The Surface State of Silicon-containing Steel has an Effect on the Hot-dip Galvanized Layer

It is well known that batch hot-dip galvanizing with silicon steel will cause abnormal or active coating formation when the W Si is close to 0.1% (i.e. at the Sendrein peak) or greater than 0.3%. On the surface of silicon-containing hot-rolled steel, the active zones are usually randomly distributed. When hot-dip galvanizing these steels, coarse ζ-phase grains and thick ζ-phase layers will be formed in the coating, which will make the appearance and mechanical properties of the coating worse and the zinc consumption will increase.

Local advance growth is a typical feature of hot-dip galvanizing of hot-rolled active steel. When the surface is treated mechanically or chemically, the formation of the active coating is significantly enhanced. Numerous studies have been conducted on the effect of surface condition and cold working on the hot-dip galvanizing reaction of silicon-containing steel, but no completely consistent mechanism has been proposed to explain the cause of the formation of local active coating structure. Other factors, such as tertiary element content, grain orientation, and surface or subsurface oxidation, may play a role in the activity phenomenon. In the process of hot-dip galvanizing, although the zinc bath temperature, galvanizing time and other parameters are constant, the coating structure is very different due to the changes of the above factors during the processing process before galvanization. Therefore, correctly distinguishing the influence of various factors on the surface of silicon-containing steel on the hot-dip galvanized layer will help to understand the problem of hot-dip galvanizing of silicon-containing active steel.

1.1 Subsurface oxidation

The presence of silicon in reactive steel is an important reason for the formation of reactive coatings. Many studies have given basically the same law: when the w Si in steel is about 0.1%, the coating activity increases and the reaction rate peaks; When w_{Si} is close to 0.2%, the activity decreases; When w_{Si} is higher than 0.3%, the reaction rate increases significantly. However, the activity of silicon-containing steel is related to the solid silicon content on the steel surface. Studies have shown that silicon on the surface of steel in the form of iron-silicon compounds will increase hot-dip galvanizing activity, while silicon in the form of SiO2 will not increase activity. Therefore, when hot-dip galvanizing active steel, the solid silicon content on the surface of the steel should be considered.

The hot rolling process of silicon-containing steel leads to the formation of a subsurface oxide layer of steel, in which silicon oxides are present in the form of small particles at grain boundaries and within the grain. Since the oxide formation energy of silicon is greater than that of iron, the silicon in solution will preferentially react with oxygen to form a stable inert compound that exists at subsurface grain boundaries and grains. Therefore, the inhibition of the behavior of the active coating is related to the precipitation of these inert silicon oxides in the subsurface oxide layer. K. Nishmura et al. preheated steel plates with different silicon contents under different conditions after high-temperature pickling and polishing, and found that the speed of oxide film formation on the surface of silicon-containing steel was greater than that of silicon-free steel during preheating treatment, and the reaction between liquid zinc and steel matrix was limited. The analysis of the steel matrix shows that the silicon aggregation area appears on the surface of the steel matrix, and it is believed that the accumulation area appears during the preheating treatment, which has an inhibitory effect on the subsequent hot-dip galvanizing reactivity.

V. Leroy et al. pointed out that the silicon content of hot-rolled steel in the subsurface oxide layer near the surface increased significantly. According to ion probe (IMA) analysis, the overall silicon content of the steel matrix w_{Si} is only 0.228% on the surface, and the enrichment of silicon w_{Si} is as high as 8%. while w_{Si} is only 0.01% steel, and the surface silicon enrichment w_{Si} exceeds 1%. The determination of the elemental distribution of steel at different depths confirms that the decrease in oxygen content is consistent with the change in silicon content. For steel with a w_{Si} of 0.01%, silicon is undetected at all depths except the surface. In steel with a w_{Si} of 0.228%, silicon is clearly distributed at all depths, which may be the silicon in the solid solution state of the steel.

The two types of steel show significant differences after pickling and hot-dip plating to remove the subsurface oxide layer. Low-silicon steels form a typical tight-structure coating, while high-silicon steels form an active coating, indicating that the solid-solution silicon is sufficient to destabilize the coating.

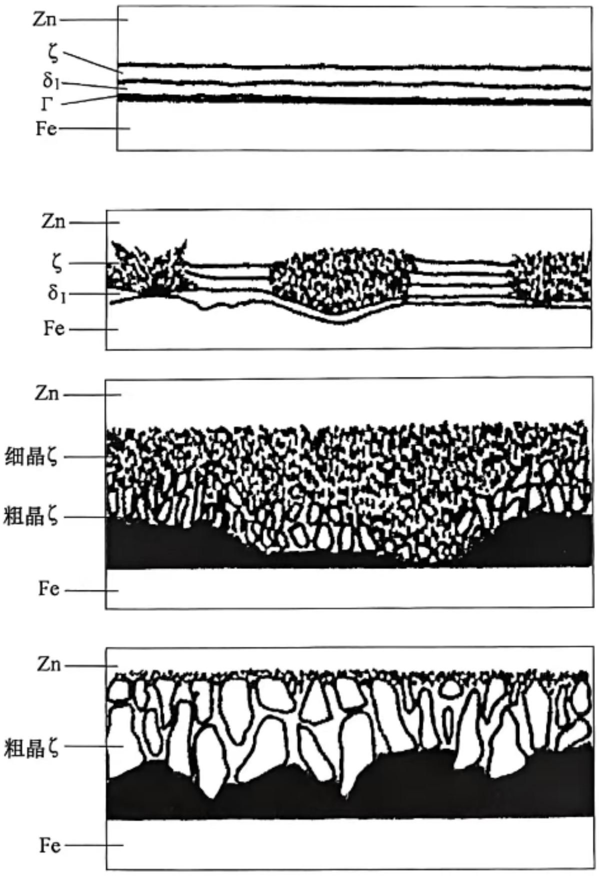

图 2-14　高硅含量钢亚表面氧化层的腐蚀深度对镀层组织的影响（由上至下腐蚀深度增加）

When hot-dip galvanizing silicon-containing active steel, the solid silicon content on the surface of the steel matrix reacting with zinc must be considered. The solid silicon content on the surface of hot-rolled silicon-containing steel is affected by two opposite effects: on the one hand, due to the oxidation of the subsurface during high temperature heating, a part of the silicon forms oxide, which reduces the solid silicon content; On the other hand, the corrosion of the oxide layer on the subsurface of the steel subsurface such as rust and pickling before plating increases the solid silicon content on the surface of the steel matrix to varying degrees. Therefore, the degree of corrosion also leads to changes in the structure of the coating. Fig. 2-14 shows the effect of corrosion depth on the coating structure of the subsurface oxide layer of steel with high silicon content. It can be seen from Fig. 2-14 that with the increase of corrosion degree, the thickness of the coating increases significantly, and the coating structure also changes from layered to dispersed. It can be seen that for silicon-containing activated steel coatings, extending the pickling time, pickling-back plating, and pre-plating sandblasting treatment will change the surface solid silicon content due to the destruction of the subsurface oxide layer, resulting in an increase in the coating activity.

Oxygen plays an important role in subsurface oxidation. To confirm the importance of oxygen in the reaction, G. Hansel hot-dip galvanized four steels with different activity (wSi 0.023%~0.06%). Low silicon content steel is active after several times of pickling and replating. When annealed in an oxidizing atmosphere (N2-O2-H2O), they become inert, while steels with high silicon content require an oxidizing atmosphere with a higher O2 content or a longer heating time to achieve the same effect. However, when annealing in a non-oxidizing atmosphere (H2), the coating morphology did not change. The results show that the inhibition of activity of silicon-containing steel by subsurface oxidation is related to the O2 content and heating time in the preheat treatment atmosphere.

1.2 Surface roughness

The surface roughness has a significant impact on the formation of hot-dip galvanized layer, and the unevenness of the surface of the steel matrix will change the growth form of the iron-zinc alloy layer. The growth form of hot-dip galvanized coating without silicon steel concave and convex surface is shown in Fig. 2-15. At the protrusion, the newly formed ζ crystal phase is separated, so that liquid zinc can penetrate near the ζ/δ interface, supporting the continuous and rapid growth of the ζ phase to form burst grains. In the depression, a tight and stable structure can be obtained because the growth is controlled by diffusion.

The formation of a stable structure in the depression of a rough surface may be due to the result of volume shrinkage, generating sufficient compressive stress

The iron-zinc alloy phase layer is stable. Once the stability layer is formed, it will remain stable regardless of whether the cause of the stability exists. In addition, there are conditions that support the formation of iron-rich layers in surface depressions. The supply of iron required for the reaction is sufficient due to the large surface area provided for the growth of the volume shrinkage alloy layer, while the supply of zinc is reduced due to the difficulty of zinc in entering the depression. In these locations, thick layers of Γ are often found.

F. Petter et al. studied the combined effects of silicon content and surface roughness of steel.

The steel plates with different silicon contents were sandblasted with coarse emery, fine emery, and glass beads, and treated with pickling methods, and different surface roughness from coarse to fine was obtained. Figure 2-16 shows the relationship between the silicon content of steel with different surface roughness and the thickness of the hot-dip galvanized layer. The test results show that the steel treated with crude emery has a thick coating in different silicon content ranges, and the relatively rough surface of the steel produces a burst ζ phase structure at the bulge and a tight structure in the depression. The steel treated with pickling and glass beads forms a typical whisker structure when the silicon content w Si is 0.08%~0.12%. When fine emery is treated with steel with 0.08% w Si, the coating thickness decreases, forming a tight continuous δ layer and a flat ζ/δ interface, but when dealing with steel with w Si of 0.12%, the coating thickness increases dramatically. This is because in steel with a w_{Si} of 0.08%, the mechanism of plating stabilization is the formation of an iron-rich layer, which no longer forms a stable Γ layer when the silicon content w Si increases to 0.12%. This transition may be the result of the system becoming unstable with a small increase in silicon content during the formation of a stable iron-rich layer.

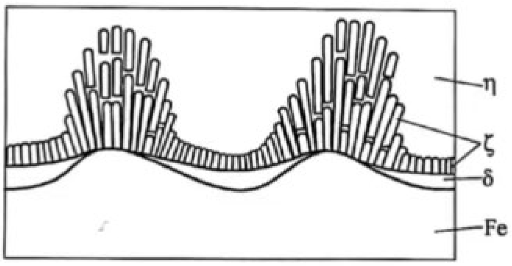

图 2-15 钢材凹凸表面的热浸镀锌层生长形态

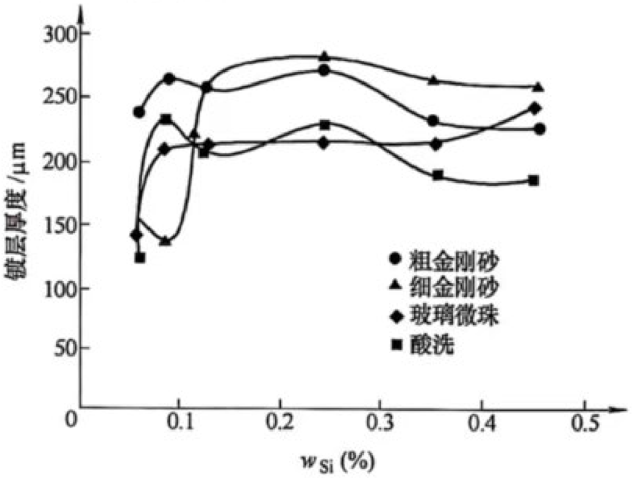

图 2-16 不同表面粗糙度钢材硅含量与热浸镀锌层厚度的关系

The above results show that although the surface roughness of fine emery and glass bead-treated steel is similar, the stability of the final coating is very different due to the different morphology. Therefore, surface roughness cannot be simply used as a parameter to evaluate whether an active coating structure is produced.

1.3 Residual stress

In practice, most steel workpieces have undergone machining before hot-dip galvanizing. A lot of research has been done on whether the residual stress increased by processing deformation changes the structure of the galvanized layer. D. Horstmann et al. believe that both hot-rolled and cold-rolled steels will have streaks or local active spots on the surface. This view is also supported by G.Hansel's results when hot-dip galvanizing hot-rolled and cold-rolled steels with the same silicon content. D. Horstmanalso found that the cold-drawn parts with critical silicon content formed streaks in the roll direction, indicating that the strain energy in the steel accelerated the diffusion of iron in the hot-dip galvanized layer and led to the activity.

Heat treatment is also used as a method to determine the effect of strain energy on the coating reaction, but these results may be caused by oxidation effects. Huacheng is matched. A.J.Vazquez et al. pointed out that heat treatment can cause changes in the growth behavior of the coating at a lower temperature of 550°C. However, G.Hansel found that recrystallization treatment at 600°C for 1 hour did not affect the activity of coating formation.

G.E. Ruddle et al. believe that different surface preparation of electropolished single crystal specimens can lead to different hardness. For these specimens, there was no tendency to increase activity due to increased surface stress.

G. Hansel pointed out that the application of additional cold rolling to the pre-cold-rolled steel plate, which reduces the thickness by about 55%, will lead to an increase in activity, and the highest silicon content corresponds to the greatest active effect, thus concluding that stress action is effective. However, in this case, the state of the surface changes, and the thickness is reduced by about half due to surface stretching, which correspondingly reduces the thickness of the subsurface oxide layer, which may be more susceptible to exposing more active points.

E. C. Mantle's study presents further evidence that stress effects do not exist in hot-dip galvanizing. After sandblasting of steel specimens, it was found that after changing the sandblasting conditions, the lattice stress changed, and these steel specimens obtained the same coating thickness after hot-dip galvanizing. This indicates that the stress effect has no obvious effect on the activity of the coating.

However, it is difficult to show that the stored strain energy has no effect on hot-dip galvanizing behavior, because other factors such as oxidation effect, silicon content and surface roughness effect may have an impact on hot-dip galvanizing behavior. Many experimental evidence suggests that stress has little effect on active phenomena.

1.4 Surface grain orientation

G. E. Ruddle et al. conducted a series of tests to determine the effect of grain orientation on hot-dip galvanizing reaction. After the steel specimen is sanded and polished to remove the defective layer on the surface, a microscopic smooth surface is obtained by chemical and electronic polishing. The results show that the steel with very low silicon content does not show activity regardless of orientation, and for coating-specific steels, the low silicon content only affects the coating on the crystal with (111) side parallel to the surface. For steel specimens with slightly higher silicon content (0.025% w_{Si}), active structures formed in all observed grain directions, although the growth mechanism of the coating was different due to different surface orientations.

The study once again confirmed the Sundrin effect, that is, the activity increased with the increase of silicon content, but the lower limit of the silicon content w Si that produced the active structure decreased to nearly 0.01%.

It is determined that the active structure of the microslippery specimen can be formed when the silicon content is as low as 0.01% w Si when the surface stress is negligible and there is no oxidation effect, and the more obvious orientation effect is observed at this transition point alone. At the silicon content close to the maximum active effect (w_{Si} is about 0.1%), the instability of the coating occurs regardless of the grain orientation. This is because at this silicon content, thermodynamic instability occurs in the alloy layer that makes up the hot-dip galvanized layer.

M.No deposited zinc and hot-dip galvanized on hot-rolled steel pipes with silicon content of 0.011%, 0.089% and 0.143% Si and a thickness of 2~3mm, respectively, to study the effect of iron grain orientation on the grain distribution of iron-zinc alloys to determine the activity of steel. The results show that due to the different orientation of iron grains on the steel surface, the density and adhesion of deposited zinc may be large or small. The (111) crystal surface of iron reacts with zinc with greater activity, and the adhesion and growth of zinc are faster, which can quickly cover the entire grain and expand to the surrounding grains. The study also believes that the solid solution silicon formed in the steel production process makes the formation of active iron grain orientation relatively easy, but the structure of the steel surface also depends on other chemical components of steel, reduction reactions and heat treatment processes in the steel production process.

1.5 Surface metallographic structure

The size and shape of the surface grains also affect the activity of the steel. It is generally believed that due to the obvious grain boundary effect, fine-grained steel is more active. However, the effect of this factor is not very certain, and experiments have shown that different grain structures have little effect on activity.

In addition, the shape and distribution of surface carbides also affect the activity of steel. A common belief is that when carburite exists
In iron grains, the activity of steel is higher than that of carburite distributed at grain boundaries.

For the influence of the above-mentioned surface conditions of silicon-containing steel on the hot-dip galvanized layer, a certain hindrance layer can be applied to the surface of the plated part before hot-dip galvanization to hinder the direct contact between zinc and the active steel surface at the initial moment of hot-dip galvanizing. Therefore, a layer of pure iron can be deposited on the surface by electroplating before hot-dip galvanizing of silicon-containing steel, or a layer of nickel can be deposited by electroplating or electroless plating before hot-dip galvanizing, which can effectively hinder the initial moment of hot-dip galvanizing, and nickel can also reduce the activity of iron-zinc alloy reaction in the later stage.