

Short Communication

Microstructure and Corrosion Resistance of Zn-Al-Mg Alloy Diffusion Coating developed on Carbon Steel by Hot Dipping

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Carbon steel samples were galvanized in Zn-6%Al-3%Mg alloy at 455°C and 475°C, respectively. Two kinds of coatings with different microstructure were obtained. The samples were examined with SEM, EDX, XRD, electrochemical and neutral salt spray test. The results show that these two coatings obtained in this study were all diffusion coatings, Al rich phase was mainly Fe₂Al₅Zn_x, and no Al phase was detected. The formation mechanism of these coatings were discussed.

Keywords: galvanizing; corrosion; diffusion; intermetallic; polarization test

1. INTRODUCTION

Hot dipping is a very efficient method to protect steels from corrosion, for the zinc coating can provide a barrier and galvanic protection for steel substrate. With the continuous requirements of improving corrosion resistance of steel, a variety of zinc-based alloy coatings have been developed, some of them have higher aluminum contents, such as Galfan(Zn-5%Al-RE)[1], Galvalume (Zn-55%Al-1.6%Si)[2], and ZAM(Zn-6%Al-3%Mg)[3,4].

One of the main purpose of low aluminum (0.2% also) addition to the Zn bath is to obtain a ductile Zinc coating by suppressing the formation of brittle Fe-Zn phases. In this case, a thin Fe-Al intermetallic interfacial layer, mainly comprised of Fe₂Al₅, is formed at the interface between the overlay coating and the steel substrate. The Fe-Al intermetallic interfacial layer is commonly referred to as the “inhibition layer”[1,5]. The morphology and thickness of this layer is affected by Al content of the bath, the temperature both of the bath and the strip, and the strip speed[6,7].

For continuous galvanizing with high aluminum content, the main object is to develop a Zn-Al alloy coating with nice formability without intermetallics at the interface. In modern continuous hot-dip galvanizing line, it takes only several seconds for the steel strip to pass through the molten Zn-Al bath.

But there is now a strong indication that the high aluminum alloy will be used in batch galvanizing[8]. At such circumstance, where dipping time is usually up to several minutes, diffusion occurs across the interface and a thick intermetallic layer is formed. As for Zn-Al-Mg alloy coatings, the diffusion layer was composed of $Fe_2Al_5Zn_x$ and $FeAl_3Zn_x$. The influence of Mg content and addition of Si to the molten bath was investigated[9,10].

In this paper, two kinds of diffusion coatings on carbon steel were prepared by hot dipping in Zn-6%Al-3%Mg alloy. The purpose of the present work was to study the microstructure, the phases, and the corrosion resistance of the diffusion coatings developed in batch galvanizing. The coating's formation mechanism was also discussed.

2. EXPERIMENTAL

The substrate is cold rolled sheet of plain carbon steel (containing in weight%: 0.17C, 0.38Mn, 0.13Si, 0.01S, 0.016P). The size of the coupons is 50mm×50mm×5mm. Hot dip experiments were completed with a crucible furnace. The Zinc alloy bath is composed of $w(Al)=6\%$, $w(Mg)=3\%$. The process for hot dip is as follows: each specimen was degreased in 10% NaOH at 70°C for 10 minutes, pickled in 10% HCl for 5 minutes in an ultrasonic cleaner, fluxed in an aqueous solution of zinc ammonium chloride at 70°C, and dried at 120 °C for 5 min, then dipped in the Zn alloy bath for 2 minutes at 475°C (Zn-Al-Mg coating1 was obtained) and 455°C (Zn-Al-Mg coating2 was obtained) respectively.

Comparative experiments were conducted with Zn-0.2%Al coating hot dipped at 455°C, with the same substrate and processing parameter with Zn-Al-Mg coating 2.

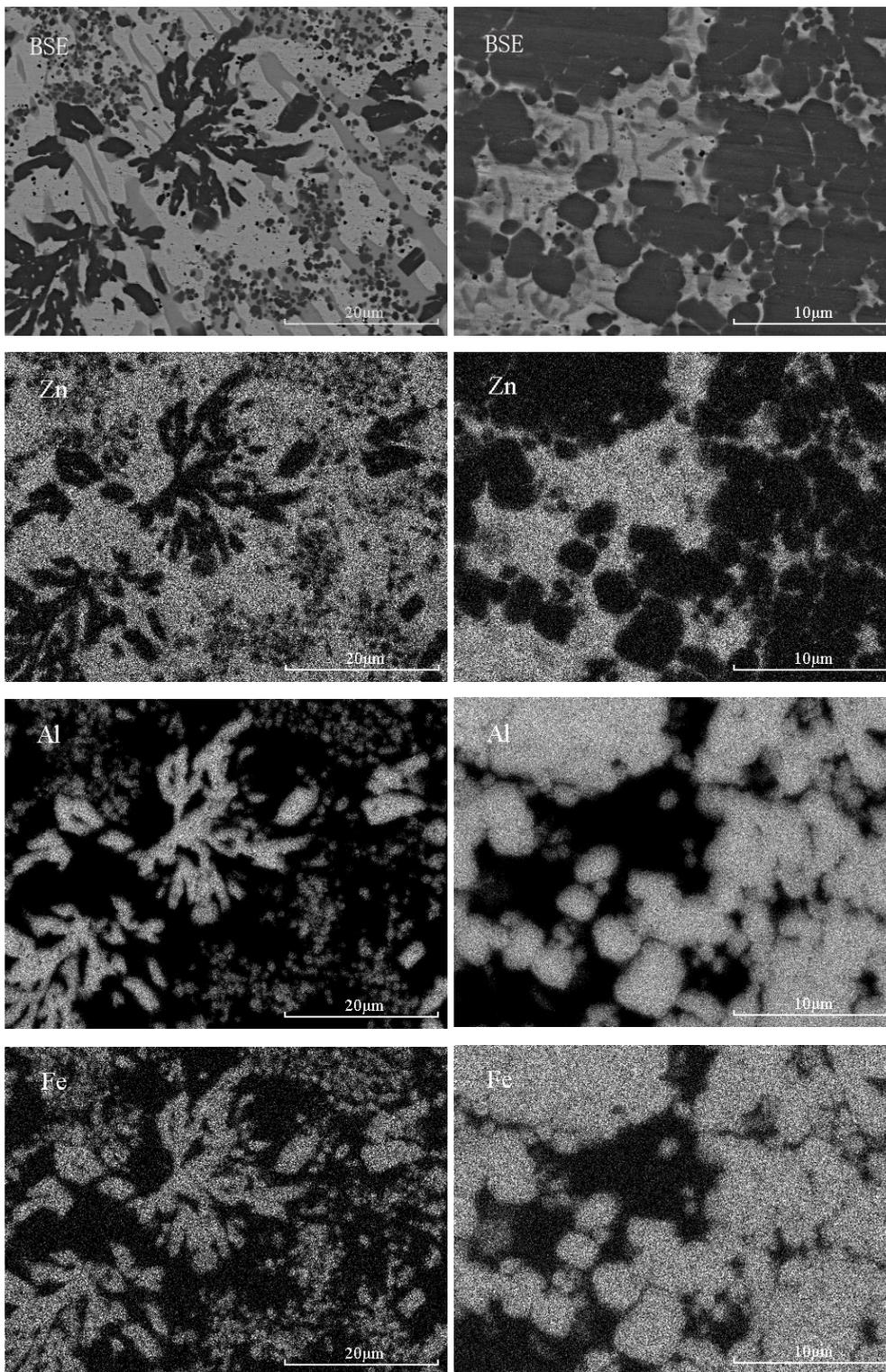
The coatings were examined using X-ray diffractometer (XRD, Panalytical X' pert Pro, Cu $K\alpha$), scanning electron microscopy (SEM, ZEISS Supra55) coupled with energy dispersive X-ray spectrometry (EDX, Oxford).

Potentiodynamic polarization (electrochemical workstation, Parstat 2273) test was conducted with a three-electrode system on the Zn-Al-Mg coatings, and on the traditional HDG Zinc coating (Zn-0.2%Al) for comparison. A 3.5% NaCl solution of pH 7.5 was used. Pt was used as auxiliary electrode, saturated calomel electrode (SCE) as reference electrode and sample as working electrode, the area was 1 cm². Scanning rate was 0.5mV/s. Scanning range was from -0.25V to 0.25V, vs. open circuit potentials. The neutral salt spray test was performed according to ISO9227 with NaCl solution of 50 g/l, the test temperature was 35°C, Average collection rate was 1.5ml/h.

3. RESULTS AND DISCUSSION

3.1 Morphologies and composition of the coatings

Fig.1 is the morphologies (backscattered electron image) and the corresponding element mappings of the coatings. The coatings were polished up to 1 μ m grade with diamond paste, then washed with alcohol in an ultrasonic bath and dried. Zn, Zn-Mg, Al-Fe phases exist in both coating1 and coating2 according to EDX element mappings. Zn is the main phase in coating1, and Al-Fe is the main phase in coating2.



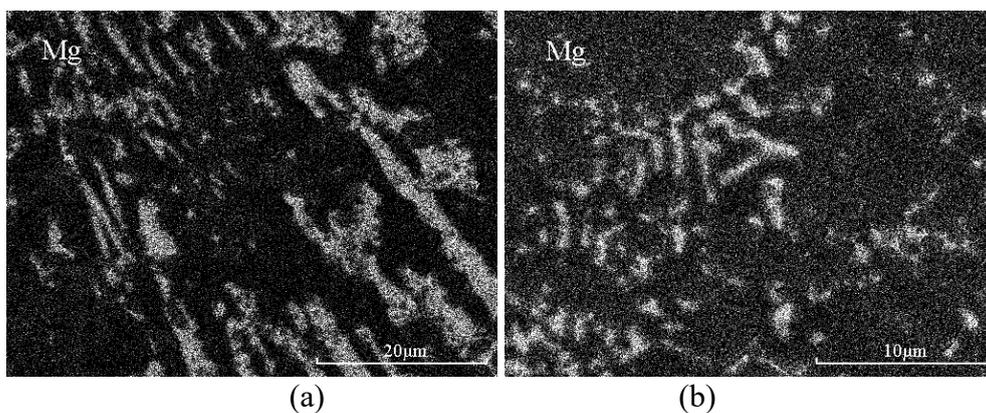
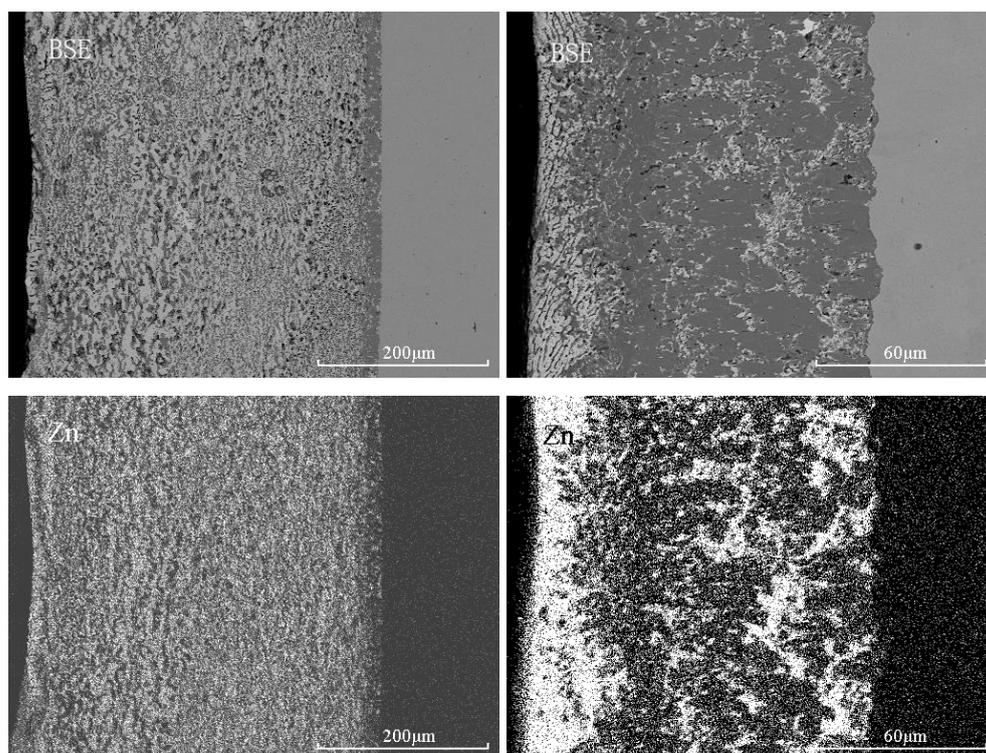


Figure 1. Backscattered electron morphologies and the corresponding element mappings of the coatings (a) Zn-Al-Mg coating1 (b) Zn-Al-Mg coating2

3.2 Cross sectional morphologies and composition

Fig.2 shows the cross sectional images and the element mappings of Zn-Al-Mg coating1 and coating 2 respectively. The result is consistent with Fig.1. In addition, coating1 consists of a mainly fine and uniform eutectic coating with a thin interface layer; coating 2 mainly consists of a columnar Al-Fe coating, with Zn rich eutectic structure exist at the top of the coating, and some eutectic exist among Al-Fe phase columnars. Mg distribution is relatively uniform across the section and is omitted here.



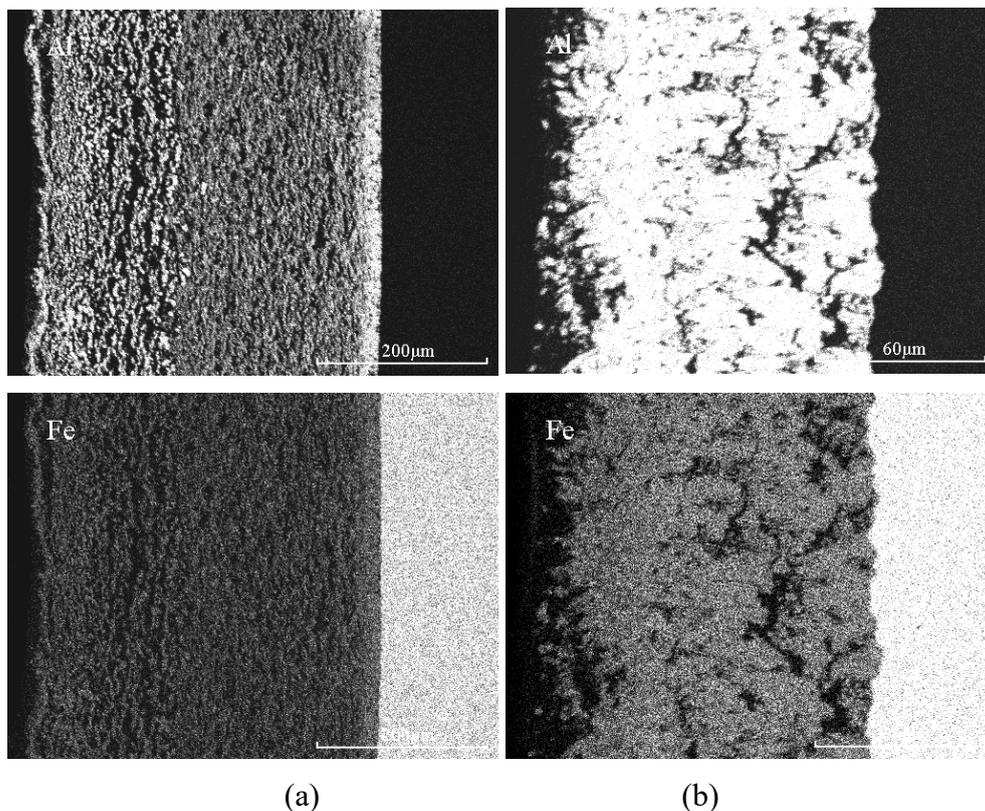


Figure 2. Cross-sectional backscattered electron images and element mappings of coatings (a) Zn-Al-Mg coating1 (b) Zn-Al-Mg coating2

3.3 Structural characterization

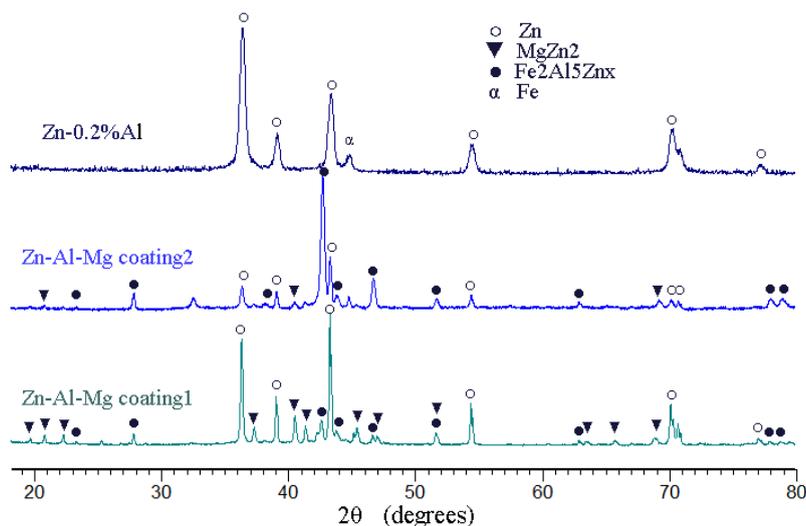


Figure 3. XRD spectra of Zn-Al-Mg coating1, coating2 and Zn-0.2%Al

Fig.3 shows the XRD spectra of Zn-0.2%Al, Zn-Al-Mg coating 1 and coating 2. The coatings were polished up to 1 µm grade with diamond paste, and washed with alcohol in an ultrasonic bath. Zn rich eutectic structure at the top of the coating 2 was removed by polishing. Zn-0.2%Al coating mainly consists of Zn phase. There exist Zn, MgZn₂ and Al₅Fe₂Zn_x in Zn-Al-Mg coating 1 and Zn is the

dominating phase. Similarly Fe₂Al₅Zn_x, Zn, MgZn₂ exist in Zn-Al-Mg coating 2, but Fe₂Al₅Zn_x is the main phase in coating 2.

3.4 Corrosion test

Zn-Al-Mg coating 2 has a higher corrosion potential than Zn-Al-Mg coating 1 and Zn-0.2%Al. The corrosion current I_{corr} of coating 2 is slightly smaller than coating 1. Both of the Zn-Al-Mg coatings have much smaller I_{corr} than that of Zn-0.2%Al (Fig. 4). Corrosion parameters are listed in table 1.

The samples for neutral salt spray test were polished to a remaining thickness of 50μm before test. The coating life was determined by 5% rust area percentage, and is an average value calculated from three individual values for each kind of coatings. The corrosion resistant life of Zn-Al-Mg coating 1 (1850 h) and coating2 (2248h) is approximately 6 and 7.3 times that of Zn-0.2%Al (308h).

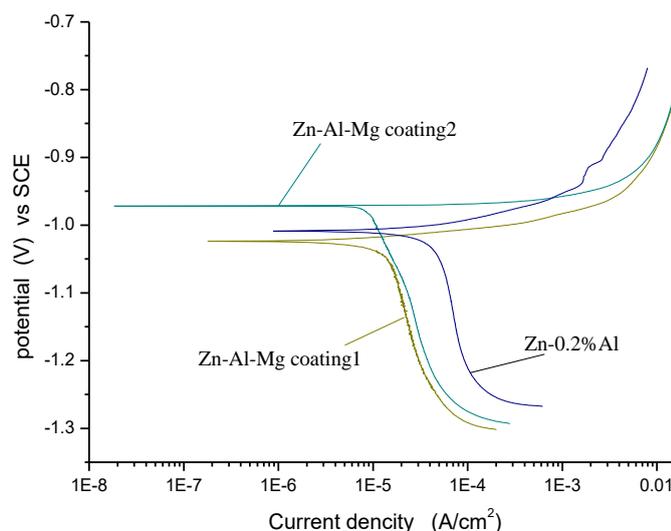


Figure 4. Potentiodynamic polarization plots of Zn-Al-Mg coating1, coating2 and Zn-0.2%Al in 3.5%NaCl

Table 1. A comparative list of corrosion parameters of different coatings

	Zn-0.2%Al	Zn-Al-Mg coating 1	Zn-Al-Mg coating2
Potential (E _{corr}), V	-1.012	-1.021	-0.979
Current (I _{corr}), mA/cm ²	4.982×10 ⁻⁵	1.336×10 ⁻⁵	9.245×10 ⁻⁶

3.5 Discussion

In the traditional industrial galvanizing, a small amount of Al (0.2 wt% also) is added into the molten zinc bath, which can slow down the Fe/Zn interface reaction. An extremely thin layer of Fe₂Al₅Zn_x is formed at the Fe/Zn interface, immediately when the steel sheet is dipped into the zinc

bath. This thin layer then act as a barrier to inhibit or retard the formation of the brittle Fe–Zn intermetallic compounds at the interface, and thus is called inhibition layer[1].

After the nucleation stage, the growth of the interfacial layer is controlled by diffusion of aluminum and zinc from the melt to the intermetallic/steel interface and of iron from the substrate to the intermetallic/melt interface[8,11,12]. The interfacial layer is mainly composed of $\text{Fe}_2\text{Al}_5\text{Zn}_x$ [13,14], FeAl_3 is also found in some studies[15,16].

The results of EDX element mapping and XRD show that both coating1 and coating2 are diffusion coatings. Al containing phase is $\text{Fe}_2\text{Al}_5\text{Zn}_x$, Al phase is not detected in either of coating1 and coating2.

The formation of Al-Fe compound is a strong exothermic reaction. With high Al content, inhibition layer has no opportunity to form because the reaction proceeds rapidly[1,17,18]. The thickness of coating2 is usually thinner ($100\mu\text{m}$ also) than coating1, probably because the volume expansion when $\text{Fe}_2\text{Al}_5\text{Zn}_x$ is formed and the stress in the coating causes cracking and spalling during coating growth. Evidence for the spalling is that steps obviously exist on the surface of coating 2.

Coating1 can be very thick (up to $400\mu\text{m}$ at testing condition). Al and Fe diffuse in melt, intermetallic compounds form when they encounter. The viscosity of the melt near the sheet increases with Al-Fe compounds in it, so thick coating adheres to the steel sheet when drawing out of the melt.

4. CONCLUSION

Different from the overly eutectic coating, two coatings obtained in this study in hot dipping Zn-6%Al-3%Mg alloy were all diffusion coatings, Al containing phase was mainly $\text{Fe}_2\text{Al}_5\text{Zn}_x$, no Al phase was detected in the coatings. One coating is Zn rich and the other is Al rich. Both of them have excellent corrosion resistance.

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