

Introduction

Continuous hot-dip galvanized sheet is manufactured almost exclusively on coating lines where the molten zinc contains a small amount of aluminum. This has been the case for many years and is, in fact, the primary reason that galvanized sheet is used today for a wide variety of very demanding products. The addition of aluminum is not made to enhance corrosion performance, but to ensure good coating adhesion during forming of the sheet. This GalvInfoNote explains the influence of aluminum and why it is so important to the successful manufacture and use of continuous hot-dip galvanized sheet.

Metallurgy of the Coating

Continuous hot-dip galvanized sheet is made by immersing steel sheet, as a continuous ribbon, into a bath (pot) of molten zinc. The process is explained in detail in GalvInfoNote 2.1 and again in GalvInfoNote 2.3. Both sides of the steel sheet are very clean and free of surface oxides when introduced into the coating bath. Typically, the sheet is cold rolled steel and receives an in-line anneal at temperatures above 1200°F [650°C] ahead of the pot, and is then cooled to approximately 875-925°F [470-490°C] before it enters the bath. The zinc, which melts at 787°F [419°C], is usually at a temperature of 870°F [465°C]. Steel sheet has sufficient high temperature strength so that it can be pulled through both the annealing furnace and the zinc bath without tearing or deforming.

During the time that the sheet is immersed in the bath (on some coating lines, as brief as ~2 seconds), the steel and molten zinc undergo a metallurgical reaction. What happens? The surface atoms of the steel sheet, which are in the solid state, interact with the zinc atoms in the bath, which are in the molten state. This interaction is called **diffusion**. Zinc atoms move in the direction of the steel and iron atoms in the steel migrate towards the molten zinc. The result is the formation of a solid “mixed” layer between the steel and the molten zinc. This layer contains zinc and iron atoms in specific proportions, and is called an **intermetallic** compound. The mixing of atoms of different metals is known as **alloying** and the diffusion zone that is formed during galvanizing is an **intermetallic alloy**. It is this alloy zone, when properly formed, which provides the excellent bond between the steel and the zinc coating.

Surface tension forces cause a layer of molten zinc to adhere to the sheet when it exits the bath. After excess zinc is wiped off, the remaining liquid solidifies when it cools below 787°F [419°C]. The final product (galvanized sheet) consists of the steel core, with an intermetallic alloy layer and outer zinc layer on both surfaces.

If the zinc bath was aluminum free, a cross-section of the coating might look similar to that in Figure 1.

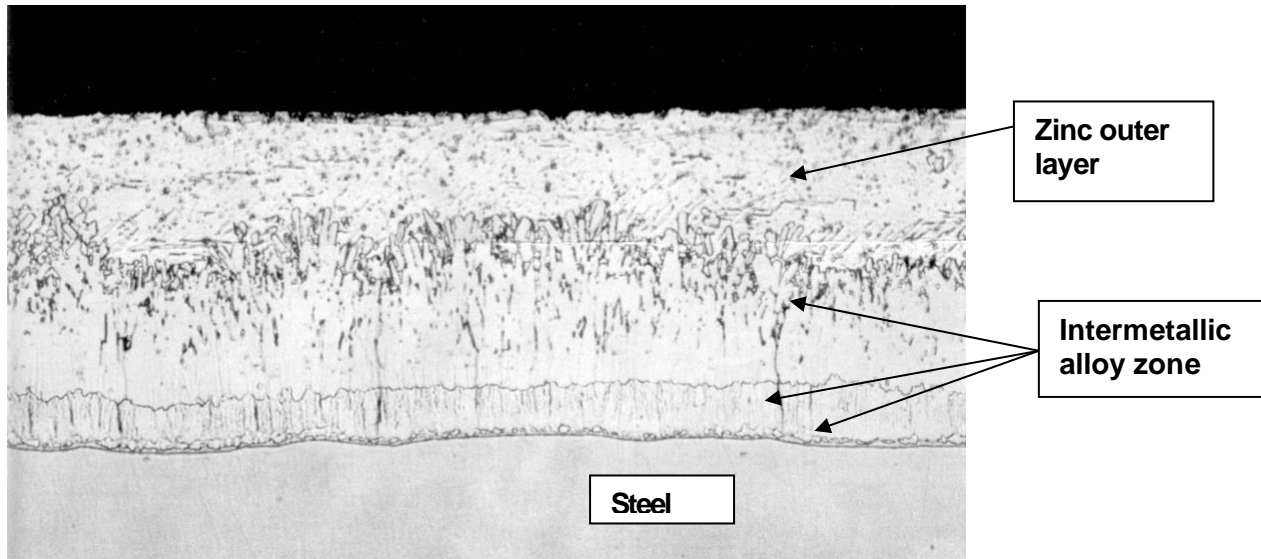


Figure 1: Cross section of coating produced in an aluminum-free galvanizing bath

The intermetallic alloy layers shown in Figure 1 are a mixture of zinc and iron atoms. They provide a high degree of bonding between the steel and the zinc outer coating. Unfortunately, these alloys have very poor ductility, i.e., they are hard and brittle. When the sheet is formed into a shape, there is a high probability of shear cracks developing in the alloy, and the zinc coating flaking off. This behaviour seriously limits the ability to form the sheet into shapes such as drawn cups, roofing panels, tight lock seams, or highly stretched automotive fenders.

Overcoming the Brittle Alloy Layer

An alloy layer is vital to achieving a good bond between steel and zinc. This layer must also be continuous (over the entire surface area of the sheet) for the coating to be free from pores. Without interfering with the formation of an alloy bond zone, how can the nature of the alloy be changed so that forming into intricate shapes is possible?

Over 75 years ago, it was discovered that the addition of a small amount of aluminum to the coating bath is a perfect answer to this problem. Initially, the reason it worked so effectively was not understood, but it was observed that having aluminum in the zinc bath made the alloy layer very thin compared to that from an aluminum-free bath. Aluminum is an inhibitor that greatly slows down the zinc-iron reaction rate. This thinner, and hence more ductile, alloy layer allows the coated sheet to be formed into many complex shapes without loss of coating adhesion, since it is not prone to the development of large internal shear cracks.

Using aluminum, at a level of approximately 0.15%, became the standard for galvanizing baths in continuous lines. To this day an aluminum addition practice is used. However there is now a much better understanding of the metallurgy of aluminum in zinc, with the result that the aluminum concentration is more closely controlled. Some manufacturers use 0.20 to 0.30% aluminum, but most stay in the range of 0.15 to 0.19%. When making zinc-iron coatings (galvanneal), the aluminum level is lowered to the range of 0.11 to 0.135%.

Although the addition of such a small amount of aluminum has a pronounced effect on the ability to form galvanized sheet, it does not have much effect on bulk corrosion behaviour. However, as the aluminum does concentrate in the alloy layer, and to some extent at the surface of the zinc, it can adversely affect issues such as spot welding, soldering, and white rust occurrence. These drawbacks are insignificant, though, in comparison with the beneficial effect that aluminum exerts on the ability to form the sheet without loss of coating adhesion.

Why Aluminum Changes the Alloy Layer

How can this small amount of aluminum have such a pronounced influence on the alloy layer growth rate? It is because when aluminum at this level is in the coating bath, the normal zinc-iron alloy compound, FeZn_7 , that forms on the steel surface (and grows at a fast rate), is no longer the most stable compound. Aluminum has a greater affinity for iron than zinc, so immediately (within 0.15 seconds)¹ after the steel enters the coating bath, the stable intermetallic compound that forms is not a zinc-iron compound, but an aluminum-iron compound, i.e., Fe_2Al_5 . This alloy layer (also known as a **barrier** or **inhibition layer**) is extremely thin and retards the zinc-iron reaction. By the time the strip leaves the bath (~2-4 seconds later) some zinc is taken into this alloy layer, but its nature is completely different from that which occurs in the absence of aluminum. It is a very thin, ternary alloy layer composed of approximately 45% Al, 35% Fe and 20-35% Zn ($\text{Fe}_2\text{Al}_{5-x}\text{Zn}_x$). Instead of the high diffusion rate that occurs when liquid zinc and solid iron form a binary FeZn_7 alloy in aluminum-free baths, the diffusion rate is now dependent on the transport characteristics of zinc through the barrier created by the aluminum-iron compound. The reaction between zinc and iron is delayed, and the net result is that the final thickness of the alloy layer is much less than when it is dependent on the diffusion rate across a growing zinc-iron alloy zone.

The nature of the alloy layer, when aluminum is added to the galvanizing bath, is shown in Figure 2. The alloy layer is the thin layer seen near the bottom of the figure. When the alloy layer is this thin, the coated sheet can be bent or formed into many useful shapes without the alloy layer cracking and resulting in loss of coating adhesion.

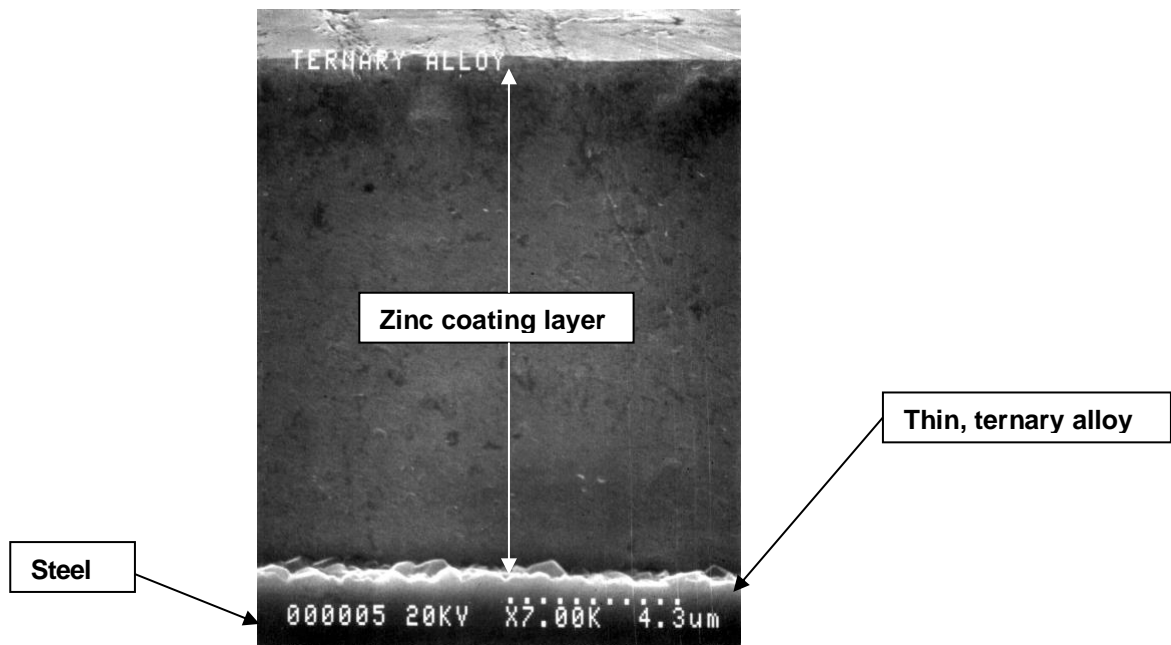


Figure 2: Cross section of galvanize coating from an aluminum containing bath (magnification 7000X)

What a discovery! This development single-handedly allowed the growth of the large continuous galvanizing industry, which now produces over 25 million tons per year of galvanize and galvaneal in North America alone. The product of these lines is used in many applications, including those that require it to accommodate very severe forming.

Aluminum Content in the Coating

Recall that for the production of galvanize, the coating bath typically contains 0.15 to 0.19% aluminum. When a coating made from such a bath is later analyzed, it is found to have bulk aluminum content of from 0.25 to 0.40%. How does this apparent increase occur? The answer lies in the strong affinity aluminum has for iron. The initial alloy that forms is Fe_2Al_5 – by atomic weight over 45% aluminum. Aluminum actually concentrates at the steel zinc interface and is taken out of the bath with the strip. The thickness of the inhibition layer is independent of coating weight (mass). This is why a lighter coating weight (mass) contains a higher overall percentage of aluminum. The rate and method of aluminum addition to the bath must take into account situations that cause its removal rate to vary, e.g., coating light gauge sheet (high surface area per unit weight) with a thin zinc coating removes aluminum at a much higher rate than running heavy gauge sheet with a thicker coating. There are other factors that control the amount of aluminum in the coating, such as: immersion time, aluminum addition rate, zinc bath temperature, and steel type. Fossen et al discuss these topics in a paper given at Galvatech '95². All these factors must be considered when planning how to replenish the aluminum in the bath. Most galvanize producers, with the assistance of their zinc suppliers; have developed aluminum addition algorithms for their zinc pots. These prediction models forecast aluminum levels depending on product mix and stipulate how to add aluminum bearing zinc to keep the aluminum in the bath at the desired concentration.

In addition to the high percentage of aluminum in the inhibition layer, the outermost ~six atomic layers at the coated zinc surface contain a significant amount of aluminum, in the form of aluminum oxide³. This occurs due to both solute rejection during freezing of the zinc coating, and the strong affinity between aluminum and oxygen. Aluminum in solution in the still liquid zinc is rejected towards the surface where it easily reduces the already formed surface zinc oxide layer to aluminum oxide. In order that they can bond to the zinc, chemical passivation and prepainting treatments are designed to remove the thin aluminum oxide layer at the surface. Passivates accomplish this with strong acidity (pH~3.1), while paint pretreatments use strong alkalinity (pH~12.9). The surface of as-coated galvanize has only 10-15% zinc present. Some post-coating galvanizing operations, such as heavy temper rolling (skin passing), can increase the surface zinc content to about 90% by significantly disturbing the surface in the process of making it extra smooth.

Aluminum in Galvanealed Coatings

Making galvaneal involves growing zinc-iron alloy compounds throughout the coating, so that it has approximately 10 to 12% bulk iron content. Refer to GalvInfoNote 1.3 for a complete description of how galvaneal is made. Since the presence of aluminum dramatically restricts growth of the alloy layer, how does this affect the production of galvaneal?

The reheating of the strip that is necessary to produce galvaneal restarts the zinc-iron diffusion reaction. Within seconds the heat breaks down the aluminum-iron inhibition layer. For this to happen consistently requires aluminum control that was not possible in the early days of continuous galvanizing. Producing galvaneal depends on the zinc and steel alloying at a rate high enough so that complete diffusion of iron throughout the coating can be accomplished in a reasonable timeframe (allowing production to be done at economical rates). Inhibition layers formed in galvaneal zinc baths are generally thinner than those formed in galvanizing baths¹. In fact, the inhibition layer formed in higher aluminum galvanizing baths may not allow the galvaneal reaction to proceed properly in the time allotted. When the aluminum concentration in the bath is reduced to less than 0.14% (in the range of 0.11 to 0.135%), the ternary alloy layer is thin enough,

and of the right composition, that reheating allows the required amount of diffusion to occur in a matter of seconds.

After the coating has been converted to galvanneal, the aluminum-iron alloy interface layer no longer exists. It, and the small amount of extra aluminum at the surface, becomes diffused into the zinc-iron coating, with the bulk of it present in the delta alloy layer (see GalvInfoNote 1.3, Table 1).

A manufacturer making both galvanize and galvanneal products on the same coating line typically uses 0.15 to 0.19% aluminum for galvanized production, and then allows the aluminum level to drop to less than 0.14% to make galvanneal. In practice, this is not as easy as it appears, since the transition needs to occur rapidly. For this, precise aluminum control is needed, requiring accurate measuring capabilities.

Summary

The inhibiting action of aluminum in a galvanizing bath was an important discovery. Continuous galvanizing lines throughout the world now use aluminum in their zinc baths. Through the years, much has been learned about the metallurgy of aluminum in galvanizing baths, which in turn has greatly influenced processing practices. The use of aluminum to reduce the thickness of the alloy layer is the one development that made continuous hot-dip galvanizing the large industry it is today. For more detailed information on aluminum in continuous galvanizing line zinc baths, refer to the associated GalvInfoNote 2.4.1 Zinc Bath Management on Continuous Hot-Dip Galvanizing Lines.

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¹ Price, S.E., et al, Formation and development of aluminum inhibition layers during galvanizing/galvannealing. La Revue de Metallurgie-CIT, Mars 1999, pp. 381-393

² Fossen, E., et al, Aluminum Control on Stelco's Z-Line, Proceedings Galvatech '95, pp. 795-800

³ Kilbane, F.M. Relationship Between Surface Composition, Steel Mill Processing and Paint Pretreatment of Galvanized Strip, Galvanizers Conference, April 14-16, 1982, Monterrey, Mexico