Study on the interface reaction layer of hydrogen reduction hot-rolled high-strength steel hot-dip galvanizing

Yihao Liu¹, Chengfa Ding¹, Jianchao Li², Rui Lu¹, Guangxin Wu¹ ⓜ and Jieyu Zhang¹

¹ School of Materials Science and Engineering & State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy, Shanghai University, Shanghai 200444, People’s Republic of China
² Department of Intelligent Manufacturing, Hebei College of Industry and Technology, Shijiazhuang 050091, People’s Republic of China

E-mail: gxwu@shu.edu.cn

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Abstract

In this paper, the instability mechanism of the Fe-Al inhibition layer produced by the interfacial reaction in the Al-containing zinc melts on the hydrogen-reduced steel is studied in detail. The results show that the surface morphology of hydrogen-reduced hot-rolled steel at different temperatures is mainly divided into porous and dense states. Due to the different surface activity of the steel after hydrogen reduction, the reaction degree of the galvanized interface is also significantly different. When the Al content is 0.2 wt%, no Fe-Al inhibition layer is detected at the interface. After that, the influence of Al content on the interface inhibition layer was explored. The research results showed that under the same reduction temperature and inhibition time, the higher the Al content, the more obvious the inhibition layer formed at the interface. Finally, by extending the dipping time, it was confirmed that the Fe-Al inhibition layer had undergone a destabilization and cracking transformation process, that is, the zinc solution permeated the Fe-Al inhibition layer, and the iron interface and the liquid zinc were in direct contact, resulting in the formation of the Fe-Zn outburst structure, which was also aggravated the process of breaking the Fe-Al inhibition layer.

1. Introduction

Hot-dip galvanizing is a method to improve the corrosion resistance of materials. It immerses a steel with clean surface in liquid zinc for 3s~30s, in order to form a protective coating on the surface of pure iron. At present, hot-dip galvanizing is still one of the most widely used, effective, and most economical processes in anti-corrosion of steel materials [1–4].

Hot-rolled steel strip is usually descaled before galvanizing. At present, the main way to remove the oxide layer is pickling [5–7]. However, pickling will cause serious environmental pollution [8–10]. It is well known that removal of oxide layer by hydrogen reduction is one of the most environmentally friendly method. The method has some advantages on high reduction efficiency, no damage to the substrate, and strong bonding in the subsequent hot-dip process [11, 12].

In the conventional continuous hot-dip galvanizing process, when the conventional Al content is probably 0.2 wt%, zinc atoms will quickly merge into the Fe-Al layer to form a zinc-rich layer, which causes the formation of the Fe₂Al₅ phase to be hindered, and the coating will appear to fall off. In addition, due to the thick coating obtained in the pure zinc bath, a small amount of aluminum is generally added to the zinc bath in order to limit the thickness of the galvanized layer on the steel in the continuous hot-dip galvanizing process. This is due to the fact that the Gibbs free energy of the reaction of Fe-Al is more lower than that of the Fe-Zn reaction, the reaction between Fe and Al is preferred in aluminum-containing zinc solution [13]. Although the affinity of Fe and Al is greater [14–16], in order to form a continuous Fe-Al layer, the Al content must reach a certain level. The method of hydrogen reduction has a series of advantages. However, in the current results, it has been shown that there is a porous iron layer with loose structure on the surface of reduced steel [12, 17, 18]. The porous iron has many pores on the surface which increases the specific-surface-area, and it will lead to a violent react with Al in the
bath, resulting in a rapid decrease of Al content in the liquid zinc at reaction interface. This may affect the subsequent interface reaction with the bath.

Up to now, there have been many reports in the literature about the effect of Al content in the bath on interfacial reaction during the continuous hot-dip galvanizing process. Tan et al.\textsuperscript{19} mentioned a hot-dip galvanizing process for porous iron surface, in which the Al content was increased to 0.5 wt% for increasing the Al content at the reaction interface. The dipping time was extended to more than 3s to promote the diffusion of Al. This process can promote the formation of aluminum-rich inhibition layer on the reaction interface. The results show that the obvious inhibition layer formed at the interface. Zhang et al.\textsuperscript{20} pointed out that in order to improve the adhesion of the coating, the Al content in the bath needs to be significantly higher. If the hot-rolled steel strip is reduced at a low temperature of 550 °C during the direct hydrogen reduction process, the same adhesion of the coating as that of pickled steel can be obtained only when the Al content is increased to more than 3%. Nevertheless, if the Al content is too high, it will cause poor weldability of the coating.

Based on the above literature summary, it can be concluded that it is feasible to replace the traditional pickling process by hydrogen reduction of hot-rolled steel strip. In addition, the influence of steel morphology and Al content in liquid zinc on the formation of Fe-Al inhibition layer and Fe-Zn phases at different reduction temperatures is rare. As a result, the influence of hydrogen reduction temperature and Al content in hot-dip galvanizing process on the formation of Fe-Al inhibition layer and Fe-Zn phases was studied by hydrogen reduction instead of traditional pickling method.

2. Experimental method

A type of hot-rolled steel with thickness about 4 mm produced by Baosteel was used in the experiment. The heating temperature of the sheet was 1200–1300 °C, the final rolling temperature was 800–900 °C, and the coiling temperature was 200–300 °C. Substrate composition (wt%): 0.1–0.2 C, 1.5–2.0 Mn, 1.0–1.5 Si, 0.3–0.5 Al, 0.01–0.05 Ti, Fe balance. The size of the sample for each experiment was 40 mm × 10 mm × 4 mm. The isothermal reduction experiments were performed on a high-temperature tubular vacuum furnace. The specific experimental steps were as follows: alkaline solution (2.5 wt% NaOH + 2.5 wt% Na\textsubscript{2}CO\textsubscript{3} + 95 wt% H\textsubscript{2}O) was prepared in a beaker and heated to 80 °C in a water bath. The steel was washed in a hot alkali solution for 15 min to remove oil stains on the surface. Subsequently, the residual lye was rinsed with deionized water, and then dried. Plug it into the quartz tube, close the flange, turn on the vacuum pump to evacuate to −0.1 MPa, hold it...
for 3–5 min, and observe whether the barometer indication changes; if there is no change, pass into high-purity nitrogen (99.999%) to atmospheric pressure and repeat 3 times to completely exhaust the air in the furnace tube. After the high temperature furnace reaches the target temperature, the quartz furnace tube is quickly pushed into the furnace cavity and kept for 5 min after the temperature is raised to the target temperature and then the high-purity nitrogen is switched to 30 pct H₂-N₂ mixture with a gas flow rate of 1 l min⁻¹. After the reduction for 1 min, 3 min, and 5 min, the reduction atmosphere was switched to high-purity nitrogen, the furnace tube was quickly drawn out, and it was cooled to room temperature under a high-purity nitrogen atmosphere. Then take out the sample and enter it into the dipping equipment for galvanizing under the protection of nitrogen atmosphere.

The aluminum content of the liquid zinc used in the galvanizing experiment is 0.2 wt%, 0.5 wt%, 1.0 wt%, respectively, and the bath temperature is about 470 °C. The surface of the reduced steel is dipped in the zinc bath for 5s, 10s, 15s, 30s. After the process is completed, the steel is taken out of the zinc pot quickly and quenched to prevent the interface reaction from continuing. All experiments were repeated under the same conditions to rule out the chance of experiment. The samples was cut into 2 × 10 × 4 mm, and then ultrasonic cleaning, drying, inset polishing and corroding were performed respectively. The polished sample was corroded with 4 vol% nitric acid + 96 vol% namyl alcohol for 3–10s. VEGA-LMUH scanning electron microscope was used to take the microstructure pictures. The specific parameters were as follows: working distance of 25 mm, acceleration voltage of 0.2–30 kV. The energy spectrometer produced by Oxford Company was used for qualitative and quantitative analysis of components, and the analysis software was the INCA software of the energy spectrometer.

### 3. Results

#### 3.1. Surface and cross-section morphology of reduction layer

The surface morphology of the reduced sample of hot-rolled steel strip is shown in figure 1 [21]. It could be seen that, the surface of the sample has extremely small pores reduced at 500 °C; at 600 °C, the micropores on the surface of the sample become larger and accompanied by cracks; at 700 °C, the pores on the surface continues to expand and presents irregular shapes; after reduced at 800 °C, the sample surface sintered and shrank, and the pores are evenly distributed, individual holes shrink, and the overall porosity becomes larger.

**Figure 2.** The cross-section scattered morphology of samples reduced at different temperatures for 5 min: (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C.
Figure 2 [21] shows the cross-section morphology of the sample after reduced at different temperatures for 5 min. After being reduced at 500 °C, the cross-section morphology of the oxide scale is still similar to that of the original steel, which is in a relatively dense state; at 600 °C, small holes and multiple cracks appeared in the cross section of the reduced layer; at 700 °C, the number of holes and cracks in the oxide layer section increased sharply, and white bright sintered iron appeared at the same time. Several small cracks appeared under the interface between the reduction layer and the substrate, indicating that internal oxidation of the sample occurred here; when the temperature is 800 °C, the number of holes and cracks in the cross-section of the reduction layer increased sharply. The number of fine cracks increases below the junction of the reduction layer and the substrate, and the internal oxidation phenomenon intensifies.

3.2. The morphology of interface reaction layer

The surface morphology of the oxide layer of hot-rolled steel strip is different after hydrogen reduction at different temperatures, and the surface morphology has a great influence on the interfacial reaction in the continuous hot-dip galvanizing process. According to the work reported by Lu et al. [21], when the hydrogen reduction temperature is 500 °C for 5 min, the oxide layer of hot-rolled steel strip is not completely reduced to pure iron, and there is still some residual Fe₃O₄ in the reduction layer, so the steel under this reduction temperature could not be used as the original steel of hot-dip galvanizing. Therefore, the effect of the reduction surface morphology at 600–800 °C on the interface of Zn-0.2 wt% Al was studied. In addition, after experimental attempts, it was found that when the dipping time was less than 15s, the adhesion of liquid zinc was poor at various temperatures, thus the dipping time of more than 15s is selected for this study.

In the experiment, the hydrogen reduction temperature is 600–800 °C and the time is 5 min. The dipping time and temperature is 15s, 30s, 470 °C, respectively. Figure 3 shows the cross-section morphology after corrosion. During the process of hot-dip, the Fe at the interface of the reduced hot-rolled steel strip dissolved in
Figure 4. Scanning of interface elements of reduced surface galvanized at 700 °C for 15s.

Figure 5. Interface of galvanizing on reduced surface at 700 °C for 15s.

Figure 6. Interface of reduction galvanizing at 600 °C/800 °C (a-d: 600 °C 5s, 10s, 15s, 30s; e-h: 800 °C 5s, 10s, 15s, 30s).
the liquid zinc and form granular Fe-Zn phase. It can be seen from a2-b2 in figure 3 that after hot-dip at 600 °C for 15s and 30s respectively, obvious changes have taken place at the interface, in which the Fe-Zn particle layer generated by dipping for 30s is obviously thicker than that of hot-dip galvanizing for 15s. After being reduced at 700 °C, the microstructure of Fe-Zn on the surface of zinc coating is more obvious. With the extension of the reaction time, the Fe-Zn phase is gradually broken, and the Fe-Zn granular diffuse into the zinc layer. At 800 °C, the Fe-Zn phase is almost completely broken, and the granular Fe-Zn phases diffuse into the zinc layer. After galvanized for 30s, the Fe-Zn layer is completely broken. Except for part of the Fe-Zn phase granularities attached to the side of the substrate, the remaining granularities are completely diffused into the zinc layer.

Figure 4 shows the scanning distribution of the interface elements with hydrogen reduction temperature of 700 °C, reduction time of 5 min and dipping time of 15s. It can be seen that the Fe-Zn layer with a thickness of about 8–10 μm is formed on the surface of the substrate. The Al content is also significantly higher than that of the upper zinc layer. It can be judged that the structure of this layer is mainly the Fe-Zn phase with a small amount of aluminum. Based on the analysis of the interface morphology and element distribution, the Fe-Al layer may be directly broken and dispersed to the zinc layer when galvanized in Zn-0.2 wt% Al bath. Due to the high activity of pure iron on the reduced surface, the reaction between liquid zinc and pure iron is more intense, and Fe-Zn phase is easily formed.

According to the points analysis in figure 5 and table 1, point 1 and 3 are Fe-Zn phase granularities in the zinc layer. The point 5 and 6 are located in the Fe-Zn layer on the upper side of the substrate, and the Fe content is higher than that of the other points. And the point 7 and point 8 are located on the substrate and the galvanized layer respectively, and the content of each element is in line with the expected results.

According to the above results, since the hydrogen reduction at 500 °C is not completely reduced. When the hot-rolled steel strip surface after hydrogen reduction is galvanized in the bath with Al content of 0.2 wt%, the surface of the hot-rolled steel strip can not be effectively galvanized. In addition, when the hydrogen reduction temperature is 600–800 °C and the dipping time is less than 15s, it could not be effectively galvanized. If the time exceeds 15s, the Fe-Al inhibition layer is not found, but a large amount of Fe-Zn phases appear. For this reason, the experiment tried to adjust Al content in the liquid zinc to explore the influence of Al content on the microstructure of the galvanizing interface.

Next, hot-dip galvanizing was carried out in 0.5 wt% Al bath. Due to the similar surface morphology of the reduced samples at 700 °C and 800 °C, in order to make the experimental phenomenon more obvious, hydrogen
reduction steel at 600 °C and 800 °C were selected for galvanizing at different times. Figure 6 shows the interface morphology of hot-rolled steel strip with hydrogen reduction temperature of 600 °C/800 °C and hydrogen reduction time of 5 min after galvanizing for 5s, 10s, 15s and 30s, respectively. Figure 7 shows the distribution of Al element at the galvanized interface of the reduced steel at 600 °C/800 °C for 5s and 15s.

It can be seen from figure 6 that the morphology of the pure iron surface at the same reduction temperature is different after various galvanizing times. After being reduced at 600 °C and galvanized for 5s, it can be seen from the element surface scanning results that there is an obvious aluminum enrichment layer at the galvanized interface. When the galvanizing time was extended to 15s, the aluminum enrichment layer had disappeared. After 5s of galvanizing on the reduced surface of 800 °C, the Fe-Al layer has been broken at the galvanizing interface from the scanning results, and only a slight aluminum enrichment layer remains. As can be seen from the morphology diagram in figure 6, the Fe-Zn phase is formed on the upper layer of the interface at this time. If the time was extended to 15s, the aluminum enrichment layer disappeared and the amount of Fe-Zn phases increased.

Summarize the above results, when the reduced hot-rolled steel strip surface is galvanized in Zn-0.5 wt% Al bath, the obvious enrichment layer can be seen after galvanized for 5s at 600 °C. While, after galvanizing for 5s, only a slight enrichment layer of aluminium remained on the reduced surface at 800 °C. When the dipping time was extended to 15s, the enrichment layer of aluminium disappeared. However, during the galvanizing process, the enrichment layer of aluminium can effectively avoid the formation of Fe-Zn phases. In order to improve the surface quality of galvanized steel, the Al content in the bath was further increased.

Then, Zn-1.0 wt% Al bath was used in the experiment. Figure 8 shows the surface morphology of hot-rolled steel strip galvanized for 5s, 10s, 15s and 30s after reduced at 600 °C/800 °C for 5 min. It can be seen that the surface morphology of pure iron with the same reduction temperature has obvious regularity after different dipping time. After the surface is reduced at 600 °C and galvanized for 5s, the interface was relatively dense and there were no obvious precipitate particles; when the dipping time was extended to 10s, a small amount of diffused particles appeared above the interface. When the dipping time exceeded 15s, a large number of granular
phase structures appeared on the upper layer of the interface. If the reduction temperature and dipping time are 800 °C and 5s respectively, the density of the interface is significantly lower than that at 600 °C, some small particle phases appear on the interface as well; After the dipping time was extended to 10s, a large number of small particle phases appeared in the galvanizing layer, and the contact between the coating and the substrate was found to be closer than that of galvanizing for 5s; when the dipping time exceeds 15s, more granular and rod-like phases appeared in the galvanizing layer, and the densification of 30s dipping time was smaller than that of 15s.

Figure 9 shows the distribution of Al at the interface of hydrogen reduced steel after 5s and 15s galvanizing at 600 °C and 800 °C, respectively. It can be seen from the results of the element surface scan that the surface after reduction at 600 °C for 5 min, there is an obvious enrichment layer of Al at the interface for 5s. When the galvanizing time was extended to 15s, the enrichment layer of Al was still obvious. According to the Al element distribution, the granular phase above the interface is also the Al enrichment phase, indicating that the enrichment layer of Al has begun to be broken off at this time, but the Fe-Al layer has not been completely broken, and no granular or rod-shaped Fe-Zn structure has been formed. If the time reaches 30s, the enrichment phase of Al had been largely broken, and a large number of aluminium enrichment granularities appeared above the interface. After the surface was reduced at 800 °C and galvanized for 5s, it can be seen from the element surface scan results that there is a very continuous enrichment layer of Al at the galvanized interface, but the enriched layer has a tendency to break. It can be seen from the morphology that the Fe-Al phase in the upper layer of the interface has fallen off to the zinc layer. When the time was extended to 15s, the enrichment layer of Al disappeared, and the rod-shaped and granular Fe-Zn structures appeared above the interface layer. The microstructure of Fe-Zn began to break and most of the rod-like Fe-Zn phases changed to granules when the dipping time was prolonged to 30s.

According to the above results, when the Al content is 0.5 wt%, the enrichment layer of Al at the interface was not obvious after hydrogen reduction at 800 °C for 5s. After increasing the Al content in the bath, an obvious aluminium enrichment layer appeared in the interface layer after the sample was reduced at 800 °C for 5s. Figure 10 and table 2 show the EDS point analysis results of the reduced surface galvanized at 800 °C for 5s. The upper layer of the interface is galvanized layer and the lower layer is substrate. Point 1 and 2, which are the points on the Fe-Al layer, and there are point 3 and 4 on the granular phases that fall off to the galvanized layer. From the table, it can be seen that contents of each element are in line with the expected results.
4. Discussion

In the process of continuous hot-dip galvanizing of modern steel strip, when the Al content in the zinc bath is greater than 0.15 wt%, Al and Fe will react to form inhibition layer, which inhibits the Fe-Zn reaction and prevents the deterioration of the coating property \[17, 22\]. However, during the immersion process, the Fe-Al inhibition layer does not persist as the dipping time prolongs \[23\]. Jordan et al \[24\] pointed out that the inhibition time depends on the Al content of the liquid zinc and the surface quality of the original steel. This indicates that the Fe-Al inhibition layer will fracture and even dissolve due to the erosion of liquid zinc. The Fe-Zn phase is formed by the violent chemical reaction between the substrate and the molten Zn that is the instability of the Fe-Al inhibition layer. Due to the large number of micro pores and cracks in the reduced iron. It is easy to form local bath chemistry in the area where the Al content decreases rapidly and the supplement of Al is difficult to reach. Thus, the Fe-Zn alloy nucleates in these locations and grows into outburst lumps. At the same time, in porous reduced iron, since the orientation of Fe-Al crystal grains formed on its matrix would be more disordered than under random conditions, this inhibition layer would be easily penetrated by Zn diffusion \[11\]. Wu et al \[17\] believe that specific surface area of steel strip is the main factor causing the difference between porous surface and relatively dense surface. The increase in specific surface area means that more Al atoms are needed to form a complete inhibition layer. Due to the increase of nucleation rate and Fe concentration caused by the increase of specific surface area of porous matrix, the aluminum atoms in the front of interface reaction are consumed in a very short time and lead to serious depletion layer. The depletion of aluminum atoms will lead to the rapid instability of Fe$_2$Al$_5$ inhibition layer and promote the corrosion and dissolution of Fe.

According to the above experimental results, it can be seen that when the surface of reduced hot-rolled steel strip is galvanized in 0.2 wt% Al. If, the dipping time is less than 15s, the zinc cannot be effectively plated. On the other hand, the Fe-Al inhibition layer cannot be detected effectively once the dipping time is more than 15s. At the same time, a large number of Fe-Zn structures are formed on the surface of the galvanizing interface. When the Al content in the bath is adjusted to 0.5 wt%, the continuous Fe-Al inhibition layer can be observed at 600 °C for 5s. After prolonging the dipping time to 15s, the Fe-Al inhibition layer is completely broken. At 800 °C for 5s, only a slight aluminum enrichment layer was observed at the galvanizing interface, meanwhile, the rod-shaped Fe-Zn phase structure began to appear above the interface. When the dipping time is extended to 15s, the thickness of the Fe-Zn layer continues to increase. Once the Al content in the bath is adjusted to 1.0 wt%, the Fe-Al inhibition layer can be effectively detected at 600 °C for 5–15s. Yet, the dipping time is prolonged to 15s, the Fe-Al inhibition layer begins to break. The Fe-Al inhibition layer can be observed on the surface of steel by hydrogen reduction at 800 °C and the dipping time is 5s. However, there is a partial fragmentation tendency. If the dipping time is extended to 15s, the Fe-Al inhibition layer disappears completely.

Bari et al \[25\] pointed out that the solubility of Fe in liquid zinc is related to the Al content. With the increase of Al content, the concentration of Fe atoms at the front of the interface will decrease. The concentration of Fe atoms at the front of the interface decreases with an increase of Al content, which avoids the problem of aluminum depletion at the interface and promotes the growth of Fe-Al inhibition layer. Isono et al \[26\] pointed out that an iron atom adsorbed by 7 aluminum atoms at the galvanizing interface. With the increase of Al content in liquid zinc, the formation driving force of Fe-Al inhibition layer will be enhanced, it is conducive to the growth of Fe-Al inhibition layer, and inhibition of Fe-Zn phases formation within a certain time. The
number of Al atoms at the interface will decrease with an increase immersion time, resulting in forming an aluminum-poor layer. At this time, the formation of Fe-Zn phases occurs in three stages: after densification, discontinuity, and spalling of the Fe-Al inhibition layer. The liquid zinc diffuses along the random large-angle grain boundaries generated during the nucleation and growth of Fe-Al grains, further penetrates the Fe-Al inhibition layer to reach the substrate, and reacts violently with Fe atoms.

The Fe solubility formula (equation (1)) proposed by Tang [27] also explained that the solubility of Fe in liquid zinc is related to the aluminum content. With the increase of aluminum content, the concentration of Fe atoms at the front edge of the interface will decrease, which solves the problem of aluminum depletion at the interface and promotes the growth of Fe-Al inhibition layer. In addition, increasing the Al content in the liquid zinc solution will increase the driving force of forming the Fe-Al inhibition layer, and increase the content of Al atoms at the interface, which is conducive to the growth of the Fe-Al inhibition layer, and inhibit the formation of Fe-Zn tissue within a certain dipping time [2].

$$\ln [Fe]^{3}[Al]^2 = 28.1 - \frac{33066}{T} \quad (1)$$

Due to the surface of hot-rolled steel strip after hydrogen reduction is more active. During the Al content in liquid zinc is low, the Fe-Al inhibition layer is not formed on the surface of reduced sheet when reacting with liquid zinc, but Fe-Zn structure is formed directly. Based on this, the fracture mechanism diagram of Fe-Al inhibition layer was drawn, as shown in figure 11. When the Al content in the liquid zinc reaches a certain level, Fe will react with Al preferentially in the bath to form Fe-Al inhibition layer. The Al content at the front of the interface decreases with the extension of the dipping time. The liquid zinc directly contacts with the pure iron at the substrate through the Fe-Al phase grain boundary, resulting in Fe-Zn phase granularities, and the Fe-Al inhibition layer will be unstable and broken. With the extension of the dipping time, the microstructure of Fe-Zn continues to grow, and then the microstructure of the upper part of the Fe-Zn layer is broken into small granularities from the rod-shaped morphology, finally, the Fe-Zn outburst structure is formed.

5. Conclusion

According to the basis of our previous research, the surface of steel strip at different reduction temperatures was galvanized by hydrogen reduction method. Further, the influence of different Al content in the bath on the formation and instability of Fe-Al inhibition layer was discussed. The following conclusions were drawn:

(1) The morphology of hot-rolled steel strip reduced by hydrogen at different temperatures is mainly divided into two types: porous and dense. The surface of steel strip reduced at different temperatures has a great influence on the formation of Fe-Al inhibition layer on the galvanized interface.

(2) The surface reduced with hydrogen cannot be effectively galvanized in Zn-0.2 wt% Al bath. When the Al content in the bath reaches 0.5 wt%, a continuous Fe-Al inhibition layer can be obtained by galvanizing under 600 °C reduction. In order to generate a continuous Fe-Al inhibition layer, the aluminum content must be greater than 1.0 wt% on the surface of galvanizing at 800 °C by reduced.

(3) Due to the different activity of the surface after hydrogen reduction, the reaction degree of the galvanizing interface is also different. There is no Fe-Al inhibition layer with low aluminum content in the bath. After the Al content reaches a certain amount, the Fe-Al inhibition layer can be unstable and broken by prolonging the dipping time.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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