Formation of periodic layered structure during hot-dip galvanizing in Al-Zn-Mg bath

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Abstract

This study investigated the effect of Al and Mg content and immersion time on the formation of periodic layered structure during hot-dip galvanizing in Al-Zn-Mg bath. The steel substrates were immersed in Al-Zn bath for 10 s to 120 s, with five levels of Al content in the range of 15 to 55 wt.%, and four levels of Mg additions, in the range of 0.5 to 3.0 wt.%. The microstructure and constituent phases of the periodic layered structure were characterized by optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The coating with periodic layered structure contains a thin light gray $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer near substrate and outer periodic layered structure. The periodic layered structure consists of alternating light gray layer (FeAl_3Zn_x) and black

gray layer (Al dendrites and Zn-rich interdendritic regions). The formation of periodic layered structure requires an incubation period t_1 , while if the immersion time is over t_2 , the periodic layered structure is destroyed. In addition, t_1 and t_2 varies with the Al content and Mg addition.

Keywords: Hot-dip galvanizing; Al-Zn-Mg coating; Periodic layered structure; Immersion time

1. Introduction

Al-Zn coatings are predominantly used to improve the corrosion resistance of steel, due to the sacrificing protection from Zn and the long lasting physical barrier from aluminum oxide [1]. In recent years, a large amount of studies have been focused on the investigation of Al-Zn coatings by alloying a number of elements to acquire improved corrosion resistant performance [2-5]. Magnesium is one of the most popular elements added into the Al-Zn bath because of the excellent performance of Al-Zn-Mg coatings, such as corrosion resistance, wear resistance, welding characteristic [5-6]. The published reports in Al-Zn-Mg coatings are mainly focused on low Al content [5-9], while few studies are focused on Al-Zn-Mg coatings with high Al content. Recently, as Wang [10] analyzed the microstructure and corrosion behavior of 45Al-Zn-Mg coatings, he found a typical periodic layered structure in some samples. The results of salt spraying testing showed that the corrosion resistance of the coating with periodic layered structure was excellent. This interesting discovery led the authors to investigate the Al-Zn coatings with Mg additions furtherly.

The periodic layered structure was found for the first time by Liesegang in liquid-gelatine systems [11]. The formation of periodic layered structure in solids was firstly discovered by the research group of Osinski et al. in 1982 [12]. This discovery indicated that such periodic layered structure consists of a periodic sequence of layers which grow parallel to the substrate. After that, various reports have been published that are focused on the formation of such periodic layered structure in solid-solid reaction systems, such as NiCoFe/Mg [13], SiO₂/Mg [14], Co₂Si/Zn [15], SiC/Ni [16], Sn/Ni-7 wt. % V [17], Fe₃Si/Zn

[18] and $\text{Ni}_3\text{Si}/\text{Zn}$ [19-20]. Recently Liu et al. [21] observed the periodic layered structure with alternating layers in the reactions of FeCr alloys and molten Zn. However, the information about the periodic layered structure formed in hot dip galvanizing is still insufficient.

In this work, the formation of periodic layered structure during hot-dip galvanizing in Al-Zn-Mg bath, with different Al and Mg contents and immersion time was investigated.

2. Experimental procedure

2.1. Sample preparation

Q235 steel (ASTM A284 Grade D), the composition of which is shown in Table 1, is selected as sample material. The steel is cut into regular shape with the dimension of $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ by wire electric discharge machine. The bath materials, 99.99% purity Zn, Al ingots and Mg-Al alloy are melted in the KGPS-30-8 medium frequency induction furnace. The designed composition of all baths and corresponding dipping temperature are listed in Table 2. The Mg additions in this work are designed according to the research of Wang [10], who found that the corrosion resistance of 45Al-Zn coating was significantly improved when the Mg additions were in the range of 0.5 to 3.0 wt.%.

Prior to hot dipping, the steel substrates are firstly degreased in alkaline solution for 4 minutes at $75\text{ }^\circ\text{C}$, followed by rinsing in water, and pickling in hydrochloric for 3 minutes at $75\text{ }^\circ\text{C}$. Secondly, the steel specimens are covered by a flux, the constituent of which is shown in Table 3, for 3 minutes at $75\text{ }^\circ\text{C}$, and then dried for 10 minutes at $90\text{ }^\circ\text{C}$. Thirdly, the steel substrates are dipped in Al-Zn-Mg baths for 10s, 20s, 40s, 60s, 80s or 120s, then withdrawn

from the baths and cooled in water. Finally, the steel substrates are embedded in resin, followed by polishing to a mirror surface and corroded by 10 vol.% HNO₃ solution.

2.2. Sample characterization

The CQ-45B2 optical microscopy (OM) and JSM-6360 scanning electron microscopy equipped with an energy dispersive spectroscopy (SEM-EDS) are conducted to analyze the structure and the composition of the phases. The ESCALAB-250Xi X-ray photoelectron spectrometer (XPS) with an Al K α X-ray source and a 650 μ m measuring spot diameter, is carried out in order to reveal information about the state of the chemical bond of the specific elements on the periodic layered structure. D/MAX-2500 X-ray diffraction (XRD) with Cu K α radiation coupling continuous scanning at 40 kV and 40 mA is performed to determine the phases in the coatings. The sample is scanned with 2θ ranging from 10° to 90°, the scanning speed of 5°/min and step space of 0.02°.

3. Results and Discussion

3.1. Microstructure and phase constituent of the periodic layered structure

As the microstructure and phase constituent of the coatings consisting of the periodic layered structure are similar, the sample dipped in 55Al-Zn-0.5Mg bath for 60 s at 610 °C with typical periodic layered structure, is illustrated as follows as a representative.

Fig. 1(a) shows the overview of the whole coating and Fig. 1(b) is the detail view of the area near the substrate. The periodic layered structure consists of alternating light gray layer and dark gray layer. The individual layer is parallel to the substrate. Fig. 2 presents the SEM

mapping of the region in Fig. 1(b). The SEM mapping analysis shows that Mg is homogeneously distributed over the whole coating. To identify the nature of Mg in the coatings, XPS analysis is carried out. From Fig. 3, it can be gained that the binding energy of Mg is 1303.5 eV. According to the study of Fuggle et al. [22], Mg exists in its elemental form. The above analysis indicates that Mg does not take part in the formation of intermetallic compound.

The morphology of the dark gray dendritic layers are analogous to that of the overlay (or solidified bath) shown in Fig. 4. Selverian et al. [23] found that three features, i.e. the alpha Al dendrite size, the Zn-rich interdendritic regions and the Si particles defined the part of the coating in 55Al-Zn-Si (Galvalume) referred to as the overlay. According to the Al-Zn binary phase diagram [24], as the 55Al-Zn bath solidifies from 610 °C, the Al-Zn liquid decomposes into Al-rich and Zn-rich solution. On the basis of above analyses, it can be deduced that the dark gray layers consist of Al dendrites and Zn-rich interdendritic regions, marked as (Al+Zn) layer.

To analyze the light gray layers of Fig. 1(a), the compositions of areas marked A, B, C, D, E and F is ascertained by EDS. The compositions of areas B, C, D, E and F correspond to $\text{Fe}_{23.06}\text{Al}_{72.49}\text{Zn}_{4.45}$, $\text{Fe}_{22.69}\text{Al}_{72.74}\text{Zn}_{4.57}$, $\text{Fe}_{22.30}\text{Al}_{73.04}\text{Zn}_{4.66}$, $\text{Fe}_{20.43}\text{Al}_{73.04}\text{Zn}_{5.53}$ and $\text{Fe}_{19.01}\text{Al}_{74.55}\text{Zn}_{6.44}$, respectively. The Al and Fe content in the five areas is similar. The composition of area A, close to the substrate, is $\text{Fe}_{28.50}\text{Al}_{65.56}\text{Zn}_{5.93}$. According to the EDS analysis, it can be deduced that the composition of light gray layer near the substrate is different from the outer alternating light gray layers. Then, XRD analysis is carried to obtain more information about the phases of the coating. Close to the sample surface (roughly

corresponding to line 1 from the right SEM micrograph of Fig. 5), (Al), (Zn) and FeAl_3 are identified by XRD analysis as shown in Fig. 5(a). After grinding with SiC paper to remove the first approximate 300 μm (roughly corresponding to line 2), the (Al), (Zn) and FeAl_3 are found to be the dominant phases via XRD analysis in Fig. 5(b). (Al), (Zn) and FeAl_3 are identified again in the XRD patterns of Fig. 5(c) in the section after grinding the second approximate 300 μm (roughly corresponding to line 3). The distinct phases identified in the XRD patterns of Fig. 5(d), which are obtained at the region near the substrate of the sample after removing the third approximate 300 μm (roughly corresponding to line 4), are (Fe), (Al), (Zn), FeAl_3 and Fe_2Al_5 . According to the study of Peng et al. [25, 26], Zn dissolved within FeAl_3 and Fe_2Al_5 during the reactions between the Fe substrate and Al-Zn baths. On the basis of the above results, combining the informations in literatures [25-27], it can be deduced that the inner light gray layer near the substrate belongs to $\text{Fe}_2\text{Al}_5\text{Zn}_x$ and outer light gray layers to FeAl_3Zn_x .

The ordering of phases in the coatings that are identified by XRD, is determined by line scan analysis. The scanning line is perpendicular to the interface, between the substrate and the coating, as shown in Fig. 6. The SEM-EDS line scan results show that the concentration of Al and Fe presents a periodic variation between the coating surface and the light gray layer close to the substrate.

The ordering of individual phases in the periodic layered structure is schematically presented in Fig. 7. A light gray FeAl_3Zn_x layer and a dark gray (Al+Zn) layer is defined as a layer pair. The periodic layered structure consists of multiple layer pairs. In addition, the coating contains a thin light gray layer near the substrate which is identified as $\text{Fe}_2\text{Al}_5\text{Zn}_x$.

3.2. Effect of immersion time on periodic layered structure

The samples dipped in 45Al-Zn-0.5Mg and 55Al-Zn-0.5Mg baths for different immersion times are characterized and analyzed in details, as illustrated in Fig. 8 and 9 respectively.

Fig. 8 represents the SEM micrographs of the coatings, obtained by dipping Q235 steel substrates in 45Al-Zn-0.5Mg, for different immersion times at 590 °C. At the beginning of hot dipping for relatively short immersion time, 10 s, the coating consists of a $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer, a FeAl_3Zn_x layer and a (Al+Zn) layer, similar to the common microstructure formed during Al-Zn hot-dip galvanizing in literatures [2-4,23], as illustrated in Fig. 8(a). When the immersion time increases to 20 s, the periodic layered structure with few layer pairs is formed in the coating, as shown in Fig. 8(b). With the further increase of immersion time, the number of the layer pair continues increasing, as represented in Fig. 8(c), (d) and (e). And when the immersion time is 80 s, the periodic layered structure becomes the most pronounced, compared to 40 s and 60 s. When the steel substrate is immersed for a period of time longer than 120 s, the periodic layered structure begins to deteriorate and the banded FeAl_3Zn_x layers near the sample surface are transformed to blocky compounds, as shown in Fig. 8(f).

Fig. 9 shows the SEM micrographs of the coatings obtained by dipping the steel substrates in 55Al-Zn-0.5Mg, for different immersion times at 610 °C. When the immersion time is 10 s, the periodic layered structure with few layer pairs is formed in the coating, as represented in Fig. 9(a). As the immersion time continues increasing, the layer pair increases and the periodic layered structure becomes more and more pronounced, as illustrated in Fig.

9(b), (c) and (d). When the immersion time is 80 s, the periodic layered structure begins to deteriorate and the banded FeAl_3Zn_x layers close to sample surface are transformed to blocky FeAl_3Zn_x , as shown in Fig. 9(e). As the sample immerses for a longer time, 120 s, more band FeAl_3Zn_x layers are transformed to blocky compounds, as illustrated in Fig. 9(f).

According to above experimental results, it can be found that the formation of periodic layered structure requires an incubation period marked as t_1 , while as the immersion time reaches another period marked as t_2 , the periodic layered structure begins to be destroyed. Therefore, the model of the development of the periodic layered structure with the immersion time is built, as presented in Fig. 10. When the immersion time is shorter than t_1 , the periodic layered structure is not formed. As the time is in the range of t_1 to t_2 , the layer pairs increase with the immersion time, while if the immersion time is over t_2 , the periodic layered structure begins to be destroyed. As Liu et al. [21] investigated the formation kinetics of the periodic layered structures in Fe30Cr70/Zn system, they also found that formation of periodic layered structure require an incubation period. And when the immersion time is too long, the growth rate of Fe-Al intermetallic layer decreases, the Fe-Al intermetallic layer is gradually attacked by the liquid phase of the bath according to Chen et al. [28] and Nishimoto et al. [29]. Thus the banded FeAl_3Zn_x layers is attacked by liquid phase from bath and transformed to blocky ones.

3.3. Effect of Al content on the periodic layered structure

The structures of the coatings obtained in Al-Zn-0.5Mg baths for 40 and 80 s, with Al content in the range of 15 to 55 wt.%, is presented in Fig. 11 and 12 respectively.

When the Al content in Al-Zn-0.5Mg bath is 15 wt.%, the coating immersed in the bath for 40 s consists of a $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer, a FeAl_3Zn_x layer and a (Al+Zn) layer. As the Al content increases to 25 or 35 wt.%, many cracks parallel to the substrate appear within the intermetallic layer. When the Al content in the bath is 45 wt.%, the periodic layered structure with few layer pairs is formed. As the Al content increases to 55 wt.%, the layer pair increases and the periodic layered structure becomes more pronounced.

When the Al content in Al-Zn-0.5Mg bath is 15 wt.%, the microstructure of the coating obtained for 80 s is similar to the coating for 40 s, but the thickness of intermetallic layer increases and the internal cracks appears. As the Al content increases to 25 wt.%, more cracks appear within the intermetallic layer. When the Al content increases to 35 wt.%, the periodic layered structure with few layer pairs is formed. As the Al content in the bath is 45 wt.%, the layer pair increases and the periodic layered structure becomes more pronounced. When the Al content increases to 55 wt.%, the periodic layered structure begins to deteriorate and the banded FeAl_3Zn_x layers near sample surface are transformed to blocky FeAl_3Zn_x .

According to the experimental results, it can be concluded that the Al content in bath could affect the transformation process of the periodic layered structure. The incubation period t_1 of the formation of periodic layered structure is shortened as the Al content increases. In addition, the immersion time t_2 for the deterioration of the periodic layered structure is reduced with the increase of Al content. The growth of intermetallic layer between substrate and overlay layer is controlled by the reaction between Fe from the substrate and Al from the bath [30,31]. When the Al content in bath increases, the reaction of Fe-Al aggravates and FeAl_3Zn_x layers grow faster. Thus, the incubation period of the periodic layered structure is

shortened.

3.4. Effect of Mg addition on the periodic layered structure

The samples dipped in 45Al-Zn and 55Al-Zn baths for 40 s with different Mg additions are investigated, as represented in Fig. 13 and 14 respectively.

The scanning SEM micrographs of the coatings obtained in 45Al-Zn baths, for different Mg additions for 40s, are represented in Fig. 13. When Mg addition is 0.5 wt.%, the periodic layered structure with few layer pairs is formed in the coating. When the Mg addition increases to 1.5 wt.%, the layer pairs increase and the periodic layered structure becomes distinct. When Mg addition is 2.5 wt.%, the banded FeAl_3Zn_x layers close to the sample surface are destroyed. When the Mg addition increases to 3.0 wt.%, all banded FeAl_3Zn_x layers in the periodic arrangement are replaced by blocky FeAl_3Zn_x .

Fig. 14 shows the SEM micrographs of the coatings obtained by dipping steel substrate in 55%Al-Zn baths, for different Mg additions for 40 s. When the Mg addition is 0.5 wt.%, the distinct periodic layer is formed in the coating. As the Mg addition increases to 1.5 wt.%, the periodic layered structure is completely destroyed.

According to the above experimental results, as the Al content is constant, the incubation period t_1 and destruction time t_2 of the periodic layered structure is reduced with the increasing of Mg addition. The experimental results in 3.1 indicate that Mg does not take part in the formation of intermetallic compound and it exists in the coatings as elemental form. Unwin et al. [5] and Tong et al. [32] proposed that Mg addition in the Al-Zn bath promoted the interface reaction and the growth of the Fe-Al intermetallic layer, making the intermetallic

denser, due to the implementation of grain refining. Therefore, Mg refines the grain of the coating and then affect the transformation kinetics of the periodic layered structure.

This work investigates the effect of Al and Mg content and immersion time on the periodic layered structure in details, and the formation mechanism of the periodic layered structure will be investigated in next paper, on the basis of additional experiments.

4. Conclusions

The effect of immersion time, Mg additions and Al content, on the periodic layered structure in Al-Zn-Mg coatings are investigated. The following conclusions could be drawn from the present study:

1. The alternating layers of the periodic layered structure consist of a FeAl_3Zn_x layer and a (Al+Zn) layer. In addition, the coating contains a thin $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer existing between the substrate and the periodic layered structure.
2. The formation of the periodic layered structure requires an incubation period t_1 . In addition, when the immersion time is over t_2 , the periodic layered structure is destroyed by the liquid phase of the bath.
3. The incubation period t_1 when periodic layered structure is formed and the immersion time t_2 when periodic layered structure is destroyed, is shorten with the increase of Al content and Mg addition.

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Fig.1. SEM micrograph of typical periodic structure in the coating obtained by dipping steel substrate in 55Al-Zn-0.5Mg for 60 s at 610 °C: (a) overview of the entire coating, (b) detail view of the area near the substrate.

Fig.2. SEM mapping to area in Fig. 1(b).

Fig.3. XPS analysis, showing the high-resolution Mg spectra of the cross section of the coating obtained by dipping steel substrate in 55Al-Zn-0.5Mg for 60 s at 610 °C.

Fig.4. SEM micrograph of coating obtained by dipping steel substrate in 35Al-Zn-0.5Mg for 20 s at 570 °C, showing the dendritic morphology of the overlay.

Fig.5. XRD of the coating obtained by dipping steel substrates in 55Al-Zn-0.5Mg for 60 s at 610 °C at different sections. (a) at section 1 near the coating surface, (b) at section 2 after grinding with SiC paper to remove the first approximate 300 µm, (c) at section 3 after removing the second approximate 300 µm, (d) at section 4 near the substrate after removing the third approximate 300 µm.

Fig.6. Line scan analysis of the cross section of the coating obtained by dipping steel substrate in 55Al-Zn-0.5Mg for 60 s at 610 °C.

Fig.7. Diagram of ordering of phases in the periodic layered structure.

Fig.8. SEM micrographs of the coatings, obtained by dipping steel substrate in 45Al-Zn-0.5Mg for different times: (a) 10 s, (b) 20 s, (c) 40 s, (d) 60 s, (e) 80 s, (f) 120 s.

Fig.9. SEM micrographs of the coatings, obtained by dipping steel substrate in 55Al-Zn-0.5Mg for different times: (a) 10 s, (b) 20 s, (c) 40 s, (d) 60 s, (e) 80 s, (f) 120 s.

Fig.10. Model of the development of the periodic layered structure with the increase of immersion time. The time t_1 presents the period when the periodic layered structure begins to be formed, and t_2 presents the period when the periodic layered structure begins to be destroyed.

Fig.11. SEM micrographs of the coatings, obtained by dipping steel substrate in Al-Zn-0.5Mg bath with different Al content for 40 s: (a) 15 wt.%, (b) 25 wt.%, (c) 35 wt.%, (d) 45 wt.%, (e) 55 wt.%.

Fig.12. SEM micrographs of the coatings, obtained by dipping steel substrate in Al-Zn-0.5Mg bath with different Al content for 80 s: (a) 15 wt.%, (b) 25 wt.%, (c) 35 wt.%, (d) 45 wt.%, (e) 55 wt.%.

Fig.13. SEM micrographs of the coatings, obtained by dipping steel substrate in 45Al-Zn-Mg bath with different Mg additions for 40 s: (a) 0.5 wt.%, (b) 1.5 wt.%, (c) 2.5 wt.%, (d) 3.0 wt.%.

Fig.14. SEM micrographs of the coatings, obtained by dipping steel substrate in 55Al-Zn-Mg bath with different Mg additions for 40 s: (a) 0.5 wt.%, (b) 1.5 wt.%, (c) 2.5 wt.%, (d) 3.0 wt.%.

Table 1: Composition of base steel

Element	C	Mn	Si	S
Composition (wt.%)	0.12%-0.20%	0.30%-0.70%	0.20%-0.30%	<0.045%

Table 2: Composition of baths and corresponding immersion temperature

bath	Al(wt.%)	Mg(wt.%)	Temperature(°C)
1	15	0.5	530
2	15	1.5	530
3	15	2.5	530
4	15	3.0	530
5	25	0.5	550
6	25	1.5	550
7	25	2.5	550
8	25	3.0	550
9	35	0.5	570
10	35	1.5	570
11	35	2.5	570
12	35	3.0	570
13	45	0.5	590
14	45	1.5	590
15	45	2.5	590
16	45	3.0	590
17	55	0.5	610
18	55	1.5	610
19	55	2.5	610
20	55	3.0	610

Table 3:Composition of flux

Compound	ZnCl ₂	NaCl	SnCl ₂	KCl	K ₂ ZrF ₆	CaCl ₂
Composition(g/50ml)	15	1.2	4	0.5	1.2	0.6