# ADVANTAGES OF GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY (GDOES) IN THE ANALYSIS OF DIFFERENT TYPES OF ZINC COATINGS ON STEEL

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**Abstract**

In this paper, the main advantages of GDOES profiling analysis in evaluating the thickness of zinc coating applied using hot-dip and electroplating technology on steel sheets are assessed, including the evaluation of electroplating zinc coating with a chromate and chromite passivation layer.

Zinc coating is one of the surface treatments of steel products and structures in order to protect them against corrosion attack by the surrounding aggressive environment and contributes to increasing their service life. The thickness, phase structure, and chemical composition of the Zn coating influence its protective properties. In addition to destructive and non-destructive methods, optical and electron microscopy, which require time-consuming preparation of Zn-coated steel sheet samples, are also used to evaluate Zn coating. Based on the experimental work and its results, it was found that the use of GDOES profiling analysis can replace optical and electron microscopy with high accuracy.

**Keywords:** Zinc coating, GDOES profiling analysis, optical microscopy

## 1. INTRODUCTION

Surface treatment is one of the important engineering technologies that provide corrosion protection for steel products and structures, modifying their external appearance and functional properties, including increasing their service life.

The appearance and properties of zinc coatings depend on the technology of their production. The article deals with the evaluation of zinc coatings applied to steel sheets using the hot-dip galvanising in molten zinc, galvanising method, and zinc coating with a chromate and chromite passivation layer.

Various destructive or non-destructive measurement methods are used to check the thickness of the Zn coating [1]. The measurement methods are determined by the type of substrate material, the type of coating, and its expected thickness. The methods for measuring the coating thickness are given by EN ISO 3882 [2]. In industrial practice, Zn coating thickness is most often determined by the magnetic method. Optical microscopy is a time-consuming and instrumentally demanding but accurate method for evaluating coating thickness, but it requires the time-consuming preparation of experimental samples. Similarly, the thickness and chemical composition of the coating can be determined by electron microscopy, which also requires the time-consuming preparation of experimental samples. In some scientific papers, glow discharge optical

emission spectrometry (GDOES) is reported for Zn coating thickness measurement, which, on the other hand, does not require the time-consuming preparation of experimental samples [3,4].

The principle of GDOES consists in the interaction of electromagnetic radiation with atoms, during which electrons move from their original energy level to higher energy levels (excitation) and then return to their original level. The excitation source of the glow discharge is a Grimm lamp, which consists of a cathode and a hollow anode. A discharge, which is confined to a circular area on the surface of the sample, is ignited by putting a high voltage between the anode and cathode. The argon atoms are ionised, accelerated in an electric field, and fall onto the surface of the sample (cathode). From there, the sample atoms are excited mainly by collisions with the incident argon ions. This is called cathodic sputtering, which is actually the atomisation of the sample (**Figure 1**). The released atoms of the sample are then excited in the discharge and subsequently emit radiation that is characteristic of the individual elements of the sample. A crater is formed on the surface of the sample (**Figure 2**).

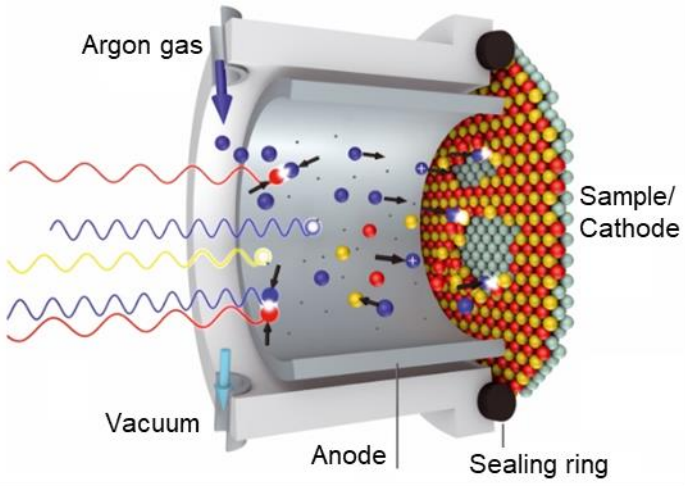


**Figure 1** Excitation mechanism [5]

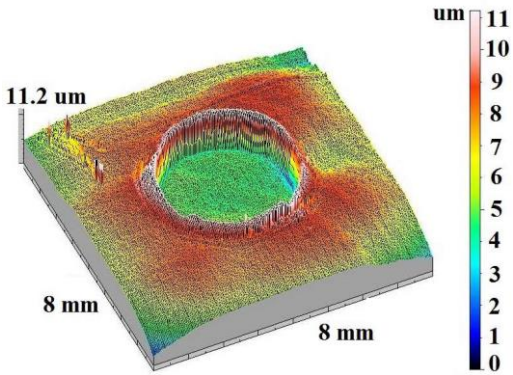


**Figure 2** 3D profile of the crater after GDOES analysis [6]

## 2. EXPERIMENTAL METHODS

GDOES profiling analysis to determine the thicknesses of the conductive zinc coatings and their chemical composition was performed under excitation conditions of 1,000 V and 15 mA using a Spectruma Analytik GMBH glow discharge optical emission spectrometer (model GDA 750) operated at the Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB - Technical University of Ostrava. In the case of the analysis for determination of the thickness of zinc coatings with a non-conductive passivation layer, a radiofrequency excitation source was used [7] (excitation conditions: 800 V and 2 hPa).

The determined thicknesses of the zinc coatings were compared with the results of optical microscopy (Olympus GX51 optical microscope, operated at the Faculty of Mechanical Engineering, VŠB - Technical University of Ostrava). Standardly prepared samples for optical microscopy were analysed in cross-section. Etching was performed with Nital 4% reagent.

### 2.1 Evaluation of hot dipped zinc coating

The first objective of the experimental work was to verify the suitability of using GDOES profiling analysis to assess the thickness and quality of the zinc coating formed by hot dip galvanising.

Hot-dip galvanising is one of the most effective and widely used methods of protecting steel against corrosion [8]. It makes it possible to obtain high-quality coatings and thus ensure long-term corrosion protection at relatively low operating costs for coatings. The material most commonly hot-dip galvanised is ferritic or ferritic-perlite structural steel in various grades [9].

Depending on the composition of the steel, the temperature and composition of the zinc bath, the thickness of the galvanised steel, the lag time in the bath, the condition of the surface, and the method and rate of cooling after the steel is removed from the zinc bath, an alloy coating composed of various Fe-Zn intermetallic compounds is formed. The layers composed of these compounds have different grain composition and morphology, thickness, and mechanical properties. They are denoted by letters of the Greek alphabet, i.e. gamma (Γ), delta (δ), zeta (ζ) or eta (η). The iron content of the alloy coating increases from the outer surface to the substrate material. Similarly, the zinc content increases from the underlying steel material to the outer surface [10].

**Figure 3** shows a profiling analysis of the S235JR galvanised steel. The record shows that the zinc coating layer (70% Zn) reaches a depth of about 73 μm. At a depth of approx. 79 μm, the zinc content is 50%, and at a depth of 84 μm, the zinc is practically absent (the apparent presence in the figure is due to detector noise). The beginning of the curve, where the zinc content is 100%, represents the phase $\eta$. At a depth of 9 μm, the beginning of a more pronounced decrease can be observed in the zinc curve, which ends about 28 μm from the surface and corresponds to the transition zone $\eta + \zeta$ (with variable zinc content from 100% to 95%), followed by a band of phases $\zeta$ and $\delta$. These two zones are difficult to distinguish by GDOES analysis. The end of the δ zone is at a depth of 73 μm, corresponding to a zinc concentration of 70%. The chemical composition of the base material (S235JR steel) determined by GDOES analysis is given in **Table 1**.

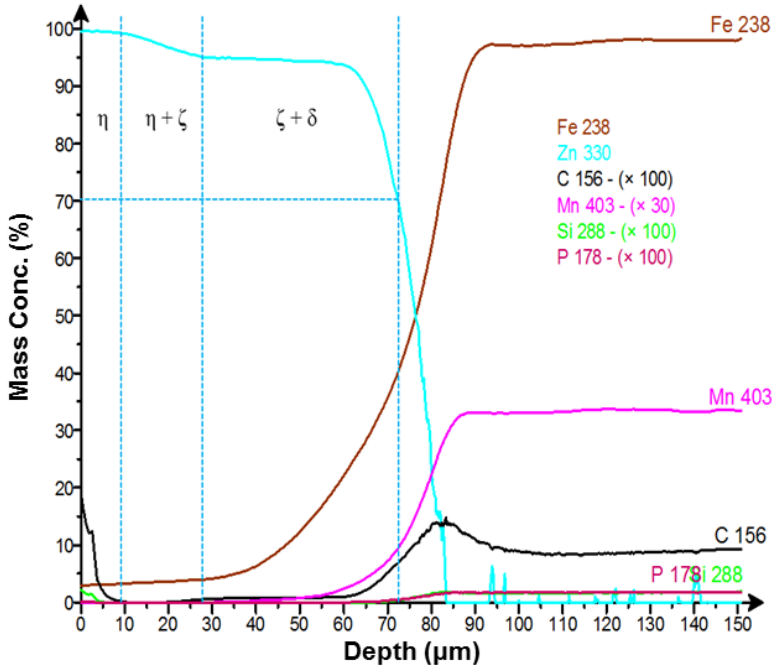


**Figure 3** GDOES profiling analysis of hot-dip galvanised S235JR steel

**Table 1** Chemical composition of the base material (S235JR steel) determined by GDOES analysis

| C | Mn | Si | P | S | Cr | Ni | Mo | Cu | Co | Pb | V | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| wt.% | | | | | | | | | | | | |
| 0.109 | 0.994 | 0.015 | 0.013 | 0.008 | 0.033 | 0.014 | <0.001 | 0.025 | 0.005 | 0.002 | <0.001 | 0.053 |

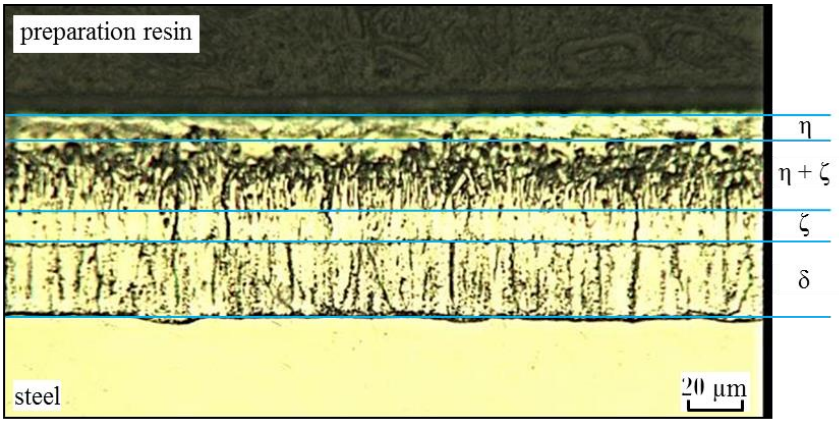


**Figure 4** Metallographic image of S235JR hot dipped Zn coated steel, cross-section, etched with 4% Nital

The result of the GDOES profiling analysis corresponds to the metallographic analysis (see **Figure 4**). The thickness of the zinc coating on the S235JR structural steel sample is in the range of 72-76 µm. On average, the zinc coating reaches a thickness of 74 µm. The picture shows a layer of pure zinc $\eta$ (on the surface); underneath, there is a layer of monoclinic crystals $\zeta$ and then the phase $\delta$, which is uniform and homogeneous. Between the phases $\eta$ a $\zeta$, there is a mixed phase $\eta + \zeta$.

### 2.2 Evaluation of galvanic zinc coating with a passivation layer

The second objective of the experimental work was to verify the suitability of using GDOES profiling analysis to assess the thickness and quality of the non-conductive passivated zinc coating formed by electroplating. In the case of a non-conductive coating, it is necessary to use a radio frequency source (RF-GDOES).

The anti-corrosion properties of the zinc coating are significantly improved by passivation. The passivation of Zn coating consists in the formation of a conversion layer on its surface, i.e. the chemical dissolution of the surface layer of zinc and the formation of a “nobler” coating containing metals other than zinc. The traditional treatment is so-called chromating (see **Figure 5**), in baths containing hexavalent chromium, which is highly toxic. During chromating, approximately 0.5 mg of zinc is dissolved. A more environmentally friendly solution to passivation of the zinc coating is chromiting in trivalent chromium baths, which produces a similar, but usually thinner, conversion coating (see **Figure 6**). The zinc removal rate during chromiting is about twice that of chromating, with about 1 µm of zinc coating dissolved. The undisputed advantage of passivation by chromiting over chromating is that, in addition to environmental protection, it also preserves the corrosion resistance of the coating under thermal stress, for example, during so-called dehydrogenation [11]. For photos of galvanised samples with passivation layer (see **Figure 7**).

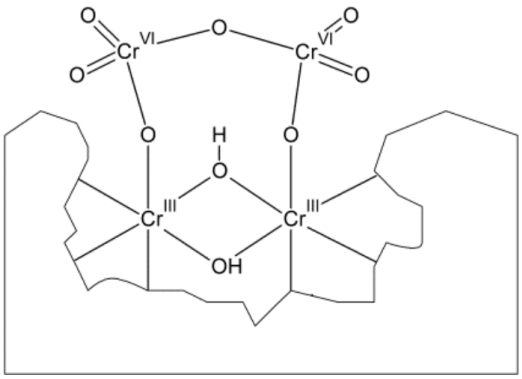


**Figure 5** Structure of chromated zinc coating [11]

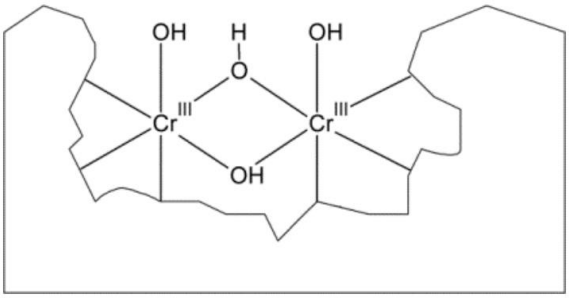


**Figure 6** Structure of chromited zinc coating [11]

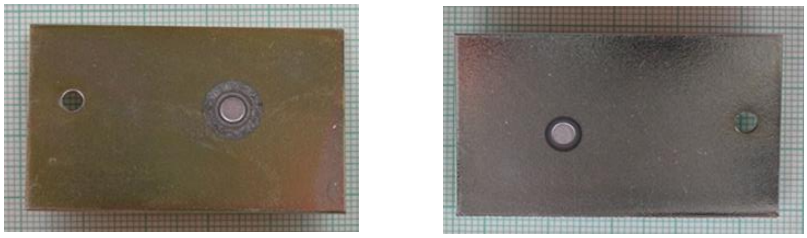

**Figure 7** Samples with galvanic Zn coating (left: Zn + chromate; right: Zn + chromite)

The profile record of the galvanised sheet with chromate coating is shown in (**Figure 8**).The thickness of the total zinc coating is 15.8 µm (it is read at the point where the iron and zinc curves intersect - indicated by the dashed blue line in the record). **Figure 9** is a profile record of a galvanised sheet with a chromite passivation layer. The thickness of the zinc coating here is 13.9 µm. **Table 2** shows the chemical composition of the base material. The GDOES results confirm the assumption made in [11] that chromiting produces a thinner Cr coating than chromating. **Figure 9** shows an increased carbon content in the coating, which could be due to failure to comply with the technological procedure for coating.

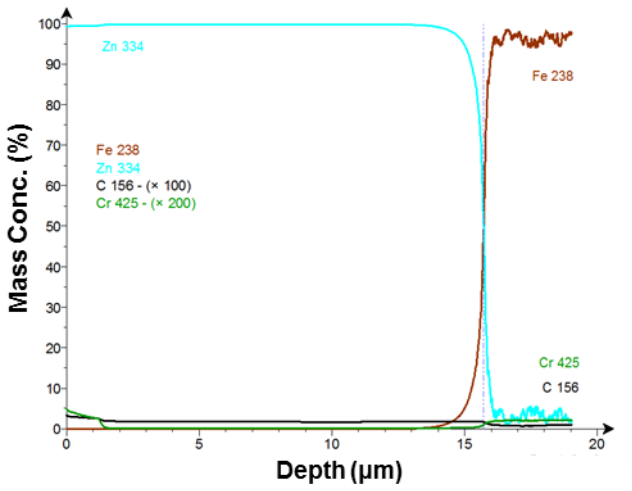


**Figure 8** Record of RF-GDOES profiling analysis of galvanised sheet with chromate coating

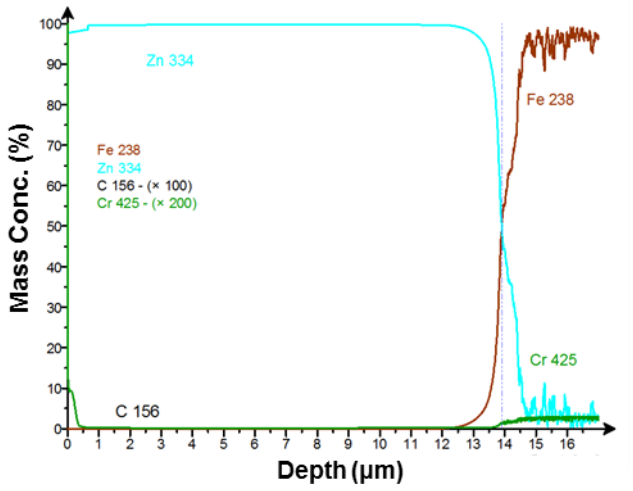


**Figure 9** Record of RF-GDOES profiling analysis of galvanised sheet with chromite coating

**Table 2** Chemical composition of the base material determined by GDOES analysis

| C | Mn | Si | P | S | Cr | Ni | Mo | Cu | Co | Pb | V | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| wt. % | | | | | | | | | | | | |
| 0.034 | 0.449 | 0.011 | 0.016 | 0.006 | 0.014 | 0.047 | 0.013 | 0.034 | <0.001 | <0.001 | 0.014 | 0.054 |

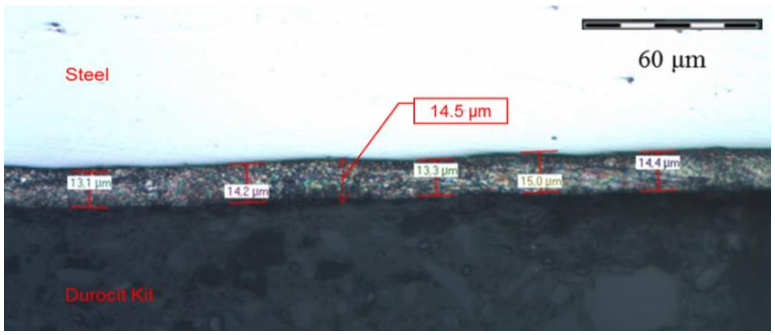


**Figure 10** Optical microscopy image of Zn + chromate coated sample; cross-section, etched with 4% Nital

The GDOES results were compared with optical microscopy (results in **Table 3)**. As an example, a metallographic image of a chromate-passivated galvanic zinc-coated steel plate sample is shown in (**Figure 10**). The thickness of the coating was measured ten times and after confirming the normality of the data with no outlying values, the data were averaged to a thickness value of 14.5 μm.

**Table 3** The zinc layer thicknesses determined by optical microscopy, GDOES analysis and magnetic method

| **Sample** | **Zinc coating thickness (μm)** | | | | |
|---|---|---|---|---|---|
| | **optical microscopy** | | **GDOES** | | **magnetic method** |
| hot-dip galvanised | 74 | η ≈ 9<br>η + ζ ≈ 25<br>ζ ≈ 12<br>δ ≈ 28 | 73 | η ≈ 9<br>η + ζ ≈ 19<br>ζ + δ ≈ 45 | 78 |
| galvanic Zn + chromate | 14.5 | | 15.8 | | 17.3 |
| galvanic Zn + chromite | 12.9 | | 13.9 | | 15.6 |

## 3. CONCLUSION

The aim of the experimental work was to compare the advantages of using profile GDOES for the analysis of zinc coatings, especially their thickness, compared to the traditional evaluation using microscopic methods. It was found that:

- GDOES gives statistically consistent results for zinc coating thickness measurements with optical microscopy,
- When evaluating hot-dip zinc coatings by GDOES, the phase structure of the coating, i.e. eta-phase, zeta-phase, delta-phase, and gamma-phase, can be detected and determined,
- probable technological indiscipline in galvanising (presence of carbon in Zn coating) can be detected,
- the chemical composition of zinc (and also alloy) coatings with a passivation layer (including the thickness of the passivation layer) can also be determined,
- after the GDOES profiling analysis, a BULK analysis can be performed immediately to determine the exact chemical composition of the base material,
- GDOES does not require sample preparation, i.e. the analysis is less time and cost consuming and can replace optical microscopy, which can be used to determine the thickness but not the exact chemical composition of coatings.

## ACKNOWLEDGEMENTS

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