Indian Steel Sheet Building Group: Technical Note 2.4.1

Coating Processes and Surface Treatments

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Zinc Bath Management on Continuous Hot-Dip Galvanizing Lines

Introduction

This GalvInfoNote expands on Note 2.4 to provide more detailed information on the management of the zinc bath chemistry and other parameters needed to produce high quality zinc-coated sheet products on continuous coating lines.

General

- Control of the steel-zinc reaction has a major effect on coating quality, i.e., coating adherence, formability, weldability, uniformity, and appearance. In successfully managing these important characteristics, it is also vital that the strip surface be free of oxides and soils as it enters the zinc bath.
- A clean strip surface, free from iron debris, is also critical to minimizing dross formation.
- In a zinc bath without aluminum, there is a high diffusion rate between the molten zinc and any immersed steel, with the alloy layer growing very fast. This is the case in batch galvanizing. Various brittle, binary FeZn intermetallic alloys immediately form, resulting in poor coating adherence if the material is later formed. It is for this reason that batch galvanizing is done after all fabrication/forming is complete.
- Small amounts of aluminum added to the zinc act as an inhibitor, greatly restricting the rate at which the zinc-iron alloying reaction proceeds in the early stages of immersion.
- When aluminum is at the correct level, the zinc reaction with the steel instantly forms a very thin interfacial, ternary alloy layer (see Fig 2 in Note 2.4) with a composition of 45% Al, 35% Fe, and ~20% Zn ($Fe_2Al_{5-X}Zn_X$). The extent of this ternary alloy reaction (and the amount of zinc incorporated into it) is very sensitive to the amount of Al in the bath, to the immersion time, and to the bath and strip temperatures.
- During the typical immersion times in a CGL zinc bath (2 to 8 seconds depending on line speed) the ternary alloy remains stable if there is sufficient Al present. However, a high zinc temperature and/or long immersion time will begin to overwhelm and consume any ternary layer. Obtaining a ternary composition with a low percentage of zinc is extremely important for good coating adherence.
- Dross is a by-product of hot-dip galvanizing and consists of iron-containing particles that form in the zinc bath, and which can detract from the coating quality. The particles can be aluminum-iron-zinc (top dross, or η-$Fe_2Al_{5-X}Zn_X$) or zinc-iron (bottom dross, or δ-$FeZn_7$), with the iron coming from strip dissolution and any iron fines on the surface.

Understanding Effective Aluminum (Al_{EFF})

- Total aluminum (Al_{TOT}) is all of the Al in the bath; Al in solution in zinc and Al that is part of all the intermetallic dross phases. Al_{TOT} is determined by chemical analyses of bulk bath samples.
- Effective aluminum (Al_{EFF}) is the aluminum dissolved in the molten zinc, and is the determining factor in forming the desired coating microstructure[i]. It does not include the aluminum that is tied up in intermetallic dross particles, since that is not available to react with the iron in the steel strip. Using computer programs to make necessary adjustments for bath temperature and Fe level, Al_{EFF} is measured indirectly using techniques such as AA, OES, or ICP.
- Aluminum changes the solubility of iron in molten zinc:

- Increasing Al decreases the amount of Fe that the zinc can hold without precipitating top dross particles in the bath.
- Zinc with no Al at 860°F [460°C] can hold in excess of 0.035% Fe in solution, whereas with Al at 0.20% it can only hold about 0.010% Fe in solution (refer to Figure 1).

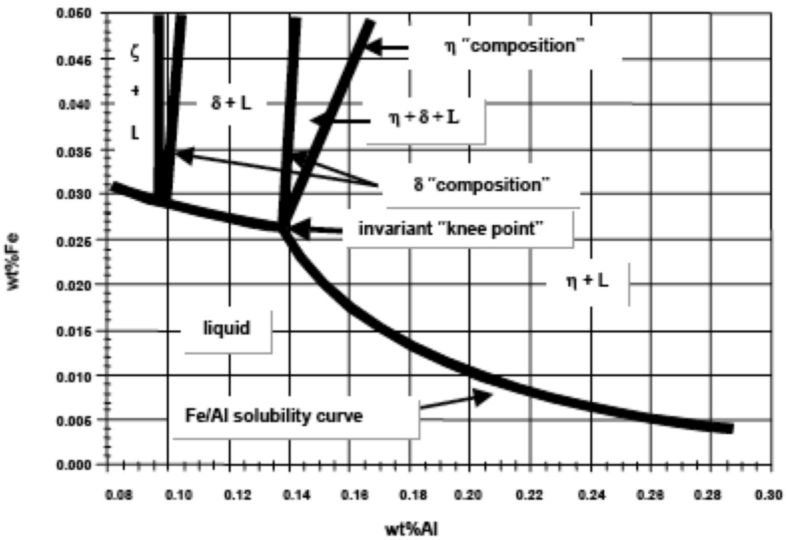

Figure 1 – Phase diagram of the Zn-rich corner of the Zn-Fe-Al system at 860°F [460°C] as per reference 1

- When producing galvanize (η + L region of Fig 1), determining Al_{EFF} consists of plotting the bath analysis results for Al and Fe on a phase diagram that is correct for the bath temperature at the time of sampling. A tie line is then drawn parallel to the intermetallic composition line, as shown in Fig 2. In this example, Al_{EFF} is the intersection of the tie line drawn from the 0.20% Al/0.035% Fe point, parallel to the η "composition" line (see Fig 1), to where it intersects the Fe/Al solubility line at 0.175% wt% Al. Again, this is only correct for a given temperature (in this case 860°F [460°C]) because the solubility curves shift up or down with the bath temperature.

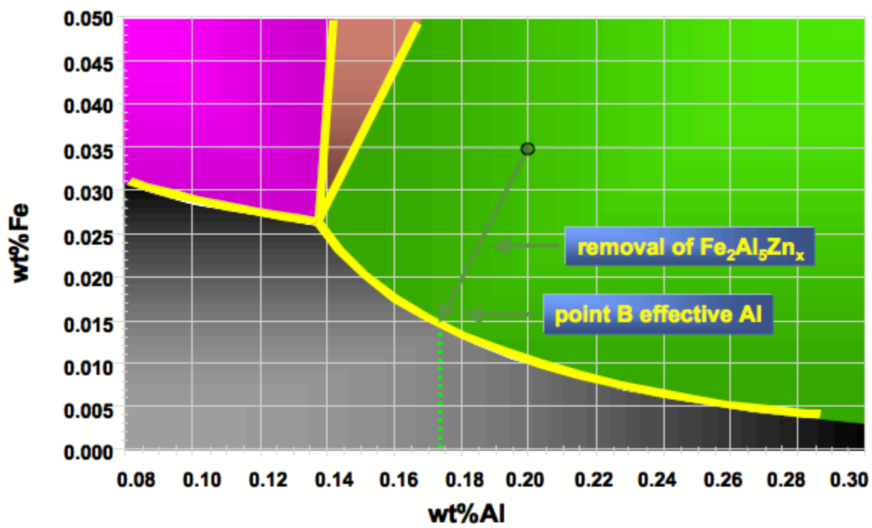

Figure 2 – Determining Al_{EFF} using the Zn-Fe-Al phase diagram (Courtesy of Xstrata)

- It is important to emphasize that the solubility diagrams vary as a function of temperature, which affects the determination of Al_{EFF}. To obtain correct Al_{EFF} results the sampling temperature must be known.
- Because of the effect of temperature on Al_{EFF}, it is impractical to use multiple solubility curves for its determination. Fortunately, zinc suppliers have developed computer tools that can determine Al_{EFF} for the complete range of bath chemistries and operating temperatures used by galvanizing companies.

Zinc Bath Operations

- Coatings with good surface quality, and having a proper composition and appearance, require a stable bath composition/temperature and effective control of dross build-up.
- Most CGL lines today use lead-free zinc, resulting in galvanize with a spangle free, smooth appearance.

Bath Compositions

- Total aluminum (Al_{TOT}) – typically 0.16 to 0.20% for galvanize, and 0.11 to 0.14% for galvanneal.
- Iron (Fe) – typically 0.015 to 0.03%.
- Lead (Pb) – typically zero (0.007% max); may be up to 0.10% if a spangle is desired.
- Antimony (Sb) – typically zero; may be up to 0.10% if a spangle is desired.
- Zinc (Zn) – Balance.

NOTE: Most galvanized sheet produced in the western world is spangle-free, i.e., zero Pb or Sb.

Bath and strip temperatures

- Bath temperatures range from 855 to 880°F [455 to 470°C] (typically 865-870°F [463 to 465°C]).
- Incoming strip temperature runs from 800 to 900°F [425 to 480°C], although the aim is to be at, but no more than, 5°F [2°C] above the bath temperature in the case of ceramic pots. This brings just enough excess heat into the bath so as to minimize the need to operate the inductors to keep the zinc at the correct temperature. The bath is more quiescent when the inductors are not operating.
- Whatever temperature practice is employed, it is important to maintain it consistently in order to avoid zinc temperature fluctuations. The reason for this is explained in the section on dross control.
- A high entry temperature can result in an uncontrollable rise in bath temperature, plus zinc dust build-up in the snout – leading to surface defects.
- An entry temperature that is too high can also result in more enrichment of Al in the ternary alloy layer, causing a higher depletion rate of Al from the bath and overall poor Al level control. It also results in more dissolution of the steel strip – leading to more dross generation.

Producing Galvanize (GI)

- Effective Al levels above 0.14% produce adherent coatings. When Al_{EFF} is below 0.14%, binary FeZn intermetallics can form, which are brittle and can lead to poor adherence.
- At 0.14% Al_{EFF}, the entire zinc coating (including the ternary alloy layer) contains about 0.20% Al. The higher the Al level is above 0.14%, the higher the bulk Al level in the coating. If the bulk Al content of the coating reaches levels above 0.30%, spot weldability problems could result.
- When Al in the bath is at the appropriate level (0.14% and higher), the galvanizing reaction forms a thin, interfacial, ternary alloy layer on the steel having a composition of 45% Al, 35% Fe, and 20% Zn ($Fe_2Al_{5-X}Zn_X$).
- Spangles are the zinc crystals or grains formed during solidification of the coating. The difference in crystal orientation from spangle to spangle manifests itself as variations in reflectivity. Spangles are thickest at the center and thinnest at the grain boundary, more so in the case of large spangles.
- Pure zinc freezes on most steel substrates with a very small (< 0.5mm diameter) spangle that is barely discernible to the naked eye, resulting in a very smooth and evenly reflective surface. To achieve a larger spangle, additions of lead or antimony must be made to the zinc bath. These elements have the effect of reducing the number of nucleation sites, and/or increasing the dendrite growth velocity, allowing spangles to grow larger before touching their neighbors. Refer to GalvInfoNote 2.6 for more information on spangles.

- Lead reduces surface tension and enhances fluidity and wettability. It increases the propensity for crazing at bends and can cause intergranular corrosion and delayed adhesion failure. Lead increases the tendency for sagging of the coating at low line speeds and produces a high relief spangle. At levels of 0.10% - 0.15% the spangles can be very large (~ 25 mm diameter). The small spangle that results from lead free zinc is very flat and easy to convert to extra smooth by temper passing.
- Antimony also reduces surface tension and enhances wettability. Its presence can result in a brittle coating if the aluminum level is not proper. Antimony produces a smaller spangle than lead, all other factors being equal.
- If the strip is too hot at bath entry it causes Al content in the coating to increase, while if it is too cold the Al in the coating will decrease. It is very important to control the strip temperature as it enters the zinc bath. Ideally the strip should be at the liquid zinc temperature to no more than 5°F [2°C] above it. Operating in this fashion on lines with a ceramic pot brings in a small amount of extra heat to minimize the need for the inductors to be on, helping to keep the bath quiescent.
- The reason for the above behavior is the strong affinity between Al and Fe, the speed of the reaction, and the effect that temperature has on this reaction. At a given bath Al level and temperature, the same amount of ternary alloy instantly forms, regardless of strip speed or total coating weight.
- Since the amount of Al extracted from the bath by the ternary alloy layer is independent of line speed and coating weight, it is important that operators know the rate of Al extraction at all times so that it can be replenished. As stated in GalvInfoNote 2.4, 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.

Producing Galvanneal (GA)

- Galvanneal is a zinc-iron alloy coating that is made by reheating the strip from as low as 820°F [438°C] to 935 to 1050°F [500 to 565°C], and holding in this range for about ten seconds. The zinc is still liquid when the strip enters the galvanneal furnace. Reheating restarts the zinc-iron diffusion reaction, breaks down the inhibition layer that formed while the strip was in the zinc bath, and after 5 to 10 seconds a dull gray matte coating is created. This coating consists of intermetallic zinc-iron alloy layers having an overall bulk iron content of between 9 and 12%. See Table 1 in GalvInfoNote 1.3 for the composition of the alloy phases in a galvanneal coating.
- The Al_{EFF} level in the zinc bath when making galvanneal is typically 0.11% to 0.13%. This level is lower than that when making galvanize in order to produce an inhibition layer that breaks down easier during conversion of the coating to galvanneal. Higher Al levels would require more heat during conversion, producing coatings with a higher iron level that would be susceptible to powdering. Keep in mind that the Al_{EFF} level used to make galvanneal is unsuitable for producing galvanize, as the ternary alloy layer formed would have a high zinc-iron content that could lead to flaking of the coating during severe forming operations.
- Most lines producing galvanneal use induction furnaces having three or more zones, which reheat the strip to 935 to 1050°F [500 to 565°C] in a few seconds. Induction furnaces, combined with soaking and cooling zones, provide the means to do this in a controlled, fast, and efficient fashion, resulting in a coating with good appearance and adherence.
- The galvanneal reaction starts at the steel interface and is dependent on: time, strip temperature reached, Al_{EFF}, bath temperature, steel grade, coating weight, and line speed. A higher Al_{EFF} content requires higher temperature and/or longer time to produce an optimum coating, with more danger of "overcooking", that could result in powdering. If the temperature is too low, the coating will not be fully alloyed. If the Al_{EFF} is too low (<0.11%), the coating adhesion will be poor, again due to powdering. Running too fast does not allow proper soak times. Keep in mind that each coating line is different and operators must determine the optimum windows for all the above variables.
- Stabilized IF substrate converts to galvanneal faster than ultra-low carbon or plain carbon substrate, and amongst IF substrates, Ti stabilized reacts faster than Ti-Nb stabilized. Rephosphorized IF steels are slower to respond to the galvanneal reaction and must be heated to a higher temperature.

Control of Dross

- Dross is an iron-containing particle that forms in the coating bath.
- Sources of iron are: strip dissolution, iron fines on the surface of the strip, and sink roll & other submerged hardware.
- Dross is a very hard, sand-like particle. Top dross is an aluminum-iron compound and bottom dross is a zinc-iron compound. Both types of dross interfere with good coating quality.
- Clean strip surface, free of iron debris, is also important in minimizing dross formation.
- At the steel-zinc interface a ternary $Fe_2\ Al_{5-X}Zn_X$ intermetallic forms, which has a density less than zinc and floats, contributing to top dross. It floats because it is less dense than zinc due to its high Al content.
- Since they float, any addition of 10% Al alloy bars to the bath results in most of the Al reporting directly to the top dross and leaving the bath on the surface of the strip. For this reason, it is a much better practice to use pre-alloyed jumbo zinc ingots, or 5% Al alloy bars (which sink), as the means of adding Al, since it will be more uniformly distributed throughout the entire bath volume.
- On many lines, robots are used to skim off top dross.
- Binary intermetallic (δ-$FeZn_7$) can also form. It has a density greater than zinc and sinks to form bottom dross. Again, by the proper use of pre-alloyed jumbo zinc ingots to control aluminum, the formation of δ-$FeZn_7$, and thus bottom dross, can be reduced.
- The aluminum level in the bath therefore affects the type of dross that is formed. At greater than about 0.14% Al_{EFF}, the stable dross particle is a primarily aluminum-iron particle – less dense than the molten zinc (top dross). The more the Al_{EFF} is below 0.14%, the more the stable dross particle that forms is a zinc-iron compound – denser than the molten zinc (bottom dross). For this reason, bottom dross can build-up during galvanneal campaigns.
- A key element in minimizing bottom dross generation is stability of the bath with respect to both temperature and aluminum content. A sudden drop in temperature can cause precipitation of zinc-iron from the melt. Also, sudden increases in aluminum percentage can generate excess top dross. Minimizing Al gradients by using modified feeding practices can control dross[1]. In short, don't shock the system.
- Again, to avoid rapid Al fluctuations, use pre-alloyed zinc jumbos, or 5% Al alloy bars, as much as possible as the means of getting Al into the bath, rather than 10% Al alloy bars. Following this practice has been found effective in minimizing bottom dross generation during long galvanneal runs. Refer to GalvInfoNote 5.2 for the range of Al levels available in jumbo zinc ingots.

Bath Control During Product Transitions (GA ⇒ GI and GI ⇒ GA)

- This article emphasizes that having stable bath operations is important to producing galvanized sheet. However, on coating lines that produce both GI and GA sheet, bath stability must be disturbed when transitioning from one product to another. Transitions are a complex topic that is too large to cover in detail here. Reference 1 contains information on the best practices to use when making these transitions. In short:
    - The GA ⇒ GI transition involves adding large amounts of Al to the bath such that the Al level is increased quickly.
    - The GI ⇒ GA transition consists of adding only SHG ingots (Al-free) to the bath so that Al decreases via removal by the strip.

Measuring and Controlling Bath Variables

- An important element of bath management involves measuring and controlling the chemistry of the zinc, the temperature of the strip and zinc, and the bath level.
- For each line a sampling plan must be developed for the bath metal. This involves:
    - The location(s) where the samples are taken
    - The sampling technique and sample type

- The method(s) of determining total and effective aluminum
- The measurement of other elements (Fe, Pb, Sb, Cd, etc.) in the bath metal

- Al_{EFF} in the zinc can be measured indirectly by a number of analytical techniques, including atomic absorption (AA), inductively coupled plasma (ICP), and optical emission spectroscopy (OES). The direct reading must be corrected, however, by knowing the values of Al and Fe measured by these techniques, and the bath temperature at the time of the sampling. Computer tools and software are available to perform this task.
- Al_{TOT} determination typically requires wet chemical analysis, as the aluminum tied up in the dross must be dissolved before it can be analyzed.
- The appropriate strip and zinc temperature and zinc level sensors must be part of the line equipment.
- Shown below are the important factors involved in good management of zinc bath chemistry:

Factors for Bath Management and Control of Effective Aluminum

1. **Material**
   - Zinc ingot chemistry
   - Aluminum/Antimony bar chemistry
   - Steel strip – chemistry, thickness, width, roughness
2. **Method**
   - Coating weight
   - Steel strip – speed, temperature
   - Bath temperature, pot heating method
   - Sampling method
3. **Machine**
   - Pot –condition, inductors or heating elements, hardware condition
   - Sampling tool
   - Sampling mold
4. **Man**
   - Additions – zinc ingot, aluminum bar, antimony bar
   - Dross removal method
   - Sampling practice and location
5. **Measurement System (accuracy, precision, resolution, calibration)**
   - OES, ICP (bath chemistry)
   - Pot thermocouple (bath temperature)
   - Sensors – strip thickness, coating weight, strip temperature, line speed

[i] McDermid, J.R., Baril, E., Goodwin, F.E., Galvanizing Bath Management During Galvanizing to Galvanneal and Galvanneal to Galvanize Product Transitions, Proceedings Galvatech '04, pp. 855-869