2. Coating Process	es and Surface Treatments
GalvInfoNote	Zinc Bath Management on
2.4.1	<b>Continuous Hot-Dip Galvanizing Lines</b>
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# Introduction

This GalvInfoNote expands (in summary form) 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. Readers desiring more detailed information are referred to the references listed at the end of this note.

# 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.
- Bath chemistry management is the management of AI, including its analysis and control.
- In continuous galvanizing, AI exerts a very powerful effect in the reaction between the steel and molten Zn and is purposely added to the bath for that reason. The reaction is governed by an equilibrium constant and takes place mainly at the liquid zinc/steel interface.
- It is important to understand that a CGL bath is, in reality, *a chemical (metallic) reactor*. Steel (Fe), Zn and Al are being transformed into zinc-coated steel and dross, governed primarily by the following reaction:<sup>1</sup>

### 2Fe + 5AI 👝 Fe<sub>2</sub>Al<sub>5</sub>

- When aluminum is dissolved in zinc the reaction with 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<sub>2</sub>Al<sub>5-x</sub>Zn<sub>x</sub>). 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. When the proper amount of Al is present, it means that both surfaces of each unit area of strip passing through the zinc bath, independent of strip thickness or line speed, always contains a thin and very adherent alloy layer containing 45% Al.
- Fe solubility in molten zinc is a function of AI content and bath temperature. Fe solubility decreases as bath AI content increases and as bath temperature decreases.
- During the typical immersion times in a CGL zinc bath (typically 2 to 8 seconds depending on line speed) the ternary alloy remains stable if there is sufficient AI 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 on GI products.
- 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 [η-Fe<sub>2</sub>Al<sub>5-x</sub>Zn<sub>x</sub>]) or zinc-iron (bottom dross [δ-FeZn<sub>7</sub>]), with the iron coming from strip dissolution and any iron fines on the surface.

## Understanding Effective Aluminum (Al<sub>EFF</sub>)

- Both Fe and Al have a limited solubility in liquid Zn. They form a variety of intermetallics in the Zn-rich corner of the Zn-Al-Fe alloy system. Al contained in intermetallics is not available to react with steel. The only Al available to react with steel is Al dissolved in Zn, otherwise known as effective Al (AleFF).
- Aluminum content of the zinc bath is the key to understanding and controlling the CGL process, and this is achieved by the control of pot chemistry, viz., the AlEFF level.
- Total aluminum (AI<sub>TOT</sub>) is all of the AI in the bath; AI in solution in zinc and AI that is part of all the intermetallic dross phases. AI<sub>TOT</sub> is determined by chemical analysis of bulk bath samples.
- Al<sub>EFF</sub> is aluminum dissolved in molten zinc, and is the determining factor in forming the desired coating microstructure<sup>2</sup>. It does not include aluminum tied up in intermetallic dross particles, since that is not available to react with iron in the steel strip. Using computer programs to make necessary adjustments for bath temperature and Fe level, Al<sub>EFF</sub> is measured indirectly using techniques such as AA, OES, or ICP, and directly in the zinc bath using a laser induced breakdown spectroscopy (LIBS) instrument.
- Aluminum changes the solubility of iron in molten zinc:
  - Increasing AI decreases the amount of Fe that 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).





• When producing galvanize ( $\eta$  + L region of Figure 1), determining Al<sub>EFF</sub> consists of plotting the bath analysis results for Al<sub>TOT</sub> and total 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 Figure 2. The slope of this line represents the ratio in which Fe and Al combine in this region of the phase diagram. In this example, Al<sub>EFF</sub> is the intersection of the tie line drawn from the 0.20% Al/0.035% Fe point, parallel to the  $\eta$  "composition" line (see Figure 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 Aleff 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<sub>EFF</sub>. To obtain correct Al<sub>EFF</sub> results, the temperature of the bath must be known at the time of sampling.
- Because of the effect of temperature on Al<sub>EFF</sub>, it is impractical to use multiple solubility curves for its determination. Fortunately, zinc suppliers have developed computer tools that can determine Al<sub>EFF</sub> for the complete range of bath chemistries and operating temperatures used by galvanizing companies. Al<sub>EFF</sub> can also be measured directly using the LIBS technique.
- In practice, the CGL bath is always supersaturated with respect to Fe solubility when in the η + L region, so intermetallic particles are always present in the bath. The determination of Al<sub>EFF</sub> by first measuring Al<sub>TOT</sub> is essentially an exercise of 'mathematically or graphically' removing Al present in intermetallic particles.

## **Effect of Steel Chemistry**

- The reaction between steel strip and an AI containing Zn bath is extremely complex.<sup>3</sup>
- The inhibition layer is primarily composed of Fe<sub>2</sub>Al<sub>5</sub> and contains Zn in solution with the possible inclusion of small amounts of Mn, P, and O. The amount of Zn in the layer increases with immersion time.
- There appears to be a Mn depletion zone immediately below the inhibition layer substrate interface, suggesting that Mn has diffused outwards to become incorporated into the inhibition layer structure. There is also the chance of a similar effect with P in a Ti-P IF substrate.
- There is little effect of the substrate chemistry on the formation of the inhibition layer with the exception of the growth of a thicker layer on Ti-P IF.
- For immersion times of 1-10 s, a thicker inhibition layer forms in a galvanizing spelter than in a galvannealing spelter.
- After the initial rapid nucleation and growth of the layer in a galvanizing spelter, the degree of further growth is greater than that seen in a galvannealing spelter, perhaps due to a localized depletion of AI in the latter.
- A slightly thicker inhibition layer forms on the Ti-P substrate than on Ti IF substrate. This may provide a clue as to why the rate of the Fe-Zn galvannealing reaction is relatively slow on rephosphorized substrates. The growth of the thicker layer may support the theory that P promotes nucleation of Fe<sub>2</sub>Al<sub>5</sub>.
- When producing GA, most substrate steel chemistries should be run in the three-phase field of the phase diagram to gain the benefits of a stable knee point effective AI, and top dross formation, which can extend GA runs by reducing bottom dross build-up.
- Some substrate chemistries (e.g., re-P BH) may not fully galvanneal in the η+δ+L region, therefore a bath chemistry in the two phase δ+L field should be employed to ensure the GA coating microstructure develops fully.

• 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.

## 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 zero spangle, smooth appearance.

#### Bath Compositions

- Total aluminum (Altor) typically 0.16 to 0.20% for galvanize, and 0.11 to 0.135% for galvanneal.
- Iron (Fe) typically 0.015 to 0.03%.
- Lead (Pb) typically zero (0.007% max).
- Antimony (Sb) typically zero; may be up to 0.10% if spangle is desired.
- Zinc (Zn) Balance.
  - NOTE: Most galvanized sheet produced in the western world is zero spangle, i.e., Pb or Sb less than 0.005%.

#### Zinc Addition Practices

- The melting of a CGG alloy jumbo weighing one ton, would result in a 10°C drop for a mass of 60 tons of bath metal, and would result in a significant amount of dross particles being formed. In a 300 ton bath the drop would be 2°C, i.e., a larger bath is more stable as its temperature is less affected by cold zinc additions.
- And, as Al<sub>EFF</sub> is mostly influenced by bath temperature variation, a larger mass of metal in a bath reduces dross generation due to charging.
- To minimize dross formation in lower mass baths it is beneficial to reduce the charging rate of ingots. Gradual ingot immersion results in a slower increase of dross and a smaller quantity of dross generated.<sup>4</sup>
- During steady state GI operation, approximately 50% of the AI from 10% brightener bars is recovered to the CGL bath whereas the recovery is near 100% when 5% bars are used. This is most likely the result of the fact that 10% brightener bars float whereas 5% bars sink, resulting in lower losses to oxidation (and top dross) for the latter material.
- Also, as 5% bars are near the eutectic composition of the Zn-Al system, they melt more uniformly and at a lower temperature than the surrounding Zn bath. The 10% Al bars contain a primary high Al phase, which melts at a temperature considerably higher than that of the Zn bath.
- It is recommended that 5% Al brightener bars be used for Al additions if the Al is not being added via alloy jumbos. This is especially important on CGL lines coating very thick substrate with heavy coatings. Such lines sometimes run very slow, resulting in poor mixing of the bath metal. This may result in Al starvation in the Zn near the bottom of the snout where the strip enters. The inhibition layer that forms in such conditions may tend to being brittle and not be able to withstand subsequent forming of the product. Flaking of the coating can occur. Using 5% Al alloy bars help prevent this situation.

#### 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 that it remain consistent 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 AI in the ternary alloy layer, causing a higher depletion rate of AI from the bath and overall poor AI control. It also results in more dissolution of the steel strip – leading to more dross generation.

## Producing Galvanize (GI)

- Effective AI levels above 0.14% produce adherent coatings. When AI<sub>EFF</sub> is below 0.14%, binary FeZn intermetallics can form, which are brittle and can lead to poor adherence.
- At 0.14% Al<sub>EFF</sub>, 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 AI in the bath is at the appropriate level (0.14% and higher), the galvanizing reaction forms a thin, interfacial, ternary alloy layer that adheres to the steel and has a composition of 45% AI, 35% Fe, and 20% Zn (Fe<sub>2</sub>Al<sub>5-x</sub>Zn<sub>x</sub>).
- 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 difficult to discern by 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 spangle formation.
- 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 very 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, which minimizes the need for the inductors to be on, helping to keep the bath more quiescent and save energy.
- The reason for the above behavior is the strong affinity between AI and Fe, the speed of the reaction, and the effect that temperature has on this reaction. At a given AI<sub>EFF</sub> level and temperature, the same amount of ternary alloy instantly (< 0.15 s) forms, regardless of strip speed or total coating weight.
- Since the amount of AI 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 AI extraction at all times so that it can be replenished. As stated in GalvInfoNote 2.4, most galvanize producers, with the assistance of their Zn suppliers, have developed AI addition algorithms for their Zn pots. These prediction models forecast AI levels depending on product mix and stipulate how to add AI-bearing zinc to keep AI in the bath at the desired concentration.

# Producing Galvanneal (GA)

- Galvanneal is a Zn-Fe 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 Zn coating is still liquid when the strip enters the galvanneal furnace. Reheating restarts the Zn-Fe diffusion reaction, breaks down the inhibition layer that formed while the strip was in the bath, and after 5 to 10 seconds a dull gray matte coating is created. This coating consists of intermetallic Zn-Fe 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<sub>EFF</sub> level in the Zn bath when making galvanneal is typically 0.11% to 0.13%. This level is lower than 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 Fe level that would be susceptible to powdering. Keep in mind that the Al<sub>EFF</sub> level used to make galvanneal is unsuitable for producing galvanize, as the ternary alloy layer formed would have a high Zn-Fe 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<sub>EFF</sub>, bath temperature, steel grade, coating weight, and line speed. A higher Al<sub>EFF</sub> 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 Al<sub>EFF</sub> 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.
- To improve line operation efficiency and produce the highest product quality in GA coatings, the inhibition layer formed in the hot-dip stage should be as thin as possible, yet the formation of bottom dross should be avoided. These two conflicting requirements require compromises, which can best be achieved by producing GA in baths containing an AI level marginally higher than the knee point in the Zn-AI-Fe system, i.e., slightly more than 0.0138% AI. By using such a composition, bottom dross formation is largely avoided. The inhibition layer is still thin and patchy and readily dissolves in the annealing treatment. When producing GI, the bath aim AI level should be no higher than 0.15-0.16%, so that transition to GA can be accomplished quickly.

## **Control of Dross**

- Dross is an Fe-containing particle that forms in the coating bath. Sources of Fe are: strip dissolution, steel 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 Al-Fe compound and bottom dross is a Zn-Fe compound. Excess amounts of both types of dross interfere with good coating quality.
- Clean strip surface, free of steel debris, is also important in minimizing dross formation.
- At the steel-Zn interface a ternary Fe<sub>2</sub> Al<sub>5-x</sub>Zn<sub>x</sub> intermetallic forms, which has a density less than zinc and floats, contributing to top dross. It floats because it is less dense than Zn due to its high Al content.
- Since they float, any addition of 10% AI alloy bars to the bath results in most of the AI reporting directly to the top dross, with some 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% AI alloy bars (which sink), as the means of adding AI, 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<sub>7</sub>) can also form when the bath chemistry is in the GA region. This intermetallic 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<sub>7</sub>, and thus bottom dross, can be reduced.
- The Al level in the bath therefore affects the type of dross that is formed. At greater than about 0.14% Al<sub>EFF</sub>, the stable dross particle is a primarily Al-Fe particle less dense than the molten zinc (top dross). The more the Al<sub>EFF</sub> is below 0.14%, the more the stable dross particle that forms is a Zn-Fe compound denser than the molten zinc (bottom dross). For this reason, bottom dross can build-up during galvanneal campaigns.
- Aluminum is mainly consumed by the formation of the inhibition layer at the substrate/Zn interface. Dross formation normally accounts for less than 10% of the total Al added to the bath.
- In the bulk of baths, a dynamic equilibrium prevails so the concept of an equilibrium constant can be used to minimize dross formation. The higher the AI content in the ingot, the higher the resultant AI in the bath and the more dross particles form following charging.
- To minimize dross formation, use a CGG alloy that simply replenishes the amount of Al consumed in the charging interval.

- 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 Zn-Fe from the melt. Also, sudden increases in Al percentage can generate excess top dross. Minimizing Al gradients by using modified feeding practices can control dross<sup>1,5</sup>. In short, <u>don't shock the system</u>.
- Again, to avoid rapid Al fluctuations, use pre-alloyed Zn 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 Zn ingots.

# Bath Control During Product Transitions (GA $\Rightarrow$ GI and GI $\Rightarrow$ GA)

• This GalvInfoNote emphasizes that having stable bath operations is important in 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.

#### GA to GI transition

- The GA ⇒ GI transition involves adding large amounts of AI to the bath such that the AI level is increased quickly.
- The  $\delta$ -phase is no longer thermodynamically stable in the bath at higher Al concentrations. It undergoes a transformation to  $\eta$ -phase according to the reaction:

$$2 \delta$$
-FeZn7 + 5AI  $\Rightarrow \eta$ - Fe<sub>2</sub>AI<sub>5-x</sub>Zn<sub>x</sub> + (7-X) Zn

This transformation of bath intermetallics consumes large amounts of bath AI and will tend to decrease AI<sub>EFF</sub> below target levels unless properly compensated for.

In Figure 2 the transition starts at point A and proceeds to points B or C with a target bath chemistry of O.20 wt% Al. If the target is Al<sub>TOT</sub> = 0.20% the end point is B; if it is Al<sub>EFF</sub> = 0.20%, the end point is C. Both of these targets will create considerable top dross. To minimize top dross creation, the solution is to increase the bath Al content to just above the knee point of ~ 0.14%. For galvanizers wishing to run cleaner baths seen at higher Al contents, the solution is to use only Al<sub>EFF</sub> for bath control.



Figure 3 – Representation of the GA to GI transition (from reference 2)

 A long-standing practice for the GA to GI transition is to "spike" the bath AI using brightener bars and then feed only AI containing jumbos during the time the bottom dross is converting and floating to the surface. This can result in a significant gap in the total versus effective AI readings, creating the generation of new top dross particles. The larger the gap, the more top dross particles are generated. If AI<sub>TOT</sub> is being used to control the bath, it gives large misrepresentations of the state of the bath chemistry.

- An additional factor complicating the GA to GI conversion is the conversion of bottom dross particles (1.5% AI) to top dross particles (45% AI). This causes AI deportment to dross to be greater than experienced during steady state GI operation. Also, bath Fe levels are higher during normal GA operation than during normal GI operation since Fe solubility in Zn is significantly higher in the GA region.
- In transitioning to the GI mode, Fe solubility is significantly lowered, which results in additional AI being consumed in the creation of new top dross particles.
- It is an advantage to use 5% AI brightener bars when transitioning since they sink, allowing the AI to get to the bottom dross more quickly. Their efficiency in doing so is close to 100%, compared to 10% AI brightener bars with a lower efficiency of 50 to 75% due to the fact they tend to float and AI is lost to top dross and oxidation.
- One GA to GI conversion practice that allows the target Al<sub>EFF</sub> to be achieved earlier and to eliminate brightener bar additions after the initial spike addition is to use 1% Al jumbos to feed the bath. Doing this supplies additional Al for dross particle transformation while not detracting from getting to the aim Al<sub>EFF</sub>.
- Note also that AI demands of the bath can be reduced during the transition period by producing high coating weight products and lowering the strip entry temperature, as these actions will lower the %AI in the coating.

#### GI to GA transition

The GI ⇒ GA transition consists of adding only SHG ingots (Al-free) to the bath so that Al decreases via removal by the strip and dross production from the GI composition in the η + L field to the to the desired GA bath composition in either the three-phase η + δ + L region or the δ + L field. The transformation reaction is:

 $\eta$ -Fe<sub>2</sub>Al<sub>5-X</sub>Zn<sub>X</sub>  $\Rightarrow$  2[Fe]+ 5[Al] + X Zn ([] brackets mean element in liquid Zn solution)



Figure 4 – Representation of the GI to GA transition (from reference 2)

- The dissolution reaction is a consequence of the bath soluble Fe increasing with decreasing Al content. This reaction can increase bath Al and delay reaching the desired GA composition.
- In Figure 4, points A and A' have the same Al<sub>EFF</sub>, but A' has a larger mass of η intermetallics that will dissolve back into the bath during the initial stages of the transition and retard attainment of the GA composition. This means that the GI to GA should start from Al<sub>TOT</sub> bath composition rather than from Al<sub>EFF</sub> composition in order to take the additional Al from the intermetallic decomposition into account. To do this effectively, multiple analyses from pre-transition bath samples should be taken so as to establish a consistent and reliable starting point.
- The transition end point computations and timing should be based on the strip area throughput rather than time, as it is the former that controls AI depletion of the bath.

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• There are other simple remedies to increase AI output via the strip, such as coating thin sheet (higher line speed), light coating weights, use of wide strips and higher strip entry temperatures in order to shorten the transition time. These actions all contribute to faster removal of AI from the bath.

### **Measuring and Controlling Bath Variables**

- An important element of bath management involves measuring and controlling the chemistry of the Zn bath, the temperature of the strip and Zn bath, 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<sub>TOT</sub> in the zinc can be measured by a number of analytical techniques, including atomic absorption (AA), inductively coupled plasma (ICP), optical emission spectroscopy (OES) and. To obtain Al<sub>EFF</sub>, the Al<sub>TOT</sub> result must be corrected using the total Fe value, the bath temperature at the time of the sampling and the appropriate phase diagram for the temperature. Computer tools and software are also available to perform this task.
- A technology known as LIBS (Laser Induced Breakdown Spectroscopy) is also available. It provides a real time quantitative analysis of the concentration of dissolved AI (Al<sub>EFF</sub>) and Fe in the molten zinc bath<sup>6,7</sup>. The dross content is also determined at the same time. The precision of the measurements of dissolved AI and Fe is ±15 ppm. Real time results allow improved scheduling of the GA to GI and GI to GA transitions.

<sup>7</sup> Nadeau, F., Warnement, C., Stechschulte, J., *"Lab Free Pot Chemistry Monitoring: LIBS Brought to the Next Level"*, Galvatech 2015 Proceedings, Toronto, ON, June 2015.

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<sup>&</sup>lt;sup>1</sup> Tang, N-Y, "Demystifying CGL Bath Management", 2000 Galvanizers Association Conference, Toronto, ON.

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<sup>&</sup>lt;sup>3</sup> Price, S.E., et al, "Study of aluminum inhibition layer formed during hot dip stage of galvannealing on titanium interstitial free and rephosphorized titanium interstitial free substrates", Ironmaking and Steelmaking, 1999, Vol 26, No. 5, pp. 378-386.

<sup>&</sup>lt;sup>4</sup> Ajersch, F., *"Numerical Simulation of the Rate of Dross Formation in Continuous Galvanizing Baths"*, Iron and Steel Technology, August, 2006, p. 101.

<sup>&</sup>lt;sup>5</sup> McDermid, J.R., Dewey, C., <u>Optimizing the GA to GI Transition at Pro-Tec CGL#1</u>, 92<sup>nd</sup> Galvanizers Association Meeting, Toronto, ON, October 29 - November 1, 2000

<sup>&</sup>lt;sup>6</sup> Nadeau, F., "Online Monitoring od Effective Aluminum and Total Iron", Galvatech 2011 Proceedings, Genoa, Italy, June 2011.