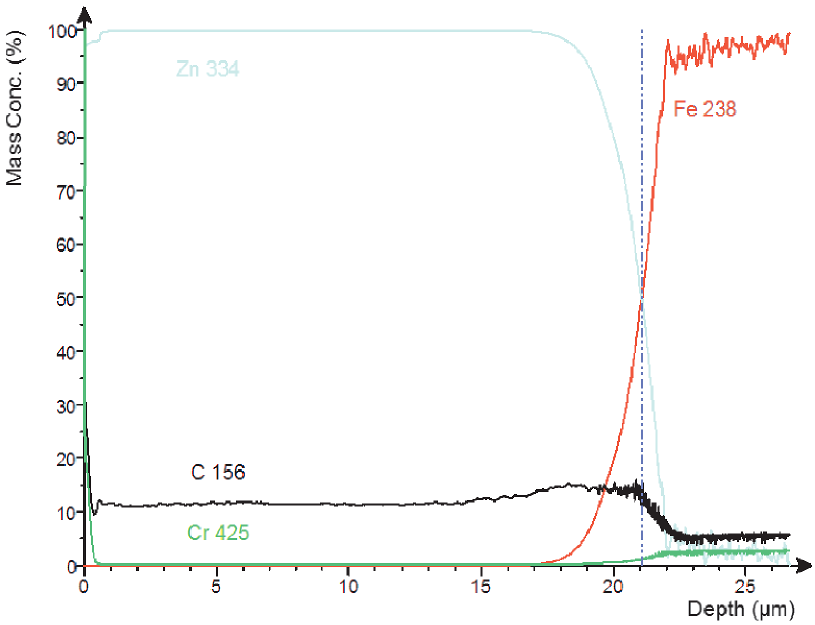

Figure 6 RF-GDOES spectrum of sample 3A (Zn coating + blue chromate)

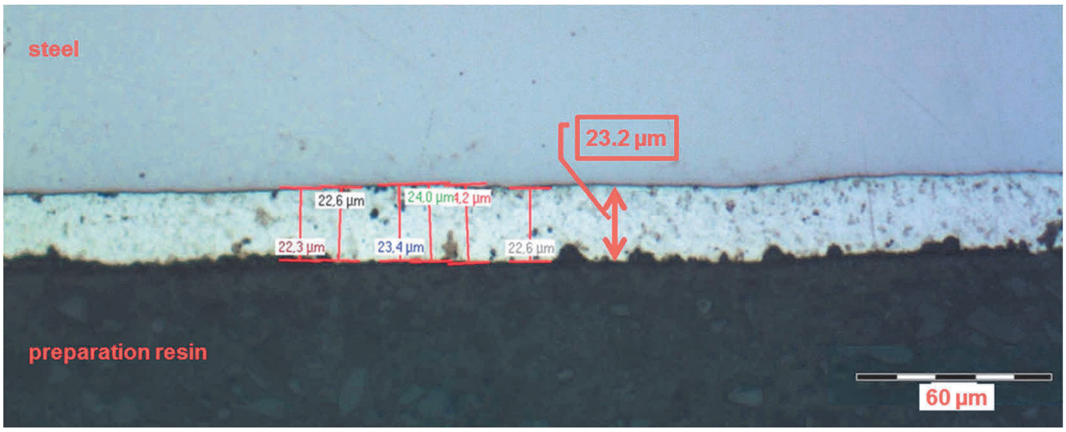

Figure 7 Metallographic image of sample 3A (Zn coating + blue chromate)

The following table (**Table 2**) shows the results of metallographic and RF-GDOES analysis. The data were evaluated using the software QC-Expert using the "Compare Two Selections - Pairwise Comparison," method and it was demonstrated that the differences are not statistically significant. The correlation coefficient is 0.989, indicating a very good match of data measured by both methods.

Table 2 Comparison of the results obtained by optical microscopy and RF-GDOES

Sample	Chromate coating	Metallography	RF-GDOES
		µm	
1A	-	10.1	9.0
1B	-	12.3	8.5
2A	yellow	6.0	3.9
2B	yellow	3.5	4.8
3A	blue	23.2	21.0
3B	blue	32.0	28.0

5. CONCLUSION

This paper aimed to verify the possibility of using RF-GDOES for the analysis of galvanized metal sheets and to assess the thickness of the zinc coating in dependence on the conditions of the galvanizing process.

On the basis of the results obtained, it can be stated that the quantity of galvanized material and the location of the sample on the hanger in the zinc bath are the parameters with substantial influence on the thickness of the Zn coating.

From the comparison of the methods used for determining the thickness of the zinc coating, it can be concluded that RF-GDOES is a suitable method for this purpose. Differences in zinc thickness measured using RF-GDOES and optical microscopy are not statistically significant. The influence of chromate layer on measurement of the thickness of the zinc coating was not confirmed.

ACKNOWLEDGEMENTS

This work was supported by the project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education. Youth and Sports of the Czech Republic and by VŠB-Technical University of Ostrava: SP 2018/60 „Specific research in the metallurgical, materials and process engineering“.

REFERENCES

[1] PODJUKLOVÁ, J., SUCHÁNKOVÁ, K., ŠRUBAR, P., KOPANAKOVÁ, S., and HRABOVSKÁ, K. Study of influence corrosive environment on characteristics protective coatings used for long-term corrosion protection of steel substrate. In *METAL 2013: 22nd International Conference on Metallurgy and Materials. Ostrava: TANGER*, 2013, pp. 953-958.

[2] MARDER, A. R. Metallurgy of zinc-coated steel. *Prog. Mater. Sci.*, 2000, vol. 45, no. 3, pp. 191-271.

[3] KUKLÍK, V. and KUDLÁČEK, J. *Hot-Dip galvanizing of steel structures*. 2016. 209 p.

[4] FUKUMURO, N., NISHIYAMA, J., SHIGETA, K., TAKAGAMI, H., YAE, S., and MATSUDA, H. Confirmation of hydroxide in electroless cobalt alloy films by GDOES". *Trans. Inst. Met. Finish.*, 2007, vol. 85, no. 2, pp. 111-112.

[5] VONTOROVÁ, J., DOBIÁŠ, V., and MOHYLA, P. Utilization of GDOES for the study of friction layers formed on the surface of brake discs during the friction process. *Chemical Papers*, 2017, pp. 1507-1514.

[6] LIU, Y., JIAN, W., WANG, J. Y., HOFMANN, S. and SHIMIZU, K. Quantitative reconstruction of the GDOES sputter depth profile of a monomolecular layer structure of thiourea on copper. *Appl. Surf. Sci.*, 2015, vol. 331, pp. 140-149.

[7] VONTOROVÁ, J.; VÁŇOVÁ, P. Determination of carburized layer thickness by GDOES method. *AIMS Materials Science*, 2018, vol. 5, no. 1, pp. 34-43.

[8] ESCOBAR GALINDO, R., FORNIÉS, E. and ALBELLA, J. M. Compositional depth profiling analysis of thin and ultrathin multilayer coatings by radio-frequency glow discharge optical emission spectroscopy. *Surf. Coatings Technol.*, 2006, vol. 200, no. 22-23 SPEC. ISS., pp. 6185-6189.