Research Article

Study on the Corrosion Mechanism of Zn-5Al-0.5Mg-0.08Si Coating

Shiwei Li, Bo Gao, Ganfeng Tu, Yi Hao, Liang Hu, and Shaohua Yin

School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110004, China

Correspondence should be addressed to Bo Gao, ljiaojiao@163.com

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A new type of hot-dip Zn-5Al-0.5Mg-0.08Si and Zn-5Al alloy coatings was performed on the cold rolled common steel. The hot-dip process was executed by self-made hot-dip galvanising simulator. SEM and EDS test results demonstrated that Mg was mainly distributed in crystal boundaries. XRD test results showed that the corrosion product of Zn-5Al-0.5Mg-0.08Si alloy coating was almost $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. The features of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ are low electric conductivity, insolubility and good adhesion. The corrosion resistance of alloy-coated steels was detected by neutral salt spray test. The microstructural characterization of the coating surface after neutral salt spray test and removing the corrosion products revealed that the corrosion process of Zn-5Al-0.5Mg-0.08Si coating was uniform and the coating surface was almost flat. As a result, the corrosion resistance of Zn-5Al-0.5Mg-0.08Si coating has a remarkable improvement with a factor of 9.2 compared with that of Zn-5Al coating.

1. Introduction

Owing to excellent mechanical properties, large production, and low-cost manufacture, steels are applied widely in nearly every field, such as machinofacture, building, and dunnage. But its resistance to atmospheric corrosion is very low in most environments [1–7]. Hot dipping is a very efficient method to protect steels from corrosion, and zinc coating can provide a barrier and galvanic protection for steel substrate [1, 2, 5]. The corrosion resistance of zinc coating can be enhanced by adding alloying elements, for example, Al, Mg, RE, and Ni [5–12]. The effect of Mg element is the most remarkable among them. But detailed information on the structure and properties of the coating is limited in published literatures [4], and the reason for enhanced corrosion resistance has not yet been clarified definitely [2, 8, 13]. In this paper, the corrosion mechanism of hot-dip Zn-5Al-0.5Mg-0.08Si coating was studied in detail by the coating microstructure and corrosion products analysis.

2. Experimental Procedures

2.1. Materials. Purities of Zn, Al, Mg, and Si were 99.99%, 99.7%, 99.94%, and 99.93%, respectively. The substrate was common cold rolled steel (DC01D).

2.2. Process of Pretreatment and Hot Dipping. The process of pretreatment and hot dipping was as follows: alkaline degreasing (NaOH, 15 wt. %) at 80°C for 5 minutes with a soft brush → water flush → remove iron oxides with HCl solution (18 vol.%, 70°C) → water flush → electrolysis fluxing (the parameters was according to China patent, no. 201010296310.4) → dried at 120°C for 20 minutes in an oven → hot-dip. Table 1 shows some factors [14, 15] that affect thickness of coating in hot-dip process and the actual parameters used in this experiment.

2.3. Examination of Coatings. The surface microstructure of the coatings, the corrosion products after neutral salt spray test, and the morphology of coatings after removing the corrosion products were examined by means of scanning

TABLE 1: Relative parameters that influence coating thickness.

Parameters classification	Experiment parameters	Parameters classification	Experiment parameters
Rising rate of steel	150 [m/min]	Air pressure	0.01 [Mpa]
Ingredient of alloy	Zn-5Al Zn-5Al-0.5Mg-0.08Si	Distance between air bells 12 knife and steel	20 [mm]
Hot-dip temperature	450 [°C]	Air bells knife angle	-5 [°]
Hot-dip time	8 [S]	Distance between air knife and melting zinc surface	20 [cm]

FIGURE 1: SEM image of Zn-5Al coating and corresponding results of EDS in A and B dots.

electron microscopy (SEM, SSX-550 equipped with EDS). The analysis of corrosion products was carried out on a PANALYTICAL X'Pert Pro MPD(PW3040/60). The neutral salt spray test was carried out by salt spray testing chamber (DCTC1200p, produced by Germany Siemens company) for 96 hours continuously. (Other parameters adopted in this study in the neutral salt spray test were according to China national standard GB/T10125-1997.)

3. Results and discussion

3.1. SEM and EDS Analysis of Coatings Surface. Figure 1 shows the surface morphology image of Zn-5Al coating and corresponding results of EDS in A and B dots. From Figure 1, it can be found that the coating consists of coarse $\beta(\text{Zn})$ and Zn-Al binary eutectic phases. Owing to the potential difference between the two phases, when the coating is put in the corrosive environment, the phase of lower electrode potential will accelerate corroding process, while the phase of higher electrode potential will be protected from corroding. So the corrosion resistance of Zn-5Al coating is not very high.

Figure 2 indicates SEM images of Zn-5Al-0.5Mg-0.08Si coating. It can be seen that the dendritic arm spacing of Zn-5Al coating is significantly decreased from $\sim 10 \mu\text{m}$ to $2\text{--}5 \mu\text{m}$ after adding alloying elements Mg and Si; meantime, some new phases are formed expect $\beta(\text{Zn})$ (A), such as Al-rich(B) and MgZn_2 -Zn-Al ternary eutectic(C) [2]. Magnesium is only distributed in crystal boundaries, and it can make the grains fine and restrain the crystal boundary corrosion [16].

3.2. XRD Analysis of Corrosion Products. Figure 3 shows the XRD patterns of the corrosion products of Zn-5Al and Zn-5Al-0.5Mg-0.08Si coatings. As shown in Figure 3(a), the corrosion products of Zn-5Al are $\text{Zn}(\text{OH})_2$

and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. Figure 3(b) shows that the corrosion product of Zn-5Al-0.5Mg-0.08Si coating is only $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, so it can be concluded that the addition of Mg can promote the conversion process from $\text{Zn}(\text{OH})_2$ to $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ [17]. $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ with characteristics of electric conductivity, insoluble and Good adhesion [18, 19] can better protect the coating compared to Zn-5Al coating.

3.3. SEM Analysis of Morphology of Corrosion Products. Figure 4 shows SEM images of corrosion products for Zn-5Al and Zn-5Al-0.5Mg-0.08Si coatings. Figure 4(a) shows that the corrosion products of Zn-5Al coating are smooth and loose, and there are some holes on the surface, so the corrosion products cannot prevent the corrosion media from penetrating itself. Figure 4(b) indicates that the corrosion products of Zn-5Al-0.5Mg-0.08Si are very dense and the size of grain is very fine. Thus, it can protect the coating effectively. Therefore, it can be concluded that corrosion resistance of Zn-5Al-0.5Mg-0.08Si is much better than that of Zn-5Al coating. The related literatures [10, 20–22] have reported that the densely packed corrosion products can prevent the oxygen diffusion and improve the corrosion resistance of the coating.

3.4. SEM Analysis of Coating Surface after Removing the Corrosion Products. Figure 5 shows SEM images of the microstructure of coating surface after removing the corrosion products of neutral salt spray test. As shown in Figure 5(a), the Zn-5Al coating has been exfoliated during the neutral salt spray test, and many narrow cracks were found on the surface. Therefore, the corrosion media can penetrate the coating, and the corrosion rate would be

FIGURE 2: SEM images of Zn-5Al-0.5Mg-0.08Si coating and EDS microanalyses (composition in wt%).

FIGURE 3: XRD patterns of corrosion products of Zn-5Al and Zn-5Al-0.5Mg-0.08Si coatings ((a) Zn-5Al coating, (b) Zn-5Al-0.5Mg-0.08Si coating).

FIGURE 4: SEM images of corrosion products of Zn-5Al and Zn-5Al-0.5 Mg-0.08Si coatings ((a) Zn-5Al coating, (b) Zn-5Al-0.5Mg-0.08Si coating).

FIGURE 5: SEM images of coatings surface after removing the corrosion products of neutral salt spray test ((a) Zn-5Al coating, (b) Zn-5Al-0.5Mg-0.08Si coating).

accelerated. The corrosion process of Zn-5Al is dominated by crystal boundary and exfoliation corrosion. But the surface of Zn-5Al-0.5Mg-0.08Si coating was almost flat, as given in Figure 5(b), so the corrosion process of Zn-5Al-0.5Mg-0.08Si coating is dominated by uniform corrosion. It can be concluded that the addition of Mg can effectively restrain crystal boundary and exfoliation corrosion, which is an important reason for the improvement in corrosion resistance of Zn-5Al-0.5Mg-0.08Si coating.

3.5. Corrosion Resistance of Coatings. After neutral salt spray test, the corrosion products were dissolved with saturated ammonium acetate solution. The corrosion rates of Zn-5Al and Zn-5Al-0.5Mg-0.08Si coatings were measured by weight loss method were 0.5832 and $0.0634 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, respectively. So, the addition of Mg can enhance corrosion resistance of Zn-5Al coating markedly with a factor of 9.2, which shows a good application prospect for Zn-5Al-0.5Mg-0.08Si coating in the future.

4. Conclusions

- (1) After adding of Mg to the Zn-5Al coating, the grain is refined significantly.
- (2) The addition of Mg to Zn-5Al coating can promote the conversion process from $\text{Zn}(\text{OH})_2$ to $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.
- (3) The corrosion products of Zn-5Al-0.5Mg-0.08Si coating is very compact and the size is fine. It can prevent corrosion media effectively.
- (4) The corrosion resistance of Zn-5Al-0.5Mg-0.08Si coating is dramatically improved with a factor of 9.2 compared with that of Zn-5Al.

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