



Article Corrosion Behavior of Zn-Al-Mg-Si Coatings in Sulfur Dioxide-Containing Environment

Henryk Kania * D and Anżelina Marek

Department of Metallurgy and Recycling, Faculty of Materials Engineering, Silesian University of Technology, Krasińskiego 8, 40-019 Katowice, Poland; anzelina.marek@polsl.pl

* Correspondence: henryk.kania@polsl.pl

Abstract: Zn-Al-Mg-Si coatings are an excellent alternative to conventional hot-dip galvanizing coatings. Their high corrosion resistance in corrosive environments containing chlorides and CO₂ is well recognized. But sulfur dioxide is also an important stimulator of corrosion in the atmospheric environment. This article presents the results of microstructure (SEM/EDS/XRD) and corrosion behavior tests of Zn-Al-Mg-Si coatings obtained by a double hot-dip method on HSLA steel. The corrosion resistance of the coatings was determined in the sulfur dioxide test with general condensation of moisture (EN ISO 6988). In the corrosion test, Zn-Al-Mg-Si coatings showed twofold smaller weight loss compared to conventional hot-dip zinc coatings. It was found that the corrosion behavior of coatings was influenced by the structural components revealed in the outer layer: Al-rich dendritic and interdendritic areas with Zn/MgZn₂ eutectic, MgZn₂ intermetallic and Si precipitates and their electrochemical nature. The increase in corrosion resistance was caused by the formation of beneficial corrosion products: layered double hydroxides (LDHs) based on divalent Mg²⁺ and Zn²⁺ cations, trivalent Al³⁺ cations and SO₄²⁻ anions, and zinc hydroxysulfate—Zn₄SO₄(OH)₆·5H₂O. The presence of Si precipitates could cause pitting corrosion of coatings.

Keywords: hot-dip galvanizing; double hot-dip method; Zn-Al-Mg-Si coatings; corrosion resistance; sulfur dioxide test

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1. Introduction

Zinc coatings are the most commonly used protection for steel against corrosion. Currently, more than half of the world's zinc production is used in the hot-dip galvanizing process [1]. Batch hot-dip galvanizing technology also generates the greatest zinc losses as a result of the generation of zinc-rich waste, such as galvanizing ash and hard zinc. However, unjustified zinc consumption also results in the formation of too thick coatings and insufficient zinc flow from the surface of the product after removal from the galvanizing bath. Research has been conducted for many years to reduce zinc loss. The result is the development of many galvanizing bath compositions containing small additions of Al, Ni, Pb, Bi and Sn [2,3]. This line of research is still being continued. Galvanizing baths are developed taking into account the specificity of materials and products, based on alloy additives that have not been used on an industrial scale before, such as Ti [4]. Alloy additives to the bath improve the technological efficiency of the hot-dip process and the quality of coatings, which reduces material costs. However, limited zinc resources and its constantly increasing price [1] create the need to look for more effective solutions to reduce zinc consumption.

An alternative to conventional galvanizing baths are baths containing large additions of Al and Mg. Zn-Al-Mg coatings on steel developed over the last thirty years, such as ZAM (ZnAl6Mg3) [5], Super Dyma (ZnAl11Mg3Si0.2) [6], MagiZincTM (ZnAl1.5Mg1.5) [7], Magnelis (ZnAl3.5Mg3) [8], showed much better corrosion resistance than hot-dip galvanized coatings. However, their production is limited to sheet coatings using the continuous

method developed by Sendzimir. However, in the batch hot dip process, the use of a Zn-Al-Mg bath has major limitations, which primarily include the need to use a flux and the formation of a periodic layered structure, which leads to excessive coating thickness [9]. Previous research has shown that the use of the double hot-dip method allows for the repeatable production of ZnAl₅ coatings using conventional fluxes [10], and the addition of Si to the bath stabilizes the structure of the coating and eliminates the periodic layer structure [11]. Increasing the Al content in the bath causes a proportional increase in corrosion-resistant coatings. On the other hand, a higher Al content increases the solidification temperature of the bath. Nowacki et al. [12] showed that the ZnAl₁₂Mg₃ alloy solidifies at a temperature of 414.1 °C. It can, therefore, be concluded that in order to maintain the temperature for the traditional hot-dip galvanizing process, the most technologically advantageous content of the bath is 12 wt.% Al and 3 wt.% Mg.

Zn-Al-Mg coatings are very popular because they are able to provide steel with much better corrosion resistance than traditional zinc coatings. So far, many studies have been carried out to understand the corrosion mechanisms of Zn-Al-Mg coatings. The research provided important information about corrosion products. Corrosion products have been thoroughly characterized in neutral salt spray tests (NSST) [13–15], as well as in natural atmospheric environments [5,16–21]. Current data suggest that Zn-Al-Mg coatings and the corrosion products formed thereon provide significant improvements in corrosion resistance in chloride-containing environments. Person et al. [20] report that in the initial stages of atmospheric corrosion, ZnAlMg coatings are covered with layered double hydroxides (LDHs) based on Mg-Al and Zn-Al cations and CO_3^{2-} anions, while on zinc coatings, the corrosion products contain $Zn_5(OH)$ 8Cl₂·H₂O, zinc hydroxycarbonate and ZnO. Chlorides and CO2 are the most important corrosion stimulants in atmospheric environment; therefore, there is not much information available on the corrosion behavior of Zn-Al-Mg coatings in CO₂ and chloride-free environments. However, an important substance polluting the atmosphere, which also has a strong anti-corrosion effect, is sulfur dioxide. Person et al. [22] studied the initial atmospheric corrosion of ZnAl₂Mg₂ coatings in humid air containing 80 ppb SO₂. "In situ" studies show that Mg-containing sulfite forms as an initial corrosion product in environments containing SO₂, as well as SO₂ and NaCl. Cathodic reduction of oxygen promotes the oxidation of sulfite to sulfate, which, in turn, increases the initial corrosion rate of Zn-Al-Mg coatings. However, such a picture of the impact of SO_2 is incomplete and depends on other environmental conditions in which the research was conducted.

The aim of the research in this work is to analyze the corrosion behavior of Zn-Al-Mg-Si coatings in a sulfur dioxide-containing environment. The article presents the results of research on the microstructure of Zn-Al-Mg-Si coatings obtained in a bath with the ZnAl12Mg3Si0.3 composition and their corrosion behavior in a sulfur dioxide environment with general moisture condensation. This will allow for the prediction of the impact of SO₂ content in a corrosive environment on the durability of coatings.

2. Materials and Methods

2.1. Materials and Hot Dip Procedure

Zn-Al-Mg-Si coatings were made on $50 \times 100 \times 2$ samples made of high-strength cold-forming HSLA steel (SSAB, Hämeenlinna, Finland). The chemical composition of the steel according to the manufacturer's certificate is presented in Table 1. The Si content in this steel (0.20% wt.%) classifies it as Sebisty steel [3].

Zn-Al-Mg-Si coatings were produced using the double batch hot-dip method. Before the hot-dip process, the steel surface was cleaned by degreasing, pickling and fluxing. Steel samples were initially immersed in a Zn bath and then in a Zn-Al-Mg-Si bath. The temperature of each bath was 450 °C. The samples were immersed in each bath for 60 s. Then, the samples were cooled in air. The procedure for producing the coatings was selected based on detailed research conducted in [15]. A conventional galvanizing bath with Al and Bi technological additives was used as the zinc bath. The content of alloying additives in the Zn-Al-Mg-Si bath was kept at 12 wt.% Al, 3 wt.% Mg and 0.3 wt.% Si, while the Zn bath contained standard Al additives at the level of 0.006 wt.% and Bi at the level of 0.06 wt.%. (Table 1).

Table 1. Chemical composition of HCLA steel and research baths.

		Content [wt.%]					
		С	Si	Mn	S	Р	Fe and Others
Steel	HSLA	0.06	0.20	0.80	0.003	0.009	rest
		Al	Fe	Si	Mg	Bi	Zn and others
Bath	Zn-Al-Mg-Si Zn	11.86 0.0059	0.024 0.031	0.32 0.001	3.15 0.002	0.0001 0.061	rest rest

2.2. Characterization Methods

Investigations of the microstructure of coatings and corrosion products were performed using Hitachi S-3400 N scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscope (EDS) (Hitachi, Tokyo, Japan). Noran Instruments—System Six software (Thermo Fisher Scientific, Waltham, MA, USA) was used for the tests. X-ray phase analysis was performed on a Philips X'Pert 3 X-ray diffractometer (Malvern Panalytical, Malvern, UK) using a copper anode lamp (λ CuK α = 1.54178 Å) powered by a current of 30 mA and a voltage of 40 kV and a graphite monochromator.

Sulfur dioxide testing with general moisture condensation was carried out in accordance with the EN ISO 6988 standard [23]. The tests were carried out in a Koesternich Hygrotherm model 519 chamber with a working capacity of 300 dm³. The daily cycle consisted of 8 h of exposure of samples in a closed chamber in a humid environment containing sulfur compounds at a temperature of 40 ± 1 °C and 16 h of exposure to ambient atmosphere. The smoothness and changes on the surface of the samples were monitored every 24 h. Gravimetric tests were performed every 5 daily cycles. The final result was the average of 5 samples of the same type and three measurements for each sample. The total testing time was 30 daily cycles. The corrosion rate was determined on the basis of the unit mass change of the samples after subsequent periods of exposure in the Koesternich chamber.

3. Results and Discussion

3.1. Top Surface Microstructure of Coatings

Figure 1 shows SEM images of the top surface of the coatings, while the chemical composition characteristics of the micro-areas of the coating are presented in Table 2. Structural components with a characteristic dendritic structure can be observed on the coating surface (Figure 1a). The morphology of the interdendritic areas includes components with a lamellar eutectic structure and areas with a compact and coherent structure, which may be characteristic of intermetals (Figure 1b). EDS analysis indicates that the dendrite region is rich in Al (Figure 1c, point 1), while the intermetallics regions contain mainly Zn and Mg (Figure 1c, point 2). The Zn concentration in the dendrites indicates that it is most likely a solution of Zn in Al (β). The atomic fraction of Zn to Mg in the intermetallic region is close to 2, which may correspond to the $MgZn_2$ phase. Bright lamellars in the eutectic (Figure 1d, point 3) contain a Zn-rich phase, which, due to the Al content, is a solid solution of Al in $Zn(\alpha)$. Dark lamellars contain mainly Zn, but also significant amounts of Mg (Figure 1d, point 4). The most probable phase is $MgZn_2$ intermetallic, although the chemical composition cannot clearly confirm this due to the very fine structure of the eutectic. The local occurrence of characteristic, approximately equiaxed precipitates was also observed on the coating surface, the chemical composition of which indicates that they are Si precipitates (Figure 1d, point 5).



Figure 1. SEM images of top surface of Zn-Al-Mg-Si coatings: (**a**,**b**) structural components on the coating top surface; (**c**) EDS analysis points in dendrites and intermetallics; (**d**) EDS analysis points in eutectics and Si precipitation.

Table 2. Results EDS analysis of the top surface of Zn-Al-Mg-Si coatings and the corresponding phase (analysis points as shown in Figure 1).

Point No.	Mg (at.%)	Al (at.%)	Si (at.%)	Zn (at.%)	Phase
1	-	80.9	-	19.1	Al-rich phase
2	32.8	-	-	67.2	MgZn ₂ intermetallic
3	0.6	9.1	-	92.8	Zn-rich phase
4	9.4	7.2	-	83.4	MgZn ₂ intermetallic
5	-	1.1	98.1	-	Si

Figure 2 shows the XRD spectra of top surface of the Zn-Al-Mg-Si coating. This study shows that aluminum, zinc and MgZn₂ intermetallic are present on the coating surface. The Al peaks confirm the existence of the Al(β) solution as Al-rich dendrites. The MgZn₂ peaks confirm that the Mg- and Zn-rich phases that appeared in the interdendritic region and the dark lamellars are composed of MgZn₂ intermetallics. The peaks for Zn confirm the presence of the Zn(α) solution as bright lamellars. The light and dark lamellars, therefore, form the Zn/MgZn₂ eutectic. Only two weak peaks for Si were identified in the XRD pattern. However, the corresponding EDS analysis can sufficiently confirm the occurrence of Si precipitates on the coating surface.



Figure 2. XRD spectra of top surface of the Zn-Al-Mg-Si coating.

3.2. Cross-Section Microstructure of Coatings

Figure 3 and Table 3 show the cross-sectional microstructure of Zn-Al-Mg-Si coating and corresponding EDS analysis. The general image of the coating shows a two-layer structure: outer layer and diffusion layer (Figure 3a). The main structural components of the outer layer are Al-rich dendrites (point 1), MgZn₂ intermetallic and lamellar eutectic structure in interdendritic areas. The microstructure of lamellar eutectic is shown in Figure 1c. It consists of light lamellars of Zn-rich phase (point 4) and dark lamellars of MgZn₂ intermetallic. Si precipitates (point 3) are also located in the outer layer. The structure of the outer layer can, therefore, be described as dendrites of the Al(β) solid solution with interdendritic spaces filled by MgZn₂ intermetallic and the Zn/MgZn₂ eutectic, in which Si precipitates occur locally.

Table 3. Results of EDS analysis of a cross-section of Zn-Al-Mg-Si coatings and the corresponding phase (analysis points as shown in Figure 2).

Point No.	Mg (at. %)	Al (at. %)	Si (at. %)	Fe (at. %)	Zn (at. %)	Phase
1	-	89.3	-	-	10.7	Al-rich phase
2	34.9	-	-	-	65.1	MgZn ₂ intermetallic
3	-	6.3	91.6	-	2.1	Si particles
4	0.6	11.1	-	-	88.3	Zn-rich phase
5	6.7	3.2	-	-	90.1	MgZn ₂ intermetallic
6	-	60.9	5.8	24.9	8.4	Fe(Al,Si,Zn) ₃
7	-	59.1	6.1	25.4	9.4	Fe(Al,Si,Zn) ₃

The diffusion layer of the coating consists of two zones (Figure 3d). The compact layer of low thickness that forms near the substrate (point 7) turns into a zone of crystals with a regular structure (point 6). The structural components of these zones, although they show different morphologies, have similar chemical compositions, and EDS analysis allows the identification of Al, Fe, Zn and Si in their micro-area (Table 3, points 6 and 7). These results correspond very well with the content of components in the diffusion layer of ZnAl12Mg3Si0.3 coatings in FeAl₃ intermetallics [15]. Si and Zn have high solubility in Fe-Al intermetallics in the solid state [24]. As the authors show in their work [15], the total content in at.% (Al+Si+Zn) is close to 75 at.%, which, with a Fe content close to 25 at.%, gives the atomic ratio (Al+Si+Zn)/Fe corresponding to FeAl₃ intermetallics. The atomic ratio (Al+Si+Zn)/Fe at points 6 and 7 is 3.01 and 2.93, respectively. This may suggest that



Figure 3. SEM images of a cross-section of Zn-Al-Mg-Si coatings: (**a**) general view of the coating; (**b**) outer layer; (**c**) Zn/MgZn₂ eutectics; (**d**) diffusion layer.

3.3. Corrosion Resistance Determined via Sulfur Dioxide Test with General Condensation of Moisture

The corrosion resistance of Zn-Al-Mg-Si coatings was determined comparatively on the basis of mass changes during the sulfur dioxide test with general condensation of moisture. The comparison coating was conventional zinc hot-dip coating. The relationship between mass changes and the test duration is shown in Figure 4a. The graph shows that the Zn-Al-Mg-Si coating is characterized by an initial mass increase. Then, its weight decreases. Comparative Zn coating shows a weight loss from the beginning of the corrosion test. The mass loss of Zn coating is relatively rapid and much more intense than that of Zn-Al-Mg-Si coating. After 30 cycles of exposure in the Koesternich chamber, the average specific mass loss of Zn-Al-Mg-Si coating was 12.63 ± 2.32 g/m², while for Zn coating, it was 26.27 ± 3.29 g/m². The dissolution intensity of Zn-Al-Mg-Si coating was approximately two times lower than the comparative Zn coating.

The appearance of the coating surfaces after 30 cycles of testing in the Koesternich chamber is shown in Figure 4b. After completing the corrosion test, it can be stated that the tested coatings remain continuous and have not penetrated the substrate. The thicknesses of the coatings measured before starting the corrosion test were $43.27 \pm 3.2 \,\mu$ m, respectively, for Zn-Al-Mg-Si coating and $69.23 \pm 4.6 \,\mu$ m for Zn coating. The thickness of the coatings determines whether the protection remains effective in this corrosion test. Distinct grains are visible on the surface of Zn coating, while the appearance of Zn-Al-Mg-Si coating after the corrosion test is much grayer and matte (Figure 4b). The microstructure of Zn coating

(Figure 4c) and the comparison of the morphology of its structural components indicate the typical structure of the phases of the Fe-Zn system: outer layer of η phase (solid solution of Fe in Zn) and diffusion layer of $\delta 1$, ζ intermetallics [3]. The presence of grains on the Zn coating surface after the corrosion test confirms that the corrosion wear occurred in the outer layer of coating. Taking into account that the weight loss of Zn-Al-Mg-Si coating was smaller, it can be concluded that corrosion wear also occurred in the outer layer of this coating.



Figure 4. Results of the sulfur dioxide test with general condensation of moisture: (**a**) development of unit mass change of coatings; (**b**) surface appearance of coatings after the 30 cycles exposure; (**c**) structure of the comparative Zn coating (δ_1 —FeZn₁₀, ζ —FeZn₁₃, η —solid solution of iron in the zinc).

3.4. Corrosion Bechaviour Characterization

Figure 5 shows the SEM images of the corroded Zn-Al Mg-Si coating surface, which was exposed to the sulfur dioxide test with general condensation of moisture for 30 day cycles. The appearance of the coating surface reveals defects in the form of holes (Figure 5a) and cracks (Figure 5b). Two structural components of the coating are also clearly visible: Al-rich dendrites and Zn/ZnMg₂ eutectic.



Figure 5. SEM images of corroded Zn-Al-Mg-Si coating surface after 30 cycles of exposure in the sulfur dioxide test with general condensation of moisture: (**a**) holes on the coating surface; (**b**) structural components of the coating—Al dendrites and Zn/MgZn₂ eutectic and corrosion cracks.

The EDS spectrum from the surface of Al-rich dendrites (Figure 6) shows the presence of Al, but also small amounts of S and O (point A). In the $Zn/MgZn_2$ eutectic area, there is



a high S content. Zn is also concentrated in this area, as well as small amounts of Al, Mg and O (point B).

Figure 6. SEM images and corresponding EDS patterns of the corroded Zn-Al-Mg-Si coating after the sulfur dioxide test with general condensation of moisture.

SEM images also indicate the presence of characteristic corrosion products located in interdendritic areas (Figure 6, red square). The micro-structure of these corrosion products shows a very heterogeneous structure (Figure 7). The EDS spectrum in the micro-area of these corrosion products shows high content of Zn, Al and Mg (area C). At the same time, a significant S content is concentrated in it, and the presence of O can also be noticed.



Figure 7. SEM images and corresponding EDS patterns of the LDH area of Zn-Al-Mg-Si coating after the sulfur dioxide test with general condensation of moisture.

The XRD pattern from the coating surface after the corrosion test is shown in Figure 8. A clearly identified corrosion product, zinc hydroxysulfate, is present on the coating surface— $Zn_4SO_4(OH)_6 \cdot 5H_2O$. The results of the EDS analysis allow for the conclusion that these are eutectic $Zn/ZnMg_2$ areas. These areas contain mainly Zn, S and O (Figure 6, point B), which are components of zinc hydroxysulfate. Additionally, the location of this corrosion product may be confirmed by the small content of Mg, which is a component of $Zn/ZnMg_2$ eutectic.



Figure 8. XRD spectra of corrosion products on the Zn-Al-Mg-Si coating surface after the sulfur dioxide test with general condensation of moisture.

The XRD pattern clearly confirms the presence of layered double hydroxides (LDHs) in the corrosion products. LDH is a hydroxyl compound with a crystalline layered structure of hydrotalcite. LDHs are hydroxides of two metallic elements with the general formula $[M^{2+}_{1-x}M^{3+}_{x}\cdot(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$. M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and the anion A^{n-} is an interlayer anion [26]. The tested Zn-Al-Mg-Si coatings can be a source of divalent cations $(Zn^{2+} and Mg^{2+})$, as well as a trivalent cation (Al^{3+}) . When exposed to corrosive environments, its aggressiveness is determined by the presence of high concentrations of carbonates, chlorides or sulfur dioxide. Therefore, under the influence of corrosive atmospheres, the most probable anions are CO_3^{2-} , Cl^- and SO_4^{2-} [17]. The morphology of corrosion products in the interdendritic area (Figure 7) indicates the location of LDH there. EDS analysis in micro-area C, including high concentrations of Zn, Mg and Al, indicate the presence of divalent cations Zn²⁺ and Mg²⁺, as well as trivalent cation Al³⁺. However, the high S concentration and O content indicate that the SO₄²⁻ anion has been incorporated into the LDH structure. As previous long-term field exposure studies of ZnAlMg coatings show [17,18], it is possible that SO_4^{2-} anions may exist in the structure of corrosion products, but they have not been clearly confirmed. However, it is known that LDH compounds easily exchange both cations and anions [26], which, due to the complex composition of the atmosphere in these studies [17,18], may change the identity of interlayer ions. The presence of two different divalent cations Zn²⁺ and Mg^{2+} may indicate the coexistence in the corrosion products of the tested coatings of two compounds, Zn-Al SO₄ LDH and Mg-Al SO₄ LDH, in which SO₄²⁻ anions are incorporated into the layered structure. The coexistence of two LHD compounds based on Zn-Al and Mg-Al cations in the corrosion products of ZnAlMg coatings was demonstrated by the authors [19-21], although, due to the more complex composition of the environment and the research time, these compounds were based on CO_3^{2-} anions, which are the most stable, but can simultaneously cause the exchange and release of other anions [26].

In LDH structures, both divalent and trivalent cations (M^{2+} and M^{3+}) can be replaced by other metal ions of the same valency and similar ionic radius [27]. Therefore, it cannot be ruled out that in the corrosion products formed on the surface of the tested coatings, Zn²⁺ and Mg²⁺ cations occupy their positions interchangeably, forming Mg/Zn-Al SO₄ LHD ternaries. However, the precise identification of LDHs is very complicated due to the diversity of their stoichiometry. Additionally, the identification of LDHs in corrosion products by XRD may be difficult due to the variability of crystallographic parameters related to differences in the ratios between various cations and anions caused by the ability of LDH structures to easily undergo ion exchange [16]. The mechanism of LDH formation in the corrosion products of ZnAlMg coatings has not yet been clearly explained. The structure and morphology of the phases of the tested Zn-Al-Mg-Si coatings are very complex. Structural components detected on the surface of coatings have different corrosion potential values. The corrosion potential of Al in the passive state in aqueous solutions is higher than in the active state [28]. It can be assumed that Al-rich dendrites are in a passive state. This is confirmed by the presence of oxygen in the EDS analysis (Figure 6, point A). In an aqueous solution in 0.6 M NaCl, the corrosion potential E_{corr} vs. SCE (Saturated Calomel Electrode) of Al has a value of -849 [mV], while E_{corr} vs. SCE for Zn and MgZn₂ is -1028 and -1095 [mV], respectively [29]. Therefore, the interdendritic areas of the coating containing Zn/MgZn₂ eutectic and MgZn₂ intermetallic precipitates will act as an anode in relation to the more noble Al-rich dendrites. Under these conditions, the dissolution of MgZn₂ intermetallic and Zn interdendritics leads to the enrichment of these areas by Mg²⁺ and Zn²⁺ cations.

SO₂ reacts with water or moisture to form sulfuric acid [30]. In acidic solutions, Al dissolves, forming Al^{3+} ions [31]. Reduction of oxygen at the cathode (Al dendrites) may lead to alkalization of the corrosive environment in the immediate vicinity of Al-rich dendrites. Under such conditions, the formation of a passive $Al(OH)_3$ layer is possible [31]. Chu and Savinell [32] proposed a mechanism of Al dissolution in which there are two fast stages—aluminum ionization and the reaction of Al(OH)₃ formation—combined with a slow stage of dissolution of the passive layer as a result of the interaction of OH⁻ ions. The instability of the $Al(OH)_3$ passive layer is also confirmed by the Pourbaix diagram for aluminum, according to which the passive layer dissolves in solutions close to neutral [33]. Olge et al. [34] claim, however, that the passive layer dissolves as a result of the increase in pH at the surface during cathodic polarization. The presence of an Al(OH)₃ layer on the surface of the tested coatings can be confirmed by the XRD pattern (Figure 8). Although, the presence of only two weak peaks of this phase may indicate its small share and low durability. Al-rich dendrites can, therefore, provide Al^{3+} cations both as a result of direct ionization of Al as well as the dissolution of passive layers. However, it should be noted that sulfur compounds are an important factor in the corrosion of aluminum. In their presence, passive layers of oxide or hydroxide are formed on the Al surface [35]. EDS analysis of the surface of Al-rich dendrites (Figure 6, point A) also indicates the presence of S in this area. It can, therefore, be assumed that SO_4^{2-} ions are involved in the formation of corrosion products on the surface of Al-rich dendrites. In industrial atmospheres rich in sulfur compounds, it is most often aluminum sulfate hydrate. However, its structure is amorphous, hence the XRD pattern is not able to confirm the presence of this phase in the corrosion products on the coating surface.

It has been proven that the dissolution of Mg from MgZn₂ intermetallic is preferential to the dissolution of zinc [20,36]. Wint et al. [37] found that MgZn₂ intermetallic platelets in eutectic also preferentially dissolve into Zn platelets. Therefore, it should be expected that Mg²⁺ cations will be released earlier and their concentration at the coating/corrosion environment interface in the initial phase of the corrosion process will be higher than the concentration of Zn²⁺ cations. Therefore, the initial formation of the LDH structure will be based on Mg-Al cations. However, due to the high capacity for ion exchange in LDH structures, further exchange of Mg²⁺ cations and their replacement with Zn²⁺ cations should be expected, leading to the formation of an LDH structure based on Zn-Al cations. However, at the current stage of research, it cannot be confirmed whether this is the coexistence of two compounds Zn-Al SO₄ LDH and Mg-Al SO₄ LDH, or rather the formation of the ternary Mg/Zn-Al SO₄ LHD.

The presence of Mg in LDH structures is beneficial because it improves corrosion resistance. Corrosion studies of Zn-Al-Mg alloys indicate that LDH structures containing Mg, both binary Mg-Al LDH and ternary Mg/Zn-Al LDH, constitute a better barrier to oxygen diffusion [38]. Also, Johnson and Glasser [39] claim that the thermodynamic stability of LDH is greater than that of the corresponding divalent hydroxides, and the

solubility constant of MgAl—LDH is five orders of magnitude greater than that of ZnAl— LDH. However, the XRD pattern (Figure 8) detects peaks for Al and Zn. Detection of structural components of the coating through the layer of corrosion products may indicate a small thickness of this layer.

An important structural component of the tested Zn-Al-Mg-Si coatings for their corrosion behavior is the presence of Si precipitates in the outer layer. Figure 9 shows a cross-section of the coating after corrosion in place of the holes visible on the surface (Figure 5). EDS analysis indicates a high concentration of Si in this area (Figure 9, point D), which confirms the location of Si precipitates in this place. Intensive dissolution of the matrix is observed around Si precipitates. Si, as a structural component of the coating, has the most cathodic character (E_{corr} vs. SCE = -452 [mV] [29]).



Figure 9. SEM images and corresponding EDS patterns of the of the cross-section of the Zn-Al-Mg-Si coating after the sulfur dioxide test with general condensation of moisture.

It can, therefore, create the most effective corrosion cell with interdendritic areas containing Zn and MgZn₂. But, its corrosive effect in a cell with Al-rich dendrites can also be effective. The corrosion products around Si precipitates contain the most Zn, but EDS analysis also detected Mg and Al content (Figure 9, point E). Si corrosion itself cannot be ruled out, as high O and S contents were found (Figure 9, point D). However, corrosion of Si precipitates can be considered beneficial. Its tendencies, especially to oxidize and form SiO_2 oxide on the surface, may limit the galvanic connection with the matrix [40], which will consequently reduce the effectiveness of the Si corrosion cell. The Si content has a positive effect on the structure of the coating, but its local corrosive effect may promote pitting corrosion of the coating.

4. Conclusions

The microstructure of Zn-Al-Mg-Si coatings and their corrosion behavior in a humid environment containing sulfur compounds were investigated. The following conclusions can be drawn from the obtained research results:

- Zn-Al-Mg-Si coatings have a complex layered structure. Coatings are composed of a diffusion layer of Fe(Al,Si,Zn)₃ intermetallic and an outer layer of Al-rich dendritic and interdendritic areas with Zn/MgZn₂ eutectic, MgZn₂ intermetallic and Si precipitates. The structural components of the outer layer have a different electrochemical character, which leads to the creation of effective links between the structural components of the coating, especially on the top surface of coatings.
- In the sulfur dioxide test with general condensation of moisture, Zn-Al-Mg-Si coatings showed better corrosion resistance than conventional Zn coatings due to the formation

of favorable corrosion products. In this environment, the coating is locally covered with layered double hydroxides (LDHs) based on divalent cations Mg^{2+} and Zn^{2+} , trivalent cation Al^{3+} and SO_4^{2-} anion, while the interdendritic areas of lamellar eutectic are covered with a layer of zinc hydroxysulfate— $Zn_4SO_4(OH)_6 \cdot 5H_2O$. An $Al(OH)_3$ layer is formed on the surface of Al-rich dendrites, which can constitute a passive protective layer. This configuration of corrosion products changes the electrochemical system of the structural components of the coating and constitutes an effective barrier protection, delaying the corrosion process.

• The addition of Si to the bath effectively limits the excessive thickness of the diffusion layer of coatings, but its precipitation in the outer layer and on the top surface of coatings may promote pitting corrosion due to its cathodic nature and the creation of effective corrosion cells with other structural components of the coatings.

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