

Effect of Silicon-containing Reactive Steel on Hot-dip Galvanizing

1.1 Hot-dip galvanizing reaction of silicon-containing active steel

It is generally believed that the steel suitable for hot-dip galvanizing is boiling steel with low silicon content. The US Metal Manual specifies that the silicon content is less than 0.05%. After hot-dip galvanization, this type of steel can obtain a tight, continuous and uniform intermetallic compound structure.

In ISO 14713-2:2009 "Zinc coating - Corrosion protection guidelines and recommendations for steel structural parts - Part 2: Hot-dip plating", the relationship between the chemical composition of steel and typical coating characteristics when hot-dip galvanizing is performed at a temperature of 445~460°C is given, see Table 2-8.

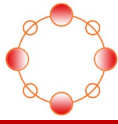
Table 2-8 Relationship between chemical composition of steel and typical plating characteristics

category	Chemical composition	Typical plating features	Description
A	$w_{Si} \leq 0.04\%$, $w_P < 0.02\%$		$w_{Si} + 2.5 w_P \leq 0.09\%$ of steel will also perform These characteristics; For cold-rolled steel, the steel composition exhibiting these characteristics is $w_{Si} + 2.5 w_P \leq 0.04\%$
B	$w_{Si} = 0.14\% \sim 0.25\%$	The surface of the coating is bright and densely organized; The surface of the coating contains a zinc layer	Iron-zinc alloys can grow to the surface of the coating; The thickness of the coating increases with the increase of silicon content. Other factors may also affect reactivity; When the w_P in the steel is greater than 0.035%, the reactivity will increase
C	$w_{Si} = 0.04\% \sim 0.14\%$	The surface of the plating is gray and the structure is coarse; The iron-zinc alloy layer is the main layer in the coating, and the iron-zinc alloy layer grows to the surface of the coating	Excessive plating may form
D	$w_{Si} > 0.25\%$		The thickness of the coating increases with the increase of silicon content

Note: 1. The presence of alloying elements (such as nickel) in zinc alloys has a significant impact on the coating characteristics shown in the table. This table does not provide relevant guidelines for high-temperature galvanizing (i.e., hot-dip galvanizing temperature of 530~560°C).

2. The composition of the steel shown in the table will change under the influence of other factors, and the composition range of each category will also change accordingly.

The popularization of continuous steel casting technology has brought new problems to hot-dip galvanizing. Unlike traditional ingot technology, continuous steel casting technology requires adequate deoxidation before casting, often using lower-cost silicon as the deoxidizer. Therefore, the



steels produced by this technology are all sedated or semi-calmed steels with a high silicon content. When hot-dip galvanizing, the silicon in the steel will significantly increase the reactivity of iron and zinc, so this type of silicon-containing steel is called "reactive steel". When silicon-containing active steel is hot-dip galvanized, there is often a gray, ultra-thick and poor adhesion coating, which significantly reduces the product quality. Therefore, the issue of hot-dip galvanizing of silicon-containing active steel has always attracted much attention.

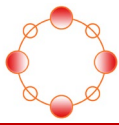
There are two main ways to solve the "activity" problem of silicon-containing active steel hot-dip galvanizing: one is to change the temperature of liquid zinc; The second is to add trace alloying elements to liquid zinc. To this end, hot-dip galvanizing technologies such as hot-dip plating poly-zinc alloy, zinc-nickel alloy, zinc-manganese alloy, zinc-magnesium alloy, and high-temperature galvanizing have been developed. These techniques can control the iron-zinc reaction through the action of alloying elements or by changing the reaction temperature to obtain a coating with a tight and continuous layered structure, appropriate zinc layer thickness, good appearance quality, and corrosion resistance and adhesion.

Silicon-containing active steel contains silicon that remains as an oxygen absorber from continuous steel casting and is specially added to increase the strength of the steel. The Shengdelin effect showed that the reaction between iron and zinc was significantly increased when the silicon content was 0.07%~0.1% and 0.3% or more, which showed that the activity and growth rate of the hot-dip galvanized layer increased significantly.

J. Foct et al. divided the silicon-containing steels into sub-Shendelin steel, Shendelin steel and pass-Shendlin steel according to the silicon content at the peak of the Sundelin effect reaction. For Yashendlin steel, similar to pure iron, at normal hot-dip galvanizing temperature, the coating structure obtained is Γ phase ($\Gamma + \Gamma$ 1 from the steel matrix), δ phase, ζ phase and η phase solidified by the surface free zinc layer, the phase layers are closely arranged and continuous, and the growth of the coating is parabolic. When Sundelin steel is galvanized, the iron-zinc reaction does not slow down with the increase of zinc immersion time, and the ζ phase in the intermetallic compound layer has always had a fast growth rate. When most of the ζ phase grows to the surface of the coating, the surface free zinc layer is no longer continuous, forming a coating with a gray surface, increased thickness and poor adhesion. The microstructure of the coating is characterized by the formation of extremely thick and discontinuous ζ phases. For the pass-Shengdelin steel with a w Si of close to 0.3%, the coating structure is composed of a fairly thick ζ phase layer and a $\delta + \zeta$ phase layer with iron-silicon predeposits, and its growth rate conforms to the linear law.

1.2 Effect of silicon on the growth of iron-zinc intermetallic compounds

When silicon-containing active steel is hot-dip galvanized, the structure, thickness and formation process of the iron-zinc intermetallic compound phase layer mainly depend on the



presence or absence of silicon in the steel. Under the influence of silicon, the reaction between the steel matrix and zinc is controlled by the initial dissolution process, and the growth of the coating is linear with time. When silicon oxides are formed on the surface of silicon-containing steel, the reaction is controlled by the diffusion in the phase layer of iron-zinc intermetallic compounds, and the growth of the coating is parabolic.

The effect of silicon content in steel on the growth rate (thickness change) of the intermetallic compound layer is related to the hot-dip plating time and dip plating temperature. As shown in Fig. 2-11, the growth rate of the intermetallic compound phase layer does not increase with the increase of silicon content when the silicon content of steel with a silicon content of less than 0.4% w Si is dipped for a short time ($\leq 20s$), and the growth rate of the phase layer increases when the dipping time reaches 2 minutes. For steels with a silicon content of more than 0.4% w Si, the growth rate increases with the increase of silicon content after a short period of dipping. This phenomenon is also related to the hot-dip plating temperature, which makes the growth rate change more obvious. The above results show that the effect of silicon in steel on the phase layer growth of intermetallic compounds does not play a role in the short dipping time, and only after a certain period of dipping reaction does silicon play a role in the phase layer growth behavior.

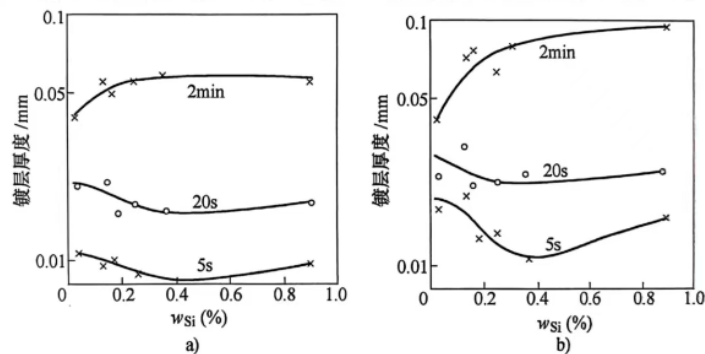
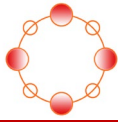


图 2-11 钢中硅含量对金属间化合物相层厚度的影响
a) 430°C b) 460°C

Silicon in steel affects the growth of iron-zinc intermetallic compound layers during hot-dip galvanizing, mainly affecting the diffusion of iron and zinc. Because the affinity of silicon atoms with iron atoms is greater than that of silicon and zinc, silicon atoms dissolve into iron to form iron-silicon compounds. Iron-silicon compounds first exist in a very fine, separate form and migrate as inert substances through the still thin intermetallic compound phase layer to the molten zinc interface. If these iron-silicon compound particles are fine enough and have sufficient supersaturation at the molten zinc interface at the ζ layer interface, they will promote the nucleation of the ζ phase in the molten zinc and form a broken phase layer. When the iron-silicon compound particles exceed the critical size, their effect decreases, the reaction no longer occurs, and a tight iron-zinc intermetallic phase layer will be formed.

The effect of silicon on the growth of hot-dip galvanized layer has been put forward by some

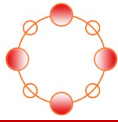


researchers to Γ the instability of the phase layer. They believe that when steel contains a certain amount of silicon, its ζ phase and the most iron-rich Γ phase will change significantly. With the increase of silicon content, the instability of the Γ phase layer occurs at the same time as the growth of ζ crystals, and the instability of the Γ phase layer plays a major role in the growth of the coating. For the coating of low-silicon mild steel, the Γ phase morphology is a thick columnar Γ phase layer, and there are only a few irregular phases at the Γ/Γ_1 interface, which is likely to be the result of different Γ_1 phase formation rates caused by different grain orientations in Γ phase. In the mild steel coating corresponding to the silicon content corresponding to the reaction peak, the Γ layer has instability, and Γ and Γ_1 interpenetrate to produce a jagged Γ/Γ_1 interface. The growth of γ_1 is obtained by diffusion of zinc to the surface of α -Fe and the reaction with α -Fe. When the $\Gamma_{\text{phase 1}}$ is formed continuously, the small grains of the Γ phase are separated from the iron surface, and at the same time, Γ_1 transforms into the δ phase, and the Γ grains move through the Γ_1 layer, but not through the Γ_1/δ interface, where it dissolves and disappears. For the transport mechanism of silicon in the hot-dip galvanized layer, this will allow the silicon to remain in the Γ phase because the solubility of silicon in Γ_1 is much smaller than in the Γ phase. When the silicon content exceeds a certain value, the Γ phase instability forms small solitary particles, and the Γ particles move to the Γ_1/δ interface in the Γ_1 layer through a strong Kirkendall effect. Since the solubility of silicon in the δ phase is greater than that of the Γ phase, silicon is easily transported and exists in the δ phase, and the silicon-rich δ phase can then be converted into the ζ phase.

K. Osinski et al. used diffusion coupling technology to study the reaction between silicon-containing mild steel and zinc and explained the reaction of hot-dip galvanized coating. They believe that the reaction is a ternary diffusion reaction, which is different from the binary diffusion reaction in that the addition of the third element increases the degrees of freedom, resulting in unstable and irregular diffusion and uneven forms. Regarding iron-silicon compounds, it is believed that iron-silicon compounds only exist in the earliest formation of ζ phase close to zinc, and with the prolongation of reaction time, the high silicon and high iron content at the beginning near the iron-silicon compound will decrease with the formation of iron-silicon compounds.

Some studies have suggested that silicon has zero solubility in the ζ phase, and it is present in δ phase and iron-silicon compounds. However, silicon favors the heteronucleation of the ζ phase in the liquid phase and makes the ζ layer more prone to diffusion, and the high supersaturation of iron is the main driving force for the formation of the ζ phase, which greatly reduces the critical size of the ζ crystals of heterogeneous nucleation.

J. Foct et al. studied the effects of different silicon contents on the nucleation and growth of hot-dip galvanized coatings. The zinc-rich angle of the Fe-Zn-Si ternary phase diagram at 450°C was calculated by thermodynamic calculations (Fig. 2-12). According to this phase diagram, both



silicon-containing liquid-phase zinc and iron-silicon compounds cannot coexist with ζ -phase binary equilibrium, they can only coexist with δ -phase binary equilibrium, so the silicon in the zinc bath can only be released by generating iron-silicon compound particles or by nucleating and growing in δ phase, and a model to explain the effect of silicon on the hot-dip galvanized iron-zinc reaction is proposed (see Fig. 2-13).

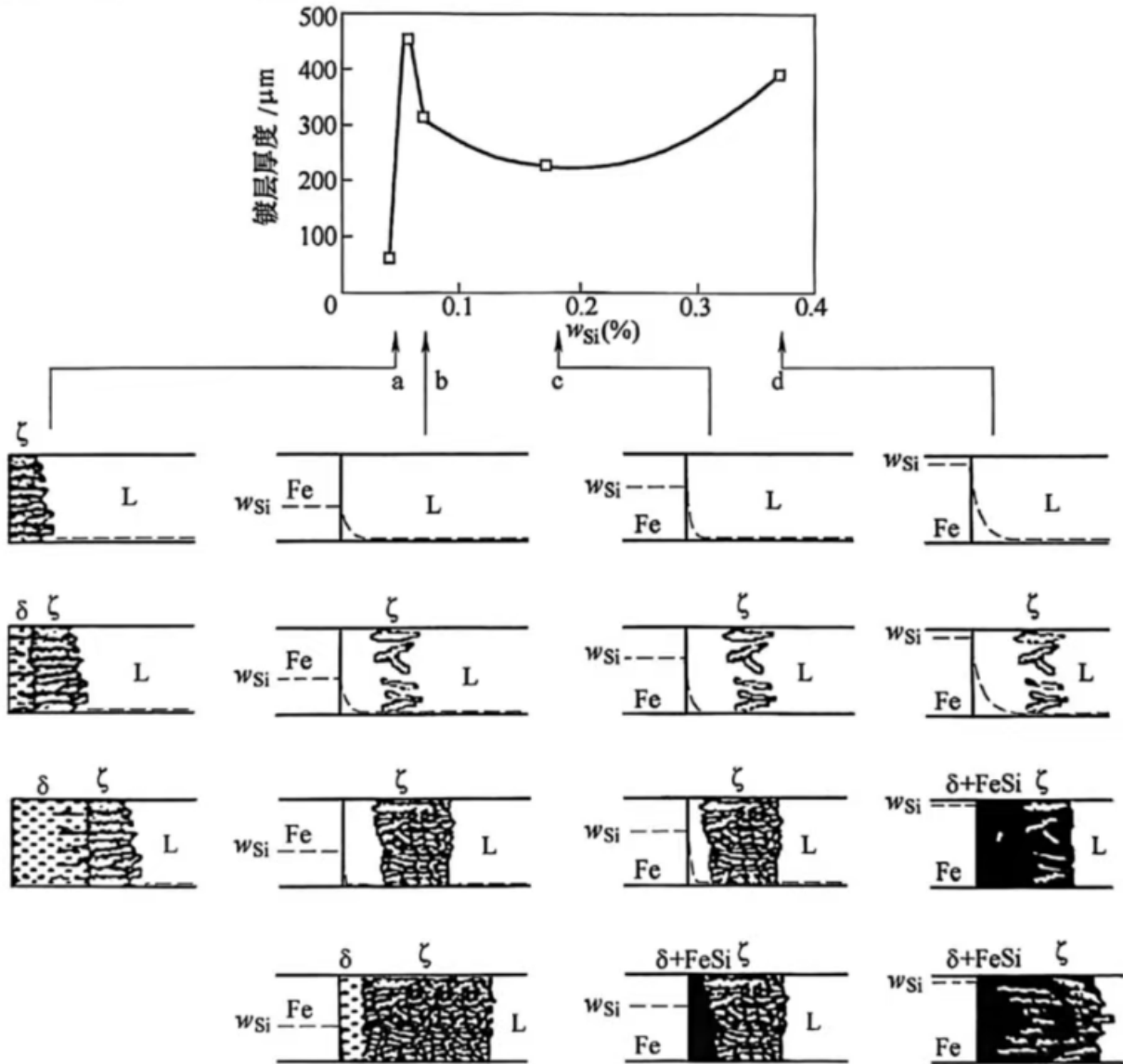
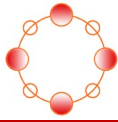


图 2-13 硅对热浸镀锌铁锌反应影响的模型

1) In the reaction between pure iron and liquid zinc, it is ζ the first iron-zinc alloy formation phase because the ζ is the easiest to achieve the content and energy conditions and its structure is simple. For sub-Shenderin steel and pure iron, the silicon content is not enough to inhibit the ζ phase formed at the initial stage of contact with the surface of the steel matrix, ζ it can be attached to the heterogeneous nucleation of the steel matrix. When the iron content in the ζ phase in contact with the steel matrix increases and meets the formation conditions of the δ phase, the δ phase will be generated, and then a very thin Γ layer can appear between the α -Fe and the δ phase, but the



growth of the Γ layer is affected by two aspects: first, the Γ will grow in the direction of the steel matrix; Second, the growth of δ will consume part of the Γ . All these phase growth mechanisms conform to the diffusion law, and the plating growth follows the parabolic law of $t^{1/2}$ (t represents growth time).

2) When the silicon content (w_{Si}) of the steel matrix is close to the Sendling peak (0.07%), the silicon will accumulate in the liquid phase next to the solid-liquid interface. Since the ζ phase cannot coexist with the liquid zinc binary equilibrium containing silicon, it cannot ζ attached to the heterogeneous nucleation of the steel matrix. However, at a distance from the steel matrix in the liquid phase, there is no or little silicon, and ζ grains can still be formed, which is ζ homogeneous nucleation. In this mesosphere liquid layer, iron transport can be carried out in a convection manner, which speeds up the transfer. As long as this intermediate liquid layer exists, the growth of the coating will accelerate and grow linearly until the iron content of the intermediate liquid layer increases to meet the formation conditions of the δ phase, and the δ phase balanced with the silicon-containing liquid zinc phase will grow between the matrix and the ζ layer, and the excess silicon will dissolve in the δ phase.

3) If the silicon content continues to increase, the liquid phase zinc is confined between α -Fe and the continuous ζ layer, a process similar to 2). However, the rapidly supersaturated silicon in liquid zinc creates conditions for the nucleation of iron-silicon compounds, and the liquid phase solidifies into a two-phase mixture of δ + iron-silicon compounds.

4) When the silicon content is larger, the ζ phase will grow homogeneously nucleated farther away from the steel matrix. On the one hand, the mixture δ + iron-silicon compounds limit the growth of the ζ phase parallel to the interface, and on the other hand, the large concentration gradient is formed due to the contact with the liquid zinc, which accelerates the growth of the coating. Although the growth of ζ grains parallel to the surface of the steel matrix and their bonding with each other are delayed, they are more likely to grow in the direction perpendicular to the surface of the steel matrix, which increases the thickness of the coating.