Effect of La on intermetallic layer of galvalume

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The effect of various La levels on the reaction between pure iron panel and 55%Al–Zn–1 wt-%Si liquid baths during hot dipping at 600°C was investigated in this work. Three bath compositions containing 0, 0.2 and 0.5 wt-%La respectively, combined with six immersion times of 10, 60, 120, 180, 300 and 600 s, were studied. It was found that La can effectively control the formation of intermetallic layer by the synergistic effect with Si. The addition of La makes Si enriched in the intermetallic layer during the hot dipping. It hinders the formation of the Fe2Al5 phase and promotes the growth of the τ5 phase. The intermetallic layer becomes more compact and uniform after the La was added. The intermetallic layer is composed of Fe2Al5 (τ7/τ9), FeAl3 and τ5 phase. The diffusion path model was introduced to interpret the effect mechanism of La and Si in this work.

Keywords: Galvalume, La, Diffusion, Si, Microstructure

Introduction

Hot dip galvanising is widely used to enhance the iron and steel products’ corrosion resistance. The hot dip coating can effectively protect the iron and steel products as a barrier and prolong the products’ working life.1–4 In recent years, a series of coatings has been studied, which were basically made up of zinc alloys: Al–Zn alloys, Zn–Ti alloys, Zn–Mn alloys, Zn–Co alloys and Al–Zn–Mg–RE alloys.5–8 Among those alloys, the galvalume (55%Al–Zn–1 wt-%Si) coated steel has a better anticorrosive performance than zinc coating and has a high temperature oxidation resistant property like that of aluminium coating. In addition, the galvalume coating has uniform and beautiful spangles. Those distinct advantages make the galvalume become the popular alloys in the building trades and home appliance industries.9

The reaction between the iron substrate and the Al–Zn bath is extremely rapid and strongly exothermic in hot dipping, which will bring a harmful effect to the performance of the coating.10 The earlier studies showed that a small amount of Si element added into the bath can prevent the excessive growth of the intermetallic layer at the iron substrate/coating interface.11–14 Some literatures reported the effects of rare earth addition on the properties of galvalume coating. Wu et al.15 studied the effects of 0–2 wt-% rare earth addition on microstructure and thickness of galvalume coating. It was found that La substitution in the Fe2Al5 and FeAl3 phase could grab electronic charges from Al atoms and weaken the formation of the Fe–Al compounds. Yang et al.12 detected that adding proper amounts of La can improve the corrosion resistance of the galvalume coating. In the work of Li et al.,16 55 wt-%Al–Zn bath with appropriate (0–1–0.3 wt-%) rare earth, the performance of coating and the corrosion resistance to salt water were improved and the grain was refined from 100 to 50 μm. However, less attention has been devoted to the growth and microstructures of the intermetallic layer in galvalume baths with different content of La.12,15–17

Galvalume baths in industry line are saturated with Fe (~2 wt-%). In fact, the bath is a Fe–Al–Zn–Si quaternary system. There are two important ternary intermetallics (τ7 and τ5) in the Al rich corner area of the Fe–Al–Si ternary system. Based on the Al–Fe–La ternary phase diagram at temperature relevant to hot dipping galvalume, several ternary intermetallics (LaFe2Al5 and Fe2Al5) can be observed in the Al rich corner area.18 When La is added to galvalume bath, the existence of two ternary intermetallics may have the similar effect as τ5 and τ6. It would achieve the synergistic effect that La and Si control the reaction between the iron substrate and bath.

The former researchers almost focus their attention on the overlay of the coating and found that La added into the bath can improve the corrosion resistance and refine overlay’s grain. In the work of Wu et al.,15 they only studied the immersion time of 5 s at 625°C. The purpose of the current study is to experimentally investigate the effect of La on the microstructure and growth kinetics of the intermetallic layers at 600°C. The diffusion path model was introduced to interpret the mechanism.

Experimental

The purities of the bath raw materials, Al, Si, La and Zn, are 99–99 wt-%. A pure iron was used as the substrate in
this study, and its chemical composition is Fe–0.003Mn–0.003Si–0.005C–0.001Al (wt-%). The pure iron panel was cut into 12 × 12 mm plates, and its thickness is 2.0 mm. The specimens were first polished with sandpaper, and the following steps were carried out just before dipping:
(i) degrease in 10 wt-%NaOH solution at 80 °C for 3 min
(ii) rinse in running water
(iii) pickle in 15 wt-%HCl solution for 5 min
(iv) rinse in running water
(v) hold in a aqueous solution consisting of 5 wt-% potassium fluorozirconate (K₂ZrF₆) and 3 wt-% potassium chloride (KCl), which was kept at 80 °C for 5 min
(vi) hold in a drying oven at 100 °C at 5 min to dry.

Then, the iron panels were dipped in galvalume baths saturated with Fe at 600 °C and the temperature fluctuation was ±3 °C. The dipping time ranged from 10 to 600 s (10, 60, 120, 180, 300 and 600 s). After the desired time, the iron panels were withdrawn and immediately water quenched to maintain the microstructure of the panel as it exists in the bath. The content of La in galvalume baths was 0, 0.2 and 0.5 wt-%. These baths were identified as bath A, bath B and bath C, as shown in Table 1. In the present study, three samples were used to obtain each data of experimental condition, i.e. bath composition, bath temperature and hot dipping time.

The cross-sections of coatings were examined for all hot dipping samples. Specimens were prepared using conventional metallographic techniques and polished using Al₂O₃ and etched with 4–0%HNO₃ to observe the structure of the coating. Then, these samples were examined by JSM-6510 scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDS). An acceleration voltage of 20 kV was used. The average intermetallic compound thickness was obtained from at least seven measurements of each specimen cross-section.

Results and discussion
Analyses of microstructure and diffusion path in coating
The morphologies and structures of the coatings dipped in three baths have been analysed. The results of structural examinations of coating in baths with different La contents are presented in Figs. 1–3. The phases in coatings that were galvanised for 300 s can be distinguished by their chemical composition and colour. The compositions of all phases with standard deviations are detailed in Table 2.

The coating microstructures after being galvanised in bath A for 60, 300 and 600 s are presented in Fig. 1. There is an intermetallic layer between the iron panel and overlay coating. Peng et al.19 reported that the Fe₂Al₅ layer was not observed in panels dipped for 10 s. When the iron panel was galvanised for 60 s, there was an obvious Fe₂Al₅ layer near the panel. The t₅ layer is too thin so it is hard to distinguish clearly from the FeAl₃ layer by their colour (Fig. 1a). When the hot dipping time is up to 300 s, as shown in Fig. 1b, the intermetallic layer is composed of three clear phase layers: Fe₂Al₅, FeAl₃ and t₅. The t₅ layer appears close to the overlay, and the Fe₂Al₅ layer appears near the iron substrate. The FeAl₃ layer exists between the t₅ and Fe₂Al₅ layer.15,18,20 The corresponding chemical compositions determined by EDS are listed in Table 2. There are some bright phases inseting in the Fe₂Al₅ layer (Fig. 1b and c). The former researchers proposed that the bright phase was t₁/t₉ phase.20–22

Figure 2 presents the coating microstructures after being produced in bath B for 300 and 600 s. The
intermetallic layer consists of the Fe$_2$Al$_5$, FeAl$_3$ and $\tau_5$ layers. It can be observed that a certain amount of La can effectively influence the thickness of the alloy layer. The thickness of the Fe$_2$Al$_5$ layer decreases and the thickness of the $\tau_5$ layer increases compared with that galvanised in bath A. It suggests that the La addition in galvalume bath contributes to the growth of the $\tau_5$ phase layer and inhibits the formation of the Fe$_2$Al$_5$ phase layer. The compositions of different phase layers galvanised in bath B for 300 s are listed in Table 2.

The microstructures of coating galvanised in bath B for 600 s are shown in Fig. 3. From the investigation, it is concluded that the total thickness of the alloy layer is greatly reduced when the content of 0-5 wt-%La was added into the bath. It hinders the growth of the Fe$_2$Al$_5$ phase layer and promotes the formation of the $\tau_5$ phase layer.

The diffusion path involved in galvanising reactions between the iron substrate and the bath can be described using phase diagram. With the absence of Si in the Al–Zn bath when the immersion time is short, the diffusion path in the Fe–Al–Zn system crosses the FeAl$_3$ phase first and then crosses the (FeAl$_3$+liq.) two-phase region (shown as path 1 in Fig. 4). With the increase in immersion time, the diffusion path starts to enter the following regions: (Fe$_2$Al$_5$+FeAl$_3$+liq.), (Fe$_2$Al$_5$+liq.) and ($\alpha$-Fe+Fe$_2$Al$_5$+liq.) and finally enter the $\alpha$-Fe single phase region (shown as path 2 in Fig. 4). Since the diffusion path dissects the tie lines of the (FeAl$_3$+liq.), (Fe$_2$Al$_5$+FeAl$_3$+liq.), (Fe$_2$Al$_5$+liq.) and ($\alpha$-Fe+Fe$_2$Al$_5$+liq.) regions, liquid channels exist in the intermetallic layer and the liquid phase erodes the iron substrate directly. As a result, a violent reaction occurs between the iron substrate and liquid phase according to the study of Peng et al.

In galvalume (55%Al–Zn–1·6 wt-%Si) bath, Fe, Al, Zn and Si participated in the reaction, so this is a quaternary system. In this paper, the role of La added into the galvalume bath was studied, and the Fe–Al–Zn–Si quaternary system diffusion path model was introduced to interpret the synergistic effect of La and Si on the hot dipping. The diffusion path model (Fig. 5) was constructed based on the phase diagrams of the Al–Fe–Zn–Si system and the Al–Fe–Si system. The diffusion path established on the transformation of the phase relationship in different dipping time and the former research results. The $\tau_5$ phase replaces the equilibrium intermetallic compound in the bath. The SEM/EDS examination indicates that the $\tau_5$ phase is the first phase that occurred in the coating and closest to the overlay. The diffusion path should dissect the tie lines of the ($\tau_5$+liq.) domain and enter the ($\tau_5$+FeAl$_3$+(Al)+liq.) region. It enters the FeAl$_3$ region, as shown from path 1 in Fig. 5. Since diffusion path only dissects the tie lines of the ($\tau_5$+liq.) domain, there are liquid channels in the $\tau_5$ layer, not in Fe–Al phase layer. The compact $\tau_5$ cannot form and the liquid...
phase will contact with the Fe–Al phase. Therefore, the growth of the Fe–Al intermetallic is still fast. As can be seen in Fig. 1c, most of the alloy layer is occupied by the Fe–Al phase.

When proper amount of La is added into the Al–Zn–Si bath, no liquid occurs in the intermetallic layer and all intermetallic phases are more continuous and compact and the thickness of the Fe2Al5 phase layer decreases, as shown in Fig. 3b. The EDS examination of the three layers immersed in bath C for 300 s (Table 2) indicates that the content of Si (3-4, 2-7 and 6-6 wt-% in the three layers) is higher than that galvanised in bath B (3-2, 2-4 and 6-1 wt-%) and bath A (2-8, 1-9 and 5-5 wt-%). Based on the experimental results, the amount of La added into the galvalume bath can make Si enriched in the alloy layer during the hot dipping. Lu et al.26 had reported that the diffusion path would eventually move towards Si as the Si was enriched in the coating. The diffusion path would cross the (t5 + liq.) two-phase region following a tie line, directly enters the t5 phase region, then passes the following regions: (t5 + FeAl5), FeAl5, (Fe2Al5 + FeAl5), Fe3Al and (Fe2Al5 + t5) and finally enters the α-Fe single phase region, as shown by path 2 in Fig. 5. The diffusion path is α-FeAl3, Fe5Al8, Fe2Al5 and Fe–Al phases can form in the coating. This phenomenon of the liquid phase eroding the α-Fe phase or the Fe–Al phases directly will be avoided, and the violent reaction will be under control.

We have concluded that Si would be enriched in the Fe2Al5 phase when galvalume bath contains a proper amount of La. The Si can occupy the atom site vacancies in the Fe2Al5 phase and hinder the diffusion of Al and Zn towards the iron panel.10,20 The compact t5 phase combined with the amount of Si that occupied the atom site vacancies in the Fe2Al5 phase could suppress the diffusion of Al and Zn towards the iron panel. Therefore, the intermetallic layer thickness greatly decreases when galvalume bath contains a proper amount of La.

It can be supported that with a certain amount of La in the bath, the rapid growth of the alloy layer is inhibited and the thickness of the Fe2Al5 phase layer is greatly decreased, and the more continuous and compact t5 and the Fe–Al phases form. Thus, the microstructure, quality and thickness of the alloy layer can be improved after La was added into the bath. It contributes to prolong the service lifetime of galvalume coated steel.

**Effect of La on growth kinetics of coating**

Image analysis was used to characterise the alloy layer as a function of the La content and immersion time in galvalume baths. At least six images of the alloy layer were captured for each specimen. In this work, the content of La and immersion time has a great influence on the thickness of the reaction layer. The thickness of the total intermetallic layer, the Fe2Al5 phase layer and the t5 phase layer was measured. As shown in Fig. 6, the intermetallic layer increases with the increase in hot dipping time; however, the total thickness of the layer is lower than the coating obtained in bath A without La. It can be stated that a certain amount of La in the bath results in an inhibition growth of the reaction zone to some extent.

As shown in Fig. 1c, in the samples galvanised in bath A, the Fe2Al5 phase layer grows quickly. When iron panels were galvanised in bath A for 600 s, the thickness of the Fe2Al5 and t5 phase layer is ~15-8±0.3 and 7-5±0.5 μm, and the percentages of the Fe2Al5 and t5 phase layer in the reaction zone almost reach 51.5 and 25%. However, the percentages of the Fe2Al5 and t5 phase layer of samples galvanised in bath C for 600 s are 28 and 62%, the thickness of the Fe2Al5 phase layer decreases to 5-7±0.3 μm and the thickness of the t5 phase layer increases to 13-2±0.4 μm, as shown in Table 3. It is apparent that the addition of 0-5 wt-%La

**Table 2 Energy dispersive X-ray analysis of intermetallic layers (with standard deviations) galvanised in different baths for 300 s wt-%**

<table>
<thead>
<tr>
<th>Bath A</th>
<th>Phase</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Zn</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe2Al5</td>
<td>51.3 ± 0.3</td>
<td>42.6 ± 0.4</td>
<td>2.8 ± 0.1</td>
<td>3.3 ± 0.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>FeAl5</td>
<td>58.8 ± 0.4</td>
<td>35.4 ± 0.2</td>
<td>1.9 ± 0.1</td>
<td>3.9 ± 0.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>t5</td>
<td>57.9 ± 0.5</td>
<td>27.3 ± 0.3</td>
<td>5.5 ± 0.1</td>
<td>9.5 ± 0.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Bath B</td>
<td>Fe2Al5</td>
<td>52.6 ± 0.5</td>
<td>40.8 ± 0.3</td>
<td>3.2 ± 0.1</td>
<td>3.4 ± 0.2</td>
<td>0</td>
</tr>
<tr>
<td>FeAl5</td>
<td>56.6 ± 0.6</td>
<td>37.3 ± 0.3</td>
<td>2.4 ± 0.2</td>
<td>3.7 ± 0.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>t5</td>
<td>57.8 ± 0.5</td>
<td>28.2 ± 0.3</td>
<td>6.1 ± 0.2</td>
<td>7.7 ± 0.3</td>
<td>0.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Bath C</td>
<td>Fe2Al5</td>
<td>51.8 ± 0.5</td>
<td>41.1 ± 0.5</td>
<td>3.4 ± 0.2</td>
<td>3.7 ± 0.3</td>
<td>0</td>
</tr>
<tr>
<td>FeAl5</td>
<td>54.9 ± 0.4</td>
<td>37.4 ± 0.5</td>
<td>2.7 ± 0.2</td>
<td>4.7 ± 0.4</td>
<td>0.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>t5</td>
<td>57.3 ± 0.5</td>
<td>26.3 ± 0.5</td>
<td>6.6 ± 0.3</td>
<td>9.2 ± 0.3</td>
<td>0.6 ± 0.1</td>
<td></td>
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</table>
hinders the growth of the Fe$_2$Al$_5$ phase and promotes the formation of the $\tau_5$ phase.

To evaluate the kinetics of alloy layer growth, a power-law growth equation is generally used to interpret the growth rate data, as follows:

$$Y = Kt^n$$

where $Y$ is the intermetallic layer thickness, $k$ is the growth rate constant, $t$ is the reaction time and $n$ is the growth rate constant.

The value of $n$ can be obtained by least square fitting the intermetallic layer thickness and immersion time with the equation. The $n$ value for the coating of the iron substrate galvanised in bath A is 0.51, suggesting diffusion controlled growth. When 0.2 and 0.5 wt-%La was added into the galvalume bath, the $n$ value is reduced to 0.42 and 0.39 respectively. Therefore, the growth of the alloy layer is effectively controlled. With the increasing of hot dipping time, the Fe–Al phase in the intermetallic layer gradually changes to Fe–Al–Si phase.

### Conclusion

The microstructure and morphologies of the intermetallic layer of the pure iron panels galvanised in galvalume baths with different contents of La were detailed in this work. The diffusion path model was introduced to explain the effect of La on galvalume coating. From the above investigation, it turned out that a certain amount of La added in galvalume bath significantly affects the structure of the intermetallic layer. The following conclusions can be drawn from this work.

1. A certain amount of La that was added into the galvalume bath can make Si enriched in the alloy layer. The stable diffusion path would form: overlayer/$\tau_5$/FeAl$_5$/Fe$_2$Al$_5$/z-Fe after 0.2-0.5 wt-%La was added into the bath. The liquid phase eroding the z-Fe phase or the Fe–Al phases directly will be avoided, and the violent reaction will be under control.

2. The $\tau_5$ phase becomes more compact and uniform when the galvalume bath contains a proper amount of La.

### Table 3: Average thickness of Fe$_2$Al$_5$ phase layer and $\tau_5$ phase layer galvanised in different baths for 300 and 600 s

<table>
<thead>
<tr>
<th>Hot dipping time/s</th>
<th>Thickness/$\mu$m</th>
<th>Bath A</th>
<th>Bath B</th>
<th>Bath C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Fe}_2\text{Al}_5$ layer</td>
<td>$\tau_5$ layer</td>
<td>$\text{Fe}_2\text{Al}_5$ layer</td>
<td>$\tau_5$ layer</td>
</tr>
<tr>
<td>300</td>
<td>8.9±0.3</td>
<td>5.6±0.2</td>
<td>6.1±0.2</td>
<td>7.3±0.3</td>
</tr>
<tr>
<td>600</td>
<td>15.8±0.3</td>
<td>7.5±0.5</td>
<td>7.6±0.3</td>
<td>9.5±0.3</td>
</tr>
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</table>
La. The compact τ phase can help to suppress the diffusion of Al and Zn towards the iron panel and hinder the formation of the Fe2Al5 phase.

3. The growth rate time constant decreases from 0.51 to 0.39 after 0.5 wt-%La was added into the bath. The thickness of intermetallic layer decreases after La was added into the galvalume bath.

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References