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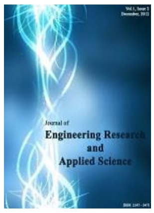

Investigation on effects of steel surface properties on galvanization behavior

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Abstract
Galvanization is a metal coating process in which a ferrous part is coated with a thin layer of zinc. The zinc coating seals the surface of the part from the environment, preventing oxidation and weathering from occurring. The primary method of galvanization is “hot dip galvanization”, which has been in use for over 150 years. While the idea of coating a part in molten zinc was first proposed by chemist Paul Jacques Malouin in 1742, the process was not put into practice until patented by chemist Stanislas Sorel in 1836. Sorel’s process has changed little since then, and still involves coating a part in molten zinc after cleaning it with an acid solution and coating the part in flux. Galvanization helps to extend the life of steel parts by providing a barrier between the steel and the atmosphere, preventing iron oxide from forming on the surface of the steel. Galvanization also provides superior corrosion resistance to parts exposed to the environment. Galvanization provides a cost-effective solution for coating steel parts, specifically those that will receive significant environmental exposure over their lifetime.

Keywords: Galvanization, galvanization behavior, coating, zinc, steel surface

1. Introduction

It is known that around 20 BC – 14 AD, brass was made by the Romans from zinc and copper. By the 14th century, zinc was recognised as the 8th metal by the Indians. Zinc was recognized in Europe as a separate metal in the 16th century when Agricola (1490 – 1555) observed when a metal called “zincum”, produced in Slesia and Paracelsus (1493 – 1541), stated clearly that “zincum” was a new metal.

In 1743, the first European zinc smelter was established in Bristol in the United Kingdom using a vertical retort procedure. A major technological improvement was achieved with the development of the horizontal retort process in Germany, which led to the erection of smelting works in Slesia, Liege, Belgium and Aachen, the Rhineland and the Ruhr areas in Germany [3].

In 1837, a French engineer Stanislaus Tranquille Modeste Sorel took out a patent for the early galvanizing process and in 1921, the first galvanizing plant opened in Australia by Lysaght. Galvanizing method has been proven as a corrosion protection method in all important applications involving iron and steel all over the world for over 160 years.

The formation of the coating is influenced by both physical parameters (eg bath temperature, immersion time, pre-galvanizing surface temperature) and chemical parameters (eg, chemical compositions, chemical composition of flux). The thickness increase of hot-dip galvanized coatings depends mainly on the interdifusion mechanism of zinc and iron atoms between zinc-based melting and bath-soaked iron-based samples.

Depending on the different chemical compositions, the interdifusion of the atoms forms an uneven coating. In the outer region, the coating is rich in zinc, whereas the coating in the inner region is rich in iron [3]. The presence of different iron / zinc ratios from the inner region to the outside creates different intermetallic phases as shown in the phase diagram (figure 1). For this reason, zinc coating can be considered as a multi-layer system composed of four phases characterized by a different thickness and mechanical properties:

- The outer layer is a ductile η phase with a maximum Fe content of up to 0.03%.
- The next layer is an isomorphous phase (ξ phase) characterized by an atomic structure containing a Fe atom and a Zn atom surrounded by 12 Zn atoms at the corners of

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a monoclinic unit cell and a light atomic icosahedron. Icosahedra is linked together to form chains and the linked chains are collected in a hexagonal sequence [1].

- δ phase is brittle which is characterized by a hexagonal crystal structure with a Fe content up to 11.5%.
- The inner phase (Γ) is a very thin layer characterized by a Fe content of up to 29% and an FCC structure.

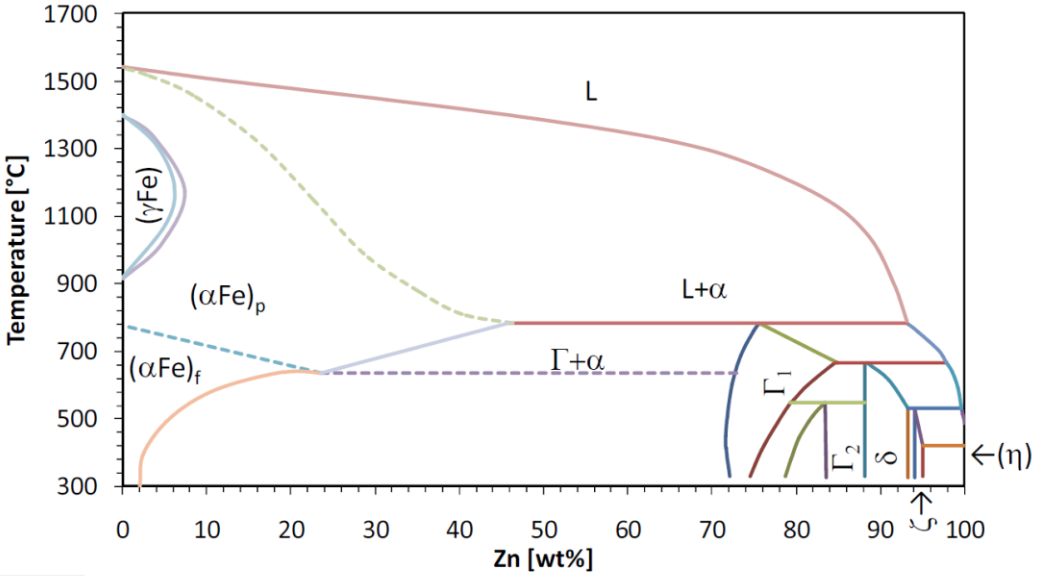

Figure 1. Zinc – iron phase diagram.

2. Galvanization process and Zinc based coating

The materials to be galvanized are immersed in a liquid solution of commercially pure zinc containing a minimum of 98% zinc. The chemical content of the bath is specified in ASTM B 6. The bath temperature should be maintained at approximately 450 ºC. The products must remain in the bath for the appropriate time to reach the bath temperature. Materials should be withdrawn slowly from the galvanized bath and the excess zinc in the surface should be removed by shaking or by the effect of centrifugal forces (figure 2.) After the material is removed from the bath, chemical reactions on the galvanized surface are continue [2]. In order to finish chemical reactions, the products must be cooled in water or in air as soon as they are removed from galvanization.

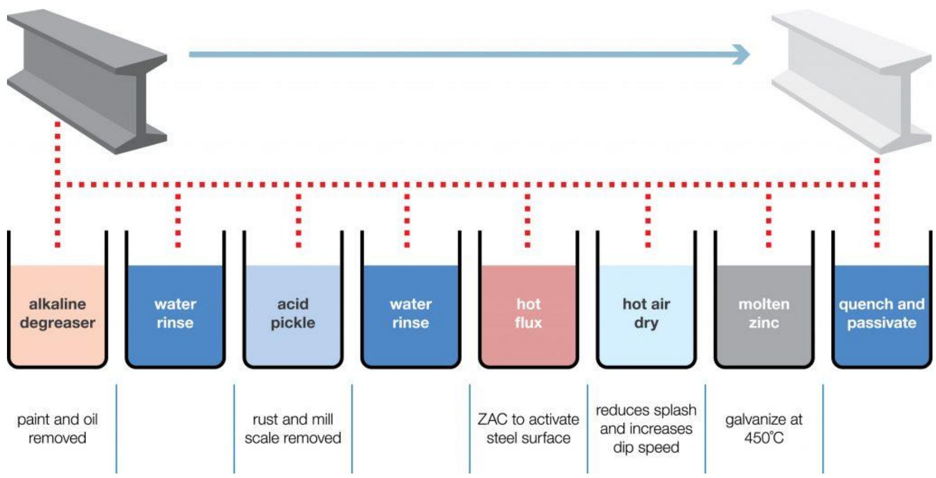

Figure 2. Steps of Galvanization Process.

In addition to creating a physical barrier to corrosion, the zinc coating also provides cathodic protection to the exposed steel. A wide range of steel products has corrosion resistance properties through galvanizing, from nails to steel structures, including bridges.

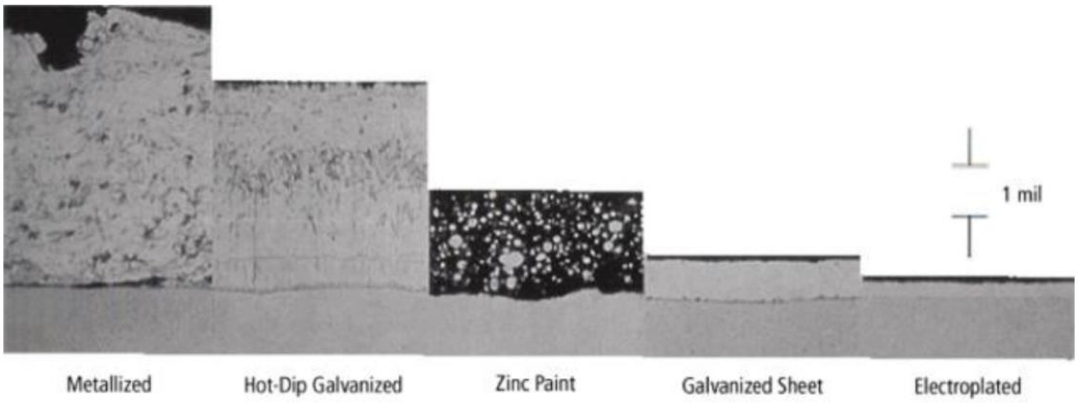

Figure 3. Zinc finishes types.

Five types of zinc-based coatings can be provided to achieve corrosion resistance: metallization, hot-dip galvanizing, zinc-based paint, galvanized coating and zinc plating (figure 3). These coatings differ in the thickness of the zinc alloy, the application methods and the duration of corrosion resistance (figure 4).

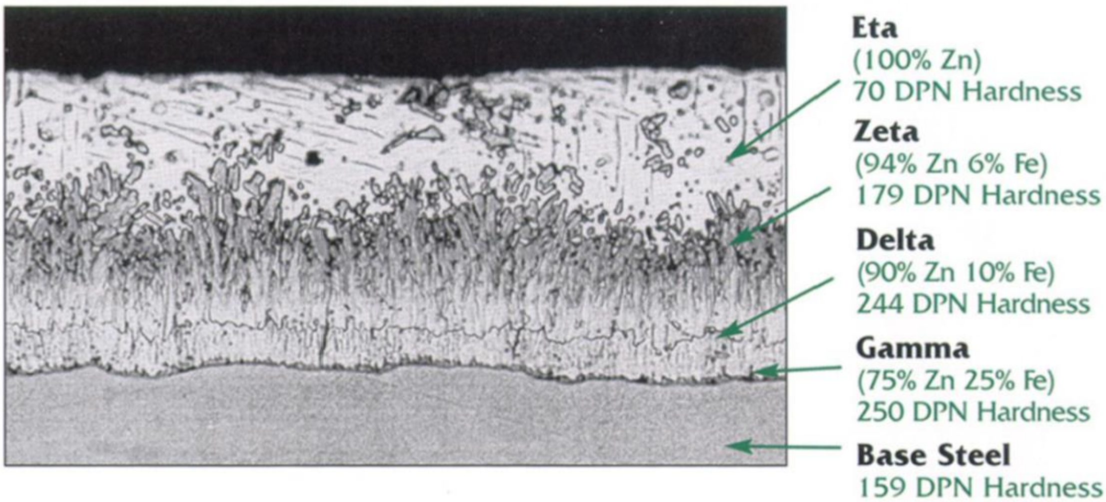

Figure 4. Microphotograph of a galvanized coating.

3. Galvanization Methods

3.1. Hot dip galvanizing:

Before immersion hot dip galvanizing, the steel part is cleaned, acidified and fluxing [1]. Prepared items are galvanized by immersion in molten zinc. The surface of the work is completely covered, producing a uniform coating of zinc and zinc-iron alloy layers whose thickness is determined principally by the mass of the steel being galvanized. Articles ranging in size from small fasteners to structures hundreds of metres high may be protected by the use of modular design techniques. Large galvanizing baths, in conjunction with modular design techniques and double-end dipping allow almost any structure to be galvanized, with greatly reduced maintenance costs and extended service life. Small items can be dipped into the molten zinc in a container which is spun or centrifuged upon removal of the molten zinc. This aids in removing excess zinc from threads and edges and provides a smooth, albeit thinner coating than batch dipped items (figure 5).

3.1.1. Wet flux galvanizing:

Wet method requires less plant tools and space. This method involves the passage of a thin layer of melt flux salt on the surface of the zinc bath to remove impurities in the surface of the steel part, and also the formation of free oxides in a portion of the surface of the zinc bath during the immersion of the steel. Generally, due to the stripping condition, the wet method tends to form a thinner coating while the piece is drawn through the flux (figure 6). The Flux layer can be made with Sodium Aluminum Fluoride or Zinc Ammonium Chloride for higher Al contents with the addition of Ammonium Chloride [7-8]. The flux layer floats freely on the surface of the bath and the interaction continues while the part is immersed. The most important functions of the flux layer:

- Cleans the surface of the component and the molten zinc, so that zinc and steel can react.
- Reduces distortion by preheating thin parts.
- Protects from overheating and burning in the second immersion.
- When wet parts are dipped, dangerous splashes are reduced.
- The melt reduces the oxidation of the surface of the zinc and thus reduces the ash formation

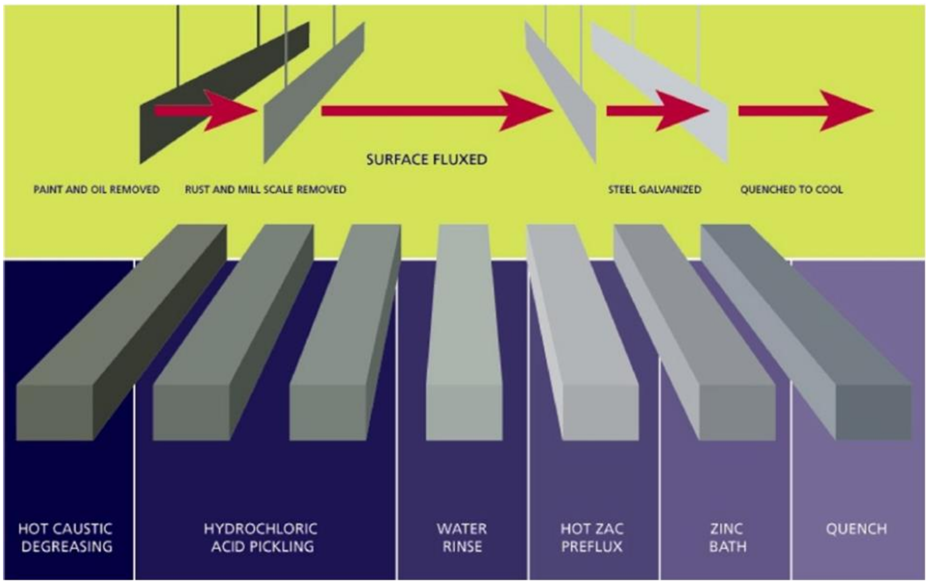

Figure 5. Hot dip galvanization process.

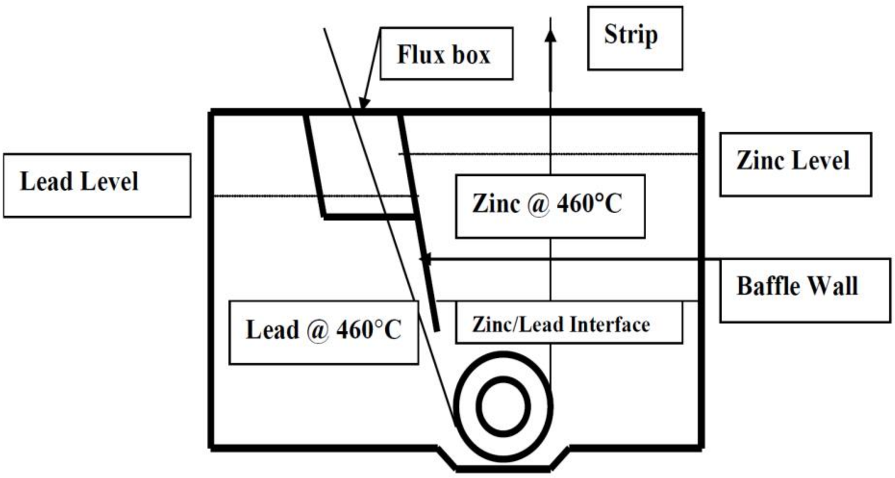

Figure 6. Wet flux galvanizing pot shematic section.

3.1.2. Galvanizing by dry method:

In the Galvanizing with Dry Method, after the parts have been cleaned, the component is pre-quenched in an aqueous solution, dried and then dipped in the zinc bath. The temperature of the pre-flux solution ranges from room temperature to 80 °C. In this process, the part must be absolutely dried before immersion in the zinc bath. For drying, the best conditions are met at a temperature of 120 °C and up to 5 minutes. Parts should be galvanized immediately after pre-fluxing and drying. In both processes, the temperature of the melt zinc galvanizing bath is maintained in the range of 445 to 455 °C, and the immersion time varies in the range of 3-6 minutes depending on the thickness of the part.

3.2. Continuous galvanizing processes (In-line galvanizing

Continuous galvanized products can usually be further processed by bending or roll forming, for example as purlins and girts, without damaging the coating. In addition, welded hollow sections formed from pre-galvanized strip are in wide use. Note welds, cut ends and drilled or punched holes may need repair to restore the corrosion protection, depending on the application and environment. In-line galvanized articles always produce thinner coatings than batch hot dip galvanizing for the same steel thickness and therefore offer less corrosion protection when exposed to the same environment.

3.3. Thermal spray

Thermal spraying or metallising is the process of spraying semi-molten zinc and other metals or their alloys to using wire heated by an arc spray or plasma heat source. Thermal spraying has the advantage that zinc coatings up to 250µm thick. The steel surface must be prepared by grit blasting. In most cases thermal spraying is more expensive than batch hot dip galvanizing for the equivalent section, but these processes are complementary and used in tandem in large structures.

3.4. Electroplating and mechanical plating

Electroplating is an economic and effective method of applying a protective coating to small steel components. It is used method of applying metallic zinc coatings to small fasteners. Mechanical plating is an electroless plating method used to deposit coatings of ductile metals. It uses mechanical energy and heat to plate and to plate zinc onto steel parts.

3.5. Thermal diffusion

Thermal diffusion are most effective for small articles. This process precludes hydrogen embrittlement so it can be used safely for high strength steels. Coating thickness are commonly coated in the 20 to 50 µm range. The coating thickness is typically dependent on the time in the rotating drum.

3.6. Zinc rich paints

Zinc rich paint coatings consist of metallic zinc dust in organic or inorganic vehicles. They are barrier coatings which also provide cathodic protection to small exposed areas of steel. Suitable zinc rich paint coatings also provide a useful repair coating for damaged or worn galvanized coatings.

4. Effects of temperature on galvanization

The rate of heating is an important factor for coating because the coating occurs when the temperature curve is sufficiently high (endothermic phenomenon) to give the system the temperature. This is due to hot or pre-heated immersion of iron, or heating of zinc and iron together. Furthermore, the material to be coated can have complex parts of different thicknesses and this will affect the calculation of the time to be applied.

Usually the thickness of the coating increases with increasing zinc bath temperature. On the other hand, the thickness of the outer layer of pure zinc decreases with the falling temperature. The removal rate is important only in controlling the thickness of this outer layer of pure zinc.

The quality of the coating thickness and the occurrence of some defects are largely due to the correlation between the bath temperature and the rate of recovery. Errors resulting from insufficient control of the bath temperature or extraction speed along with the sheet thickness are as follows: gray coating, tearing, crusting and scaling. Therefore zinc bath temperature and extraction time should be checked with plate thickness.

Table 1. Temperatures required for sheet metal thicknesses at various intervals and bath extraction speeds.

Sheet Metal Thickness (mm)	Temperature (C)	Velocity (m/min)
< **0,65**	445-450	5
0,7-0,9	450-460	4
>**0,9**	460-465	3

5. Effect of silisyum and phosphorus in galvanized steel

5
.1. Effects of silisyum:

When the silicon is not distributed homogeneously on the steel surface, it causes the coating to become rough. The reactivity of the steel depends on the ratio and distribution of silicon. At a normal galvanisation temperature of 450 °C, the usual coating is carried out, although about 0.03% Si increases the reactivity. At high Si concentrations of 3%, the reactivity of the material is much less and the iron loss decreases and the thin coating is formed. In normal hot-dip galvanizing processes, it was concluded that the amount of silicon should be limited in the following formula:

$$Si < 40.10^{-3}\ \%$$

When the amount of silicon in the steel is approximately 0.04% to 0.12% and above 0.25%, Fe-Zn alloy layers are observed to grow rapidly. In such cases, a matt gray color and a rather thick coating is formed. This color may be on one side of the coating or spread over the entire surface. In some cases, a dendritic view of the gray web is formed. In order to prevent this formation, the silicon value in the steel must be outside of the Sandelin Region values.

5.2. Effects of phosphorus

The relationship between coating thickness and phosphorus content is very similar to that observed in silicon-containing steels. Addition of 0,058% phosphorous to the phosphorus containing less than 0,020% leads to an increase of the coating thickness by approximately 50%.

5.3. Effects of silisyum and phosphorus

After hot dip galvanizing, the combination of Si and P in the steel is effective only in low Si amounts. The effect of the amount of normal phosphorus on the galvanizing properties of the material can be neglected in high silicon (> 0.12%) steels [5]. Therefore, the correct galvanizing can be achieved by providing the following two conditions:

$$Si < 0{,}040\ \%$$

$$Si + 2{,}5\ P\ \% < 0{,}09\%$$

When the amount of phosphorus was more than 0.020%, it was seen that the thickness of the coating in the structural steels increased due to the silicon values between 0.01% and 0.04%. As the amount of silicon in the steel decreases and at low temperatures, the phosphorus effect in the liquid increases. Increasing the phosphorus content in steel containing up to 0,12% Si increases the thickness of the coating at temperatures between 440 and 450 ° C.

6. Effects of surface cleaning on galvanization

In terms of the quality and appearance of the galvanizing, the cleaning of the welded area and the composition of the weld should be given the utmost importance. For successful galvanization; uncoated electrodes should be used, flaks must be cleaned, sourcing methods which do not produce slag or which produce very little should be used, for heavy sources, immersion arc method should be used and high silicon welding materials should be avoided.

The oxidation rate on the surface depends on the temperature of the zinc, the air flow on the bath and the liquid composition. For this reason, the bath temperature should be kept as low as possible, and the gas outlet holes in the corners should be designed in such a way that it does not attract a continuous air flow on the zinc surface. Moreover, the empty zinc surface must be small as the process permits and its cleanliness must be kept to a minimum. After the sheets are immersed, they are removed vertically with the help of the two cylinders and allowed to cool in the air [2-3]. Those who influence the coating quality from these processes are below. Inadequate control of the belove steps and lack of passivation result in a decrease in product quality.

- The degree of cleaning of the extraction surface of the zinc bath
- The amount of cooling of the sheets before they enter the receiving rollers.
- Distribution of airborne cooling
- Cleaning degree of the removal roller
- Pre-passivation or non-passivation

This stuation causes rough coating, flux stains, gray spots and flake formation. Gray speckles represent a ratio of 50% of these errors and result in the absence of passivation. For this reason, chromate passivation is applied to prevent white rust formation as well as such errors. The chromate film on the coating is not permanent but provides adequate protection during storage or during transportation.

7. Effects of steel surface processing and geometry on galvanization

The shape of the material to be galvanized has a remarkable effect on the coating because the alloy layers grow perpendicular to the iron interface. The convex surfaces or the outer corners can cause phase breakage and thus the material is unprotected.

The molten zinc in the galvanizing bath covers corners, seals edges, seams and rivets, and penetrates recesses to give complete protection to areas which are potential corrosion spots with other coating systems. The galvanized coating is slightly thicker at corners and narrow edges, giving greatly increased protection compared to organic coatings which thin out in these critical areas. Complex shapes and open vessels may be galvanized inside and out in one operation.

The stresses in the growing coating, compression and drawing may be caused by various reasons. Volumetric differences between the product and the resultant reaction may cause stress in the growing layer. During cooling, stresses and cracks may occur due to the difference between the expansion coefficients of the phases and the material itself. The pressure to be applied supports the more smooth coating and the continuity of the coating, this also applies to the kapla phase, which does not occur within the linear range without applying pressure.

As the thickness of the sheet increases, the coating quality tends to decrease. Thick plates require slow speeds to compensate for their high immersion temperature, smooth interaction and their high heat capacities. However, the quality of the product can be increased by 20% by providing the desired heat capacity by proper control of other operating parameters, for example, bath additives.

The condition of the surface, such as roughness and surface strain, can play an important role on the properties, structure and appearance of the galvanized coating. Most importantly, surface treatments outweigh the alloy additives in the iron or the bath. Therefore, when silisyum iron is taken into consideration, sandblasting the surface reduces the reaction rate and normal coating occurs. In the case of soft steels coated with aluminum, almost no interaction layers are formed if the steel surface is washed with acid [4,5,6].

It has been found that the advantages of precoating with zinc and nickel to prevent re-oxidation of the steel in the peeling line (table 2). Although the pre-heating time of immersion is reduced, this method is of little demand (figure 7).

Table 2. Standard Corrosion Rates for Metals in Atmospheric Conditions.

ISO 9223		**Typical enviroment**	**Corrosion rate for the first year of exposure (μm/annum)**	
Category	Description		Mild steel	Zinc
C1	Very low	Dry indoors	≤1.3	≤0.1
C2	Low	Arid/urban inland	>1.3 to ≤ 25	>01. to ≤ 0.7
C3	Medium	Coastal or industrial	>25 to ≤ 50	>0.7 to ≤ 2.1
C4	High	Calm sea-shore	>50 to ≤ 80	>2.1 to ≤ 4.2
C5	Very high	Surf sea-shore	>80 to ≤ 200	>4.2 to ≤ 8.4
CX	extreme	Ocean / off shore	>1.3 to ≤ 700	>8.4 to ≤ 25

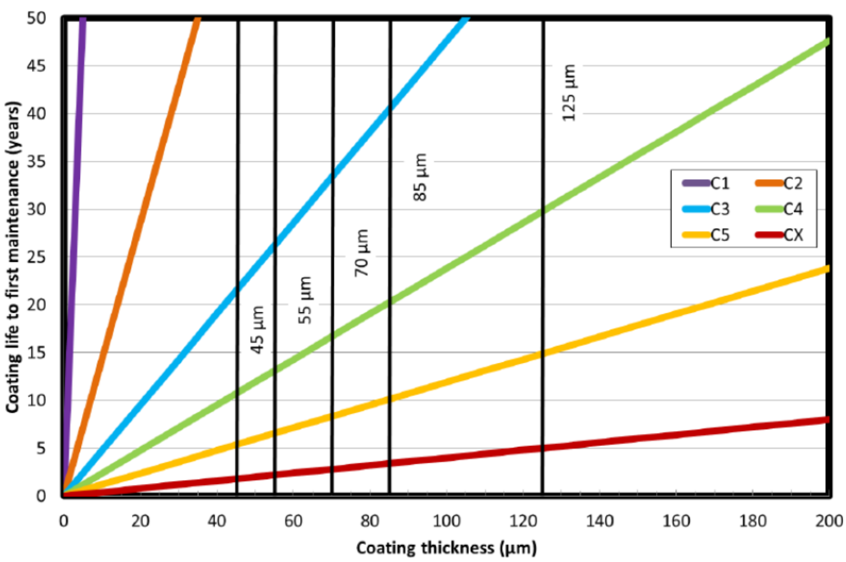

Figure 7. Coating life versus coating thickness in the macro-environment.

8. Conclusions

Atmospheric effect vehicles, bridges, railings, poles, power transmission lines, warehouses and so on. water and underground pipelines, tanks, piers, ships, pontoons, dam covers, penstock etc. boilers, pipes, gratings, electric machines etc, which are used in various branches of industry including tools and equipment. Metallic structures become unusable due to corrosion in shorter periods than expected.

Chemical composition of the sheet was observed at the beginning of the factors affecting the coating. Particularly the effect of Si and P elements was observed which effect the thickness and appearance of the galvanized coating. Companies producing according to international standards must pay attention to sheet quality, coating thickness, luster or opacity etc specified in the standard in order to produce according to standards. For example, if a material produced using St37 quality sheet will be galvanized according to EN 10240 production standard, the coating thickness according to the thickness of the sheet should be 55 µm. When the factors affecting the thickness of the coating are known, for example, the suitable sheet and the appropriate time can be immersed and the coating thickness closest to the thickness specified in the standard can be obtained. It can be seen that when the sheet having 0,01-0.03% Si range is submerged for 60 sec, this coating thickness can be approached.

Excessive zinc flow of the part coming out of the galvanizing can be controlled by gravity, temperature, and draw speed. Due to the weak yield, stalactites and mass deposits occur at the ends of the zinc-plated piece. Cleaning them after coating will incur additional costs.

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