Hot-dip Galvanized Layer

Hot-dip galvanizing is the process of immersing the cleaned and activated steel workpiece in liquid zinc, and generating an iron-zinc alloy layer on the surface of the steel through the reaction and diffusion between iron and zinc. According to different process operation methods, hot-dip galvanizing can be divided into two categories: continuous hot-dip galvanizing and batch hot-dip galvanizing.

1. Continuous hot-dip galvanizing

Continuous hot-dip galvanizing is to dip strips, steel pipes or steel wires into a zinc bath at high speed through a hot-dip galvanizing unit on a continuous hot-dip galvanizing production line for galvanizing.

(1) Continuous hot-dip galvanizing of strip steel: continuous hot-dip galvanizing of strip steel can be divided into improved according to its different pretreatment methods

Sendzimir method, US Steel method, Cook-Nortemen (Wheeling) method, and Sellas method. Their processes are as follows:

1) Improved Sendzimir method: cold rolling→ oxidation→ reduction and annealing→ cooling to hot-dip galvanizing temperature→ hot-dip galvanizing → cooling → straightening.

2) American steel joint method: cold rolling→ electrolytic alkaline degreasing→annealing→ cooling to hot-dip galvanizing temperature→hot-dip galvanizing→cooling→ straightening.

3) Cook-Nortemen (Wheeling) method: cold rolling→ hood annealing→ leveling→ pickling→ alkali washing→ solvent treatment→ preheating→ hot-dip galvanizing→ cooling→ rinsing.

4) Sellas method: cold rolling→ hood annealing→ leveling→ alkali washing→ pickling→ preheating→ hot-dip galvanizing→ cooling.

The main difference between the four processes is the different sequence of pre-cleaning and annealing processes. In the modified Sendzimir and American steel methods, cold-rolled strips are annealed in a continuous annealing furnace in a galvanizing line and then galvanized, and in order to eliminate annealing defects, the strips must be stretched and straightened before coiling. In the Cook-Nortemen (Wheeling) and Sellas processes, the strip is annealed in a hood annealing furnace, then leveled, and then sent to the galvanizing line for solvent treatment and galvanizing. Since the strip has been leveled after annealing in the hood annealing furnace, there is no need for stretch straightening before coiling. The characteristics of these four strip continuous hot-dip galvanizing production lines are shown in Table 1-4.

Table 1-4 Characteristics of continuous hot-dip galvanizing production line of strip

Production line category	Raw material strip	Pretreatment method of strip steel	Characteristics:

Improved Sendzimir method	Unannealed	Directly heat the oxidation-free furnace with gas or natural gas, adjust the excess air coefficient, so that the strip is not oxidized, and the oil on the strip is volatilized and decomposed The strip is heated to 550~650°C in an oxidation-free furnace The reduction annealing furnace is heated indirectly with a radiant tube, and a low H_2 shielding gas is introduced into the reduction furnace	The length of the furnace is significantly shorter than that of the original Sendzimir line The speed of the unit is increased, up to 180m/min Improved adhesion of the coating
U.S. Steel Union Act	Unannealed	The strip steel is first electrolytically degreased, washed, and dried before entering the reduction annealing furnace, heated to 720~750°C by the radiant tube, and cooled to 480°C after annealing into the zinc bath	The production line is long The quenching and tempering range of strip steel is wide
Cook-Nortemen (Wheeling) method	After annealing	The strip steel is washed after alkali eluting and degrease, pickled to remove the oxide scale, washed, coated with water solvent, dried and then entered the zinc bath The aqueous solvent is $NH_4Cl+ZnCl_2$ (mass fraction 40%), and the temperature is 50~70°C	The production line is shorter Low unit speed There is a problem of waste acid treatment
Sellas method	After annealing	Strip alkali eluting and degreasing before washing, pickling to remove the oxide scale and then washing Preheating and reducing the oxide film on the surface of the strip in the oxidation-free furnace	The production line is shorter Low unit speed There is a problem of waste acid treatment

The control of the thickness of the strip coating was carried out by the roller plating method in the early days, that is, when the strip steel was drawn out of the zinc bath, a pair of rollers were used to adjust the thickness of the zinc layer. However, the roll plating method limits the running speed of the strip; When the speed of the strip increases, it is easy to get an uneven coating because the zinc liquid is not replenished in time. For thin coatings, it is difficult to control precisely; The plating roller is severely corroded in the zinc liquid, which affects the continuous production. In order to improve the shortcomings of the roller plating method, the gas injection method (air knife method) is widely used, that is, the flat air flow is continuously sprayed out through a slit nozzle to blow off the excess zinc liquid brought out of the surface when the strip steel is led out of the zinc bath. The gas injection method has the following advantages: (1) the coating of the strip is uniform, and the surface quality is improved; (2) The coating adjustment range is large, which can control the thin coating and can be used to produce different-thickness galvanized strips; (3) Suitable for high-speed production lines; (4) The device is easy to maintain and can realize the automation of coating thickness control.

Galvanized strips produced by continuous hot-dip galvanizing can obtain a uniform and consistent coating. The coating is composed almost entirely of unalloyed zinc, resulting in good ductility, stamping formability and bending properties.

(2) Continuous hot-dip galvanizing of steel pipes

1) Solvent method steel pipe continuous hot-dip galvanizing process: alkali washing→ water washing→ pickling → water washing→ solvent treatment→ drying→ hot-dip galvanizing → cooling.

2) Continuous hot-dip galvanizing process of hydrogen reduction steel pipe: micro-oxidation preheating→reduction→ cooling to galvanizing temperature→ hot-dip galvanizing → cooling.

The difference between the above two processes is the difference in pretreatment, the former is basically the same as the single-sheet steel solvent method hot-dip galvanizing, and the latter is the same as the Sendzimir strip hot-dip galvanizing. The pre-treated steel pipes enter the continuous unit and are conveyed to the zinc pot through rollers. The steel pipe falls into the zinc pot and tilts into the zinc liquid, and the air in the steel pipe is discharged from the other end. The steel pipe is dialed to the other end by a slowly rotating star gear in the zinc liquid, and then lifted out of the zinc surface by a rotating axle wheel, and is immediately sucked by the magnetic roller on the upper part of it. The steel pipe moves diagonally upward with the rotation of the magnetic roller, and blows the excess zinc liquid on the surface of the steel pipe back to the zinc pot through the outer blowing ring, where the high-pressure air ejected from the ring hole blows back into the zinc pot. When the steel pipe is moved to the internal blowing device on its upper part, it is passed into the pipe by the high-pressure steam pipe for internal blowing. The blown zinc liquid and zinc particles are recovered by the cyclone. The galvanized steel pipe is then sent to the washing tank through the guide chain to cool.

(3) Continuous hot-dip galvanizing of steel wire

1) Continuous hot-dip galvanizing process of mild steel wire: annealing→ washing→ pickling→ washing→ solvent treatment→ drying→ hot-dip galvanizing→ post-treatment→ winding→ finished products.

2) Continuous hot-dip galvanizing process of medium and high carbon steel wire: degreasing→ washing→ pickling→ washing→ solvent treatment→ drying→ hot-dip galvanizing→ post-treatment→ winding→ finished products.

Low-carbon steel wires for general use and medium-high carbon wires for special purposes are slightly different in the pre-treatment stage. Before entering pickling, the mild steel wire is first recrystallized annealed to eliminate the work hardening caused by drawing, so as to maintain its good bending and ductility properties, as well as low resistivity, and to achieve the purpose of removing the residual oil stains during drawing through annealing. In order to maintain its high strength, medium and high carbon steel wires do not use annealing and degreasing.

The thickness of the coating of the wire is related to the way the wire is drawn out of the zinc solution. When drawing vertically, the thickness of the coating depends on the adhesion of the zinc liquid on the surface of the wire and the magnitude of gravity. When the lead speed is high, the adhesion is greater than gravity, resulting in a thicker and uniform coating with a coating weight of up to 300g/m². When the steel wire is drawn out at an angle of 35°, a thinner coating with a coating weight of less than 200g/m² can be obtained, but the uniformity is poor.

After the steel wire is hot-dip galvanized, the winding performance of the galvanized steel wire is reduced due to the formation of an iron-zinc alloy layer on the surface. The mechanical properties of low-carbon galvanized steel wires are related to the annealing method, while the mechanical properties of medium and high-carbon galvanized steel wires are related to the hot-dip galvanizing temperature. The mechanical properties of hot-dip galvanized steel wire are shown in Table 1-5.

Table 1-5 Mechanical properties of hot-dip galvanized steel wire

type	Carbon content (mass fraction, %)	Mechanical properties
Low-carbon galvanized steel wire	0.05~0.22	Rm =343 ~686Mpa,A =20%~40%
Medium and high carbon galvanized steel wire	0.25-0.75	Rm =1176.7~1961.2MPa

2. Batch hot-dip galvanizing

Batch hot-dip galvanizing is the process of dipping the processed steel workpiece into a zinc bath in a single piece or batch for galvanizing. Its main process flow includes: alkali degreasing → water washing→ pickling and rust removal→ water washing→ immersion solvent assisted plating→ hot-dip galvanizing→ water cooling → passivation.

The process characteristics of batch hot-dip galvanizing are as follows:

1) Batch hot-dip galvanizing is divided into dry (drying solvent method) hot-dip galvanizing and wet (molten solvent method) hot-dip galvanizing according to different solvent auxiliary plating treatment methods. The dry method is to immerse the steel workpiece in solvent aqueous solution first, and then dry it for galvanization. The wet process is to pass the steel workpiece through the molten solvent layer on the surface of the zinc bath, and then enter the zinc bath for galvanization. Because the dry hot-dip galvanizing has less explosive zinc, less zinc slag is produced, and the resulting coating has good adhesion, so most of the batch hot-dip galvanizing is currently carried out by dry method.

2) Hot-dip galvanized steel workpieces can have a large size range. From small parts (such as screws, nuts) to large steel structural parts, batch hot-dip galvanizing can be carried out, but the size of the steel workpiece is limited by the size of the zinc pot and the lifting capacity of the spreader. At present, the method of double dip plating (immersing both ends of the workpiece in a zinc bath) or progressive dipping (immersing the workpiece in a zinc bath in parts) can make some larger steel workpieces hot-dip galvanized.

3) Hot dip galvanizing can be done on steel workpieces with complex shapes. For workpieces with suitable vent and zinc venting holes, the zinc liquid can enter every corner of the workpiece to form a uniform coating.

4) Batch hot-dip galvanizing can obtain a thicker coating. The thickness of the coating is related to the thickness and size of the steel workpiece, usually the thicker the workpiece, the thicker the coating obtained. When most steels are hot-dip galvanized in batches, changes in process conditions

are relatively insensitive to changes in coating thickness. In order to obtain a thicker coating, the dipping time can be appropriately extended. Steel workpieces that have been sandblasted can also be coated relatively thickly.

3. Properties of hot-dip galvanized coating

(1) Corrosion resistance. Hot-dip galvanized layer has excellent corrosion resistance. In addition to the corrosion resistance of zinc coatings in different environments, it also has the following corrosion resistance characteristics:

1) Corrosion resistance when the hot-dip galvanized layer is all iron-zinc alloy layer. The corrosion protection effect and service life of the coating are not affected by the surface morphology. Some steels form a non-smooth gray and dark coating after hot-dip galvanization, but it does not affect their corrosion resistance. Even when red rust spots appear prematurely on the surface of the coating, it only affects the appearance and should not be considered as corroded steel matrix.

Premature red rust spots on the surface of the coating are caused by the growth of the iron-zinc alloy layer in the hot-dip galvanized layer to the surface, and the iron in the iron-zinc alloy layer is corroded. This situation mostly occurs when steel with relatively high silicon content is hot-dip galvanized, and its corrosion protection effect is not weakened. The results of long-term exposure tests show that the hot-dip galvanized coatings obtained on highly active silicon-containing steel and less active silicon-containing steel have similar corrosion resistance under equal coating thickness and the same exposure conditions.

2) Corrosion resistance at high temperatures. Hot-dip galvanized coatings still maintain good corrosion resistance under continuous exposure to temperatures up to 200°C. Exposure to temperatures above 200°C may cause the surface free zinc layer to peel off from the iron-zinc alloy layer. However, the remaining iron-zinc alloy layer can still provide good corrosion protection for the steel material matrix.

(2) Adhesion and processability: The hot-dip galvanized layer is composed of a surface free zinc layer and an iron-zinc alloy layer. In the process of hot-dip galvanizing, the steel material matrix and liquid zinc react with iron-zinc to form an iron-zinc alloy layer composed of different intermetallic compound phases on the matrix.

The test results show that the bending performance of hot-dip galvanized layer is related to the thickness of the coating. When the coating is thicker, the bending angle is smaller, and the coating is prone to cracking and peeling, which is caused by the formation of thicker brittle ζ and Γ phases in the coating. Therefore, in the production of hot-dip galvanized steel plates for stamping processing, elements such as aluminum, nickel and other elements are usually added to the zinc solution to inhibit the growth of brittle phases in the alloy layer.

(3) Hardness and wear resistance: Due to the formation of an iron-zinc alloy layer composed of

intermetallic compound phases, the existence of the iron-zinc alloy layer increases the hardness of the coating, which is close to or exceeds the hardness of ordinary galvanized structural steel, so that the hot-dip galvanized layer has good wear resistance in the application.

(4) Weldability: Hot-dip galvanized steel workpieces have good weldability and can be spot welded or seam welded. During spot welding, its welding strength is close to that of mild steel spot welding, but the welding current needs to be increased by 10%~15%.

4. Characteristics of hot-dip galvanizing technology

1) Hot-dip galvanized steel workpieces have a long service life and low service life maintenance costs. In general industrial zones and marine environments, the service life can reach 20~40 years, and in non-aggressive atmospheric environments, the service life can reach 50~100 years. Little maintenance is required during use, or for a long time.

2) Hot-dip galvanized layer can provide triple anti-corrosion protection for steel workpieces: (1) Isolation layer protection, that is, hot-dip galvanized layer provides a hard isolation layer bonded by metal bonds, which can completely cover the surface of steel workpieces and isolate steel workpieces from the corrosive environment. (2) Corrosion product layer protection, that is, the corrosion products formed after the surface corrosion of the hot-dip galvanized layer will produce volume expansion, blocking the discontinuous gap caused by the selective dissolution of the coating, thereby hindering the further corrosion of the coating and reducing the corrosion rate of the coating in the environmental corrosion medium. (3) Electrochemical protection, that is, for any small area exposed by accidental damage, such as bruises or scratches, etc., because the potential of zinc is lower than that of iron, the hot-dip galvanized layer is preferentially corroded as a sacrificial anode, so as to provide cathodic protection for steel workpieces.

3) The hot-dip galvanized layer is firmly combined with the steel material matrix and completely covered. The metallurgical combination between the plating layer and the substrate is the unique feature of hot-dip galvanizing, which makes hot-dip galvanized steel have a good resistance to mechanical damage during processing, storage, transportation and installation. All parts of the surface of the steel workpiece, including the inner and outer surfaces, as well as corners and narrow gaps, can be completely covered by the coating.

4) Reliable operation control and easy plating inspection. Due to the relatively simple hot-dip galvanizing process, it can be easily controlled for operation. At the same time, since the life of the coating mainly depends on the thickness of the coating, it is easy to observe whether its surface is continuous and bright from the appearance, and the use of a magnetic thickness gauge can easily and accurately determine whether its thickness meets the standard requirements.

5. Application of hot-dip galvanizing

Hot-dip galvanizing is a simple and effective steel material protection process, which is widely used in the protection of steel parts. At present, in addition to the mass production of semi-finished galvanized products such as galvanized steel plates, steel pipes and steel wires, many finished steel parts have been protected by hot-dip galvanization. Hot-dip galvanized products are widely used in transportation, construction, communications, electric power, energy, automobiles, petrochemicals, home appliances and other industries.

(1) Application of hot-dip galvanizing in various industries

1) Transportation industry: highway protective fences, highway signs, street lamp poles, bridge steel structures, automobile bodies, transportation machinery panels and floor plates, etc.

2) Construction industry: building steel structural parts, scaffolding, roof panels, interior and exterior wall materials, anti-theft nets, fences, blinds, drainage pipes, plumbing equipment, etc.

3) Communication and power industry: transmission towers, line fittings, microwave towers, substation facilities, wire casings, high-voltage transmission wires, etc.

4) Petrochemical industry: oil pipelines, oil well pipes, condensing coolers, oil heaters, etc.

5) Machinery manufacturing industry: housings of various machines, household appliances, ventilation devices, instrument boxes, switch boxes, etc.

(2) Application examples

1) The Sydney Opera House is located in Sydney Harbour, surrounded by the sea on three sides, and is exposed to the corrosive atmosphere of the ocean. The building features a shell-shaped concrete roof supported by hot-dip galvanized reinforcement mesh. The test shows that the hot-dip galvanized steel mesh has excellent protective performance, and covering it with 5mm thick concrete can effectively resist the corrosion of the marine atmosphere.

2) The Stainsby Hall Bridge is located in Texas, USA, and the bridge uses hot-dip galvanized steel beams. The bridge has not required any maintenance since its completion in 1974, and a recent inspection has shown that it will not require any maintenance for at least the next 25 years. This not only effectively ensures smooth traffic, but also minimizes maintenance costs.

3) The New South Wales Tennis Centre in Australia is a gymnasium built for the 2000 Sydney Olympics. The structural steel used in its external structure is hot-dip galvanized, ensuring long-term anti-corrosion effects.

4) Hot-dip galvanizing is widely used in subway, highway guardrails, traffic signs, street lamp poles and other transportation facilities.

5) Hot-dip galvanizing is used in power and communication facilities.