THE X-RAY DIFFRACTION ANALYSIS OF PHASE EVOLUTION IN ZN-AL-MG COATING LAYER

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Abstract

Variety of zinc-based coatings has been investigated in the last 35 years to improve their properties. The zinc-based coating on hot-dip galvanized steel provides excellent sacrificial protection over the steel substrate. 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 determine corrosion resistance as well. In this study 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 a 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. Inhibition layer composed of Al3Fe was identified using scanning electron microscopy as well as x-ray diffraction.

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

1. INTRODUCTION

The usage of zinc coatings for the corrosion protection of ferrous substrates is very widespread. Complex review of the topic of zinc and zinc alloy coated steel was provided by Marder [1]. 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 [2]. 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 [3]. 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 aluminum or silicon are added to the molten zinc bath to suppress the formation of zinc–iron intermetallic phases [4]. Addition of Al causes formation of the inhibition layer which was studied by number of authors [5] [6][7]. One of the major problems is that in commercial coatings are these layers too thin to be observed by light optical microscopy or conventional SEM. Similarly, the use of X-ray diffraction to identify the constituent phases in the layer is hampered by the layers' dimensions [5].

Further addition of alloying elements such Al up to 5 wt. % and Mg up to 0.5 wt. % lead to formation of equilibrium Zn11Al2 or non-equilibrium Zn2Mg intermetallic phase observed by x-ray diffraction and calculated using thermodynamic calculation in Calphad [8][9].

Diffraction experiments presented in this study examine phase evolution across the total thickness of the coating including inhibition layer which allowed assigning the layer with corresponding phases.

2. 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 exhibited total thickness ranging from 60 to 90 µm. Reaction layer thickness varied from 5 to 25 µm.

General microstructure overview was obtained using Zeiss Axio Imager.z1m light microscope. Electron microscopy was carried out using a Jeol JSM7600F scanning electron microscope employing the 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 energy dispersive x-ray analyzer (EDX) 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 were applied to the wire. Summarized in Tab. 1 are selected stripping steps and corresponding layer thicknesses removed during chemical stripping process.

XRD measurement was performed using a Panalytical Empyrean x-ray diffractometer in Theta-2Theta and 2Theta only (grazing incidence diffraction GID) geometry with incidence angle set to 0.5, 1, 2 and 3°. Characteristic CoKα₁,₂ 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 analyzed with the Panalytical search-match program Xpert High Score Plus. Quantitative results were obtained using the Rietveld method [10] implemented in program MAUD [11]. X-ray diffraction patterns taken in Theta-2Theta as well as in GID geometry were treated simultaneously for given stripping step.

Tab. 1 Stripping steps and corresponding layer thicknesses

<table>
<thead>
<tr>
<th>Strip step</th>
<th>Layer thickness (µm)</th>
<th>Strip step</th>
<th>Layer thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.step</td>
<td>5.5</td>
<td>8.step</td>
<td>2.3</td>
</tr>
<tr>
<td>7.step</td>
<td>30,000</td>
<td>9.step</td>
<td>80</td>
</tr>
</tbody>
</table>

3. RESULTS

Light microscopy images presented in Fig.1 show cross-section of three different coating layer microstructures on one investigated sample. Dendritic microstructure is displayed in Fig. 1a. Regions of wire without effective cooling with direct water sprout were exhibiting a dendritic microstructure (Fig.1b). Columnar microstructure 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. Small areas with mixed microstructure were frequently observed between the two mentioned regions (Fig. 1c). Independently of local solidification microstructure the entire coating layer could be divided into three sub-layers (Fig. 1b): alloy layer, reaction layer and inhibition (also known as interfacial) layer, respectively.
Fig. 1 Typical microstructures of the ZnAlMg coating: a) Dendritic microstructure, b) Columnar microstructure and c) Mixed microstructure. Symbols L1, L2 and L3 refer to alloy layer, reaction layer and inhibition layer, respectively.

Further microstructural analysis continued with scanning electron microscopy examination. Fig. 2 shows quantitative distribution of elements in a coating layer analyzed by EDX mapping. Documented is the area of transition from coating to substrate. Pictures in upper row show Al, Fe and Zn distribution which are followed further with Mg in lower row. Quantitative analysis is completed with line profiles of elements representing integral values of the entire analyzed area. It shows that Zn content decreases steadily and reaches its minimum at the interface with the steel substrate. Contrary, aluminum content increases with maximum localized at the interface with the steel substrate. Contribution of the iron becomes pronounced in reaction layer. Amount of iron approximately 20 to 25 at.% corresponds to Al maximum at 60 at.%. Real microstructure image shown in last image of the series is colored proportionally to the amount of each element.

Fig. 2 Quantitative EDX maps of analyzed ZnAlMg coating on the iron substrate. Colored maps show atomic concentrations of Al, Fe, Zn and Mg in analyzed area. Graph represents atomic concentrations of elements integrated over the entire analyzed area. Microstructure is superimposed with colored map of all analyzed elements.

Series of XRD patterns taken from the experiment of a step-wise removal of Zn-5Al-0.5Mg coating formed on a steel wire is shown in fig. 3. Corresponding results of quantitative phase analysis determined using MAUD program are summarized in tab. 2. Step-wise removal by chemical dissolution of the double-dip coating
showed that phase composition of the alloy layer remains very stable over its entire thickness and therefore only x-ray pattern of the stripping step 1 and 7 (last pattern exhibiting presence of Zn in the layer) are depicted in the fig. 3. X-ray pattern of the initial state confirms presence of the Zn-based solid solution, Al based solid solution and Zn$_2$Mg intermetallic phase. These phases are present in x-ray pattern after 1$^{st}$ and also 7$^{th}$ stripping step. Later mentioned diffraction pattern contains also monoclinic Al$_3$Fe phase and its quantity (Tab. 2) further increases in x-ray diffraction pattern after 8$^{th}$ stripping step. Last pattern shows bare steel substrate with ferrite and cementite identified as the only constituing phases with an amount listed in table 2. The diffraction patterns were fitted in the MAUD program using model composed of two layers: coating layer and steel substrate. This approach allowed to determined layer thickness remaining on steel substrate after stripping procedure providing the x-ray penetration was sufficient. In case of stripping step no. 7 and 8 the remaining layers exhibited thicknesses approximately 3 and 1 µm, respectively.

![Fig. 3 Series of XRD patterns taken during step-wise chemical stripping of Zn-5Al-0.5Mg coating layer](image-url)
DISCUSSION AND CONCLUSIONS

Steel wire coated with Zn-5Al-0.5Mg alloy using double dip coating technology was studied. Microstructural analysis revealed presence of 3 different solidification microstructures: dendritic, columnar and mixed microstructure observed in one sample. This effect is attributed to uneven solidification rate caused by non-uniform exposure to cooling water. The steel substrate was found uniformly coated. The entire coating layer was divided into three sub-layers: alloy layer, reaction layer and inhibition (interfacial) layer.

All three layers were characterized using SEM utilizing local characterization of chemical composition by EDX analysis. Stable concentrations of alloying elements found across the alloy layer followed with decrease of Zn and increase of Al content in reaction and inhibition layer were observed. These results are in good agreement with observations of other authors achieved by EDX or GDOES methods and published elsewhere [6],[12],[13]. Determined chemical composition corroborate well with sub-layer structure described above.

XRD analysis confirmed presence of Zn-based solid solution, Al-based solid solution present in as-solidified coating layer. The same phases were found to form coating layer after stripping to approximately 35 µm of coating thickness. The third phase found in collected diffraction patterns (initial state, 1<sup>st</sup> strip, 7<sup>th</sup> strip and 8<sup>th</sup> strip) was ZnMg intermetallic compound representing non-equilibrium phase in Zn-Al-Mg ternary phase diagram as suggested by Honda and co-workers [8]. Results of quantitative phase analysis on XRD patterns from the alloy layer exhibit decrease in amount of Zn-based solid solution which is in agreement with chemical profile in Fig. 2. Quantity of Al based solid solution does not follow chemical profile of Al. In this case further considerations taking into account further Al reach phases are necessary.

Detected chemical changes were expected to cause phase variation in vicinity of interface with steel substrate. General agreement could be observed among authors, which refers orthorhombic Al<sub>3</sub>Fe intermetallic phase as main constituent of the inhibition layer. Detailed study employing XRD and TEM was carried out by McDevitt and his co-authors [5]. They have observed Al<sub>3</sub>Fe<sub>2</sub> and Al<sub>3</sub>Fe coexisting in the inhibition layer. They have also pointed out that XRD technique is incapable of Al<sub>3</sub>Fe detection leading to an incorrect conclusion that the layer could be formed exclusively by Al<sub>3</sub>Fe. Diffraction experiment performed in our study suggests that layer could be formed also by Al<sub>3</sub>Fe phase as major constituent. Presence of Al<sub>3</sub>Fe<sub>2</sub> was not proven but cannot be completely ruled out and TEM examination of inhibition layer is required. Result of chemical microanalysis observed in this study is also in favor of Al<sub>3</sub>Fe formation because atomic concentrations of Al and Fe were observed (Fig. 2) with atomic ratio 3/1 (60at.% / 20 at. %).

TEM observation published by McDevitt suggests that Al<sub>3</sub>Fe is formed first at the interface with steel substrate. New grains of Al<sub>3</sub>Fe<sub>2</sub> were observed to grow on the expense of Al<sub>3</sub>Fe localized between Al<sub>3</sub>Fe and steel substrate. Since Al<sub>3</sub>Fe<sub>2</sub> phase was not detected in our study it is proposed that nucleation of this phase
was not initiated yet or only a minor amount of this phase formed which was below detection limit of XRD technique used in this study.

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REFERENCES