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Enhanced Fe-Al Interfacial Reaction in Hot-Dip Zn-Al-Mg Alloy-Coated Steel by Adding Si to the Molten Bath

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This study investigated the impact of Si addition on Al-Fe intermetallic layer formation and growth in a Zn-6%Al -3%Mg coating bath. The presence of trace amount of Si in the bath created a continuous η-Fe_2Al_5 layer at the Fe/coating interface at a low bath temperature, while an incomplete θ-Fe_4Al_{13} layer was formed with almost no Si added. It is widely acknowledged that Si atoms can fill vacancies along the *c*-axis of the orthorhombic Fe_2Al_5 unit cell, preventing Al diffusion and impeding the growth of Fe_2Al_5. The presence of Fe_2Al_5 containing Si can also suppress Fe dissolution. Findings of this study suggest that the addition of Si may promote the dissolution of Fe in the initial stage of Fe-Al reaction and provide a strong driving force for η phase formation at the substrate/bath interface. Therefore, with a small amount of Si added to a galvanized bath with a composition close to the eutectic point, a lower bath temperature can be used while still ensuring good Fe/coating adhesion.

Keywords: *Silicon, Interfacial reaction, Intermetallic layer,* Fe_2Al_5*,* Fe_4Al_{13}

1. Introduction

In hot-dip galvanizing, the formation of a continuous and dense inhibition layer at the Fe-Zn interface is critical for ensuring strong adhesion between the coating and substrate, and guaranteeing the formability of the coating. To inhibit the formation of brittle Fe-Zn intermetallic compounds [1], Al is deliberately added to various Zn baths, including GI coatings (<1%Al), Galfan (Zn-5%Al), Galvalume (Zn-55%Al), and a range of Zn-Al-Mg coatings. The type of Fe-Al intermetallic compounds that form depends on the Al content in the coating bath. Research has shown that Fe_2Al_5 is the ideal phase structure for the intermetallic layer at the steel/coating interface due to its superior thermodynamic stability and toughness, as suggested by Muhannad's work [2] using first-principles calculations based on density functional theory (DFT).

Although extensive studies have been conducted on the inhibition layer formed in GI baths containing 0.3%Al or less, with $Fe_2Al_{5-x}Zn_x$ being the main phase, the inhibition layer formed in GL bath, with the main phase structure still being $Fe_2(Al,Si)_{5-x}Zn_x$, there is no consensus on the inhibition layer for coatings with an Al content between 5-7%. Some studies, including those by Hinterberger [3] and Manna [4], have reported no Fe-Al intermetallic grains or layers at the steel/coating interface for Galfan coatings with 5-7%Al, using a dip temperature of 450 ºC and shorter time. Żelechower's analysis [5] of commercial Galfan coating samples found only monoclinic $FeAl_3Zn_x$ (or $Fe_4Al_{13}Zn_x$) crystals at the Fe-Zn interface, even when heated at 600 ºC for 5 minutes. Wang's study [6] on a simulated continuous hot-dip Galfan suggested that the interface layer consists entirely of $Fe_4Al_{13-x}Zn_x$ crystals. Chen *et al.* [7] found in their study that, when dipped for a longer time, the fully-formed inhibition layer for low-carbon steel in a 5%Al bath had a reaction path of Fe (substrate)/Fe_2Al_5-Zn_x/$FeAl_3$-Zn_x/Galfan (melt).

There are fewer studies on the inhibition layer formed in Zn-Al-Mg coatings with an Al content of 5-7% but Hiroki Yokoi's work [8] on the steel/coating interface layer in a Zn-6Al-3Mg bath found no inhibition layer at

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400 ºC-2s, and only Fe_4Al_{13} was observed at the steel/coating interface for 400 ºC-3600 s. Increasing the bath temperature to 460 ºC led to the formation of an η-Fe_2Al_5 phase through a solid-solid reaction with α-Fe, partially transferring the initially formed θ-Fe_4Al_{13} phase.

Galvanizing coatings, whether Galfan or Zn-Al-Mg, containing 5-7%Al, are close to the eutectic point, which lowers their melting point (approximately 380 ºC), theoretically allowing for lower bath temperatures during production. This not only improves the service life of the zinc pot equipment but also reduces cooling requirements. However, when galvanizing at lower bath temperatures, the lack of intermetallic layers at the steel/coating interface, or only the presence of Fe_4Al_{13}, cannot guarantee strong adhesion between the coating and substrate.

In this study, using a Zn-Al-Mg bath with 6%Al-3%Mg, trace amounts of Si were added to promote the formation of a continuous and dense Fe_2Al_5 inhibition layer at reaction temperatures of 410 ºC to 450 ºC. The effect of Si addition on the formation of Fe-Al intermetallic compounds was also analysed.

2. Experimental

Continuous hot-dip galvanizing experiments were carried out using 0.5 mm thick IF steel on an Iwatani simulator. The sample size was 120 × 220 mm, and the steel composition is listed in Table 1. The steel sheets were thoroughly cleaned and heated to 800 ºC, then held for 60 s at a dew point of -50 ºC under a 10%H_2-N_2 atmosphere before being cooled to the bath temperature (410 ºC, 430 ºC, 450 ºC). The samples were quickly immersed in the molten zinc pot for 3 seconds, and the zinc layer thickness was controlled to 12 μm using an N_2 gas knife. The samples were rapidly cooled to 50 ºC at a rate of 15 ºC/s. The galvanizing bath composition used in the experiment are listed in Table 2.

The adhesion between the steel sheet and coating was evaluated using the 9J ball impact test and 3M® Scotch®600 adhesive tape pull-off test. A hydrochloric acid solution containing hexamethylenetetramine was used to remove the zinc coating and observe the inhibition layer at the steel/coating interface. The microstructures of the prepared samples were observed using a scanning electron microscope (SEM) operated at 20 kV. The elemental distribution in the depth direction of the sample was studied using LECO750a glow discharge spectroscopy (GD-OES), and at least 3 points were detected on both sides of each sample to confirm reproducibility and select a representative result. A FEI Helios Nanolab 600i focused ion beam (FIB) scanning electron microscope was used to prepare cross-sectional TEM thin film samples. Prior to FIB milling, platinum deposition was used to protect the surface metal layer from damage during Ga ion milling. A JEOL 2100F high-resolution scanning transmission electron microscope (TEM) was used to observe the prepared cross-sectional thin film sample. The microstructure of the Fe-Al intermetallic layer at the steel/coating interface was studied in detail at a bath temperature of 430 ºC.

3. Results and Discussion

3.1 Adhesion between Coating and Substrate

The adhesion between the coating and substrate was assessed via the ball impact test, and the results are presented in Table 3. The results indicates that without Si addition, the bond strength between the coating and substrate was inadequate for samples obtained at galvanizing temperatures of 410 ºC and 430 ºC. Fig. 1

Table 1. Chemical composition of the IF steel used in this study

Element	Fe	C	Si	Mn	P	S	Al	Ti	Nb
wt%	Bal.	0.003	0.006	0.16	<0.015	<0.01	0.035	0.045	0

Table 2. The galvanizing bath composition

ID	Basic composition	Si content /wt%	Bath temperature / ºC
A	6Al-3Mg	< 0.005	410, 430, 450
B		0.1	

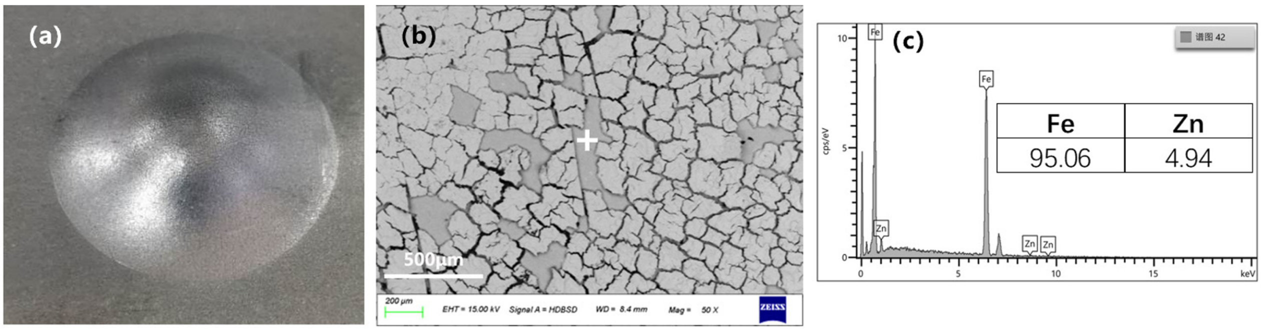

Fig. 1. Ball impact evaluation of the sample obtained in bath A at 430 ºC (a) appearance of ball impact site, (b) coatings peeled off from the substrate, (c) EDX analysis of the substrate under the peeled-off coatings

illustrates numerous cracks on the top of the 9J ball impact deformation area, and some coatings peeled off from the substrate during the 3M®Scotch®600 adhesive tape pull-off test. The area under the peeled-off coating was mainly composed of Fe with a small amount of Zn, and no Al element was detected, indicating insufficient Fe-Al reaction at this area. However, the addition of 0.1%Si into the galvanizing bath resulted in the formation of a good bond between the coating and substrate, even at 410 ºC.

Table 3. Adhesion test conducted via the ball impact test

ID	410 ºC	430 ºC	450 ºC
A	NG	NG	OK
B	OK	OK	OK

3.2 Morphology and phase change of inhibition layer

As the inhibition layer plays an essential role in ensuring adhesion between the coating and substrate, we examined the substrate/coating interface listed in Table 3 after removing the zinc coating with a hydrochloric acid solution. Fig. 2 shows that in the galvanizing bath without Si addition, needle-like substances only appeared locally at the coating/substrate interface at 410 ºC. As the bath temperature increased to 430 ºC, the needle-like substances gradually became larger and denser but still couldn't cover the substrate surface entirely. When the bath temperature was raised to 450 ºC, the morphology of the coating/substrate interface changed from needle-like to granular, with a decreased volume of each granular substance compared to the needle-like substance. After adding

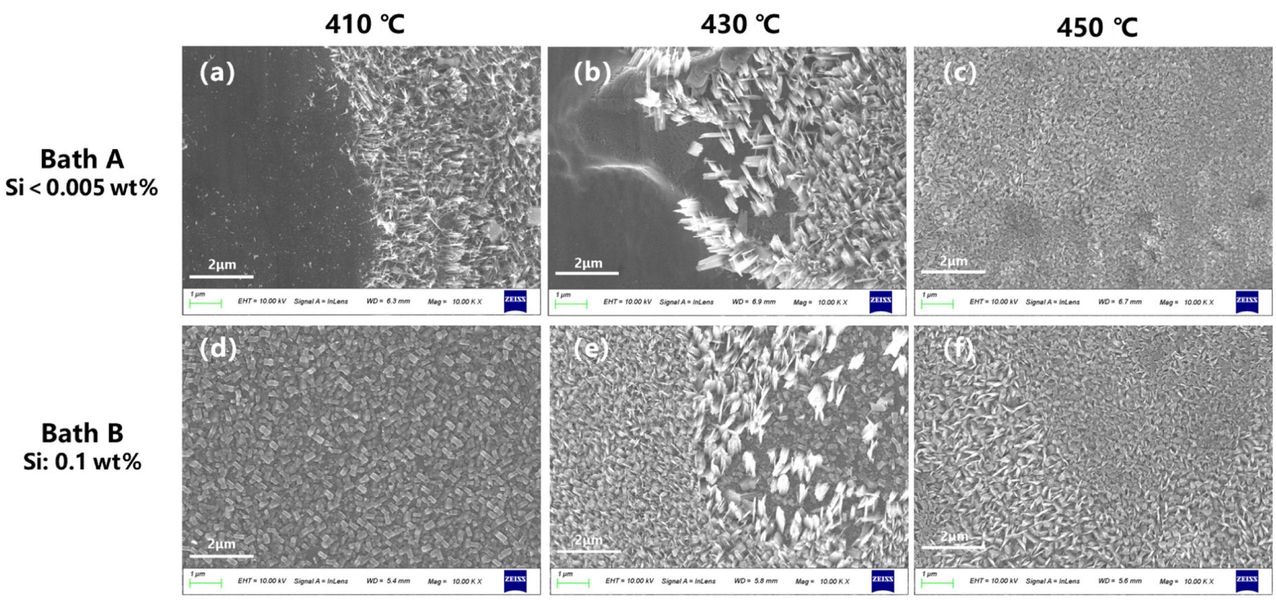

Fig. 2. The coating/substrate interface after removing zinc of the samples prepared under different conditions

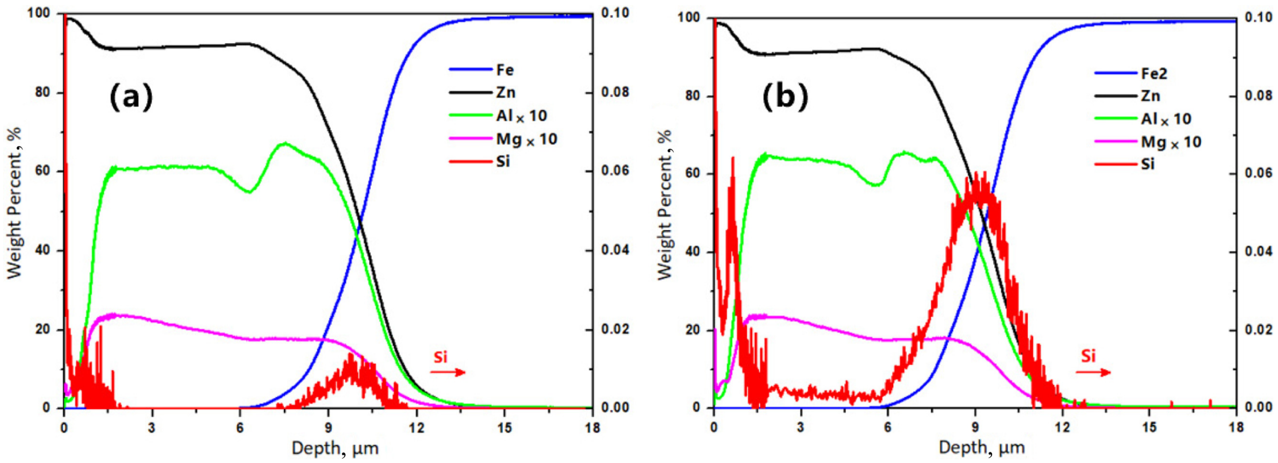

Fig. 3. GDS analysis of the depth distribution of elements in the coating obtained from samples prepared in two different baths: (a) without Si addition and (b) with Si addition at 430 ºC

0.1%Si into the galvanizing bath, a dense and uniform granular substance covered the coating/substrate interface even at 410 ºC, with the disappearance of the needle-like substance. An observation at 430 ºC showed the appearance of a needle-like substance on top of the granular substance, resulting in a bilayer structure. At a galvanizing temperature of 450 ºC, the bilayer inhibition structure tended to be complete and dense.

The GD-OES analysis of the element distribution in the depth direction of the coating presented in Fig. 3 reveals that the adjustment of the bath composition had no significant effect on the element distribution of Zn, Fe, Al, and Mg. Nonetheless, the addition of Si greatly enriched the surface of the coating and the substrate/

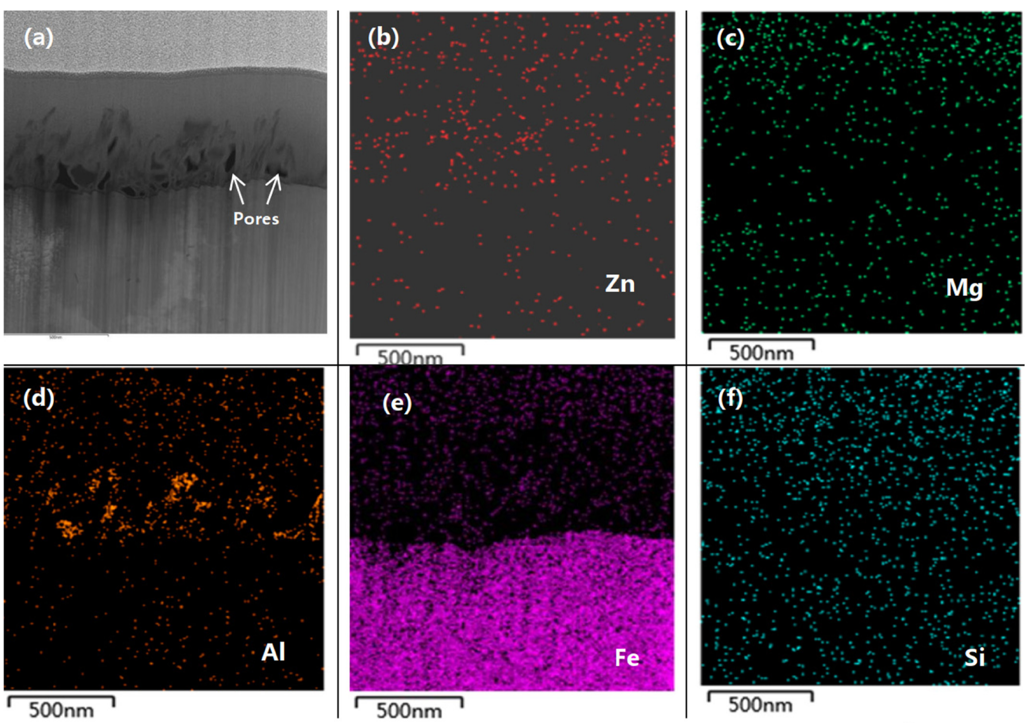

Fig. 4. EDS surface scanning analysis of the interface layer obtained in the 430 ºC galvanizing Bath A

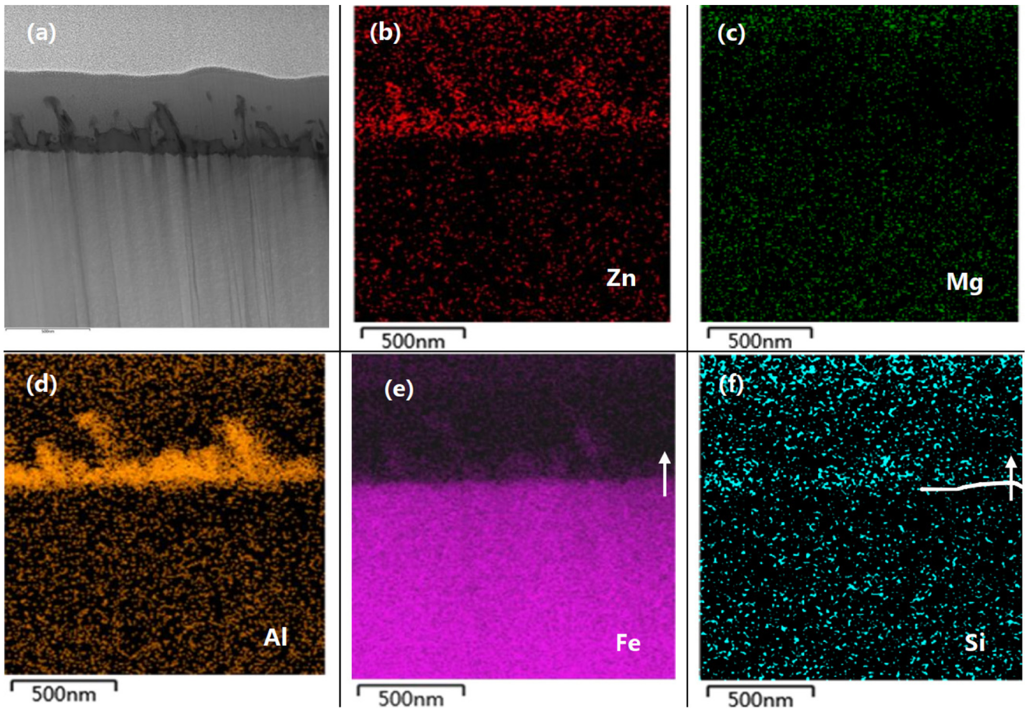

Fig. 5. EDS surface scanning analysis of the interface layer obtained in the 430 ºC galvanizing Bath B

coating interface, with a significant impact on the element distribution in the depth direction of the coating. The variations in interface layer morphology and structure shown in Fig. 2 are likely influenced by the enrichment of Si element.

Thin film samples of coating/substrate interface obtained in the 430 ºC galvanizing bath for Bath A and Bath B were prepared using FIB technology, as shown in Fig. 4a and 5a. During the thinning process by Ga ion milling, several pores were created in the inhibition layer in Fig. 4a. The inhibition layer thickness at the coating/substrate interface was only 50-500 nm due to the short reaction time between the substrate and the galvanizing bath. In comparison to the coating obtained from the bath without Si addition (Fig. 4), Fig. 5 shows evident enrichment of Al and Zn elements on the coating/substrate interface. Additionally, we observed signs of Fe dissolution from the substrate into the coating along the arrow direction, and the Si content in the coating was higher than that in the substrate.

To determine the intermetallic compound phase at the coating/substrate interface of the two compositions in the 430 ºC baths, we analysed the interfacial layer using TEM and Selected Area Electron Diffraction (SAED) techniques. The atomic coordinates of Fe_2Al_5 and $FeAl_3$ (Fe_4Al_{13}) were referenced from [9] and [10], respectively. Fig. 6 presents the analysis results of the intermetallic compounds obtained from the sample prepared in the Bath A without Si addition. In Fig. 6b, the needle-like Al-enriched substance near the substrate side was confirmed as Fe_4Al_{13} by SAED under TEM mode. The high-resolution image of the needle-like substance in Fig. 6d was identified as Fe_4Al_{13} from the Fourier Transform (FFT) diffraction spot analysis. The crystal plane spacing was measured to be 0.23 nm.

With the addition of Si, Fig. 7a presents an identifiable interface in the inhibition layer (3# region). In Fig. 7b, the high-resolution image of the needle-like substance near the coating side (1# region) revealed a crystal plane spacing of 0.202 nm from the FFT analysis, confirming the substance to be Fe_4Al_{13}. For the particle substance near the substrate side in the 2# region of Fig. 7a, the SAED pattern and simulation pattern matched only with Fe_2Al_5. From these results, we confirmed that the samples obtained in Bath B have a bilayer inhibition layer structure. Additionally, the particle-like substances consisted of Fe_2Al_5, while the needle-like substances were Fe_4Al_{13}.

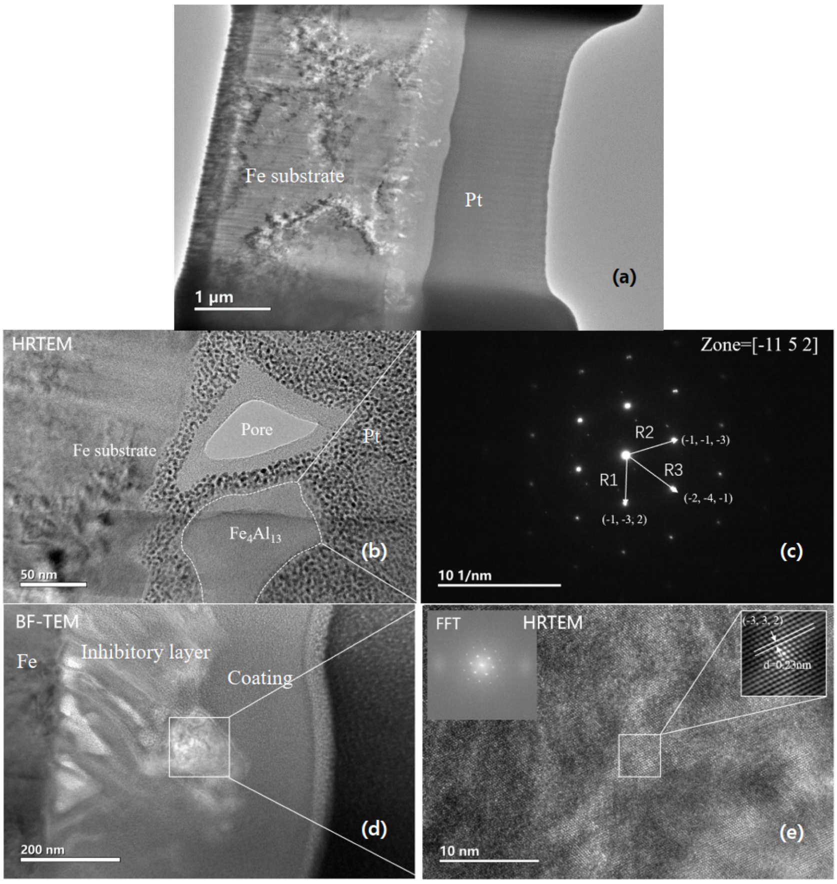

Fig. 6. TEM analysis of the coating/substrate interface obtained in the 430 ºC galvanizing Bath A: (a) bright field phase at low magnification, (b) high-resolution image of the needle-like substance near the substrate side, (c) corresponding SAED pattern of the selected area in b, (d) bright field phase at high magnification of the needle-like substance near the coating side, (e) corresponding high-resolution image of the selected area in d

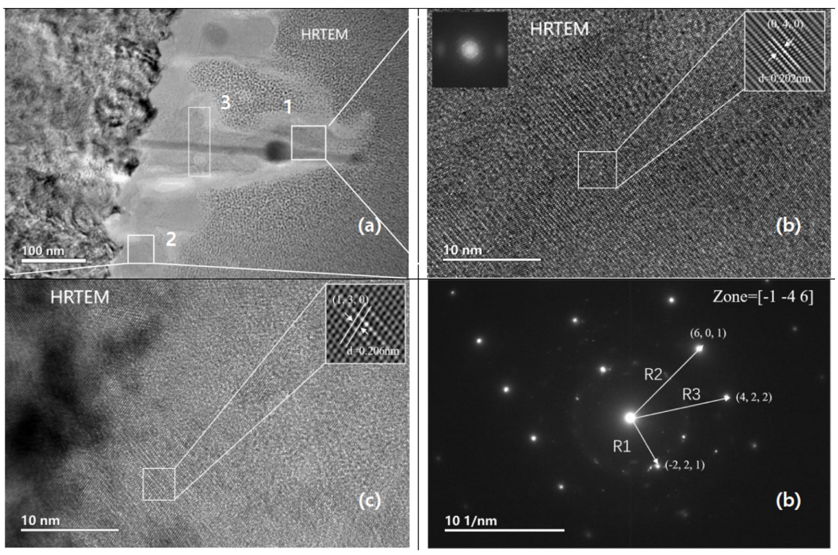

Fig. 7. TEM analysis of the coating/substrate interface obtained in the 430 ºC galvanizing Bath B: (a) high-resolution image of the coating/substrate interface substance under low magnification, (b) high-resolution image and FFT diffraction spot of the needle-like substance near the coating side at site 1 in a, (c) high-resolution image and FFT diffraction spot of the particle substance near the substrate side at site 2 in a, (d) corresponding SAED pattern of the particle substance near the substrate side at site 2 in a

3.3 Phase transformation mechanism of the inhibition layer

In this study, the Fe/Zn alloy interface layer was observed with a short immersion time and without Si addition, and it was found to be similar to that reported by Hiroki Yokoi *et al.* [8], as shown in Fig. 2. At low temperatures, only the θ-Fe_4Al_{13} phase nucleates and grows on the substrate. Hiroki's analysis suggests that the dissolution of Fe initiates the reaction between the substrate and the galvanizing bath. The dissolution of Fe provides Fe supersaturation to the Zn alloy melt near the steel, leading to the initial formation of the θ phase in the early stage of the diffusion reaction. According to the calculation of the phase diagram of Zn-Mg-Al-Fe quaternary alloy, the Fe content that triggers the transition from L + θ two-phase zone to L + θ + η three-phase zone needs to reach about 3.5 at%. Increasing the galvanizing temperature is the most effective method to increase Fe dissolution in the substrate. In this study, when the temperature was increased to 450 ºC, the θ phase underwent a transition to the η-Fe_2Al_5 phase.

It is generally believed that Si addition inhibits the growth of Fe_2Al_5 intermetallic compounds, on the one hand, by occupying the vacancies in the Fe_2Al_5 phase and blocking the diffusion channels of Al atoms, and on the other hand, by forming a barrier to further Fe dissolution from the substrate through the formation of Fe_2Al_5 containing Si and Zn. Therefore, adding Si to enhance

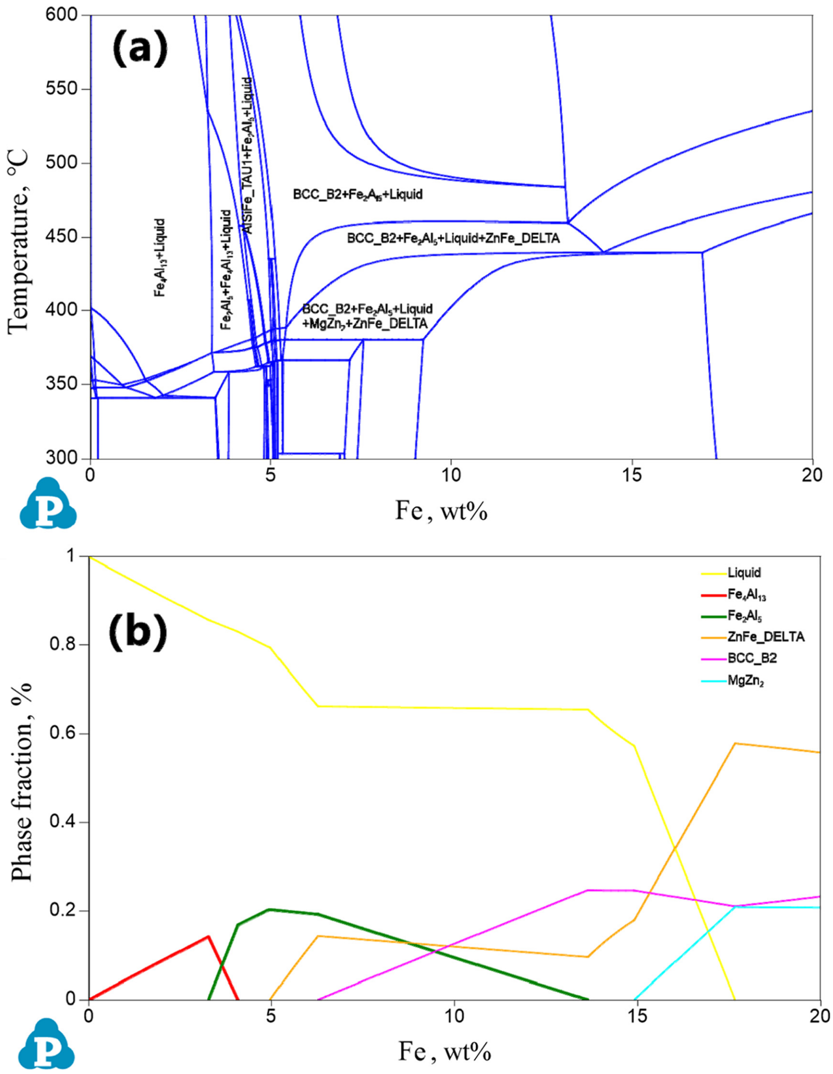

Fig. 8. The vertical sectional phase diagram (a) and the variation of precipitation phase content (b ~ c) under conditions with and without Si

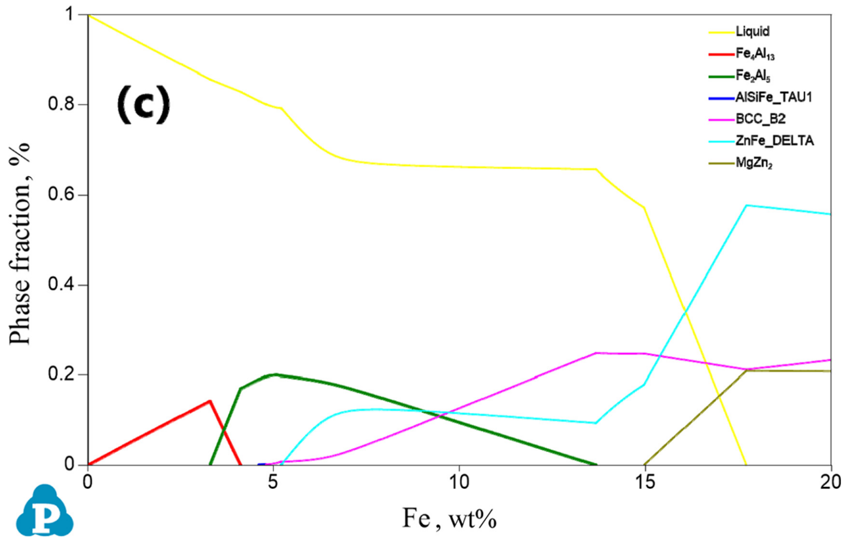

Fig. 8. (Continued) The vertical sectional phase diagram (a) and the variation of precipitation phase content (b ~ c) under conditions with and without Si

the interface reaction is not usually considered for Zn alloy coatings with low Al content (5-7 wt%) and weak Fe/Al interface reaction. In this study, 0.1%Si was added to the Zn alloy bath of composition A, and it was found that at 410 ºC, the coating/substrate interface had already formed a Fe_2Al_5 inhibition layer with better toughness than Fe_4Al_{13}, and there was no peeling of the coating in the 9J ball impact test. At 430 ºC, the coating/substrate interface formed a bilayer structure consisting of Fe_2Al_5 particles and needle-like Fe_4Al_{13} above it.

Thermodynamic phase diagrams are a powerful tool for describing the phase transformation of coating alloys. Therefore, we used Pandat software to calculate the vertical sectional phase diagram (Fig. 8a) and the variation of precipitation phase content (Fig. 8b and c) under conditions with and without Si to further explain the $\theta \rightarrow \eta$ phase transition process. The results indicate that in the absence of Si, at the initial stage of the interface reaction between the strip and the galvanizing bath, the lower free energy Fe_4Al_{13} phase is first precipitated at the interface [11], forming the $L + \theta$ two-phase region as the strip dissolves continuously. Due to the presence of a liquid channel in this phase region, Fe dissolves further and ultimately enters the $L + \theta + \eta$ three-phase region. The reaction product phase at the interface is closely related to the Fe content. When a certain amount of Si is added, the same phases precipitate at the interface and enter the $L + \theta + \eta$ three-phase region, eventually entering the $L + \eta + \tau_1$ three-phase region. These results indicate that, from a thermodynamic perspective, both the θ-Fe_4Al_{13} phase and the η-Fe_2Al_5 phase are equilibrium phases of the interface reaction between Zn-6Al-3Mg and the strip. However, the difference in their generating order may be determined by the kinetics of Fe dissolution.

Based on the experimental observations and thermodynamic calculations, it is suggested that adding Si to the Zn-6Al-3Mg galvanizing bath not only inhibits the growth of Fe_2Al_5, but also promotes its formation by facilitating the dissolution of Fe during the early stages of Fe-Al reaction. This mechanism leads to the rapid formation of a granular Fe_2Al_5 inhibition layer at the coating/substrate interface even at a lower bath temperature of 410 ºC. As the bath temperature increases to 430 ºC, the enhanced dissolution of Fe leads to the formation of a needle-like Fe_4Al_{13} layer on top of Fe_2Al_5 due to the diffusion of some Fe through the Fe_2Al_5 inhibition layer. When the bath temperature reaches 450 ºC, a denser dual layer structure is formed.

Previous research on Zn alloy baths did not report a similar effect of Si. However, a similar finding was reported in Naoki's study [12], where the presence of Si in the Fe-Si alloy samples promoted the early dissolution of substrate Fe and the formation of the η-Fe_2Al_5 phase on the surface of α-Fe, compared to pure Fe samples.

The role of Si in the interface reaction is summarized in Fig. 9. It is believed that Si promotes the dissolution

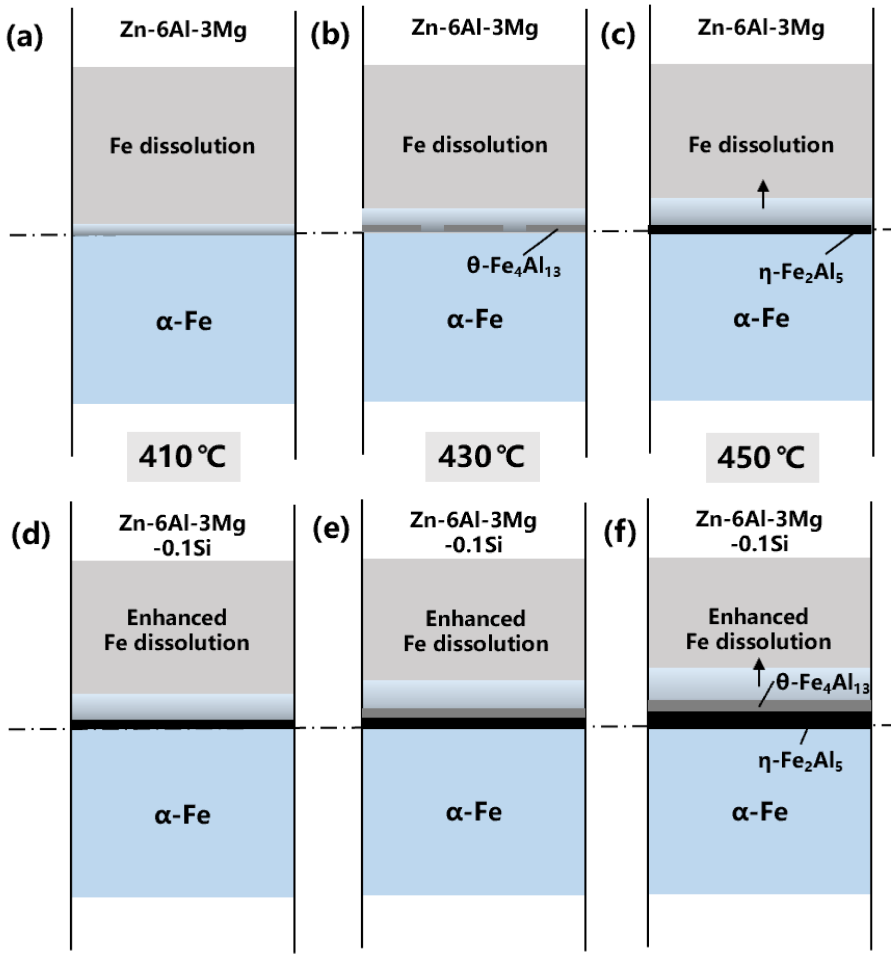

Fig. 9. Schematic diagram of the effects of bath temperature and Si addition on the interface reaction

of substrate Fe in the early stages of Fe-Al reaction, enabling Fe in the area close to the substrate to reach the condition required for the transition from the $L + \theta$ two-phase region to the $L + \theta + \eta$ three-phase region at a lower bath temperature. After promoting the formation of the Fe_2Al_5 inhibition layer, Si inhibits the further growth of Fe_2Al_5 intermetallic compounds.

4. Conclusion

This study employed a Zn-6Al-3Mg galvanizing bath to examine the impact of bath temperature and trace Si addition on the formation and growth of Fe-Al intermetallic compounds at the Fe/coating interface on IF steel surfaces.

Without Si addition, at bath temperatures of 410 ºC and 430 ºC, no complete coverage inhibition layer could be formed on the Fe substrate. The formed Fe-Al inhibition layer was a needle-like Fe_4Al_{13} structure that did not ensure good adhesion between the coating and the substrate. As the bath temperature reached 450 ºC, the inhibition layer structure gradually transformed from needle-like Fe_4Al_{13} to granular Fe_2Al_5.

With trace Si addition, even at a low bath temperature of 410 ºC, a dense and uniform granular Fe_2Al_5 inhibition layer could be formed on the Fe substrate. As the bath temperature was increased to 430 ºC, the inhibition layer structure consisted of a granular Fe_2Al_5 on the side close to the substrate, as well as a needle-like Fe_4Al_{13} on top of Fe_2Al_5 and near the side of the alloy coating. Good adhesion between the coating and substrate was obtained at all temperatures.

In addition to its acknowledged role of inhibiting the growth of Fe_2Al_5 intermetallic compounds by blocking the diffusion channels of Al in the Fe_2Al_5 phase, trace Si addition can also promote the dissolution of substrate Fe in the early stages of Fe-Al reaction. This provides a stronger driving force for the formation of Fe_2Al_5 intermetallic compounds on the substrate/coating interface.

These results suggest that by adding trace amounts of Si, it is possible to produce hot-dip zinc products close to the eutectic point at lower galvanizing temperatures while ensuring good adhesion between the coating and substrate.

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