

Effect of the Chemical Composition of the Zinc Bath on the Iron-zinc Reaction

In addition to zinc, hot-dip galvanizing baths also contain various alloying elements. Some of these elements come from plating parts and zinc pot materials (iron, silicon, etc.), some are specially added to improve the properties of coatings and plating baths (such as lead, aluminum, manganese, magnesium, nickel, etc.), and some come from zinc ingots (cadmium, germanium, etc.). The alloying elements in the zinc solution change the physical behavior of the zinc bath by affecting the melting point, viscosity and surface tension of the zinc bath, as well as the growth behavior of the intermetallic compounds, thereby changing the thickness, structure and properties of the final coating.

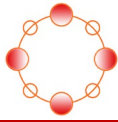
1. Iron

At 450°C (conventional hot-dip galvanizing temperature), the maximum solubility of iron in zinc liquid w_{Fe} is about 0.035%. As the hot-dip galvanizing process progresses, the iron from the steel workpiece and the iron zinc pot is continuously dissolved into the zinc bath. As the iron content continues to increase, the supersaturated iron in the zinc bath combines with zinc to form denser iron-zinc intermetallic compounds (i.e., zinc slag) that gradually sink to the bottom of the zinc pot. The formation of zinc slag increases zinc consumption. The increase of iron content in the zinc bath increases the viscosity of the zinc liquid and decreases the ability to infiltrate the steel matrix. The increase in iron content also significantly thickens the coating, and its ductility and appearance quality deteriorate.

2. Aluminum

The function of adding aluminum to the zinc bath is to improve the luster of the hot-dip galvanized layer, reduce the oxidation of the surface of the zinc bath, inhibit the excessive growth of iron-zinc intermetallic compound layers, and increase the ductility and corrosion resistance of the coating.

The test results show that when the content of aluminum in the zinc bath is 0.01%~0.12%, the gloss of the coating can be significantly improved. This is because aluminum has a greater affinity for oxygen than zinc, so a protective film of Al₂O₃ is formed on the surface of the zinc solution, which reduces the oxidation of zinc. When the aluminum content in the zinc bath reached 0.1%~0.15%, aluminum had an inhibitory effect on the growth of iron-zinc intermetallic compound layers. The inhibition of iron-zinc intermetallic compound layer is generally considered to be the inhibition effect of aluminum, and a Fe₂Al₅ barrier layer is formed on the surface of iron, which hinders the reaction between iron and zinc, thus delaying the growth of iron-zinc intermetallic layer.



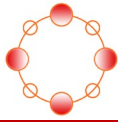
When the dipping time is long, the Fe₂Al₅ layer is destroyed, and an iron-zinc diffusion reaction will occur, and a Γ , δ , and ζ phase layer will be formed, but its thickness will be smaller than that without aluminum. When the aluminum content in the zinc bath reaches 0.3%, the corrosion resistance of the coating is significantly improved.

When the content of aluminum in the zinc bath is greater than 0.15%, the formation of brittle iron-zinc alloy phase can be inhibited, and a coating with suitable thickness and good adhesion can be obtained. This is due to the first formation of a continuous Fe₂Al₅ phase layer on the iron matrix, which inhibits the iron-zinc reaction. However, the inhibitory layer often bursts within a few seconds and loses its inhibitory effect on iron-zinc reaction. At the same time, within this content range, a large amount of scum will be generated on the surface of the zinc bath, which is easy to cause the failure of conventional plating aids. Therefore, when hot-dip galvanizing steel workpieces, the aluminum content w Al is generally controlled at 0.005%~0.02% to improve the luster of the coating. The inhibitory effect of aluminum on the iron-zinc alloy phase is widely used in continuous hot-dip galvanizing of strip steel, but it is less commonly used in batch hot-dip galvanizing of steel workpieces.

3. Lead

On the one hand, the lead in the hot-dip galvanizing bath is carried by zinc ingots, and the lead content in zinc ingots is generally 0.003%~1.75%. At 450°C, lead is about 1.2% soluble in a zinc bath, and excess lead sinks to the bottom of the pot. The lead in the zinc bath has no effect on the formation of iron-zinc intermetallic compound layers, but it can reduce the melting point of the zinc bath, prolong the freezing time of the zinc bath, and reduce the viscosity and surface tension of the zinc bath, thus increasing the wettability of the zinc bath on the surface of steel and reducing the appearance of exposed points. The addition of lead to the zinc bath also helps to form zinc flowers on the surface of the hot-dip galvanized layer.

Harvey et al. believe that lead in zinc baths is more conducive to sediment and slag retrieval. Lead exists in the form of diffuse spherical particles in solid zinc and is easily precipitated at the edge of the iron-zinc alloy phase layer. Lead has little effect on the thickness, quality, ductility and corrosion resistance of the coating. Therefore, they believe that it is not necessary to deliberately add lead due to the lead contained in zinc ingots. However, Krepski's study found that as the lead content in the zinc bath increased until it was saturated, the surface tension of the zinc bath continued to decrease. Excessive surface tension in the zinc bath will affect the smoothness of the surface of the coating, and it is easy to have defects such as droplets, bulges, and burrs at the bottom of the plating part. The zinc bath had the worst fluidity when the lead content in the zinc bath was 0.5% w_{Pb}. The poor fluidity of the zinc bath will cause the zinc liquid on the plating parts to flow poorly and produce flow marks. The test proves that the zinc bath can improve the fluidity of the



zinc bath, reduce the flow mark and reduce the zinc consumption when the zinc bath contains saturated lead. It can reduce the operating temperature and reduce energy consumption; It can improve the wettability of steel in the zinc bath and improve the ability of steel workpiece to be zinc plated between the gaps, and avoid out

Present leakage plating.

On the other hand, there are also those who deliberately add lead to zinc baths. When the solubility of lead in liquid zinc exceeds its saturated solubility, lead will be deposited at the bottom of the zinc pot, which can prevent the bottom of the zinc pot from being eroded by zinc. In addition, since lead is denser than zinc slag, the zinc slag that is constantly produced is deposited on top of the lead layer, which helps to remove zinc slag. Although the high lead content in the zinc bath has little effect on the growth of the alloy structure, due to the good fluidity of the zinc bath, the free zinc layer is thinned, making the alloy layer more likely to appear on the surface of the coating and producing gray and dark plating.

4. Antimony and tin

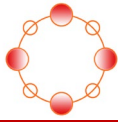
The presence of antimony in the zinc bath can improve the fluidity of the zinc bath and reduce the surface tension of liquid zinc on the steel matrix, making the coating more uniform and smooth. However, the segregation of antimony in the coating will affect the activity of the coating, and the coating will be locally blackened after a certain period of time.

When the zinc bath contains both lead and tin or antimony and tin at the same time, zinc flowers will appear on the surface of the coating, which are formed by the formation of dendrites when zinc solidifies. For hot-dip galvanizing of steel workpieces, the production of zinc flatter is not conducive to the corrosion resistance of the coating.

When only tin is contained in the zinc bath, zinc blooms do not appear on the plating. A small amount of tin ($w_{Sn} < 1\%$) had no effect on the morphology and thickness of the coating. When the tin content reaches 5%, it can inhibit the ultra-thick growth of the active steel coating.

5. Copper

When the copper content in the zinc bath w_{Cu} is less than 0.05%, the obtained coating is basically unchanged. When the copper content w_{Cu} increased to 0.6%, it had no effect on the microstructure of the coating, but the thickness was slightly thickened. When the copper content w_{Cu} increases to 0.8%~1.0%, the thickness of the coating increases, and the structure changes significantly, the δ layer thickens, the ζ phase layer gradually disappears and transforms into δ phase grain fragments, and some ζ phase small grains are mixed and diffused in the η free zinc layer. When the copper content in the zinc bath w_{Cu} is 1%~3%, the ζ phase completely disappears, and a very thin and copper-free Γ phase is formed close to the iron matrix, the outermost layer is the η phase full of small particles, and the Fe-Zn-Cu ternary phase layer with fine microcracks between



the two phase layers is the Fe-Zn-Cu ternary phase layer with fine δ microcracks, and the small particles diffused in the η phase layer are the δ phase. With the further increase of copper content, the thickness of the plating layer will increase sharply, mainly due to the intense growth of the outer layer (η + diffusion δ) phase.

Increased copper content in zinc baths increases zinc slag formation. When a zinc bath contains both copper and aluminum, the two cancel each other out.

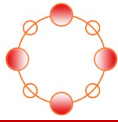
6. Cadmium

The presence of cadmium in the zinc bath can promote the reaction between the steel matrix and the zinc bath. When the cadmium content w_{Cd} was 0.1%~0.5%, it could promote the formation and growth of zinc flowers. Cadmium in a zinc bath increases the thickness of the iron-zinc intermetallic compound layer, which increases the brittleness of the coating. The increase in cadmium content in zinc baths also correspondingly increases the rate of iron dissolution. Cadmium improves the resistance of coatings to atmospheric corrosion.

A certain amount of cadmium in the zinc bath will significantly promote the growth of the ζ phase of the coating while inhibiting the growth of the δ phase. When the cadmium content in the zinc bath w_{Cd} was less than 0.6%, it had no effect on the coating structure, but the thickness increased slightly. When the cadmium content w_{Cd} is 0.8%~1.0%, the growth of the alloy layer becomes irregular, the thickness of the ζ and δ phases fluctuates greatly, and the interface of the δ/ζ phase is uneven, and there is a small amount of cadmium precipitates in the η phase and between the grains of the ζ phase. When the cadmium content w_{Cd} increased to 1.3%~2%, the structure of the alloy layer changed greatly, the thickness of the ζ phase increased significantly and became columnar, and the interface between the δ/ζ phases was obviously "jagged". When the w_{Cd} exceeds 2%, the δ phase disappears completely and the coating thickness increases dramatically, mainly due to the thickening of the outer phase (η + diffusion δ).

7. Germanium

Germanium is retained in zinc ingots when zinc is smelted through certain germanium-containing minerals. The presence of trace amounts of germanium in the zinc bath will accelerate the interdiffusion rate between iron and zinc and the overall growth rate of the hot-dip zinc coating, increase the instability of the ζ/η interface, and make the zinc bath very easy to penetrate into the ζ phase layer, thus enhancing the activity already existing in silicon-containing steel. It was found that when the germanium content in the zinc bath exceeded 0.08%, the iron-zinc interdiffusion and the growth rate of the whole coating were promoted. However, when the zinc bath also contains aluminum, when the inert steel is immersed in this zinc bath, germanium will still promote the growth of the entire coating and inhibit the growth of the δ phase; When the active steel is immersed in this zinc bath, the presence of germanium is conducive to enhancing the inhibitory



effect of aluminum on the iron-zinc reaction.

8. Nickel

On the surface of the study, the content of nickel in the hot-dip galvanizing bath w_{Ni} is 0.04%~0.12%, which can slow down or eliminate the Sundelin effect of silicon-containing reactive steel, reduce the iron-zinc reaction rate, eliminate the abnormal growth of the ζ phase when the active steel is galvanized, improve the adhesion of the coating, and form a continuous η on the surface of the coating. The phase is free of zinc layer, thus keeping its appearance shiny. It was found that there was a nickel-rich layer at the interface between the η phase and the ζ phase, and the nickel content increased with the extension of the dipping time. Obviously, the nickel-rich layer at the η/ζ interface blocks the cross-diffusion of iron and zinc atoms through the ζ layer, resulting in the slowdown of the growth of the iron-zinc alloy layer. However, for high-silicon steel (silicon content w_{Si} greater than 0.25%), the addition of nickel in the zinc bath had little effect on inhibiting the abnormal growth of the ζ phase.

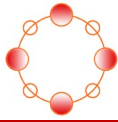
Adding nickel to the zinc bath can also improve the fluidity of the plating solution, so that the surface zinc can flow back to the zinc bath faster when the plating part is proposed to the zinc bath, thereby reducing zinc consumption, reducing the appearance of defects such as droplets and flow marks on the surface of the coating, and making the coating smoother and more uniform. However, when the nickel content in the zinc bath exceeds 0.06%, Fe-Zn-Ni ternary γ_2 phase zinc slag will be produced, which will increase the amount of zinc slag and may adhere to the surface of the coating and cause particles.

9. Magnesium

When hot-dip galvanizing silicon-containing active steel, magnesium is added to the zinc bath for the following reasons: magnesium and silicon can form stable magnesium-silicon compounds, and a small amount of magnesium can reduce the melting point of zinc alloys. These properties of magnesium can directly inhibit iron-zinc reactions by forming magnesium-silicon compounds to replace the formation of iron-silicon compounds, or indirectly by reducing the melting point of alloys.

The results of hot-dip galvanizing of mild steel with 0.1%~0.2% w Mg and 0.18%~0.25% W Si by M. Memmi et al. show that the growth of the coating can be controlled after magnesium addition, the fluidity of the zinc bath can be increased, and the hot-dip galvanizing temperature can be reduced without reducing productivity.

Early studies suggest that 0.6% wMg in zinc bath will thicken the coating, but further increase in magnesium content can reduce the thickness of the coating. When mild steel is hot-dip galvanized in a zinc bath with 0.3% W Mg, the activity will be greatly increased, resulting in a poor coating appearance. For this reason, J. Mackowiak et al. believe that adding magnesium can help



improve the coating performance, but since the appearance quality of the coating is not only related to the magnesium content in the zinc bath, but also related to the composition of the galvanized steel, the amount of magnesium added must be carefully controlled to achieve the effect.

10. Manganese

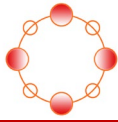
When the wMn in the zinc bath is 0.5%, manganese enters the entire intermetallic compound layer, especially in the ζ phase, affecting the diffusion of the δ/ζ interface and promoting the growth of uniform and dense δ and ζ phases. When the manganese content is 1.5%~5%, the corrosion resistance, adhesion and forming processing performance of the coating can be improved

The test results show that the thickness growth rate of the intermetallic compound layer in the hot-dip coating of silicon-containing active steel in a zinc bath with about 0.5% wMn is much smaller than that in conventional hot-dip galvanizing. Silicon-containing active steel was hot-dip plated in a zinc bath at 450 °C and 1% wMn for 9 minutes. The microstructure of the coating is similar to that of the inactive steel coating. From the perspective of thermodynamics, due to the difference in the free energy of the Gibbs formation of iron-silicon compounds and manganese-silicon compounds, the binding force between manganese and silicon is greater than that between iron and silicon, so manganese-silicon compounds are easy to precipitate and precipitate. For silicon-containing active steels, the binding of silicon in the steel to the manganese in the zinc bath does not lead to the appearance of a silicon saturated layer near the surface of the steel matrix at the beginning of hot-dip plating. Therefore, when silicon-containing activated steel is hot-dip plating, the iron-zinc intermetallic compound layer can grow in an inert way on the steel matrix, thereby eliminating the influence of silicon content in steel on the ultra-thick growth of the coating.

11. Bismuth

In conventional hot-dip galvanizing, a certain amount of lead is usually added to the zinc bath to increase the fluidity of the zinc liquid and reduce the amount of zinc adhesion on the surface of the plated part when the plating part is lifted out of the zinc bath. Due to the pollution of lead to the environment, the use of lead has been gradually restricted, so a hot-dip galvanized bismuth alloy technology that replaces lead by adding bismuth to a zinc bath has been proposed.

S. K.Kim et al. studied the hot-dip galvanizing process of adding bismuth and aluminum (w_{Bi} 0.1, w_{Al} 0.025%~0.05%) to the zinc bath, and found that the fluidity of the zinc bath was significantly improved, the zinc slag and zinc ash were reduced, the zinc consumption was reduced, and a bright coating was obtained. R. Fratesi et al. studied hot-dip galvanized bismuth alloys and found that for mild steels with a silicon content greater than 0.05%, the iron-zinc reactivity can be effectively controlled, and for steels with a silicon content of less than 0.05%, a more densely structured coating can be obtained. However, J. Perderson's study came to a different conclusion: the addition of bismuth to zinc baths with different nickel contents had no significant effect on the



thickness and structure of the coating.

Existing research work shows that in addition to affirming that bismuth can increase the fluidity of zinc liquid, the distribution, mode of action and effect of bismuth in the intermetallic compounds of the coating are still unclear, and further research is needed.

12. Titanium

Titanium is a highly blunt metal and has strong blunt stability, when it is exposed to atmospheric or aqueous solution, it can form a layer of TiO₂ oxide film with good stability, strong adhesion and excellent protection, so that the coating is in a passivated state. This film also has good self-healing properties, and when it is damaged by corrosion, the passivation film can quickly repair itself.

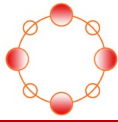
The results show that adding a certain amount of titanium ($w_{Ti} \leq 0.1\%$) to the hot-dip pure zinc bath can inhibit the reactivity of silicon-containing steel ($w_{Si} 0.04\% \sim 0.18\%$) hot-dip galvanizing to varying degrees, stabilize the ζ phase, and promote the continuous dense δ phase thickening. With the increase of titanium content in the zinc bath, the alloy phase layer gradually decreases. When the addition of titanium in the zinc bath w_{Ti} is $0.03\% \sim 0.05\%$, it can completely inhibit the Sundelin effect of conventional hot-dip galvanizing of steel with w_{Si} of 0.09% . But for steel with a w_{Si} of 0.36% , the role of titanium is not obvious. When the addition of titanium in the zinc bath $w_{Ti} \geq 0.05\%$, the hot-dip coating containing silicon steel with w_{Si} of $0.04\% \sim 0.36\%$ appeared in the η phase layer, and the γ_2 phase particle nucleus grew by absorbing the titanium atoms in the η phase and the iron atoms dissolved at the front of the ζ phase, and increased and grew with the increase of titanium content and dipping time in the zinc bath.

The corrosion test results show that the corrosion rate of hot-dip zinc-titanium alloy coating is smaller than that of pure zinc coating, and its polarization resistance and AC impedance increase, the corrosion current density decreases and the corrosion resistance is improved.

13. Rare earths

Rare earths (RE) have high chemical activity and large atomic radii, and are commonly used for hot-dip galvanizing Rare earth elements include cerium, Lanthanum and others.

After the rare earth elements are added to the zinc bath, some of the rare earths will undergo redox reactions with zinc oxide, replacing zinc and forming rare earth oxides suspended on the surface of the zinc bath, which hinders the contact between zinc liquid and air, thereby protecting zinc from oxidation and reducing the oxidation loss of zinc. Rare earths can reduce the surface tension of liquid baths, reduce the wetting angle, reduce the viscosity of zinc baths, and improve the fluidity of zinc baths. The reduction of surface tension in the plating bath reduces the critical size of the nucleus formation, increases the nucleation core, and provides heterogeneous nuclei for alloy



crystallization. Those rare earths that have not become heterogeneous nuclei are enriched at the front of alloy crystallization, inhibiting grain growth during solidification and refining the structure of hot-dip galvanized layer.

Rare earths can improve the corrosion resistance of hot-dip galvanized layers. Some studies believe that the addition of rare earths makes the corrosion potential of the coating shift forward and the corrosion current is reduced, thereby improving its electrochemical corrosion resistance. The corrosion products of pure zinc coating are mainly ZnO, which has a loose film layer and good conductivity, which cannot effectively inhibit the progress of corrosion, while the corrosion products of the coating after the addition of rare earths are $ZnCl \cdot Zn(OH)_2$, the film layer is denser and the conductivity is poor, so it can effectively inhibit the corrosion reaction. Rare earth metals are surfactant elements that tend to enrich surfaces and form dense and uniform oxide layers. These oxide layers act as a barrier to diffusion, thereby delaying the oxidation and corrosion processes of the coating.

The amount of rare earths added is not the better, and must be controlled within a certain range. Some researchers have studied the effect of adding different contents of rare earths to the zinc bath on the corrosion resistance of hot-dip galvanized layers. The results show that when the rare earth content in the zinc bath is 0.1%, the best corrosion resistance and appearance quality of the coating can be obtained. When the rare earth content is greater than 0.2%, a large number of rare earth composite phases may be concentrated at the grain boundary, reducing the corrosion resistance of the coating and accelerating the erosion of the zinc pot.

14. Others

The silver content in the zinc bath promotes the growth of the coating, resulting in a thicker coating with better corrosion resistance. Zinc baths contain chromium, vanadium or zirconium, which can inhibit iron-zinc reactions. They form ternary compounds at the apex of the ζ phase or at the ζ /liquid-zinc interface, hindering ζ phase growth, thinning the ζ phase, and smoothing the ζ /liquid-zinc interface.