

## Study on the Corrosion Resistance of Galvannealed Coatings on Different Alloying Parameters

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**Abstract:** The galvannealed coating with different Fe contents were prepared by controlling the galvannealed process parameters of hot-dip galvanized high-strength IF steel sheet, and analyzed the influence of Fe contents on the corrosion resistance of galvannealed coating. The results show that the corrosion resistance of galvannealed coating increased with the Fe content, and it was also influenced by the phase structure and the proportion of different phases in the galvannealed coating. At the same galvannealed temperature, along with the prolongation of galvannealed time, the initiative corrosion potential of galvannealed coating changed little. The compact  $\Gamma_1$  phase in galvannealed coating could improve the corrosion resistance effectively. At the same galvannealed time, the corrosion resistance of galvannealed coating was better, when the galvannealed temperature was higher.

### Introduction

Corrosion potential of hot dip galvannealed coating was rested with the balance potential of Fe and Zn. The zinc has the low site in the EMF [1, 2], and it would result in more positive corrosion potential. The change way of corrosion potential and corrosion rate of zinc alloy is very complex in the galvannealed coating, it was not only influenced by Fe contents [3], but also influenced by the intermetallic phase and alloy fine texture [4-6]. This article aims on analyzing the corrosion resistance of galvannealed coating with different Fe contents, which was prepared in different galvannealed processing parameters. It was important to make sure the influence rule of galvannealed processing parameters to the corrosion resistance of galvannealed coating. This article researched the change rule of corrosion potential, corrosion current and corrosion rate of the high-strength IF galvannealed coating with different Fe contents, which prepared through change the galvannealed temperature and galvannealed time.

### Experimental Material and Method

**Experimental Material.** Experimental material was hot-dip galvanized high-strength IF steel sheet, thickness was 0.8 mm, galvanized coating weight was 45 g/m<sup>2</sup> in the single-sided, the composition of hot-dip high-strength IF steel sheet was shown in Table 1. Cut the plate to the same specs according to the experimental request, washed and dried in the air.

Table 1. The composition (wt.%) of hot-dip galvanized high-strength IF steel sheet.

Mn	C	S	Al	Ti	Si	P
0.50	0.005	0.008	0.028	0.023	0.094	0.055

**Experimental Method.** A set of samples was heated to 450 °C in an induction heating furnace at a heating rate of 10 °C/s, and keeping 120s, 150s, 240s, 300s and 360s respectively; another set of samples was heated to 500 °C at the same heating rate, and keeping 60s, 90s, 120s, 150s and 180s

respectively; the third set of samples was heated to 550 °C at the same heating rate, and keeping 5s, 10s, 15s, 20s and 25s respectively, then quenched with water and dried in the air.

The influence of galvannealed processing parameters on the corrosion resistance of galvannealed coating was analyzed by electrochemical method. Polarization curve of galvannealed coating were measured by Galvanostat Moldel 273. Electrolytic experiment using three electrodes system, reference electrodes were saturated calomel electrode (SCE), auxiliary electrodes was platinum electrode, electrolyte was 200 g/l NaCl solution, chose the linear sweep voltammetry, made the potential scope as -0.1~0.1 V, the scanning velocity was 25~50 mV/s, scanning gap was 0.002 V, use the galvannealed plate samples as the working electrode, weathered it after scraping with acetone. Used the wax to seal up all the samples except an area about 1cm<sup>2</sup> in one surface. After measuring the area, and input it into the experimental parameters.

Input the current density and the voltage data in the experiment into ORIGIN and drew the chart after current logarithm conversion. According to the electrochemical theory, the two beeline parts of positive pole polarization curve and negative pole polarization curve can intersect one point; the abscissa of the point is the logarithm of corrosion current density. The vertical axis of the point is self-corrosion voltage. The relationship of corrosion rate and corrosion current density is as the formula (1).

$$v = \frac{M}{nF} \cdot i_{corr} = 3.73 \times 10^{-4} \frac{M}{n} \cdot i_{corr} \quad (1)$$

where, the v is corrosion rate (g/m<sup>2</sup>·h), icorr is self-corrosion current density (mA/cm<sup>2</sup>), M is the mole mass of galvannealed coating, n is the valence of galvannealed coating.

## Experimental Results and Analysis

**Influence of the Galvannealed Processing Parameters.** When the galvannealed temperature was 450 °C, the galvannealed time was 120s, 150s, 240s, 300s and 360s respectively, the result of electrochemical analysis was shown in Fig. 1 (a). As can be seen from Fig. 1 (a) that when the galvannealed temperature was 450 °C, along with the prolongation of galvannealed time, the corrosion potential increased, corrosion rate decreased, and corrosion resistance increased.

The phase structure of galvannealed coating that galvannealed at 450 °C was shown in Fig. 2, from Fig. 1 (a) and Fig. 2 can be see that the corrosion resistance of galvannealed coating was related to the phase structure in the coating, along with the prolongation of galvannealed time, the phase structure of galvannealed coating would be change. From Fig. 2 can be seen that along with the prolongation of galvannealed time, the phase structure in galvannealed coating was changed as:  $\eta \rightarrow \eta + \zeta \rightarrow \eta + \zeta + \delta_{1p} + \delta_{1k} \rightarrow \zeta + \delta_{1p} + \delta_{1k}$ . When the galvannealed time were 120s and 150s, the galvannealed coating were all comprised by  $\eta$  phase which elbowed prismatical  $\zeta$  phase with order orientation. However, when the galvannealed time was 120s, the galvannealed coating was mainly comprised by  $\eta$  phase and a little  $\zeta$  phase, and the ratio of  $\zeta$  phase in galvannealed coating was increased obviously, when the galvannealed time was 150s. The electrochemical theory showed that single phase structure had better corrosion resistance than the polyphase structure. From Fig. 1 (a), the corrosion potential had little descend, when the galvannealed time was 120s and 150s.

When the galvannealed time was 240s and 300s, there were a lot of columnar crystals  $\delta_{1p}$  phase which perpendicular to the steel substrate and the coating interface approximately at coating section near the surface, but at the site near steel substrate, there were some random orientation connected  $\delta_{1k}$  phase and some  $\eta$  and  $\zeta$  phase. Because corrosion potential of Zn-Fe alloy rested with the balance potential of zinc and iron, Zinc has the low site in the EMF, it will result in more positive corrosion potential galvannealed with lots of elements. Little Fe cannot change the pure zinc corrosion potential obviously as usual before it achieve a certain value, and the corrosion resistance of galvannealed coating will change obviously after it achieve a certain value. When the coating were mainly comprised by  $\delta_1$  phase, the Fe content was about 7.0~11.5 wt.%, more than 6.0~6.2 wt.% ( $\zeta$  phase) and 0~0.003 wt.% ( $\eta$  phase). So the corrosion potential and corrosion resistance of

galvannealed coating were increased and corrosion rate was descended. When the galvannealed time was 360s, the columnar crystals  $\delta_{1p}$  phase were disappeared entirely, and all coating section was occupied by compact  $\delta_{1k}$  phase. At this time, the corrosion resistance of galvannealed coating was increased obviously.

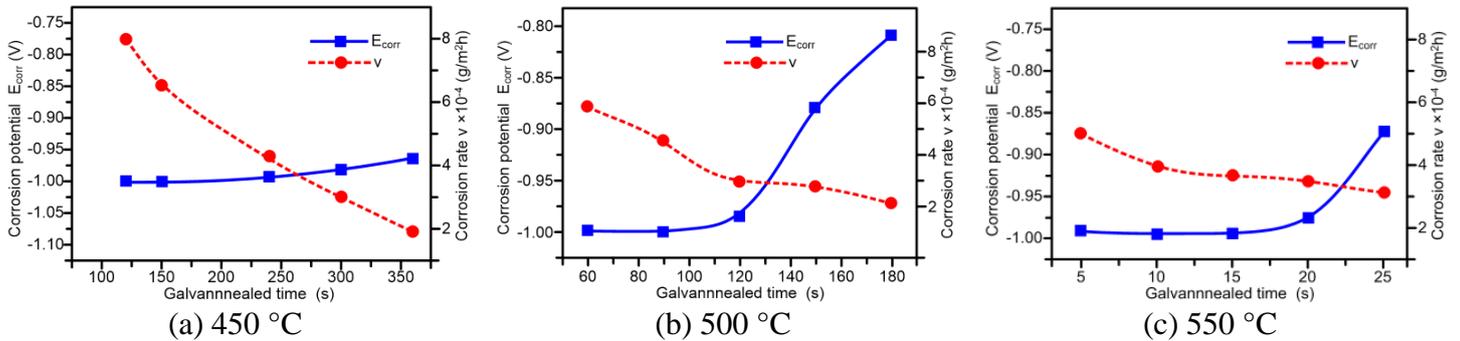


Fig. 1 The relationship of corrosion potential, corrosion rate and galvannealed time, (a) 450 °C, (b) 500 °C, (c) 550 °C.

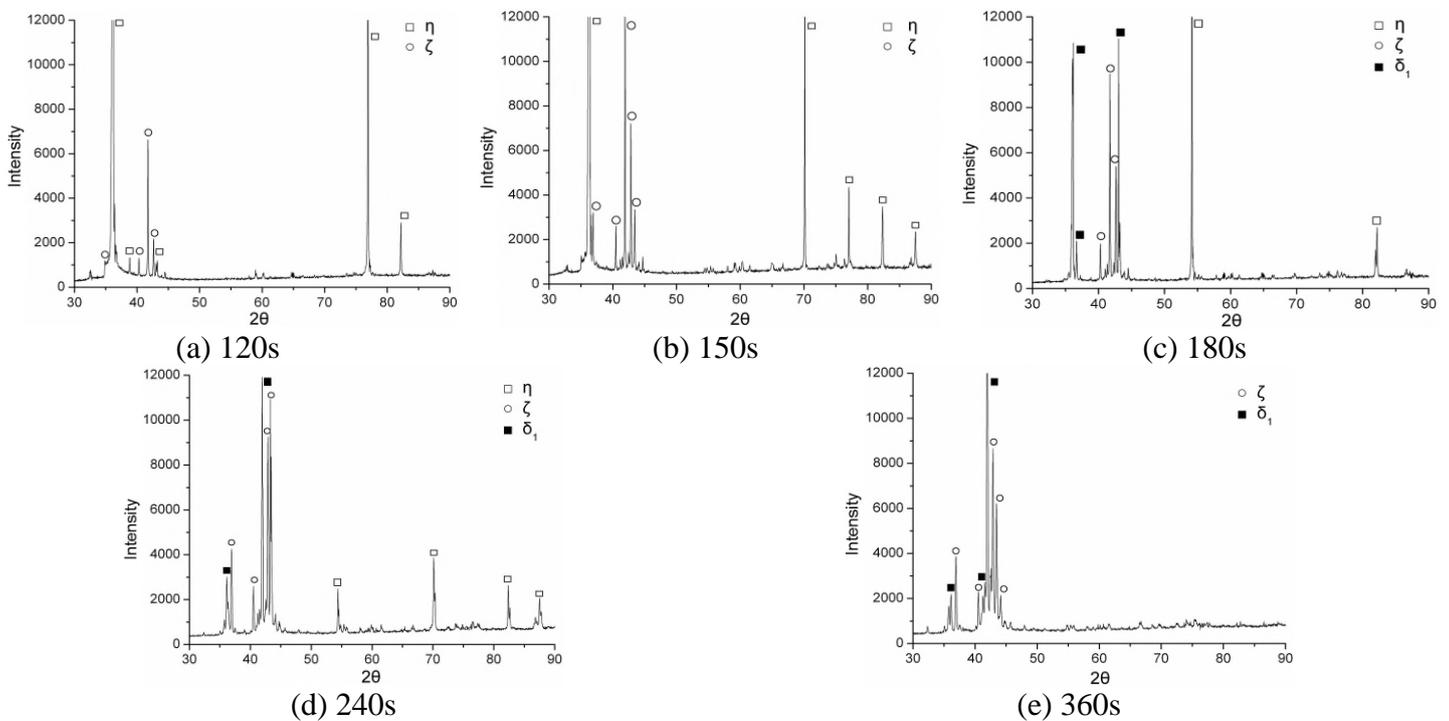


Fig. 2 X-ray diffraction patterns of different phases structure in galvannealed coating with different galvannealed time at 450 °C (a) 120s, (b) 150s, (c) 180s, (d) 240s, (e) 360s.

When the galvannealed temperature was 500 °C, the galvannealed time was 60s, 90s, 120s, 150s and 180s respectively, the result of electrochemical analysis was shown in Fig. 1 (b). As can be seen from Fig. 1 (b) that along with the prolongation of galvannealed time, self-corrosion potential increased from -0.999 V to -0.809V, corrosion rate descended from  $5.85 \times 10^{-4} \text{ g/m}^2\text{h}$  to  $2.98 \times 10^{-4} \text{ g/m}^2\text{h}$ , so when the galvannealed temperature was 500 °C, the corrosion resistance of high strength IF steel galvannealed coating was increased with the increase of galvannealed time.

The phase structure of galvannealed coating that galvannealed at 500 °C was shown in Fig. 3, from Fig. 1 (b) and Fig. 3 can be see that along with the prolongation of galvannealed time, the phase structure in galvannealed coating was changed as:  $\eta \rightarrow \eta + \zeta + \delta_{1p} \rightarrow \eta + \zeta + \delta_{1p} + \delta_{1k} \rightarrow \zeta + \delta_{1p} + \delta_{1k} \rightarrow \delta_{1p} + \delta_{1k} + \Gamma_1 \rightarrow \delta_{1k} + \Gamma_1$ . When the galvannealed time were 60s and 90s, here were lots of random shape  $\zeta$  phase in the part of coating, and the corrosion resistance of galvannealed coating had a little changed because of the increase of complex phase and Fe content.

When the galvannealed time was 120s, there was some columnar crystals  $\delta_{1p}$  phase which

perpendicular to the steel substrate and coating interface approximately at the coating section near the surface, but at the site near the steel substrate, there was some random orientation connected  $\delta_{1k}$  phase. And the corrosion potential was increased to  $-0.994V$ , corrosion rate was descended to  $3.34 \times 10^{-4} \text{ g/m}^2\text{h}$ , and the corrosion resistance of galvanized coating was increased. When the galvanized time increased to 150s, all coating section was occupied by the compact  $\delta_{1k}$  phase, which near the steel substrate and coating interface, there was a thin  $\Gamma_1$  phase between the steel substrate and coating. The coating was mainly composed by  $\delta_1$  phase, because the  $\Gamma_1$  phase was very thin, and the corrosion resistance of galvanized coating had increase. When the galvanized time increased to 180s, the galvanized coating was mainly comprised by a compact entire  $\delta_{1k}$  phase, and there was a thin tooting structure which was  $\Gamma_1$  phase. So when the galvanized times was 180s, the galvanized coating had a good corrosion resistance. However, along with the prolongation of galvanized time, the corrosion resistance of galvanized coating became good, especially when the  $\Gamma_1$  phase appeared.

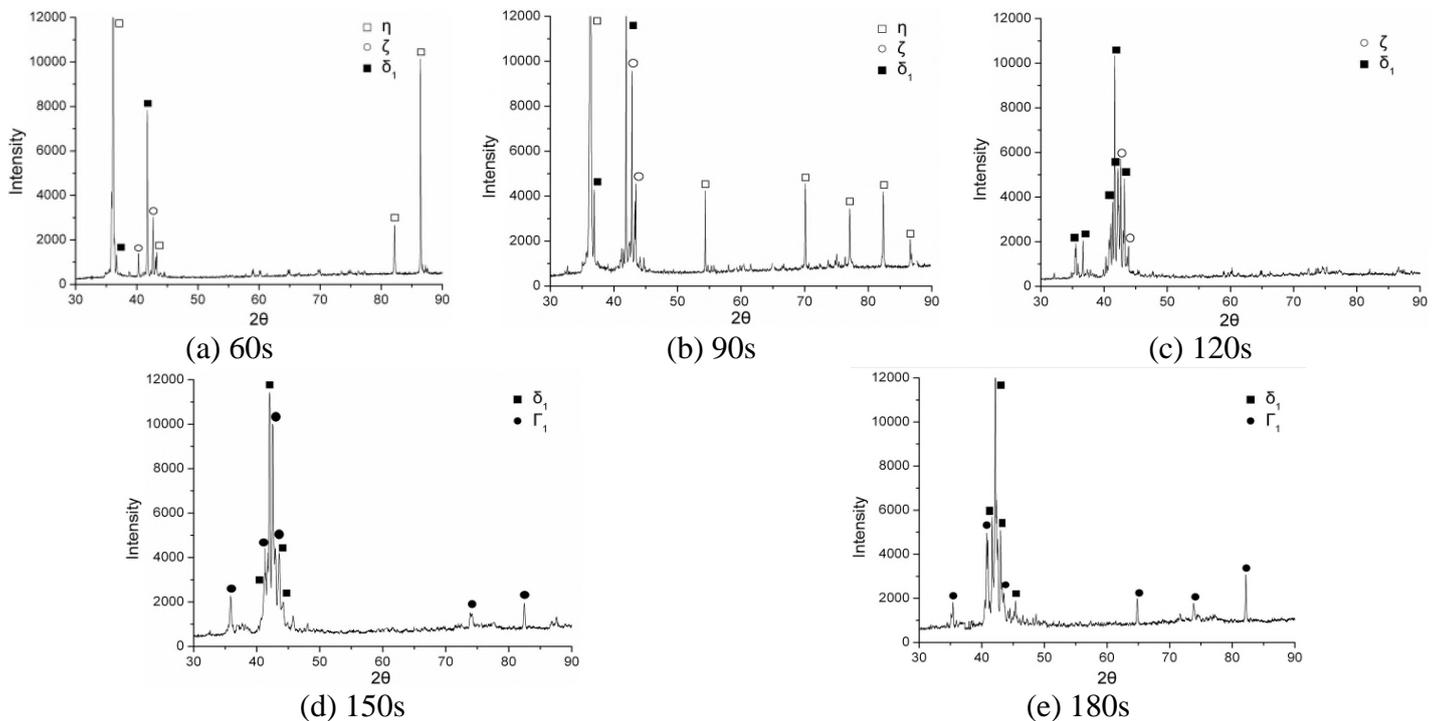


Fig. 3 X-ray diffraction patterns of different phases structure in galvanized coating with different galvanized time at 500 °C (a) 60s, (b) 90s, (c) 120s, (d) 150s, (e) 180s.

When the galvanized temperature was 550 °C, the galvanized time was 5s, 10s, 15s, 20s and 25s respectively, the result of electrochemical analysis was shown in Fig. 1 (c). As can be seen from Fig. 1 (c) that when the galvanized temperature was 550 °C, along with the prolongation of galvanized time, the corrosion potential increased, corrosion rate decreased, and corrosion resistance increased.

When the galvanized temperature was 550 °C, along with the prolongation of galvanized time, the phase structure in galvanized coating was change as:  $\eta \rightarrow \eta + \zeta + \delta_{1p} \rightarrow \eta + \delta_{1p} + \delta_{1k} + \Gamma_1 \rightarrow \delta_{1k} + \Gamma_1$ . When the galvanized time was 5s, there were lots of random stylolitic shape  $\zeta$  phase and massive  $\delta_{1k}$  phase in galvanized coating, and the corrosion potential was  $-0.990V$ , corrosion rate was  $5.01 \times 10^{-4} \text{ g/m}^2\text{h}$ . When the galvanized time was 5s and 10s, most of the galvanized coating was occupied by compact  $\delta_{1k}$  phase, only a loose  $\delta_{1p}$  phase structure near the surface and a thin tooting  $\Gamma_1$  phase near the steel substrate and coating interface, and the corrosion potential of galvanized coating increased to  $-0.996V$ . When the galvanized time increased to 20s and 25s, the coating was comprised by a compact entire  $\delta_{1k}$  phase, and there was a thin tooting structure which was compact  $\Gamma_1$  phase. The corrosion potential and corrosion resistance of galvanized coating increased obviously. So when the temperature was 550 °C, the corrosion resistance of

coating would be increased with the increase of galvannealed time. The formation of  $\Gamma_1$  phase in galvannealed coating could improve the corrosion resistance of the coating effectively.

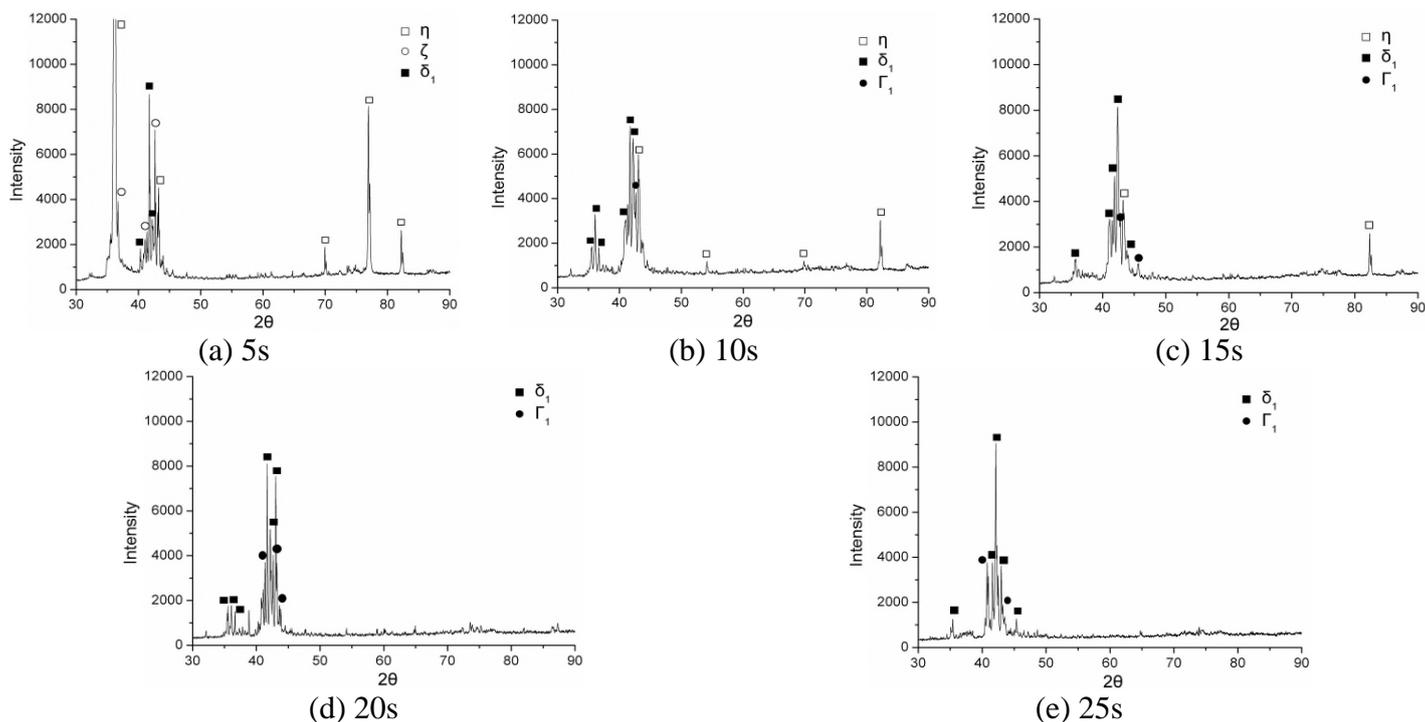


Fig. 4 X-ray diffraction patterns of different phases structure in galvannealed coating with different galvannealed time at 550 °C, (a) 5s, (b) 10s, (c) 15s, (d) 20s, (e) 25s.

From Fig. 1 (a) and Fig. 1 (b) can be seen that when the galvannealed time of high-strength IF galvanized steel sheet was 120s at 450 °C, the self-corrosion potential of galvannealed coating was -0.991 V. But when the galvannealed temperature was 500 °C, the self-corrosion potential of galvannealed coating was -0.985 V, which was higher than the galvanized steel sheet galvannealed at 450 °C. When the galvannealed temperature was 450 °C, the self-corrosion current of galvannealed coating was 0.067 mA/cm<sup>2</sup>, which more than 500 °C, that self-corrosion current was 0.030 mA/cm<sup>2</sup>, and the corrosion rate was 8.00×10<sup>-4</sup> g/m<sup>2</sup>h at 450 °C, which also more than 500 °C, that corrosion rate was 3.58×10<sup>-4</sup> g/m<sup>2</sup>h. So the corrosion resistance of coating that galvannealed at 500 °C was better than galvannealed at 450 °C.

From Fig. 1 (b) and Fig. 1 (c) can be seen that when the galvanized coating was galvannealed at 500 °C and 550 °C, the corrosion resistance of galvannealed coating was batter, when the galvannealed temperature was 550 °C, in the short time (5s), the corrosion potential of galvannealed coating was higher, when the galvannealed temperature was 550 °C than 500 °C, and the corrosion rate of galvannealed coating was lower , when the galvannealed temperature was 550 °C than 500 °C. So compared with the corrosion resistance of galvanized coating that galvannealed at different temperature, the self-corrosion potential of galvannealed coating increased, self-corrosion current and corrosion rate descended, and the corrosion resistance of galvannealed coating increased along with the prolongation of galvannealed time at the same galvannealed temperature.

**Influence of Fe Content on the Corrosion Resistance.** The relationship of corrosion potential and Fe content and the relationship of corrosion rate and Fe content at different galvannealed temperature was shown in the Fig. 5 and Fig. 6, from Fig. 5 and Fig. 6 can be see that the corrosion potential of galvannealed coating had little change, which approached the corrosion potential (-1.098V) of pure zinc, when the Fe content of galvannealed coating was low, such as the Fe content was 8.69% at 450 °C, the Fe content was 10.81% at 500 °C and the Fe content was 11.4% at 550 °C. When the Fe content in galvannealed coating reached a certain value, the corrosion potential of galvannealed coating became high obviously. From Fig. 5 and Fig. 6 can be see that the corrosion rates of galvannealed coating descended along with the increase of Fe content at different

galvannealed temperature, and the corrosion resistance of galvannealed coating increased along with the increase of Fe content.

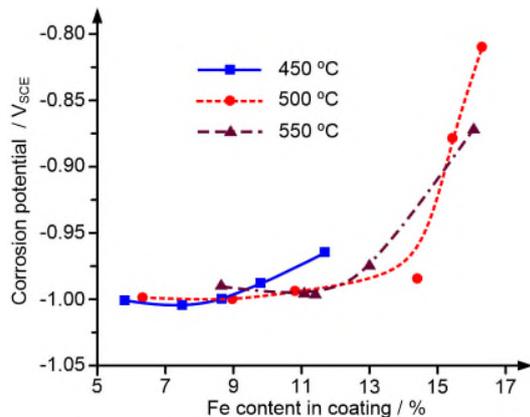


Fig. 5 The relationship of corrosion potential and Fe content.

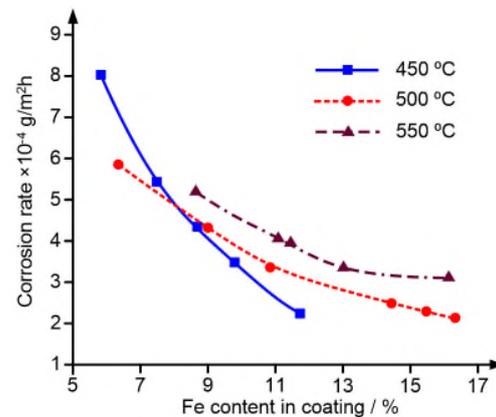


Fig. 6 The relationship of corrosion rate and Fe content.

## Conclusions

(1) The corrosion resistance of galvannealed coating was influenced by the galvannealed temperature and time obviously. Along with the prolongation of galvannealed time, the corrosion resistance of galvannealed coating became better at the same galvannealed time. And the corrosion resistance of galvannealed coating became excellent, along with the increase of the galvannealed temperature

(2) The corrosion resistance of galvannealed coating was different, when the galvannealed coating had different phase structure, when the compact  $\Gamma$  phase formed in galvannealed coating, the galvannealed coating had an excellent corrosion resistance greatly.

(3) The corrosion resistance of galvannealed coating became excellent along with the increased of Fe content in coating.

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