# The Effect of the Chemical Composition of Steel on the Iron-zinc Reaction

In the structural steel commonly used in hot-dip galvanizing, in addition to carbon elements, due to the limitations of raw materials and smelting processes, it generally contains silicon, manganese, sulfur, phosphorus and trace amounts of gas elements oxygen, nitrogen, hydrogen, etc. Among them, silicon and manganese are deoxidizers that must be added in the smelting process of steel, while sulfur, phosphorus, oxygen, nitrogen, hydrogen, etc. are brought from raw materials or the atmosphere and cannot be removed clean in smelting. There are also alloying elements deliberately added to alloy structural steels. The presence of chemical elements in steel not only affects the structure and properties of steel, but also has an impact on the hot-dip galvanization of steel.

The presence of chemical elements in steel will affect the rate of iron-zinc reactions and the properties of the coating. The reaction of steel with zinc containing chemical elements is no longer a simple binary system, and the presence of the reactive phase must be analyzed using ternary or quaternary phase diagrams. According to the phase law, there are single-phase and biphasic regions in the iron-zinc phase diagram. But in reality, the small amount of chemical elements contained in steel has little effect on the existence of these phases, and the phase produced by the reaction is very similar to that obtained by the reaction of pure iron and zinc. When the concentration of chemical elements in steel is high, its effect is more obvious, and may even lead to the formation of biphasic layers.

1. Carbon

Carbon is an indispensable element in steel, and different carbon content obtains different properties of steel. Generally speaking, during the hot-dip galvanizing process, the increase of carbon content in steel will intensify the iron-zinc reaction, thereby increasing the growth rate of the iron-zinc alloy layer. Galdman et al. studied the hot-dip galvanized coating obtained by steel with a carbon content of 0.1%~0.5% at 430~450°C, and found that when the carbon content wc in the steel increased from 0.1% to 0.5%, the growth rate time index n value of the coating could be significantly increased. In addition, with the increase of galvanizing temperature, the n-value of steel with low carbon content decreases, while the n-value of steel with high carbon content (WC is 0.5%) remains unchanged. Microscopic analysis shows that the increase of carbon content in steel will promote the growth of ζ phase and inhibit the growth of δ phase, and when the carbon content reaches 0.5%, the δ phase layer is almost completely inhibited, and the whole coating is basically composed of ζ phase.

The effect of carbon on the iron-zinc reaction depends not only on the carbon content in the steel, but also on the form in which the carbon in the steel is present and how uniformly it is distributed. The iron-zinc reaction in industrial pure iron becomes slower after carburizing, indicating that carburite is more stable than ferrite and reacts more hardly with zinc. If there are large carbide particles on the surface of the steel base, the plating will be missed because it does not react with zinc. If carbon is in the form of graphite or tempered martensitic, it has no effect on the iron-zinc reaction. But if carbon is present in spherical or lamellar pearlites, it increases the rate of iron-zinc reactions. Carburite itself is difficult to react with zinc, in pearlite steel, carburite exists as a component of pearlite, and pearlite steel intensifies the iron-zinc reaction, the reason for which is unknown. Some people think that the laminated or spherical structure of the pearlite makes the surface of the steel matrix uneven, thus increasing the iron-zinc reaction area. In addition, some people believe that the coarse $Fe_3C$ particles in the middle of the pearlite or some $Fe_3ZnC$ particles formed by reacting with zinc will rupture the surface layer of the steel matrix, thereby increasing the rate of iron-zinc diffusion reaction. This may also explain the fact that carburite, uniformly dispersed in martensitic, has no effect on the Fe-Zn reaction.

Carbon has an effect on the structure and thickness of the hot-dip galvanized layer. In general, the higher the carbon content, the more intense the iron-zinc reaction and the thicker the layer of intermetallic compounds. The effect of carbon on the iron-zinc reaction also depends on the morphology of the carbide in the steel, which is slower when the structure is more uniform in the steel.

2. Silicon

The silicon present in steel can speed up the dissolution of iron in zinc liquid, and is one of the elements that promotes the most violent iron-zinc reaction. As the silicon content in the steel increases, the iron loss value (representing the reaction rate) of the steel in the zinc liquid also increases.

The influence of silicon on the iron-zinc reaction in steel is manifested as the Sandelin effect, as shown in Figure 2-10. It can be seen from figures 2-10 that under the conventional hot-dip galvanizing temperature (450° C), when the silicon content in the steel is less than 0.03%, with the increase of silicon content, the iron-zinc reactivity can still obtain normal structure although the iron-zinc reactivity increases. When the silicon content in steel reaches 0.06%~0.1%, the iron-zinc reactivity increases sharply, and the thickness of the alloy phase layer peaks. When the silicon content in steel is close to 0.18%, the coating activity decreases,

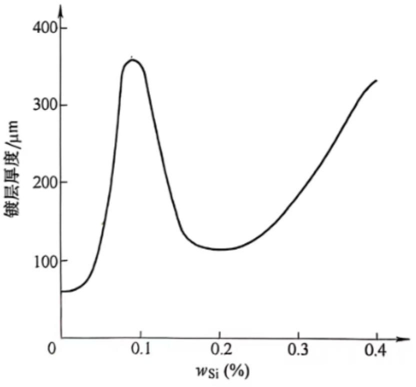

图 2-10 镀层厚度与钢中硅含量的关系（圣德林效应，450℃）

and when the wSi is higher than 0.3%, the iron-zinc reaction rate increases in a linear way.

The silicon content in steel affects the thickness of the iron-zinc intermetallic compound layer. When the silicon content in the steel is high, the ζ phase in the iron-zinc intermetallic compound layer in the coating will grow rapidly, and push the ζ phase to the surface of the coating, resulting in a rough and dull surface and a gray and dark coating with poor adhesion. Therefore, the influence of silicon in steel is also manifested in affecting the structure, appearance and properties of the coating.

3. Manganese and sulfur

In mild steel, there is less manganese and sulfur. It is generally believed that they have less impact on the structure of hot-dip galvanized layers. However, when manganese steel with more manganese content is hot-dip galvanized, there are Γ, δ, ζ and η phase layers in the coating, and the number of ζ phases is larger.

4. Phosphorus

The phosphorus in steel has a significant effect on hot-dip galvanizing, and trace phosphorus can promote the abnormal growth of the ζ phase, make the ζ phase grains coarse and inhibit the growth of the δ phase at the same time. When phosphorus is segregated on the surface of the matrix or in the growing zinc alloy layer, it will cause the advance formation of ζ phase. When the phosphorus content is about 0.15%, due to the rapid growth rate of the ζ and δ phases, the η phase layer becomes thinner, and matte spots will appear on the surface of the coating with thinner η phase. Phosphorus also affects the iron-zinc reaction rate of hot-dip galvanized layer, which is equivalent to 2.5 times that of silicon. Richard et al. found that when the silicon content in the steel is wSi <0.05%, which is not in the active range, if the phosphorus content in the steel is wp>0.03%, the ultra-thick coating will also be produced when hot-dip galvanized. Pelerin et al. studied the composite effect of silicon and phosphorus, and at a temperature of 460°C, the critical conditions for normal plating should be: if the silicon content is wSi <0.04%, wSi +2.5wp <0.09%. The French hot-dip galvanizing standard also stipulates that the steel composition suitable for hot-dip galvanizing is wSi+2.5wp≤0.09% or wSi+2.5wp≤0.11%.

5. Alloying elements

In order to change the properties of steel, some alloying elements are usually added to the steel, such as manganese, titanium, vanadium, niobium, etc. When the manganese content in steel is greater than 1.3%, the growth rate of the coating will be increased and the growth of the ζ phase will be promoted. Titanium, vanadium, niobium, etc. have basically no effect on the hot-dip galvanizing of steel workpieces, but for continuous hot-dip galvanizing, when aluminum is added to the zinc bath, the titanium, vanadium, niobium and other elements in the steel will promote the rupture of the FeAl barrier layer and make the aluminum effect in the zinc bath lose its effect prematurely. The reason is that these elements have the effect of refining the grains, which increases the grain boundaries on the surface of the steel matrix, and the grain boundaries on the surface of the steel matrix are the fast channels for zinc diffusion through the FeAl barrier layer.

When the aluminum content in steel is high, the iron and zinc reaction rate will be slowed down. When the wCr is greater than 11% or wNi is greater than 5% in steel, the coating will grow linearly. When the aluminum content in steel is low, it will promote the iron-zinc reaction, but with the increase of molybdenum content, this promotion effect will weaken, and when the wMo > 0.5%, it will slow down the iron-zinc reaction.

6. Gas

The effect of gas in steel has not been paid attention to. When the nitrogen content in steel reaches 0.02% (mass fraction), it still has no obvious effect on the iron-zinc reaction. If the oxygen contained in the steel appears in the form of oxides, it will cause the formation of an overly thick coating. Hydrogen in steel, usually produced by the pickling process, will escape during galvanizing, causing the alloy layer to crack and increase the iron-zinc reaction rate.