

## Study on growth factors of intermetallic layer within hot-dipped 25%Al–Zn alloy coating on steel

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**Abstract.** 25%Al–Zn alloy coating performs better than hot dip galvanized coating and 55%Al–Zn–Si coating with regard to general seawater corrosion protection. This study deals with the interfacial intermetallic layer's growth, which affects considerably the corrosion resistance and mechanical properties of 25%Al–Zn alloy coatings, by means of three-factor quadratic regressive orthogonal experiments. The regression equation shows that the intermetallic layer thickness decreases rapidly with increasing content of Si added to the Zn–Al alloy bath, increases with rise in bath temperature and prolonging dip time. The most effective factor that determined the thickness of intermetallic layer was the amount of Si added to Zn–Al alloy bath, while the effect of bath temperature and dip time on the thickness of intermetallic layer were not very obvious.

**Keywords.** Galvanization by hot-dipping; intermetallic layer; 25%Al–Zn alloy coating.

### 1. Introduction

Steel wire with 25%Al–Zn alloy coating was first produced commercially in 1997 by Jinzhou Wire Plant in China under the trade name RD-ZAM. The product was developed in order to obtain a coating with a better seawater corrosion protection than normal continuously hot dip galvanized steel wire. Long term immersion corrosion testing (3 years), at Zhoushan Seawater Corrosion Station for Marine Steels show that 25%Al–Zn alloy coating performs better than hot dip galvanized coating and 55%Al–Zn–Si coating as well, with regard to general seawater corrosion protection (Li 1999).

Our research activity was focused on the electrochemical and surface studies of the 25%Al–Zn alloy coating exposed to seawater (Sun *et al* 1997; Li *et al* 2000). We also analyzed the possible additional protection that could be provided by a chemical conversion treatment using a low concentration chromate solution (Li *et al* 1999). Similar to Galvalume (Borzillo and Horton US Patents 3,343,930; 3,393,089; Harey 1981; Townsend and Fisher 1982; Selverian *et al* 1986), Zn–Al alloy coating whose nominal composition was 55 wt% Al, 1.6 wt% Si and balance Zn, manufactured by hot dip process, 25%Al–Zn alloy coating was also composed of surface Zn–Al alloy overlay and intermetallic layer bonding overlay and steel substrate (Li 1999).

It is well known that a suitable amount of silicon content in the alloy bath raises the corrosion resistance and controls the formation of intermetallic layer (Ochiai

and Ohba 1990). In addition to silicon contents, bath temperature and dip time are two other major factors affecting the growth of such intermetallic layer. Because the corrosion attack will stop at the intermetallic layer which is cathodic to the 25%Al–Zn coating (Li 1999), it would thus be beneficial to obtain certain thickness of the intermetallic layer when applying an 25%Al–Zn coating for fabricated objects. This study has tried to investigate the influence of the silicon content in Zn–Al alloy bath, bath temperature and dip time on the thickness of the intermetallic layer in laboratory-prepared 25%Al–Zn coatings, and to discuss growth of the intermetallic layer in detail. It should be emphasized that the work reported here relates to batch galvanizing steel sheet. The resulting microstructures may be different from those produced in a continuous line.

### 2. Experimental

#### 2.1 Materials

Zinc used for preparation of 25Al–Zn alloy bath was electrolytic zinc with purity of about 99.99%, while purity of the aluminum was of 99.8%. The Zn–Al alloy bath was prepared by melting a suitable amount of Al, Zn, Al–Si master alloy (10.4%Si) and other alloying elements in a graphite crucible. First Al was melted at 750°C and was followed by additions of Zn, Al–Si alloy, etc.

#### 2.2 Hot-dipping procedure

The 50 × 20 × 0.8 mm size steel samples were prepared from A3 steel (0.02% C, 0.3% Si, 0.41% Mn, 0.016% S,

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0.015% P, and balance Fe) obtained from the Fushun Steel Plant. Dipping in acetone followed by hot alkaline cleaning degreased the steel specimens. The subsequent acid pickling was performed in 17% HCl solution at ambient temperature. The hot dip experiment was carried out with a flux process in this study, using a flux solution composed of 500 g ZnCl<sub>2</sub>, 10 g NaF in 500 ml distilled water. The coatings were quenched in water after withdrawal from the bath.

### 2.3 Microstructure examination

The 25%Al–Zn alloy coating samples were mounted vertically inside a cylindrical Bakelite shell by epoxy resin. Final polishing of the samples was done using  $5 \times 10^{-6}$  and  $1 \times 10^{-6}$  m diamond pastes. The coatings were etched with 200 g/l CrO<sub>3</sub> solution for 5 s to determine their structure for measurement. The metallographic examination was carried out using a CARLZEISS JENA optical microscope.

## 3. Results and discussion

### 3.1 Orthogonal regressive experimental design and results

The hot-dipping galvanization was arranged according to the 3-factor quadratic regressive orthogonal experimental design (Wei and Feng 1996), whose coding of factorial level is shown in table 1, and its measured results are shown in table 2.

Computerized treatment of the measured results yielded the following regression equation for the thickness of the intermetallic layer

$$\delta = 186.1 - 0.6859t - 0.7126\tau + 82.01w + 1.630 \times 10^{-3}t\tau - 0.1907tw - 0.2768\tau w + 6.409 \times 10^{-4}t^2 - 7.952 \times 10^{-4}\tau^2 + 48.15w^2, \quad (1)$$

where,  $\delta$  is the thickness of intermetallic layer,  $\mu\text{m}$ ;  $t$  the bath temperature,  $^{\circ}\text{C}$ ;  $\tau$  the dip time, s;  $w$  the amount of Si added to Zn–Al alloy bath, mass%.

Table 1. Coding table of factorial level.

Factor Level	Bath temp. $t$ ( $^{\circ}\text{C}$ )	Dip time $\tau$ (s)	Silicon content $w$ (mass%)
0	590.0	60.0	0.20
$\Delta$	24.7	32.9	0.16
+1	614.7	92.9	0.36
-1	565.3	27.1	0.04
+ $\gamma$	620.0	100.0	0.40
- $\gamma$	560.0	20.0	0

The partial derivatives of  $\delta$  for  $t$ ,  $\tau$  and  $w$ , therefore, are readily found to be

$$\frac{\partial \delta}{\partial t} = -0.6859 + 1.630 \times 10^{-3}\tau - 0.1907w + 1.282 \times 10^{-3}\tau \quad \frac{\partial^2 \delta}{\partial t^2} = 1.282 \times 10^{-3}, \quad (2)$$

$$\frac{\partial \delta}{\partial \tau} = -0.7126 + 1.630 \times 10^{-3}t - 0.2768w - 1.590 \times 10^{-3}t \quad \frac{\partial^2 \delta}{\partial \tau^2} = -1.590 \times 10^{-3}, \quad (3)$$

and

$$\frac{\partial \delta}{\partial w} = 82.01 - 0.1907t - 0.2768\tau + 96.30w \quad \frac{\partial^2 \delta}{\partial w^2} = 96.30. \quad (4)$$

So, for decreasing the thickness of intermetallic layer, the most effective factor was the amount of Si added to Zn–Al alloy bath. Raising bath temperature and dip time probably increased the thickness of intermetallic layer, but their effects were not very obvious which was evident from the regression coefficient.

### 3.2 Effect of Si content in bath

Equation (1) can be used to plot the curve describing the dependence of the intermetallic layer thickness on the amount of silicon added to the alloy bath. The effect of silicon content on the thickness of the intermetallic layer, when A3 steel was immersed into the Zn–Al alloy bath remained for 60 s at 560, 590 and 620 $^{\circ}\text{C}$  respectively, is shown in figure 1.

Table 2. Three-factor quadratic regressive orthogonal experimental design and its results.

Experimental points	$t$ ( $^{\circ}\text{C}$ )	$\tau$ (s)	$W$ (mass%)	$\delta$ ( $\mu\text{m}$ )
1	-1	-1	-1	7.1
2	-1	-1	1	2.1
3	-1	1	-1	13.6
4	-1	1	1	3.9
5	1	-1	-1	11.8
6	1	-1	1	5.0
7	1	1	-1	24.9
8	1	1	1	10.8
9	- $\gamma$	0	0	6.2
10	$\gamma$	0	0	13.9
11	0	- $\gamma$	0	4.8
12	0	$\gamma$	0	11.6
13	0	0	- $\gamma$	17.4
14	0	0	$\gamma$	5.4
15	0	0	0	8.3

The figure shows that the intermetallic layer thickness declined sharply even if only a small amount of silicon was added. This is attributed to the formation of Fe-Al-Si compounds between Si in the alloy bath with Al and Fe (Meng and Yang 1987). Because the diffusion of Al is essential in these compounds (Hu and Zhang 1995), a small amount of silicon addition, in fact, inhibits the diffusion of Al to the reaction interface; on the other hand, the addition of a small amount of silicon can noticeably reduce the viscosity of the alloy bath (Smithell *et al* 1976), and hence accelerate the dissolution of the intermetallic layer. Moreover, as the melting points of Fe-Al-Si compounds are always lower than those of Fe-Al compounds with similar composition (Meng and Yang 1987), the former are more soluble than the latter in the alloy bath. The alloy bath being saturated by iron prior to the experiments, it is readily found that the amount of Fe-Al dross formed in the silicon free bath, due to the dissolution of the intermetallic compounds, is obviously less than that formed in the silicon containing bath.

### 3.3 Effect of bath temperature

Bath temperature is one of the most important factors controlling the growth of the intermetallic layer, whose thickness generally increases with rising temperature. Assuming  $\tau = 60$  s,  $w = 0, 0.2$  mass%,  $0.4$  mass% in (1), the effect of bath temperature on the intermetallic layer thickness is as shown in figure 2.

As shown in figure 2, the intermetallic layer thickness increases continuously with raising bath temperature; and the average growth rate of  $0.05 \sim 0.13 \mu\text{m}/^\circ\text{C}$  for  $560^\circ\text{C}$  increases up to  $0.13 \sim 0.21 \mu\text{m}/^\circ\text{C}$  for  $620^\circ\text{C}$ . It is obvious that the accelerating diffusion of Al and Fe with the raising bath temperature, leading to the formation of the intermetallic layer exceeding the dissolution of it due to the decline in the superheat (i.e. the difference of the bath

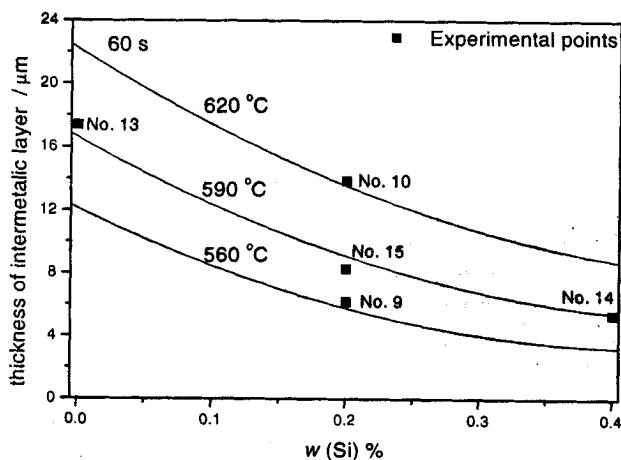


Figure 1. Thickness of alloy layer as a function of amount of Si added in Zn-Al alloy bath ( $\tau = 60$  s,  $t = 560^\circ\text{C}$ ,  $590^\circ\text{C}$  and  $620^\circ\text{C}$  respectively).

temperature and liquidus point of the ternary alloy), can explain such an increase in intermetallic layer thickness. It was also found that immersion in silicon containing Zn-Al alloy bath reduced the intermetallic layer thickness by about 40% ~ 70% compared to the thickness resulting from alloy bath containing no silicon. The addition of silicon suppresses the reactive diffusion on one hand, and accelerates the dissolution of the intermetallic layer on the other hand (Meng and Yang 1987).

### 3.4 Effect of dipping time

Dip time is another important factor controlling the growth of intermetallic layer, and generally, the thickness of intermetallic layer increases with duration. Similarly, the effect of dip time on the thickness of intermetallic layer could be observed in figure 3, assuming  $t = 590^\circ\text{C}$ ,  $w = 0, 0.2, 0.4$  mass% respectively in (1).

Figure 3 shows that the intermetallic layer thickness increases parabolically with increase in dip time. Initially the intermetallic layer grows relatively quick, at an average rate of  $0.03 \sim 0.07 \mu\text{m}/\text{s}$ , and then gradually slows down afterwards. The diffusion resistance becomes larger and larger with the increase in the intermetallic layer thickness. Furthermore, the intermetallic layer thickness resulting from the alloy bath containing silicon was thinner than the one obtained from the bath containing no silicon by 40 to 70%. As the growth of the intermetallic layer resulting from mass transfer process is accompanied by its dissolution in the molten alloy bath under conditions of galvanization by hot dipping, the addition of silicon to the Zn-Al alloy bath will decelerate the growth of the intermetallic layer and accelerate its dissolution (Meng and Yang 1987), and such effect will be more and more remarkable with the increase in silicon content. Figure 3 also shows that the formation speed of the intermetallic layer is approximately equivalent to its dissolu-

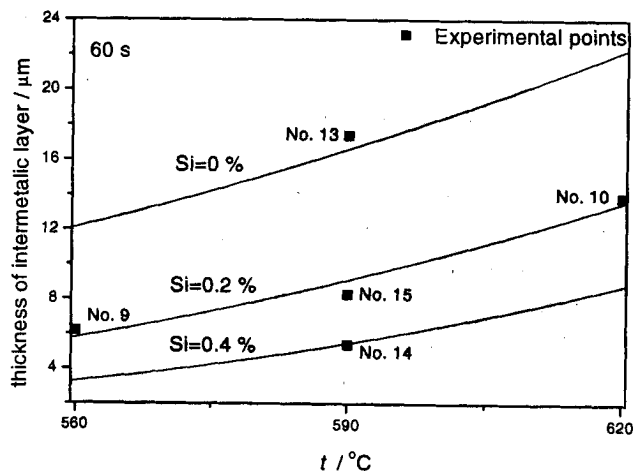


Figure 2. Thickness of alloy layer as a function of hot-dipping temperature ( $\tau = 60$  s,  $w = 0, 0.2$  mass% and  $0.4$  mass% respectively).

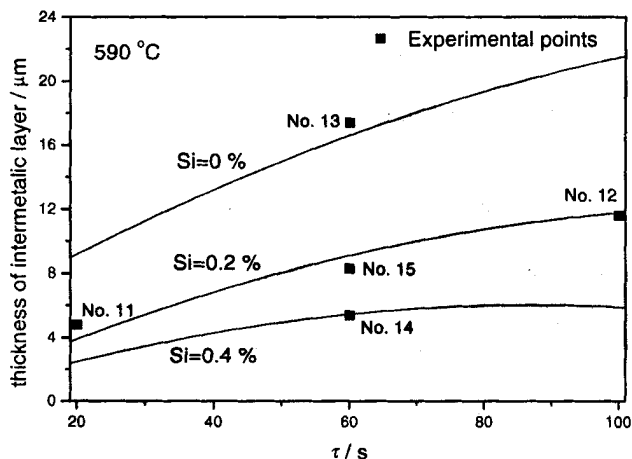


Figure 3. Thickness of alloy layer as a function of hot-dipping time ( $t = 590^{\circ}\text{C}$ ,  $w = 0, 0.2$  mass% and  $0.4$  mass% respectively).

Table 3. Check of  $F$  value.

Variation source	Sum of squares	Degree of freedom	$F$
Total	509.257	$N - 1 = 14$	
Regressive	505.848	$P = 9$	$F = 82.42 > F_{0.01}(9, 5)$
Residue	3.409	$N - 1 - P = 5$	

tion speed; assuming  $\partial\delta/\partial\tau = 0$  in (3), then the dependence of time obtaining the maximum thickness on  $t$  and  $w$  is easily found to be

$$\tau = -448.2 + 1.025t - 174.1w. \quad (5)$$

For example, when low carbon steel is dipped at  $590^{\circ}\text{C}$ , remaining for about 87 s in the alloy bath containing 0.4 mass% silicon, the intermetallic layer thickness reaches maximum value,  $6.0 \mu\text{m}$ . With extension of the dip time, the dissolution speed of intermetallic layer exceeded its formation speed, so its thickness began to decrease, as shown in figure 3.

### 3.5 Check of the regression equation

Personal computer, outputting results as shown in tables 3 and 4, did checks of  $F$  and  $t$  values. It is seen that the regression equation yielded highly significant and reliable results. Therefore, (1) can accurately describe the relationship between intermetallic layer thickness and bath temperature, dip time and silicon content added to 25Al–Zn alloy bath.

## 4. Conclusions

A mathematical model describing the growth of the intermetallic layer in an 25%Al–Zn alloy bath containing

Table 4. Check of  $t$  value.

Zero level measure	Average value	$B_0$	$t$
8.6			
8.3	8.5	9.1	$t = 0.7266 < t_{0.01}(5) = 4.032$
8.5			

silicon was obtained to be  $\delta = 186.1 - 0.6859t - 0.7126\tau + 82.01w + 1.630 \times 10^{-3}t\tau - 0.1907t\tau - 0.2768\tau w + 6.409 \times 10^{-4}t^2 - 7.952 \times 10^{-4}\tau^2 + 48.15w^2$ . For the thickness of intermetallic layer, the most effective factor was the amount of Si added to Zn–Al alloy bath, while the effect of bath temperature and dip time on the thickness of intermetallic layer were not very pronounced.

The thickness of the intermetallic layer decreases sharply with increase in the amount of Si added to the Zn–Al alloy bath; it increases continuously with the rise in bath temperature and the growth of the intermetallic layer accelerates when bath temperature raising from  $560^{\circ}\text{C}$  to  $620^{\circ}\text{C}$ ; and it increases parabolically with prolonging dip time and the growth of the intermetallic layer slows down at longer dip duration.

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