

STRUCTURE ANALYSIS OF Zn-Al-Mg COATING ON STEEL WIRE

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ABSTRACT

The corrosion resistance of zinc coatings is determined primarily by the thickness of the coating but varies with the severity of environmental conditions. In case of zinc-based alloys for steel coating the phase type and its quantity developed upon solidification determines corrosion resistance as well. In this paper the phase quality and evolution along thickness of the Zn-Al-Mg coating layer was studied by x-ray diffraction analysis. During investigation the coating was removed in controlled manner in several steps. Each individual step of removal was followed with x-ray diffraction measurement and subsequent analysis of x-ray diffraction patterns.

KEY WORDS

zinc coatings, hot-dipping, corrosion resistance, zinc-based alloys, x-ray diffraction

INTRODUCTION

The usage of zinc coatings for the corrosion protection of ferrous substrates is very widespread [1, 2]. To improve corrosion resistance of wires, the coating can have the addition of 5% Al which could be further increased to 10% for improved corrosion protection [3]. Galvanizing forms a metallurgical bond between the zinc and the underlying steel creating a barrier that is part of the metal itself. During galvanizing, the molten zinc reacts with the iron in the steel to form a series of zinc/iron alloy layers [4]. Zinc is anodic to iron and steel and as a result in the case of galvanic corrosion zinc becomes the anode, while the ferrous substrate becomes the cathode and does not corrode. Hot-dipping involves immersion of the steel in a bath of molten zinc or Zn-based alloys. Hot-dip galvanized coatings comprise essentially pure zinc provided controlled amounts of aluminium or silicon are added to the molten zinc bath to suppress the formation of zinc-iron intermetallic phases [5]. Addition of Al causes formation of the inhibition layer which is still not well understood. One reason for the lack of detailed information on the formation of the inhibition layer is that the Fe-Al layer on commercial product is often too thin to be observed in cross-section using light optical microscopy or conventional SEM and XRD analysis [6]. Diffraction experiments presented in this contribution examine whole thickness of the coating including inhibition layer which allowed assigning the layer with corresponding phases.

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EXPERIMENTAL DETAILS

An experimental material used for this study was a steel wire substrate with 6.5 mm diameter coated with Zn-5Al-0.5Mg. Dipping process started with pickling performed in HCl followed by water rinsing in water and drying. Hot dipping process was executed in two stages – double dip coating. The first stage comprised immersion of the steel substrate in zinc bath held at 450°C. In the second stage the substrate was dipped in a Zn-5Al-0.5Mg alloy bath held at 450°C. After immersion, the wire was drawn up from the bath vertically to allow for solidification in cooling water. Coatings exhibit total thickness ranging from 60 to 90 µm. Reaction layer thickness varied from 5 to 25 µm.

General microstructure overview was obtained using Zeiss Axioscope light microscope. Electron microscopy was carried out using a Jeol JSM7600EF scanning electron microscope with back scattered electron detector. All observations as well as chemical microanalysis were performed at 15 kV accelerating voltage and 89 µmA probe current. Local chemical composition was detected using an Oxford Instruments EDX analyser coupled with the scanning electron microscope.

Observation of depth resolved phase evolution in the coating was executed using x-ray diffraction analysis (XRD). Each series of XRD measurements started with the stripping of the wire in 1.5% HCl in ethanol or 10ml HNO₃ in 30ml of water [6]. Sample cleaning in water and weighting was executed after each stripping step. A Metler Toledo balance with precision of 0.1 mg was used to determine exact weight of the sample. In total 9 stripping steps summarized in Tab. 1 were applied to the wire.

XRD measurement was performed using a Panalytical Empyrean x-ray diffractometer in Theta-2Theta geometry. Characteristic CoK $\alpha_{1,2}$ radiation filtered by Fe was used during scattering experiment. Co mirror was used to generate primary parallel beam on incident arm. Detector arm was equipped with 0.27° parallel plate collimator and scintillation detector. X-ray diffraction data were analysed with the Panalytical search-match program Xpert High Score Plus.

STRIPPING STEPS AND CORRESPONDING LAYER THICKNESSES

Table 1

Strip step	Layer thickness (µm)	Strip step	Layer thickness (µm)	Strip step	Layer thickness (µm)
1.step	5.774	4.step	4.2	7.step	1.244
2.step	4.64	5.step	7.323	8.step	2.249
3.step	5.393	6.step	6.894	9.step	80

RESULTS

Light microscopy images presented in Fig.1 show cross-section of three different coating layer microstructures on one investigated sample. Columnar microstructure is displayed in Fig. 1a. It is typical for regions with high cooling rate due to direct contact with the cooling water. The columnar grains grew in one direction because of rapid heat removal. Regions of wire without effective cooling with direct water sprout were showing a dendritic microstructure (Fig.1b). Small areas with mixed microstructure were frequently observed between the two mentioned regions (Fig. 1c).

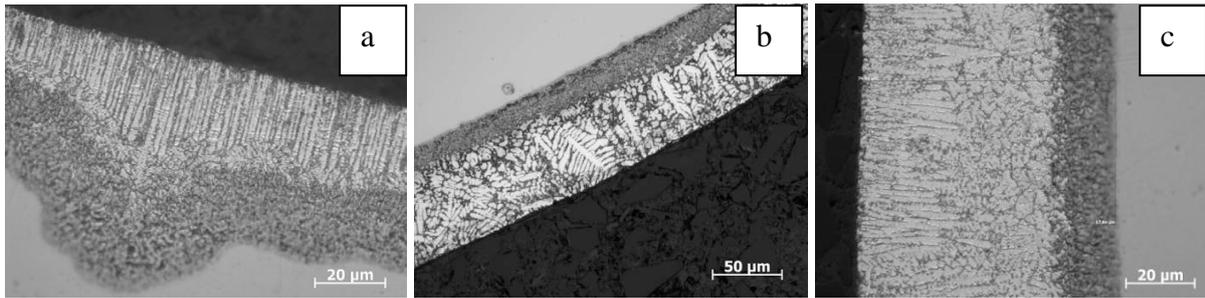


Fig. 1 Typical microstructures of the ZnAlMg coating: a) Columnar microstructure, b) dendritic microstructure, c) mixed microstructure

Further microstructural analysis continued with scanning electron microscopy examination. Two regions of interest were chosen. First, labelled by polar angle 0° with characteristic solidification microstructure is shown in Fig. 2a. Second region of interest was found at 90° and microstructure is documented in Fig. 2b.

Both regions were characterized using EDX line scan of chemical elements across the total coating thickness. Analysis focused on major chemical constituents of the coating: Zn, Al, Mg and Fe. Same features were observed in both line scans. Zn, Al and Mg are observed in alloy layer while Fe only in reaction and inhibition layer.

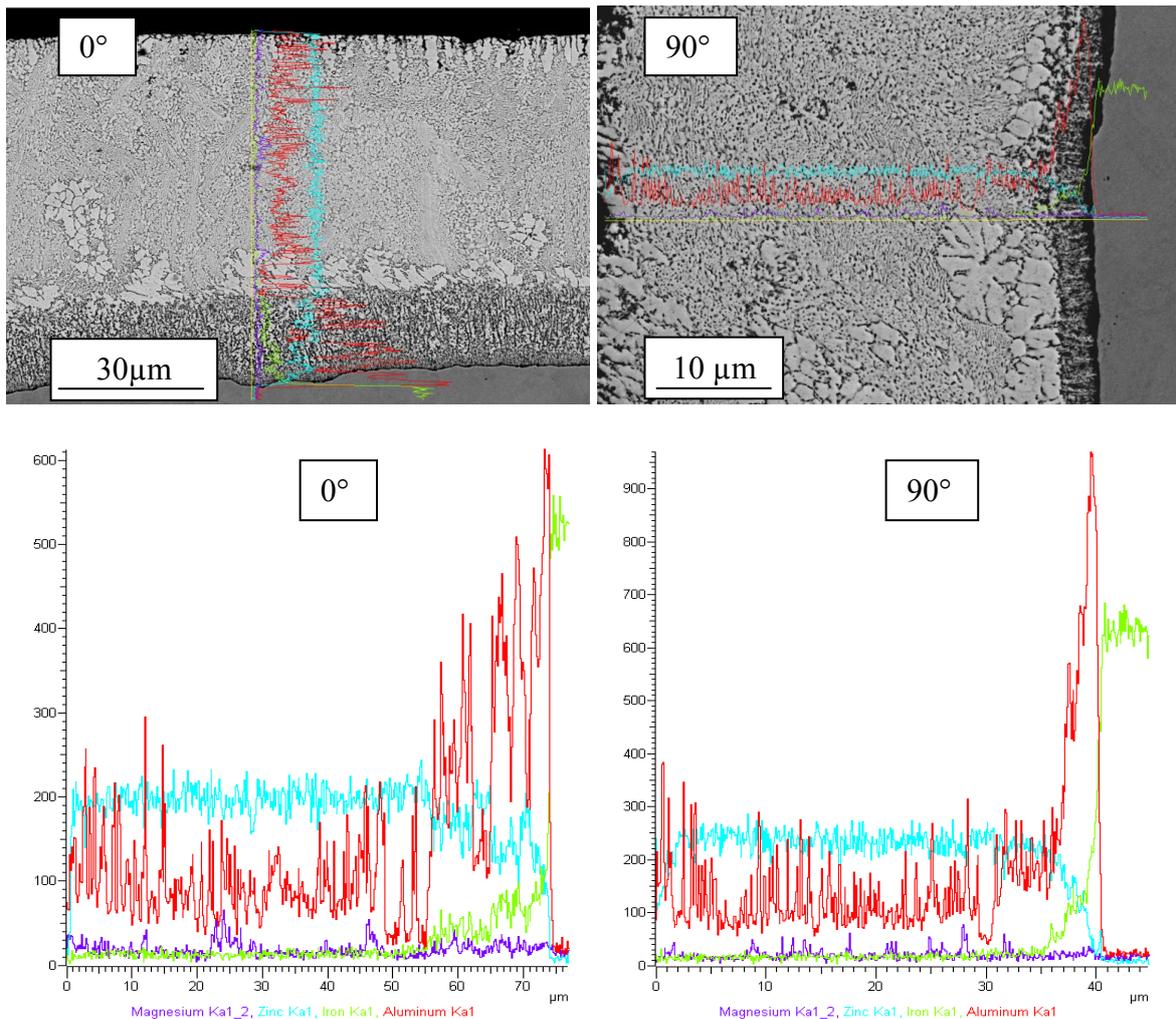


Fig. 2 Solidification microstructure of the coating taken at polar coordinates 0° and 90° with corresponding EDX line profiles of chemical elements

Series of XRD patterns taken from the experiment of a step-wise removal of ZnAlMg coating formed on a steel wire is shown in fig. 3. Thickness of each layer removed from the coating is listed in the table 1. Step-wise removal by chemical dissolution of the double-dip coating showed that phase composition of alloy layer remains stable over its entire thickness. Changes are observed close to the reaction as well as inhibition layer. Presence of Mg rich phases becomes less pronounced. Further removal of reaction layer reveals the inhibition layer adhering directly to the steel, where mainly Al₃Fe intermetallic phase was identified.

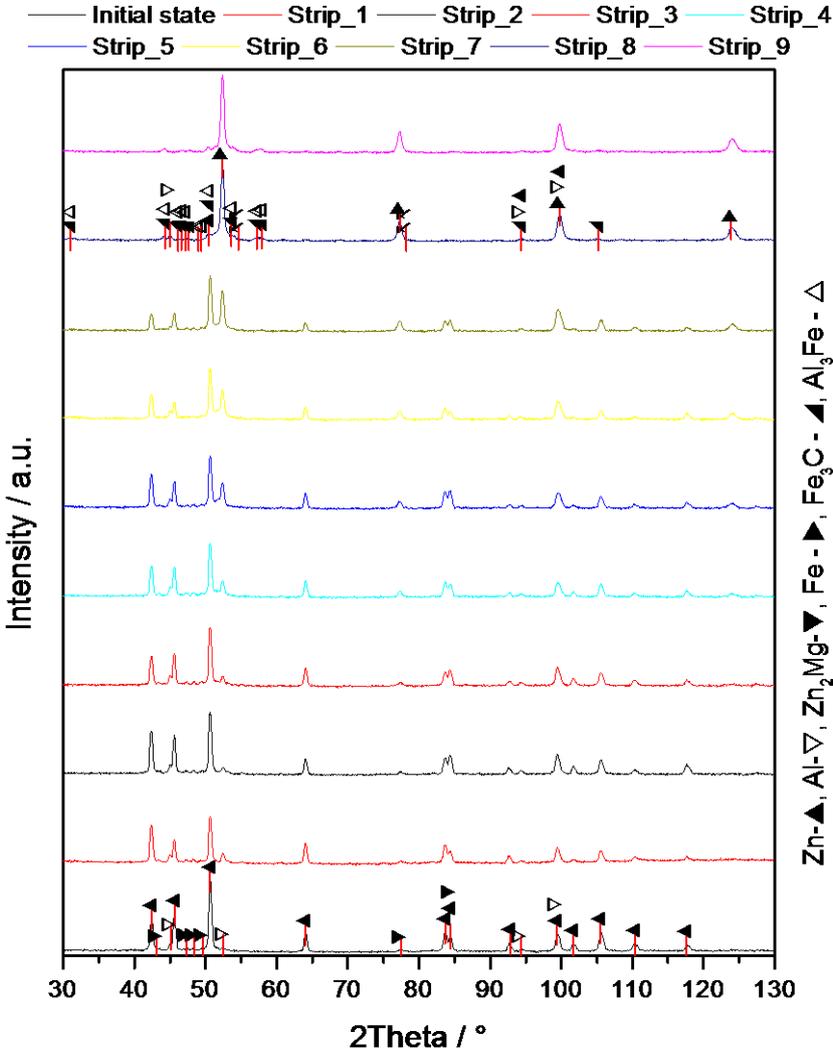


Fig. 3 Series of XRD patterns taken during step-wise chemical stripping of ZnAlMg coating layer

DISCUSSION and CONCLUSIONS

Steel wire coated with Zn-5Al-0.5Mg alloy using double dip technology was studied. Microstructural analysis revealed presence of 3 different solidification microstructures: dendritic, columnar and mixed microstructure. Coated sample was found uniformly coated. The entire coating layer could be divided into three sub-layers: alloy layer, reaction layer and inhibition layer.

All three layers were characterized using SEM in particular utilizing local characterization of chemical composition by EDX analysis. Stable concentrations of main alloy constituents were found across the alloy layer. Phase changes indicated by chemical

analysis were expected in vicinity of reaction layer. In this region x-ray diffraction analysis shows decrease in quantity of Zn₂Mg as reaction on decreasing Mg content. On the contrary, Al content increases which in return forms higher amount of Al rich solid solution. As it was shown in chemical line scans Al tends to build up a thin Al rich layer in close vicinity of the base steel. This layer is considered as an inhibition layer where Al forms intermetallic phases. According to McDevitt et.al. [6] this layer is a mixture of Al₅Fe₂ and Al₃Fe phases. Our study confirms using Al₃Fe present in inhibition layer. This is in contrast with previous studies where only Al₅Fe₂ was detected by XRD.

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REFERENCES

1. PISTOFIDIS, N., VOURLIAS, G., KONIDARIS, S., PAVLIDOU, E., STERGIOU, A., STERGIOUDIS, G. *MATER LETT*, **61**(4-5), 2007, pp. 994-997.
2. DE BRUYCKER, E., ZERMOUT, Z., DE COOMAN, B. C. 2007. *Materials Science Forum*, **539-543**, , pp. 1276-1281.
3. SUGIMARU, S., NISHIDA, S., NISHIKAWA, Y., YOSHIMURA, K., TANAKA, S., YOSHIE, A., USHIODA, A. 2004. *Wire Journal International*, Vol. 37, pp. 60-64.
4. Hot-Dip Galvanizing for Corrosion Protection of Steel products. American Galvanizers Association, 2000.
5. HOSKING, N.C., STRÖM, M.A., SHIPWAY, P.H., RUDD, C.D. 2007. *Corrosion science* 49, pp. 3669-3695.
6. MCDEVITT, E., MORIMOTO, Y., MESHII, M. 1997. *ISIJ International*, **37**(8), pp. 776-782.