CHARACTERIZATION OF Zn-Mg-Al BASED COATING

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Abstract

This paper aims to characterize Zn-Mg-Al based coating by profile analysis and determine its thickness as a basic property of the coatings. The most frequently used method for its determination is optical microscopy, but it is time-consuming and destructive. Glow Discharge Optical Emission Spectrometry (GDOES) was chosen as the second method for determining both the thickness and the chemical composition of the coating. The results show that both methods give statistically identical results. The suitability of using GDOES for Zn-layer analysis has already been demonstrated in the literature, and this work confirms these conclusions. Its use for the analysis of alloy layers has been verified by this work.

Keywords: Zn-Mg-Al layer, Zn layer, GDOES, optical microscopy

1. INTRODUCTION

The basic methods dealing with corrosion protection [1-3] include the hot-dip galvanizing method [4]. Hot-dip galvanized sheets are often used in the automotive industry, where formability is also an important feature [5]. The principle of this method consists in the contact of the iron contained in the steel with zinc [6]. The reaction occurs to form a tightly bonded alloy coating that provides corrosion protection to the steel [7]. Zn coatings have undeniable advantages, but they still corrode due to their higher electrode potential relative to steel. The dissolution rate and the difference in corrosion potential between Zn and steel can reduce the use of Zn alloy coating with Ni [8,9], Co [10] or Sn [11]. Currently, Zn-Mg-Al based anti-corrosion coating is being studied [12]. In addition to the increased corrosion resistance, the coatings obtained from these baths have higher hardness and scratch resistance [13].

The elements added to the zinc bath significantly affect the structure, appearance and corrosion resistance of the resulting coating [12]. Aluminium improves the plasticity of the coating, lightens, increases gloss and improves corrosion resistance by forming a zinc coating containing Al_2O_3. Fe-Al intermetallic phases are emitted at the solid/liquid interface during the galvanising process, forming a barrier to the reactive diffusion of zinc and preventing the growth of Fe-Zn intermetallic phases. Magnesium improves the wettability of the steel substrate, reduces the surface tension of the bath, and improves corrosion resistance.

Glow Discharge Optical Emission Spectrometry (GDOES) [14] is a method used to determine the average chemical composition of the base material [15] as well as the thickness and chemical composition of Zn layers [16]. In this paper, its use for the analysis of alloy coatings is verified. Optical microscopy is used as a comparative method [17].

2. EXPERIMENTAL MATERIAL

The thickness and composition of the Zn-Mg-Al and Zn layers (galvanized sheet without surface finishing) were characterized on two sheets of non-alloy steel (see **Figure 1**). The chemical composition of the base material was determined after evaporation of the “BULK” surface layer by Glow Discharge Optical Emission Spectrometry analysis (**Table 1**).

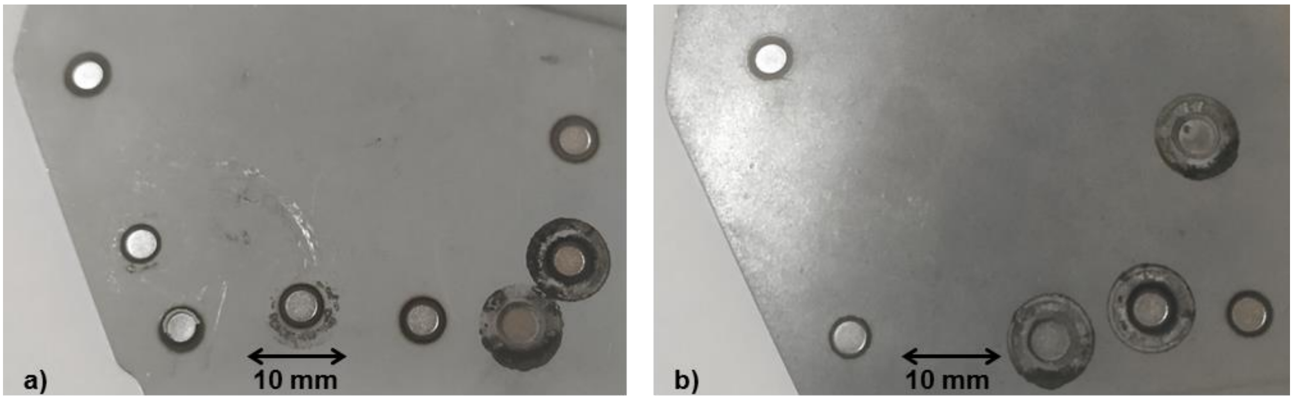

Figure 1 Samples with craters after GDOES profile analysis **a)** Zn coating, **b)** Zn-Mg-Al coating

Table 1 Chemical composition of the base material (wt. %)

C	Mn	Si	P	S	Cr	Ni	Mo
wt. %							
<0.001	0.128	<0.001	0.012	0.010	0.035	0.061	0.005
Cu	**Ti**	**Co**	**B**	**Pb**	**V**	**W**	**Al**
wt. %							
0.051	0.032	<0.001	<0.001	<0.001	0.010	<0.001	0.077

3. EXPERIMENTAL METHODS

A glow discharge optical emission spectrometer made by Spectruma Analytik GmbH (model GDA 750) was used in this work. The average chemical composition of the sample base material was determined by BULK GDOES analysis under 700 V and 35 mA excitation conditions. Profile analysis was performed under excitation conditions of 1000 V and 15 mA. Measurement of the zinc layer thickness on the sample was performed in cross-section on an Olympus IX50 optical microscope. Both of these instruments are operated at the Faculty of Materials Science and Technology, VSB – Technical University of Ostrava.

4. RESULTS AND DISCUSSION

In the following figure (**Figure 2**), two records of profile GDOES analysis of galvanized sheet and Zn-Mg-Al coated sheet are shown as an example. As expected, >99% zinc was measured on the surface of the Zn sheet (**Figure 2a**), with the proportion of zinc decreasing with increasing crater depth and the proportion of iron and other elements that were part of the base material increasing. The other elements have such low percentages that it would be meaningless to show them. Even the scales of the profile records of magnesium, aluminium, manganese, chromium, nickel and copper had to be changed for the sake of recognition - the value subtracted from the record must be divided by the constant given in the legend of the records.

In the profile analysis record of the Zn-Mg-Al coated sheet (**Figure 2b**), the concentration of Zn, magnesium and aluminium is approximately 95 %, 3.7 % and 0.7 %, respectively; their concentration decreased with crater depth. The concentration of iron and other elements contained in the base material increased analogously with decreasing Zn coating.

The curve of zinc content in the base material varied for both the conventional and modified coating. This may have been due to a non-stabilised detector or the analyser sensitivity to the dusty material redeposited on the crater wall.

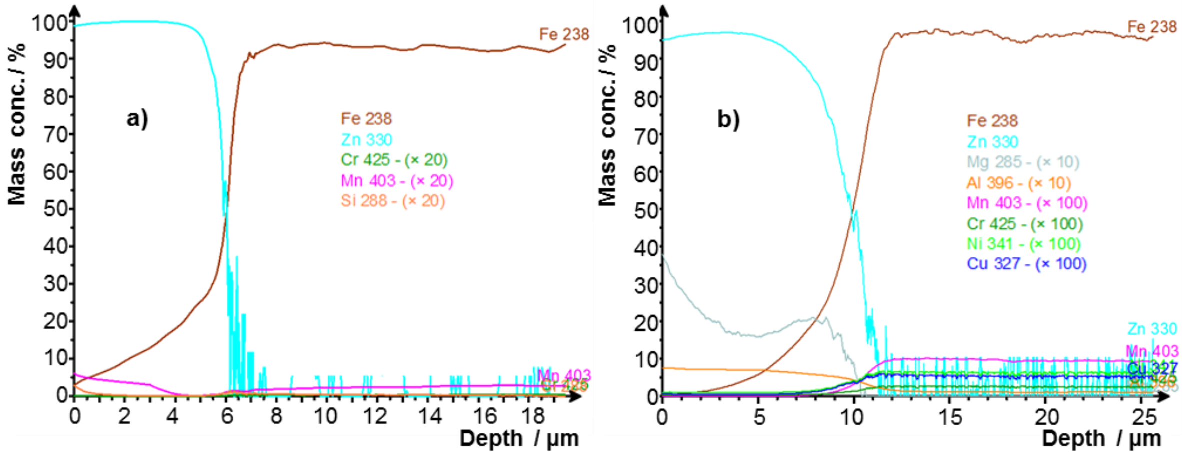

Figure 2 Profile records of GDOES analyses of non-alloy steel sheet with **a)** Zn coating, **b)** Zn-Mg-Al coating

As shown in (**Figure 1**), the records were measured repeatedly. The individual thicknesses were not statistically different and are recorded in **Table 2**. The average thickness of the Zn coating was 10.1 µm, and that of the Zn-Mg-Al coating was 6.0 µm. The coating thickness was read at the point where the Zn and Fe profile curves crossed.

Table 2 Surface layer thicknesses determined by GDOES (µm)

Sample	**Zn coating**	**Zn-Mg-Al coating**
	µm	
Measurement 1	6.1	10.1
Measurement 2	5.7	10.2
Measurement 3	6.2	10.1
Measurement 4	6.1	10.0
Measurement 5	6.0	10.3
Average	**6.0**	**10.1**

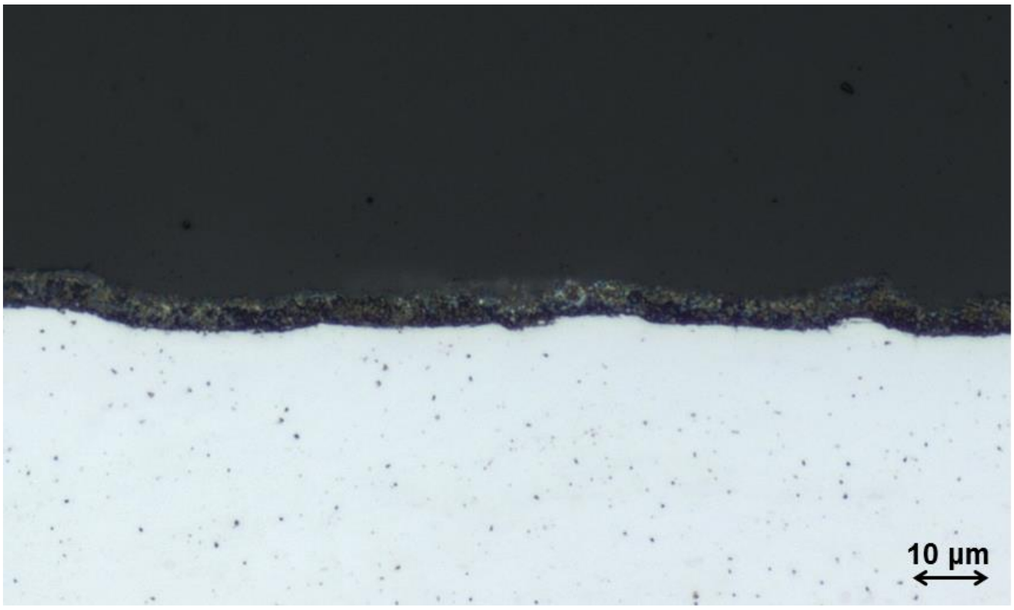

Figure 3 Zn coating – cross-section on Olympus IX70 optical microscope

Optical microscopy was chosen as the method of comparison. The samples were subjected to metallographic preparation before analysis and then observed on an optical microscope. Two samples of each type of coated sheet were prepared, and the thickness and uniformity of the coatings were assessed.

The following figures show cross-sectional images of the samples obtained using an Olympus IX70 optical microscope (**Figures 3** and **4**). The Zn-Mg-Al coated image (**Figure 4**) shows the eutectic microstructure of the coating. The classical Zn coating is characterized by a homogeneous microstructure (**Figure 3**).

Coating thicknesses were measured at 10 locations in each image (as shown in **Figure 4**). The galvanic Zn coating reached an average thickness of 5.8 μm on the first sample and 5.3 μm on the second sample. The average thickness of the Zn-Mg-Al coating was 10.2 μm (sample 1) and 11.1 μm (sample 2). All measured values are shown in **Table 3**. The measured values (20 for each type of coating) were statistically evaluated by QC Expert software and were found to have a Gaussian distribution with no outliers. Box plots confirming these conclusions are shown in (**Figure 5**).

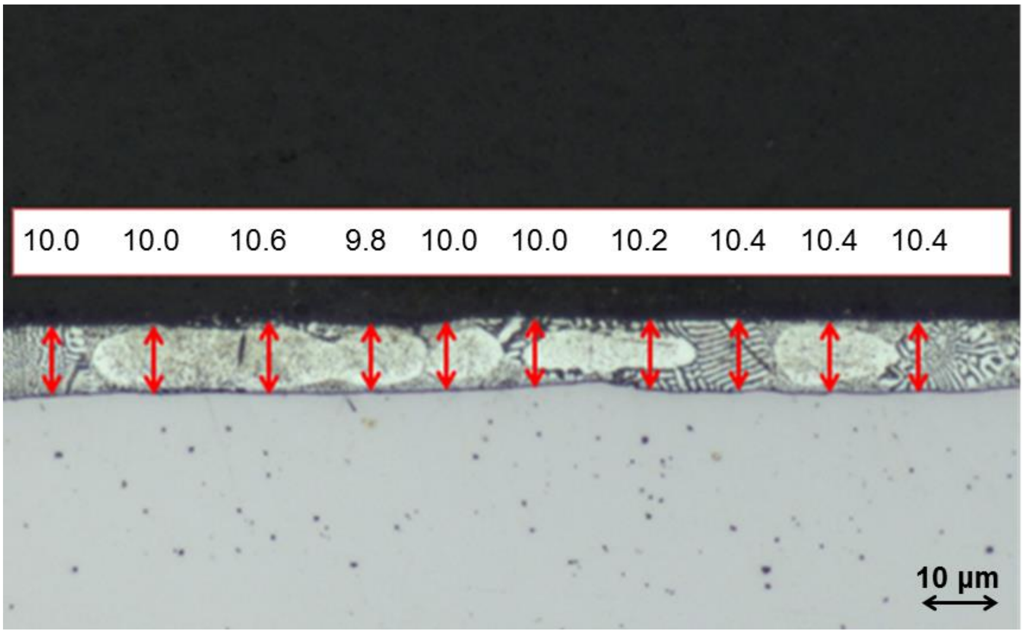

Figure 4 Zn-Mg-Al coating – in cross-section on Olympus IX70 optical microscope – with layer thickness measurement

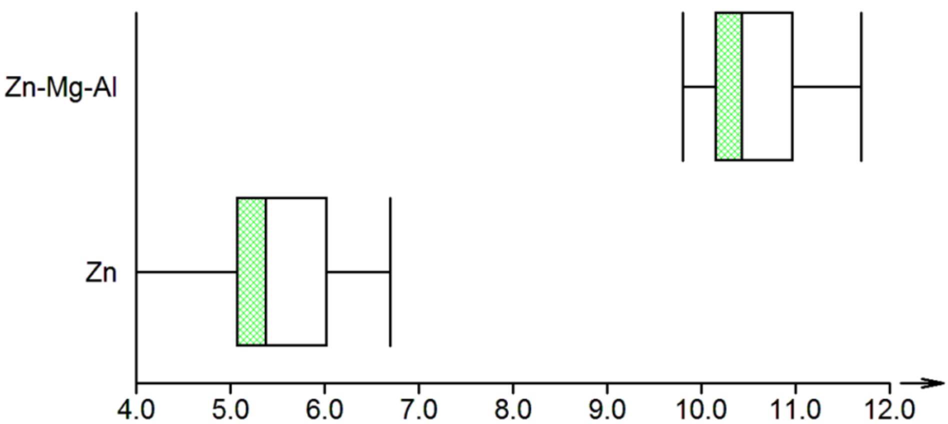

Figure 5 Box plots – evaluation of layer thicknesses of Zn and Zn-Mg-Al coatings – QC Expert software

Table 3 Surface layer thicknesses determined by optical microscopy (μm)

Sample	Zn coating		Zn-Mg-Al coating	
	model 1	model 2	model 1	model 2
	μm			
Measurement 1	5.8	5.0	10.0	11.7
Measurement 2	5.7	6.5	10.0	10.9
Measurement 3	5.8	4.6	10.6	11.3
Measurement 4	5.6	5.1	9.8	10.9
Measurement 5	6.2	5.0	10.0	10.9
Measurement 6	5.6	5.5	10.0	11.1
Measurement 7	5.7	4.0	10.2	10.9
Measurement 8	5.8	4.2	10.4	11.1
Measurement 9	6.1	6.0	10.4	10.8
Measurement 10	6.0	6.7	10.4	11.0
diameter	**5.8**	**5.3**	**10.2**	**11.1**

The following table (**Table 4**) summarises the results obtained – i.e. compares the thicknesses of the individual layers determined by the two methods.

Table 4 Comparison of results (surface layer thicknesses) determined by GDOES and optical microscopy (μm)

Sample	Average layer thickness	
	Optical microscopy	GDOES
	μm	
Zn coating	5.5	6.0
Zn-Mg-Al coating	10.6	10.1

5. CONCLUSION

This work aimed to characterize the Zn-Mg-Al coating using optical microscopy and GDOES analysis and compare it with the classical galvanic zinc coating. It was found that the thickness of the Zn-Mg-Al surface layer is larger (almost twice) and more even than that of the pure galvanic zinc layer. Furthermore, the suitability of using GDOES analysis to analyse alloy coatings was confirmed.

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