

Interpretation on Sebisty effect of hot-dip galvanized steels^①

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Abstract: Sebisty effect describes the unusual fact that the thickness of the hot-dip galvanizing coating on the steel containing 0.12%~0.25% silicon decreases with increasing temperature of zinc bath. The microstructures of hot-dip galvanized coatings on silicon-containing steels (0.14% Si) immersed in zinc bath at 723 K and 753 K were analyzed. It is found that the thickness of η and ζ layer decreases with the increase of temperature of zinc bath and Γ layer changes from discontinuous layer (at 723 K) to relatively continuous layer (at 753 K). The improvement of the fluidity of zinc bath due to the rising temperature of zinc bath makes η layer thinner. Moreover, the existence of relatively continuous Γ layer and the acceleration of the dissolution of ζ layer to zinc bath co-lead to the decrease of the thickness of ζ layer with increasing temperature.

Key words: zinc coatings; Sebisty effect; intermetallics; galvanized steel

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1 INTRODUCTION

The quality of hot-dip galvanized products is greatly influenced by many factors such as the constituents in steels^[1, 2], the elements in zinc bath^[3-5], and hot-dip galvanizing temperature. The constituents in steels that have the greatest influence on the galvanized coatings are silicon, which is frequently added to steel as a deoxidant during its production. Sandelin^[6] firstly reported that it was the silicon in steels that caused excessively galvanized coatings on steel articles. For a typical low-carbon steel article containing little silicon, a continuous and compact zinc protective coating with various intermetallic layers composed of Γ , δ , ζ and η is developed on the surface of a steel article, in accordance with a Fe-Zn binary phase diagram. The presence of silicon at certain levels (in the vicinity of 0.1% and above 0.3% (mass fraction)) in steels, known as reactive steels, can result in the rapid growth of the alloy layer, producing a coating of excessive thickness, having gray appearance and poor adherence^[7-9]. However, it is surprising that the steel articles with silicon content between 0.12% and 0.25% (mass fraction) produce continuous and compact coatings whose thickness decreases with increasing temperature of zinc bath. The unusual phenomena is first observed by Sebisty, called Sebisty effect. In galvanizing industry, silicon content in a large number of steel articles locates in the range of 0.1%~0.25%. Until now, the Sebisty effect has not been insufficient of experimental proof^[10]. In this paper, by investigating the microstructures of hot-dip

galvanized coatings on silicon-containing steels (0.14% Si) immersed in zinc bath at 723 K and 753 K, the interpretation of Sebisty effect was proposed.

2 EXPERIMENTAL

The 55 mm \times 40 mm \times 3 mm samples were hot-rolled steel sheets. Their chemical compositions are listed in Table 1.

Table 1 Chemical compositions of samples (mass fraction, %)

C	Si	Mn	P	S
0.17	0.14	0.23	0.010	0.005

Before being dipped in the zinc bath, the samples were prepared in a classical galvanizing treatment cycle. They were ground and then successively cleaned in an alkaline solution, pickled in an acid solution, fluxed in an ammonium chloride and zinc chloride solution and dried at 393 K. Fluxing enables steel samples to be protected before galvanizing and promotes the attack of the substrate by zinc during the first seconds of reaction. The samples were then dipped in pure zinc bath at (723 ± 2) K and (753 ± 2) K for immersion time varying from 3 min to 10 min in a laboratory simulator. After galvanizing treatment, they were quenched quickly in water. The cross-sections of the samples were analyzed by scanning electron microscopy (SEM: LEO 1530VP) coupled with an energy-dispersive spectroscopy system (EDS: INCA 300) after they

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were polished and etched with chromic acid liquor.

3 RESULTS AND ANALYSES

3.1 Microstructural change of coatings

When galvanized at 723 K and 753 K for 6 min, the samples have similar coatings with compact and continuous δ , ζ and η layer, just like those of low-silicon non-reactive steels, as shown in Figs. 1(a) and (b). At 723 K, the coating is about 157 μm in thickness including δ (12 μm), ζ (103 μm) and η (42 μm) layer. At 753 K, the coating thickness decreases by 36 μm , which is 121 μm including δ (13 μm), ζ (83 μm) and η (25 μm), as illustrated in Fig. 2.

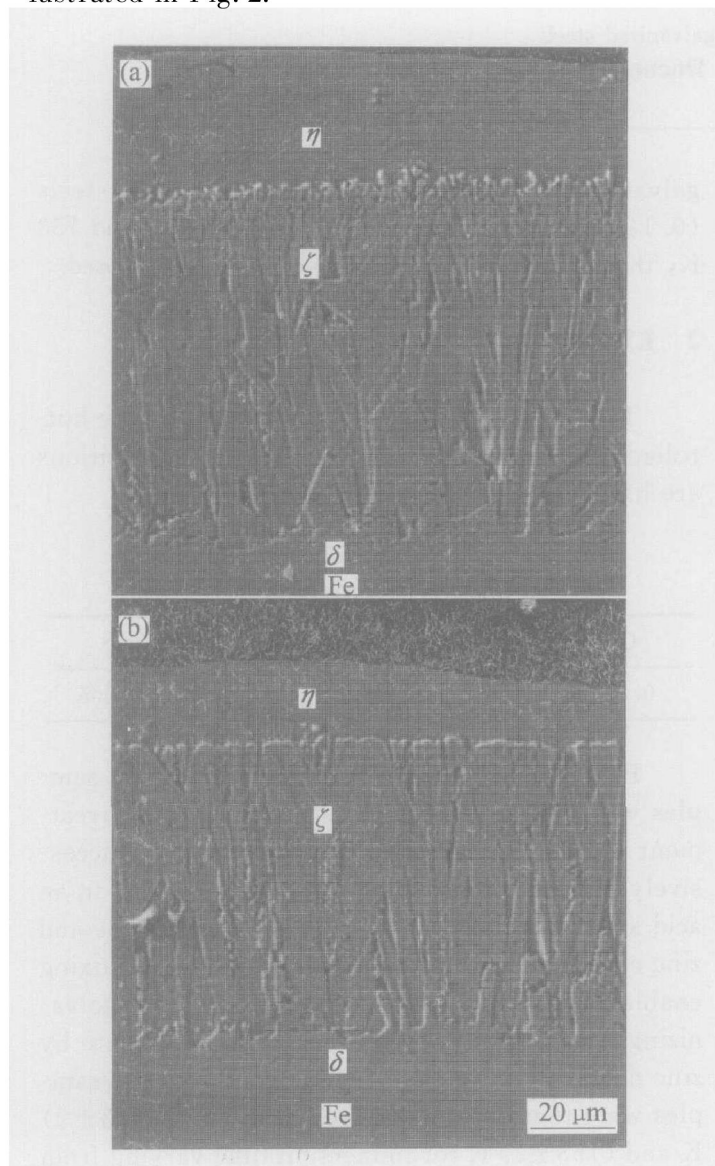


Fig. 1 Microstructures of galvanized coating on 0.14% Si steel at different temperatures for 6 min
(a) —723 K; (b) —753 K

3.2 Change of steel substrate/coating interface

The microstructure of the substrate/coating interface was observed using SEM under high magnification, as shown in Fig. 3. It is clear that Γ is

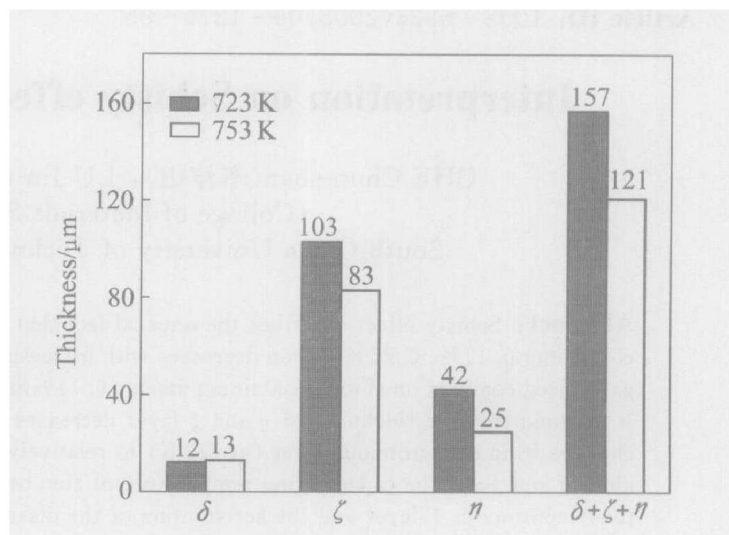


Fig. 2 Thickness of galvanized coating on 0.14% Si steel at different temperatures for 6 min

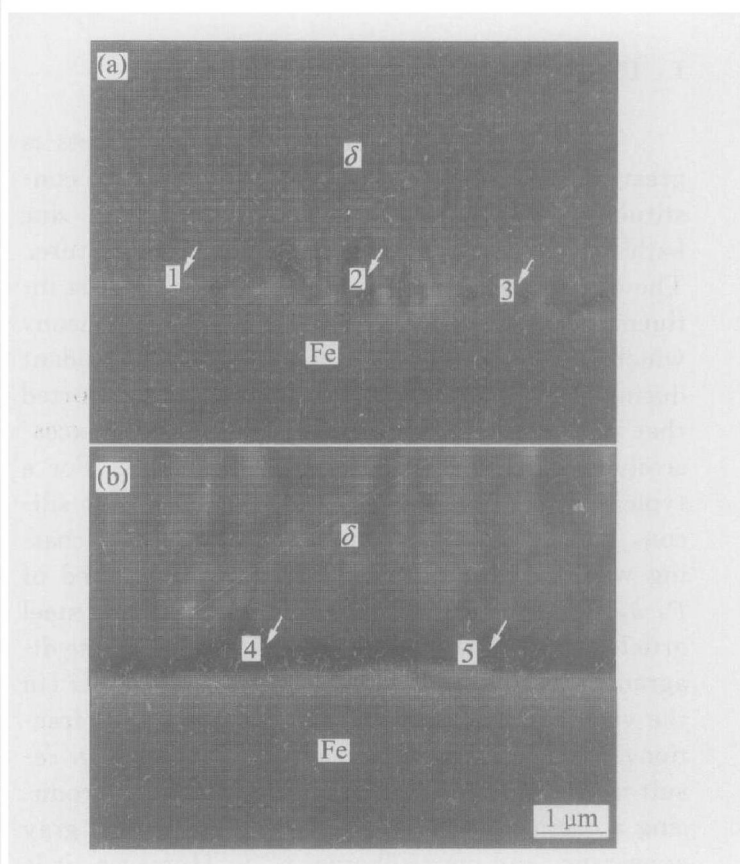


Fig. 3 Microstructures of substrate/coating interface of galvanized coating on 0.14% Si steel at different temperatures for 6 min
(a) —723 K; (b) —753 K

discontinuous at 723 K (Fig. 3(a)), while Γ becomes a relatively continuous layer with a thickness of less than 0.5 μm at 753 K, as shown in Fig. 3(b). EDS results show that the point 1 marked in Fig. 3 contains about 11% Fe (mass fraction), identified as δ phase (FeZn_{10} , 7.0%–11.5%), while the points 2, 3, 4 and 5 contain about 25%–30% Fe, identified as Γ phase ($\text{Fe}_3\text{Zn}_{10}$, 23%–27.7%).

4 DISCUSSION

By comparing the microstructure of the galvanized coating at 723 K with that at 753 K, it is found that there are three changes in the coatings with increasing temperature of zinc bath. The first one is the decrease of the thickness of the η layer, the second one is the change of the Γ layer from discontinuous to relatively continuous, the last one is the decrease of the thickness of the ζ layer.

4.1 Change of η layer

Above 693 K, zinc is in a liquid state. The viscosity μ of the zinc is dependent upon temperature, and is determined by the equation of $\mu = \mu_0 \exp(E/RT)^{[11]}$. Where μ_0 is the coefficient of viscosity at melting temperature, $0.4131 \times 10^{-3} \text{ N} \cdot \text{s}/\text{m}^2$, E is the activation energy, $12700 \text{ J}/\text{mol}$, R is the universal gas constant, $8.314 \text{ J}/(\text{mol} \cdot \text{K})$. At 723 K, the viscosity of zinc is $3.42 \times 10^{-3} \text{ N} \cdot \text{s}/\text{m}^2$. When the temperature of the zinc bath is increased to 753 K, the viscosity of zinc is decreased to $3.14 \times 10^{-3} \text{ N} \cdot \text{s}/\text{m}^2$. The decrease of the viscosity of zinc with rising temperature of the zinc bath improves the fluidity of zinc bath, which is in favor to the liquid zinc flowing back to zinc bath on the surface of the samples when they are drawn away from zinc bath, resulting in the η layer thinner.

4.2 Change of Γ layer

Temperature is one of the key factors which influence the Fe-Zn reaction. The higher the temperature is, the easier the Fe-Zn reaction takes place. The growth rate of Fe-Zn compounds is usually quickened with the increase of temperature. However, it is also possible that the growth rate of Fe-Zn compounds is lowered if phase transformation occurs during Fe-Zn reaction.

Kozdrs et al.^[12] carried on the research of the galvanizing steels with less than 0.2% silicon. It is found that Γ layer plays a major role in the growth of galvanized coatings. The modification of Γ layer occurs concurrently with bearded structure formation of galvanized coatings. He proposed that silicon destroying compact and continuous Γ layer leads to the formation of abnormal coatings.

Because of the absence of Fe-Zn-Si ternary phase diagram at the temperature higher than 723 K, it is uncertain that how temperature affects the Fe-Zn-Si phases. With regard to Seibisty steels, the substrate/coating interface is a discontinuous Γ layer at low temperature (e. g. 723 K) and the Γ layer becomes relatively continuous at high temperature (e. g. 753 K). The fact shows that Γ layer containing certain silicon can keep more stable at high temperature. Γ layer is the most iron-rich and

compact Fe-Zn compound and its stability can control the growth of galvanized coatings, which delays the growth of the Fe-Zn compound layer.

4.3 Change of ζ layer

During galvanizing, the growth of ζ layer accompanies with ζ dissolution to zinc bath. The schematic illustration of the ζ layer growth is shown in Fig. 4.

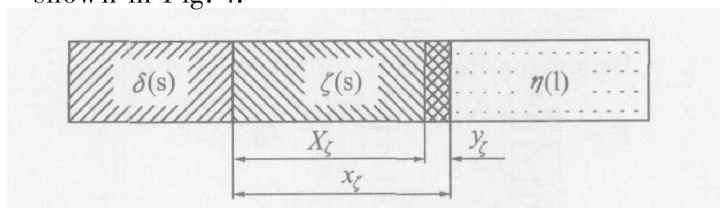


Fig. 4 Schematic illustration of ζ layer growth

The growth rate of ζ layer is given by^[13]

$$dX_{\zeta}/dt = dx_{\zeta}/dt - dy_{\zeta}/dt \quad (1)$$

where dX_{ζ}/dt is the growth rate of ζ layer, dx_{ζ}/dt is the growth rate of ζ layer without dissolution, abiding by Fick diffusion law, and dy_{ζ}/dt is the dissolving rate of ζ layer, abiding by Nernst-Brunner equation.

According to Fick law:

$$dx_{\zeta}/dt = K_{\zeta 1}/x_{\zeta} \quad (2)$$

where $K_{\zeta 1}$ is the growth coefficient.

According to Nernst-Brunner equation:

$$dC_{\zeta}/dt = K_{\zeta 2}(S/V)(C_{\text{Fe}}^S - C_{\zeta}) \quad (3)$$

where dC_{ζ}/dt is the change rate of iron concentration in zinc bath, $K_{\zeta 2}$ is the dissolution coefficient, S is the surface area of samples, and V is the volume of zinc bath and C_{Fe}^S is the iron saturated concentration in zinc bath.

$$C_{\zeta} = \rho_{\zeta} \gamma_{\zeta} S y_{\zeta} / V \quad (4)$$

where ρ_{ζ} is the density of ζ layer, γ_{ζ} is the average Fe concentration in ζ layer and y_{ζ} is the average thickness of the dissolved ζ layer.

V is approximately considered a constant as it hardly changes with the change of Fe solubility in zinc bath.

Substituting Eqn. (4) to (3) and getting

$$dy_{\zeta}/dt = -ay_{\zeta} + b \quad (5)$$

where $a = K_{\zeta 2}S/V$ and $b = K_{\zeta 2}C_{\text{Fe}}^S/\rho_{\zeta}\gamma_{\zeta}$.

Combining Eqns. (1), (2) and (5), the growth rate of ζ layer is denoted by

$$dX_{\zeta}/dt = K_{\zeta 1}/X_{\zeta} + ay_{\zeta} - b \quad (6)$$

During galvanizing, $V \gg S$, so $a \rightarrow 0$, Eqn. (6) is simplified by

$$dX_{\zeta}/dt = K_{\zeta 1}/X_{\zeta} - b \quad (7)$$

Integrating Eqn. (7) and substituting the initial conditions $t=0$, $X_{\zeta}=0$, it is obtained that

$$-(K_{\zeta 1}/b^2) \ln(1 - bX_{\zeta}/K_{\zeta 1}) - X_{\zeta}/b = t \quad (8)$$

Expanding Eqn. (8) in series and taking the first three items, it is given by

$$X_{\zeta}^2/(2K_{\zeta 1}) + (1/3)(bX_{\zeta}^3/K_{\zeta 1}^2) = t \quad (9)$$

Simplifying Eqn. (9) and getting

$$FX_{\zeta}^2 + GX_{\zeta}^3 = t \quad (10)$$

Substituting the test data to Eqn. (10) and simulating them according to the method of least squares, it is obtained that

$$\begin{cases} F \sum_{i=1}^N X_{\zeta i}^4 + G \sum_{i=1}^N X_{\zeta i}^5 = \sum_{i=1}^N t_i X_{\zeta i}^2 \\ F \sum_{i=1}^N X_{\zeta i}^5 + G \sum_{i=1}^N X_{\zeta i}^6 = \sum_{i=1}^N t_i X_{\zeta i}^3 \end{cases} \quad (11)$$

By solving Eqn. (11), it is obtained that

$$\begin{aligned} F &= \left| \begin{array}{cc} \sum t_i X_{\zeta i}^2 & \sum X_{\zeta i}^5 \\ \sum t_i X_{\zeta i}^3 & \sum X_{\zeta i}^6 \end{array} \right| / \Delta \\ G &= \left| \begin{array}{cc} \sum X_{\zeta i}^4 & \sum t_i X_{\zeta i}^2 \\ \sum X_{\zeta i}^5 & \sum t_i X_{\zeta i}^3 \end{array} \right| / \Delta \\ \Delta &= \left| \begin{array}{cc} \sum X_{\zeta i}^4 & \sum X_{\zeta i}^5 \\ \sum X_{\zeta i}^5 & \sum X_{\zeta i}^6 \end{array} \right| \end{aligned} \quad (12)$$

As C_{Fe}^S , ρ_{ζ} and γ_{ζ} are the known parameters, $K_{\zeta 1}$ and $K_{\zeta 2}$ are acquired by Eqns. (9) and (12).

Integrating Eqn. (2) and substituting the initial conditions $t=0$, $x_{\zeta}=0$, it is obtained that

$$x_{\zeta} = \sqrt{K_{\zeta 1}} \cdot t \quad (13)$$

Integrating Eqn. (5) and substituting the initial conditions $t=0$, $y_{\zeta}=0$, it is obtained that

$$y_{\zeta} = (C_{\text{Fe}}^S V / \rho_{\zeta} \gamma_{\zeta} S) \cdot [1 - \exp[-K_{\zeta 2} S t / V]] \quad (14)$$

Integrating Eqn. (1) and substituting the initial conditions $t=0$, $X_{\zeta}=0$, Eqns. (13) and (14), the thickness of ζ layer is obtained by

$$X_{\zeta} = \sqrt{K_{\zeta 1}} \cdot t - (C_{\text{Fe}}^S V / \rho_{\zeta} \gamma_{\zeta} S) \cdot [1 - \exp[-K_{\zeta 2} S t / V]] \quad (15)$$

The available parameters are listed in Table 2.

Table 2 Known physical parameters

Physical parameter	Magnitude	Comment
ρ_{ζ}	7.2 g/cm ³ [14]	Density of ζ layer
γ_{ζ}	6% [9]	Average iron concentration of ζ layer
$C_{\text{Fe}, 723 \text{ K}}^S$	0.045% [15]	Iron saturated concentration in zinc bath at 723 K
$C_{\text{Fe}, 753 \text{ K}}^S$	0.07% [15]	Iron saturated concentration in zinc bath at 753 K

Table 3 Values of F , G , $K_{\zeta 1}$ and $K_{\zeta 2}$ of ζ layer of galvanized coating on 0.14% Si steel at 723 K and 753 K

Temperature/ K	$F/(s \cdot \mu\text{m}^{-2})$	$G/(s \cdot \mu\text{m}^{-2})$	$K_{\zeta 1}/(\mu\text{m}^2 \cdot \text{s}^{-1})$	$K_{\zeta 2}/(\mu\text{m}^2 \cdot \text{s}^{-1})$
723	3.83×10^{-2}	4.65×10^{-2}	13.05	6.68
753	1.36×10^{-5}	1.00×10^{-4}	10.74	22.43

Fig. 5 shows the thickness of ζ layer of the galvanized coating on 0.14% Si steel at 723 K and 753 K as a function of immersion time. It is clear that the thickness of ζ layer increases with increasing immersion time whereas it decreases with increasing temperature of zinc bath. By substituting the values ($X_{\zeta i}$) to Eqn. (12), the values of F , G , $K_{\zeta 1}$ and $K_{\zeta 2}$ are acquired, as shown in Table 3. $K_{\zeta 1}$ is the growth coefficient of ζ layer and its value reflects the growth controlled by the diffusion mechanism. It is shown from Table 3 that $K_{\zeta 1}$ decreases from 13.05 to 10.74 with the increase of galvanizing temperature from 723 K to 753 K. It is inferred that the growth of ζ layer controlled by the diffusion mechanism is declined, which may be due to the change of Γ layer from discontinuous to relatively continuous, delaying the Fe-Zn diffusion. $K_{\zeta 2}$ is the dissolution coefficient and its value reflects the dissolution of ζ layer to zinc bath. It is also seen from Table 3 that $K_{\zeta 2}$ increases from 6.68 to 22.43 with the galvanizing temperature from 723 K up to 753 K. It is inferred that the dissolution of ζ layer to zinc bath accelerates with rising temperature. By combining Eqn. (15), it is found that the value of X_{ζ} decreases, that is, the thickness of ζ layer decreases, if the value of $K_{\zeta 1}$ decreases and the value of $K_{\zeta 2}$ increases.

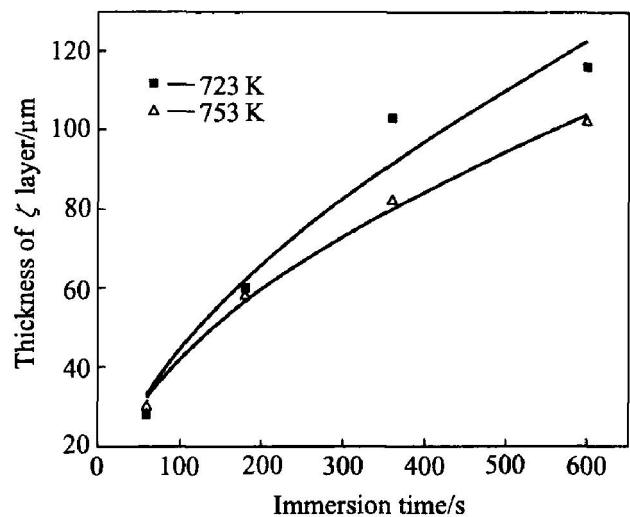


Fig. 5 Thickness of ζ layer of galvanized coating on 0.14% Si steel at 723 K and 753 K as function of immersion time

5 CONCLUSIONS

1) The thickness of galvanized coatings on 0.14% Si steels decreases with increasing temperature at 723 – 753 K.

2) There are three changes in galvanized coatings with increasing temperature: the decrease of the thickness of ζ and η layer and the change of Γ layer from discontinuous to relatively continuous.

3) The improvement of fluidity of zinc bath due to the rising temperature of zinc bath makes η layer thinner.

4) The existence of relatively continuous Γ layer and the acceleration of the dissolution of ζ layer to zinc bath co-lead to the decrease of the thickness of ζ layer with increasing temperature.

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