Effect of Mg on Fe–Al interface structure of hot–dip galvanized Zn–Al–Mg alloy coatings

Yiye Xie, An Du, Xue Zhao, Ruina Ma*, Yongzhe Fan*, Xiaoming Cao

Key Lab for New Type of Functional Materials in Hebei Province, Tianjin Key Lab Material Laminating Fabrication and Interface, School of Material Science and Engineering, Hebei University of Technology, Tianjin 300132, People's Republic of China

ARTICLE INFO

ABSTRACT

Zn–5 wt% Al–x Mg (x = 0, 1, 2, 2.5, 3, and 5 wt%) alloy coatings were prepared by the flux process. The morphology, phases, and microstructures of the interface reaction layer of the alloy coatings prepared at different Mg contents were analyzed by field emission–scanning electron microscopy, X-ray diffraction, and transmission electron microscopy studies. The results show that the intermetallic layers formed on the steel plate surfaces in the Zn–Al–Mg bath consist of Fe_4Al_{13} and $Fe_2Al_5Zn_{0.4}$ phases. With increase in the Mg content, the thickness of the Fe–Al interface reaction layer decreased. Magnesium dissolved in the crystal lattice of the Fe–Al intermetallic compounds, resulting in a change in the lattice constants of the Fe–Al intermetallic compounds. This leads to lattice distortion and inhibition of the $Fe_2Al_5Zn_{0.4}$ phase growth. In addition, the grain size decreased, and the interface between the coating and the steel matrix tends to be straight with increase in the Mg content. The Mg element segregates at the grain boundaries of the Fe–Al intermetallic, resulting in grain refinement.

1. Introduction

Hot–dip galvanized zinc and its alloy coated steels are widely used in various fields [1]. With excellent corrosion resistance, hot–dip galvanized Zn–Al–Mg coating is an ideal alloying material for the hot dipping process [2–4]. However, the presence of Mg causes poor surface quality of the coating, which hinders its large–scale application and popularization. Therefore, it is important to study the influence of Mg element on the interface structure of hot–dip galvanized Zn–Al alloys. It is known that the Fe–Al interface reaction layer consists of mainly $FeAl_3$ and Fe_2Al_5 phases [5–6]. During hot-dipping, the reaction between substrate and bath is extremely rapid and intense which can lead to a decrease in the coating toughness. This causes rupture and flaking of the coating [7–9]. If the Fe-Al interface reaction layer is thick, it may even delaminate from the substrate. Therefore, the reaction layer should be as thin as possible [8–10].

Addition of a small amount of an alloying element to the hot-dip bath can influence the thickness of the Fe-Al interface reaction layer [11–12]. Extensive studies have shown that the addition of elements such as Vanadium, Titanium, Silicon, Copper, and Rhenium into the Zn-Al bath affects the structure of the Fe-Al interface. Vanadium [13] and Titanium [14–16] occupy the vacancies of Fe_2Al_5 lattice, thereby promoting the nucleation of Fe_2Al_5. This suppresses the growth of the Fe-Al

phase and leads to a thinner reaction layer. Rhenium [17] distributes in the grain boundaries and promotes grain refinement. Copper acts in synergy with Silicon to effectively control the Fe-Al reactivity and hinder the growth of the Fe_2Al_5 phase [18]. Silicon, when added in the Zn–Al bath, suppresses the rapid exothermic reaction between the Zn-Al bath and the substrate by forming a solid reaction layer and reducing the reaction rate. Thus, Silicon prevents excessive growth of the alloy layer at the coating-steel interface [19]. The addition of Mg promotes the interface reaction and shortens the formation time of the reaction layer, resulting in the formation of a uniform and dense reaction layer [20]. Li et al. speculated that the interface structure of hot-dip galvanized Zn-Al alloy is composed of a $FeAl_3Zn_x$ phase, primary zinc-rich phase, and dendritic aluminum rich phase, arranged in a periodic manner. The presence of Mg was considered to destroy this periodicity and densify the reaction layer [21].

At present, most of the Zn-Al-Mg coated steels produced in the world are obtained by sheet galvanization after being prepared by the gas reduction process, this process has the advantages of fast production speed, high output, and zero pollution [22–24]. But, it is a difficult technique and requires complex equipment. Furthermore, the gas reduction process is not suitable for high strength steel and large structural components. However, the flux process is simple and easy to operate and can be used to obtain a thin coating. Complex-shaped and

---

discontinuous samples for galvanizing are usually prepared by the flux process. This research aims to provide a foundation for galvanization of steel plates and structural components prepared by the flux process. Therefore, the flux process was used in this study to prepare discontinuous hot-dip galvanized coatings.

Even though there are many studies on hot-dip coating of zinc alloys, very few studies report the effect of Mg on the grain refinement. In this work, steel sheets were hot-dipped in a bath containing Zn-5 wt% Al-x Mg (x = 0, 1, 2, 2.5, 3, and 5 wt%) alloy, and the effect of Mg on the microstructure of the reaction layer was studied. In addition, the location and the chemical state of Mg in the reaction layer were determined by performing transmission electron microscopy (TEM) studies.

2. Experimental details

2.1. Materials preparation

The hot-dip experiments were carried out in a medium frequency induction furnace equipped with a silicon controlled rectifier. The Q235 steel sheets, used as the substrate in this work, were cut into $80 \times 80 \times 3$ mm sample plates. All the samples were degreased with NaOH (150 g/l) solution and then etched with HCl (20 vol%) solution to remove surface rust. Subsequently, they were dipped in a fluxing agent (consisting of 20 wt% $ZnCl_2$-8 wt% KCl-8 wt% NH_4Cl-0.5 wt% $BiCl_3$-1 wt% HCl-62.5 wt% H_2O) at 25 °C for 30 s and dried before being dipped in the baths. The dipping alloy consists of pure zinc ingot (99.9 wt%), pure magnesium ingot (99.9 wt%), and pure aluminum strip (99.9 wt%), which were all obtained from Zhuzhou Smelts Group Co., Ltd. (China). The Zn-5 wt% Al-x Mg (x = 0, 1, 2, 2.5, 3, and 5 wt%) alloy was prepared with different contents of Mg. The compositions of the immersion baths are given in Table 1. The traditional dipping process used in the present study. The samples were dipped into the Zn-Al-Mg bath (540 °C) for 40 s, and the Zn-Al-Mg coatings were formed after solidification in the air for 50 s.

To investigate the characteristics of the intermetallic layer between the overlay and the steel substrate, the overlaid Zn-Al-Mg coating was removed by corrosion in an acid solution. Subsequently, 10×10 mm samples were cut from the sheets using a linear cutting machine. The samples were dissolved in dilute HCl (5 vol%) containing a corrosion inhibitor (2 vol% $(CH_2)_6N_4$) for 30 s (defined as 1#) and 90 s (defined as 2#) to expose the surfaces of the Fe-Al intermetallic compounds. Then the as-prepared samples were taken out and cleaned with deionized water and anhydrous alcohol for later use. Meanwhile, for TEM studies, the substrate and the overlay were first removed by mechanical thinning to 50 μm and later thinned by ion beam thinning. The reaction layer was then transferred for TEM studies.

2.2. Characterizations

The phase structures of the Zn-5 wt% Al-x Mg (x = 0, 1, 2, 2.5, 3, and 5 wt%) alloys were examined by X-ray diffraction (XRD; D8 Advance, Bruker, Germany) at 25 °C using Cu K_{α} radiation (1.54059 Å). The morphology of the interface of the Fe-Al intermetallic compound layer was characterized by field emission scanning electron microscopy

Table 1
Composition of the immersion baths (wt%).

Label	Zn	Al	Mg
0 Mg	Bal.	5.16	0.00
1 Mg	Bal.	5.03	1.12
2 Mg	Bal.	5.21	1.98
2.5 Mg	Bal.	5.13	2.49
3 Mg	Bal.	5.01	3.11
5 Mg	Bal.	5.09	4.95

(FE-SEM; Nova Nano SEM450, FEI, USA) and energy dispersive spectroscopy (EDS). The morphologies of the particles were characterized using a field emission transmission electron microscope (FE-TEM; Tecnai G2 Spirit TWIN, FEI, USA) equipped with EDS.

3. Results and discussions

3.1. Phase structure of the cross-section

Fig. 1 shows the cross-sectional microstructures of the Zn-5 wt% Al-x Mg (x = 0, 1, 2, 2.5, 3, and 5 wt%) alloy coating. The reaction layer is divided into two regions: one close to the overlay, which is sparse, and another close to the substrate, which is dense. The compositions of the reaction layer determined by EDS are listed in Table 2. The SEM-EDS analysis shows that the sparse region is composed of Fe_4Al_{13} phase, and the dense region is composed of $Fe_2Al_5Zn_{0.4}$ phase. Furthermore, the amount of $Fe_2Al_5Zn_{0.4}$ phase in the reaction layer is more than that of the Fe_4Al_{13} phase. There are many gaps in the reaction layer, and the microstructure of the gaps is similar to that of the overlay. The reaction layer forms the Fe_4Al_{13} phase instead of the $FeAl_3$ phase, because the reaction temperature in this work is higher than that reported in previous papers. The thickness of the reaction layer and the total coating thickness are shown in Fig. 2. With increase in the Mg content, the thickness of the reaction layer decreases gradually, but the thickness of the overlay increases. Therefore, the total thickness of the coating does not change consistently with change in the Mg content. At the same time, the Fe_4Al_{13} phase becomes dense, and the interface between the substrate and the reaction layer tends to be straight. Meanwhile, the interface between the overlay and the reaction layer becomes apparent with increase in the Mg content.

3.2. Phase structure of the reaction layer

The SEM images of the surface morphology of the reaction layer in 1# at low magnification are shown in Fig. 3. The compositions of the surface were also determined by XRD, and the XRD patterns are shown in Fig. 4. The SEM-EDS and the XRD analyses indicated that the banded structure in Fig. 3 is primary zinc–rich phase, hexagonal (Fig. 3(c)) and columnar (Fig. 3(d)) structures correspond to $MgZn_2$ and the agglomerated particles are Fe-Al intermetallic compounds. High–magnification SEM images were recorded to further characterize the agglomerated particles of Fe-Al intermetallic compounds in the reaction layer. The SEM images of the surface morphology of the reaction layer in 1# at high magnification are shown in Fig. 5. Table 3 shows the elemental composition and the relative content of the reaction layer of the sample at points 1–7 marked in Fig. 5. The reaction layers of the samples with different contents of Mg are composed of block, granular and banded structures. The SEM-EDS and the XRD analyses indicated that the banded structure is primary zinc-rich phase of the overlay, block structure is Fe_4Al_{13} phase, and granular structure is $Fe_2Al_5Zn_{0.4}$ phase. In the absence of Mg (Fig. 5(a)), the content of Fe_4Al_{13} phase in the reaction layer is more than that of the $Fe_2Al_5Zn_{0.4}$ phase. The size of the Fe_4Al_{13} grains is approximately 2–3 μm, and the distribution of the Fe_4Al_{13} phase is sparse. Whereas, the size of the $Fe_2Al_5Zn_{0.4}$ grains is approximately 1 μm, and the distribution of the $Fe_2Al_5Zn_{0.4}$ phase is dense. At a Mg content of 1 wt% (Fig. 5(b)), the amount of Fe_4Al_{13} phase decreases, and the size of the $Fe_2Al_5Zn_{0.4}$ grains is approximately 0.5 μm. When the Mg content is increased to 3 and 5 wt% (Fig. 5(c) and (d)), the amount of Fe_4Al_{13} phase reduces drastically, and the size of the $Fe_2Al_5Zn_{0.4}$ grains becomes significantly smaller, approximately 0.2 μm or less. With further increase in the Mg content, the amount of $Fe_2Al_5Zn_{0.4}$ phase increases, and the size of the $Fe_2Al_5Zn_{0.4}$ grains decreases from 3 to 0.2 μm.

The surface morphology of the reaction layer in 2# exhibited a granular structure as shown in Fig. 6. Table 4 shows the elemental composition and the relative content of the reaction layer of the sample