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Abnormal Coating Buildup on Si Bearing Steels in Zn Pot During Line Stop

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A hot-dip simulator was utilized to replicate abnormal coating buildup observed during line stops at galvanize lines, assessing the influence of processing conditions on buildup (up to 14 mm/side). Steel samples from 19 coils (comprising IF, BH, LCAK, HSLA, DP600-DP1180, Si: 0.006 - 0.8 wt%, P: 0.009 – 0.045 wt%) were examined to explore the phenomenon of heavy coating growth. It was discovered that heavy coating buildup (~3 mm/h) and rapid strip dissolution (~0.17 mm/h) in a GA or GI pot can manifest with specific combinations of steel chemistry and processing conditions. The results reveal the formation of a unique coating microstructure, characterized by a blend of bulky Zeta crystals and free Zn pockets/networks due to the "Sandlin" growth mechanism. Key variables contributing to abnormal coating growth include steel Si content, anneal temperature, dew point in heating and soaking furnaces, Zn pot temperature, Zn bath Al%, and cold-rolling reduction%. At ArcelorMittal Dofasco galvanize lines, an automatic online warning system for operators and special scheduling for incoming Si-bearing steels have been implemented, effectively preventing further heavy buildup occurrences.

Keywords: *Abnormal Zn coating growth, Steel strip dissolution, Si bearing steels, AHSS steels, Galvanize processing*

1. Introduction

During line stops at galvanize lines, sometimes, a heavy coating layer (up to 14 mm/side) could be built-up on the strip submerged in the Zn pot (for immersion time of only 3 ~ 5 hours), which is ~10x faster coating growth than a normal situation. The Zn buildup can break away and fall from the GA tower (40 ~ 60 m height) after exiting the Zn pot, causing a safety hazard by directly falling onto the pot area and/or causing Zn splashing, and damaging equipment. The heavy buildup also corresponds to fast strip dissolution, leading to strip breakage. It is necessary to understand the cause, and to avoid the heavy buildup or strip breakage.

2. Experiment Method

2.1 Heavy coating buildup at production galvanize lines (cgls) and sampling

Fig. 1 shows an example of heavy coating buildup on a HSLA steel (0.33Si) after being submerged in the GI pot for 3.5 hours at ArcelorMittal Dofasco's #6CGL. The buildup coating (~9 mm thick) was cracked and separated from the strip at the top roll of the GA tower (63 m height), with some of coating falling back to the Zn pot area. Fig. 2 shows another HSLA strip (1.2 mm) was completely dissolved in the GI pot after being submerged for 7.5 hours (buildup was not observed due to strip dissolution). Samples (steel and/or coating) from these two cases were submitted for investigation.

In total, 10 cases of heavy coating buildup (or strip dissolution) were observed at 5 different CGLs in ArcelorMittal in recent years. It was noticed that all incidences occurred on Si bearing steels (Si: 0.04 ~ 0.8 wt%) with Zn pot Al of 0.13 ~ 0.22 wt%, and dipping time of 1 – 8 hours.

2.2 Validation with hot dip simulator

A hot dip simulator (HDS) was used to reproduce the coating buildup and to determine the impact of processing conditions on the buildup.

Steels samples from 19 coils (including IF, BH, LCAK, HSLA, DP600-DP1180, Si: 0.006 - 0.8 wt%, P: 0.009 – 0.045 wt%) were used for the simulation. A hot-rolled

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Fig. 1. Example of Heavy Coating Buildup During Line Stop at #6CGL (HSLA, 0.33Si, 3.5 hrs)

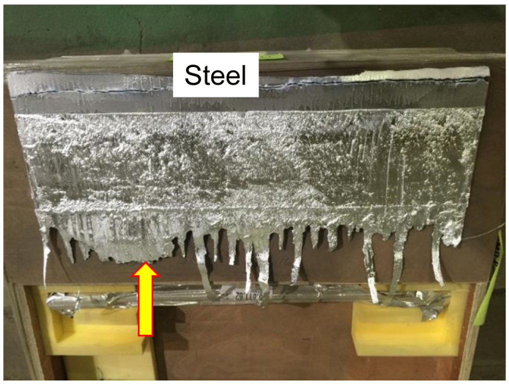


Fig. 2. Example of Strip Dissolution in the Zn Pot During Line Stop (HSLA, 0.35Si, 7.5 hrs)

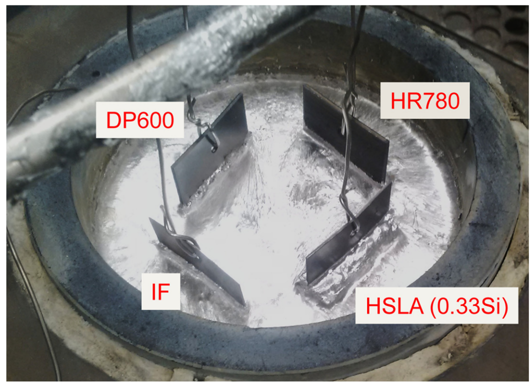


Fig. 3. Dipping Experiment for As-cold (or hot) Rolled Steels; Open GI Pot, 460 °C, Dip Time: 3.5 hrs

steel (HR780: 0.59Si) was cold-rolled to a 50% reduction by a lab scale rolling mill to investigate the impact of rolling conditions on the buildup.

Pre-oxidation was carried out in the hot dip simulator at various temperatures in air (to simulate the extreme situations). Whereafter, the samples were cooled at the fastest possible rate to room temperature by N_2 and then heated up again to target anneal temperatures in a controlled atmosphere before being dipped in the Zn pot.

Target Hot Dip Simulation Conditions (based on possible production situations during line stops):

Anneal-T (°C): 25 (as-rolled), 450, 500, 550, 750, 850 (for 60 – 180 s)
Strip Entry-T (°C): 25, 300, 460
Pot T (°C): 450, 460, 470, 480
Pot Al (wt%): 0.13, 0.20, 0.25 (Fe saturated)
Dew Point (°C): +5, -10, -45, -70,
Furnace H_2 (%): 0, 5
Submerging Time (hour): 0.15, 0.25, 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5
Pre-oxidation before annealing: 200 - 700 (°C) for 1 s in air
Post-oxidation after annealing: 450 °C for 10 s in mix of N_2 and air

As-cold (or hot) rolled samples of various steel grades were submerged directly in the open Zn pot together when target Anneal-T and Snout-T were at 25 °C (room temperature, Fig. 3).

2.3 Sample characterization

Optical image, SEM-EDS and wet chemical (ICP) etc. were used to characterize the samples.

3. Results and Discussions

3.1 Coating buildup (or strip dissolution) on hot dip simulation samples

Fig. 4 shows some of test results for various as-cold (or as-hot) rolled steels submerged in an open GI pot for 3.5 hours. Abnormal heavy coating growth (8 ~ 20 mm/side) occurs for the Si bearing steels (HSLA, DP780, DP980 and DP1180: 0.29 ~ 0.8 Si), confirming their heavy growth observed at production CGLs. It is noted that no heavy buildup (i.e. ≤ 1 mm) can be observed on IF (0.006Si), BH (0.009Si - 0.045P), LCAK (0.005Si),

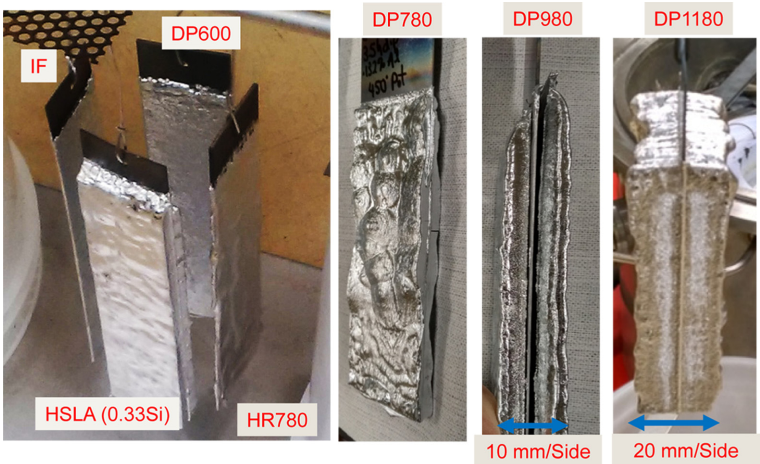


Fig. 4. Zn Coating Buildup (observed in cross-section) on Different Grades; Open GI Pot, 450-460 ºC, Dip Time: 3.5 hrs

HSLA

Ser No	C (wt%)	Mn (wt%)	Si (wt%)	P (wt%)	Coating Thk (mm/side)
M48692	0.032	0.151	0.049	0.009	3.4
M48702	0.042	0.174	0.038	0.013	0.6

Fig. 5. Zn Coating Buildup (observed in cross-section) on HSLA Steels with Different Si Levels; Open GI Pot, 460 ºC, Dip Time: 1.5 hrs

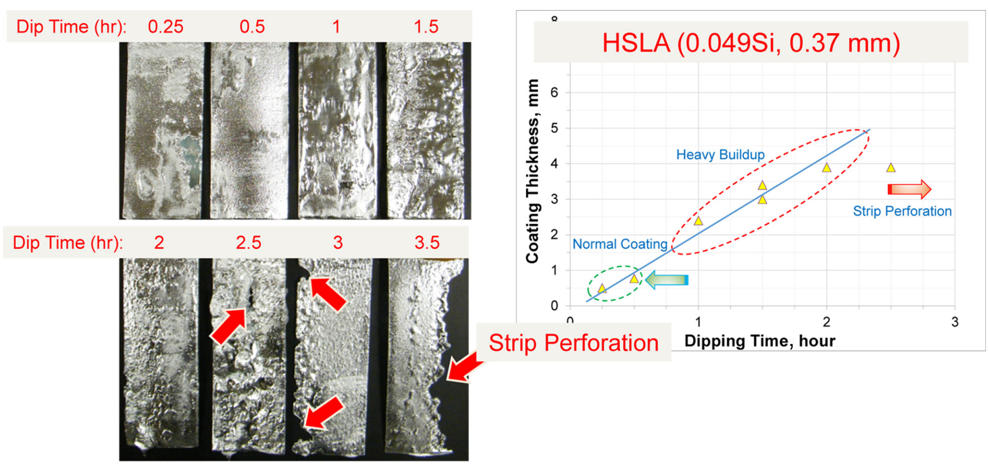


Fig. 6. Zn Coating Buildup or Strip Dissolution (arrowed) on HSLA CR Steels; for Various Dipping Times, at 460 ºC, GI Pot

DP600 (0.18 Si) and HR780 (0.59Si, as-hot rolled) steels. Similar results were observed with the GA pot too.

For a low Si HSLA grade, abnormal coating growth occurs on the steel with 0.049 wt% Si, but not on the steel with 0.038 wt% Si (Fig. 5), indicating the safe limit for avoiding the heavy coating growth is: Si < 0.04 wt%.

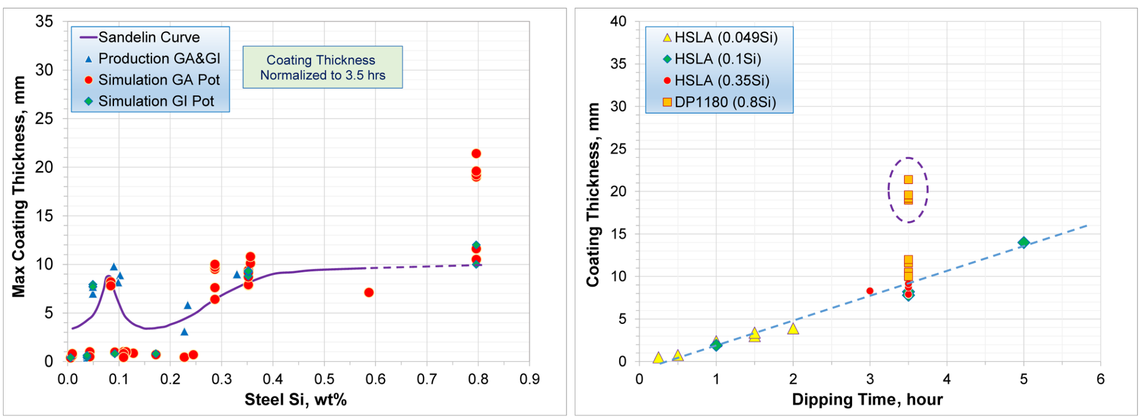
Fig. 6 shows an example of the buildup with increasing of dipping time. In general, no heavy buildup occurs for dipping time of 30 minutes or less regardless of steel chemistry. Significant buildup occurs after ~1 hour dipping, at which time the coating surface becomes very rough due to severe Fe-Zn alloying. The coating thickness can reach 3.4 mm after 1.5 hours dipping. The strip (0.37 mm) can be perforated after 2.5 hours dipping. The heavy buildup can fall back into Zn pot after 3 hours due to significant strip dissolution.

3.2 Effect of steel chemistry and processing conditions on heavy buildup & strip dissolution

As shown in Fig. 7a, in both GA and GI pots (bath Al%: 0.1 ~ 0.2 wt%), the max coating thickness (including production samples) follows (approximately) the well-known "Sandelin" Curve [1-6]. That is, the heavy coating growth occurs either in the Si range of 0.04 ~ 0.12 wt% or > ~ 0.23 wt%. However, the buildup cannot always be reproduced by the HD simulator when the Si is between 0.04 wt% to 0.23 wt% where the buildup is highly sensitive to other processing conditions as discussed later.

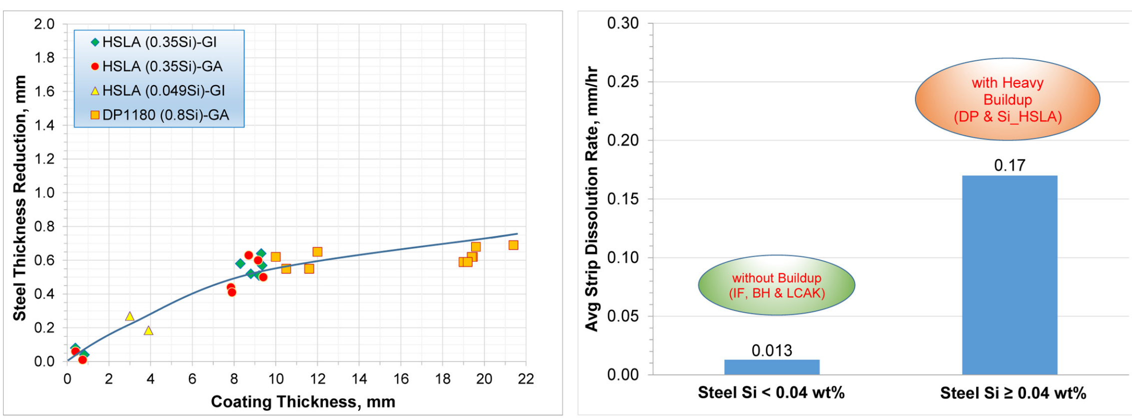
When the heavy buildup occurs, in general, the coating thickness increases linearly with dipping time (Fig. 7b), indicating the existence of liquid Zn diffusion channels (or Free Zn networks) during the Fe-Zn coating growth. If the coating growth were controlled by interdiffusion of Fe and Zn in solid state (i.e. through newly formed Fe-Zn alloy layer), it would have followed a sigmoid (or S-shape) curve and at a much slower growth rate (i.e. square root of dipping time [1-4]). It is noted that the thickness of some of DP1180 coatings can be 2x thicker than other heavy buildups for a given dipping time, indicating the buildup is not affected by Fe-Zn diffusion alone.

The heavy coating buildup of the Si bearing steels (Si ≥ 0.04 wt%) also corresponds to fast strip dissolution in the Zn Pot (~ 0.17 mm/h), which can be ~13x faster than the normal situation (Fig. 8a,b). Therefore, a 1.2 mm thick



(a) (b)

Fig. 7. Effect of Steel Si% & Dipping Time on Coating Buildup



(a) (b)

Fig. 8. Relationship between Heavy Coating Buildup and Strip Dissolution in Zn Pot (450 ~ 465 °C)

HSLA (0.35Si) strip can be completely dissolved after just 7.5 hours of submersion at #6CGL as observed previously, leading to an extended line stop in order to re-thread the strip through the furnace. It is also noted that steel thickness reduction increases almost linearly with coating thickness when the coating is ≤ 12 mm, but further reduction becomes very small for the extremely thick coatings (18 ~ 22 mm, DP1180). In fact, high Si (0.8 wt%) in the steel can lead to much thicker (less dense) coating for a similar amount of Fe available for formation of Zeta phase.

As shown in Fig. 9a, the buildup at anneal-T of 450 ~ 500 °C is similar to that for a sample dipped at room

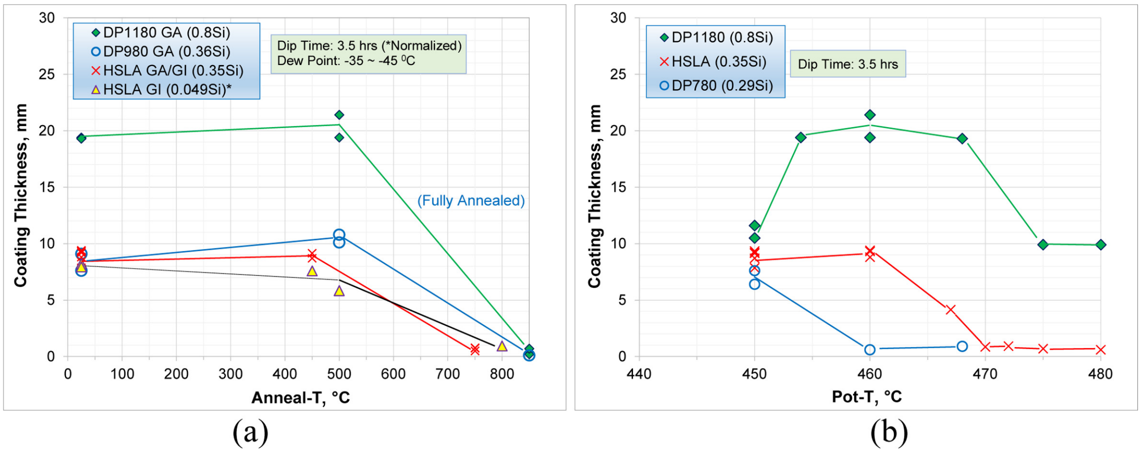


Fig. 9. Effect of Anneal-T & Pot-T on Coating Buildup

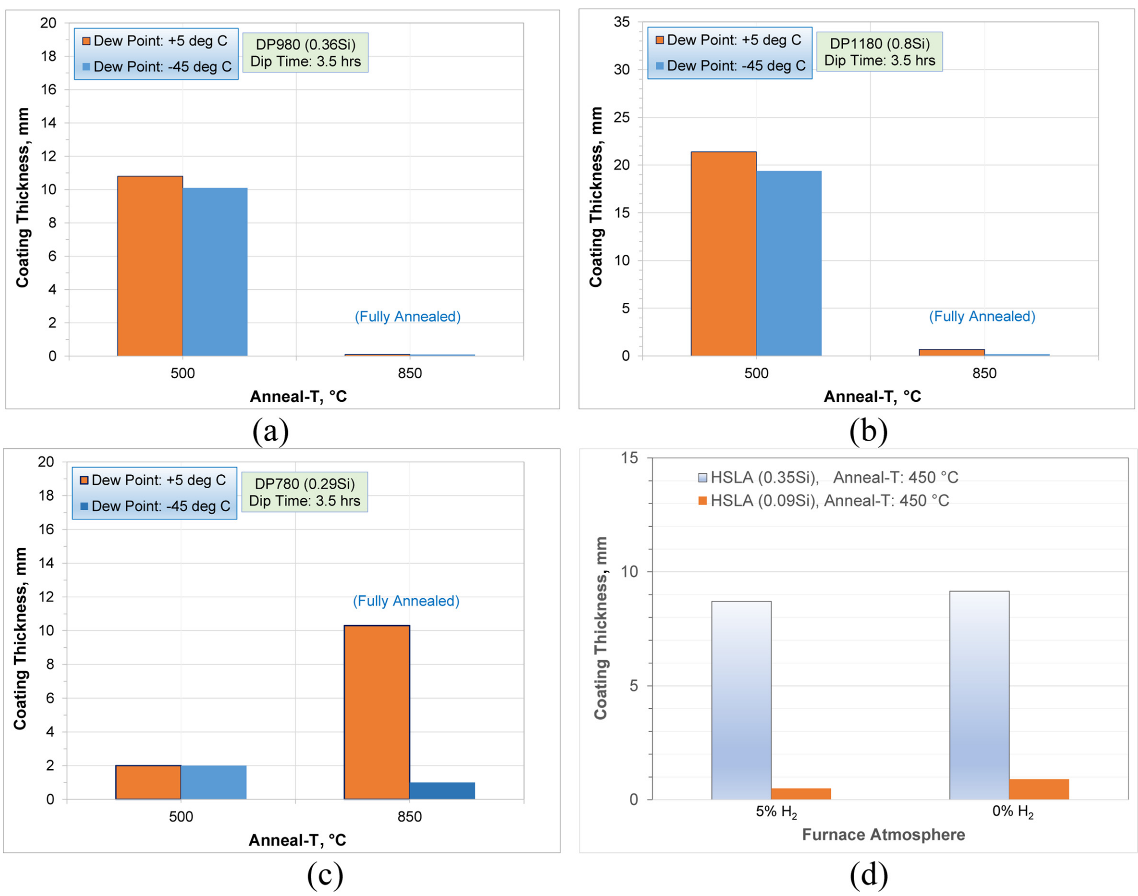


Fig. 10. Effect of Furnace Dew Point or H_2% on Coating Buildup

temperature, whereas no heavy buildup occurs when anneal-T is ≥ 750 ºC (i.e. fully recrystallized) regardless of the grade (Dew point: -35 ºC ~ -45 ºC).

The effect of Zn pot temperature shows different trends for different grades (Fig. 9(b)). For DP780 (0.29Si), no buildup is observed when the pot-T ≥ 460 ºC, and for HSLA (0.35Si), the buildup decreases significantly when the pot-T ≥ 467 ºC. For DP1180 (0.8Si), the buildup occurs at all temperatures tested (450 ºC - 480 ºC), and it is ~2x thicker when the pot-T at 455 ºC - 467 ºC, resulted from large amount of free Zn networks existing between the bulky Zeta crystals.

For DP980 & DP1180 (0.33-0.8Si), the effect of furnace Dew point on the buildup is small (Fig. 10a,b). However, for DP780 (0.29Si), high Dew point (+5 ºC) promotes heavy buildup even at 850 ºC anneal-T (Fig. 10c), and the effect of Dew point is not observed at 500 ºC anneal-T (both have only light buildup). The effect of furnace H_2% (0-5%) is not observed (Fig. 10d). The above results show the complicated interactions between steel Si%, Dew point and anneal-T. More work should be done to understand the effect of steel microstructure and steel surface chemistry on the buildup.

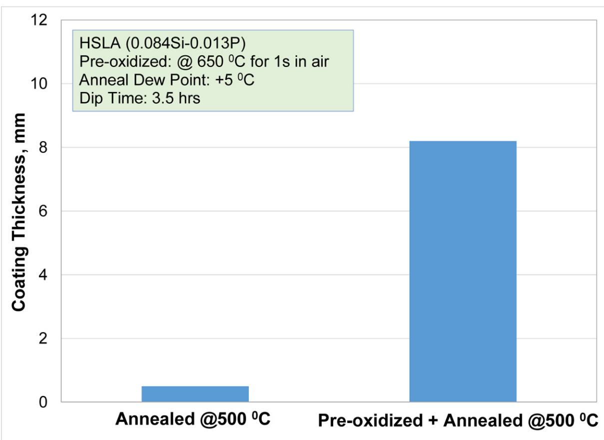


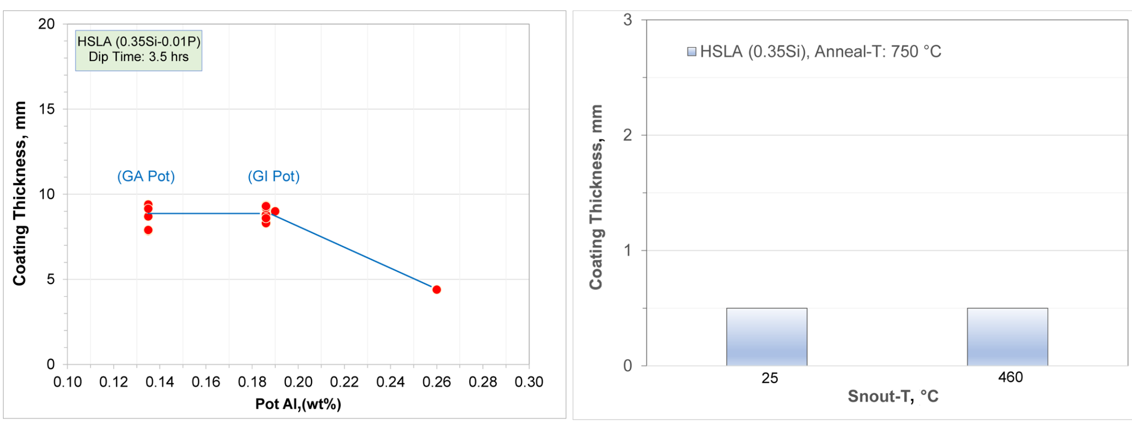
Fig. 11. Effect of Pre-oxidation on Coating Buildup

It is well known that pre-oxidation (e.g. at DFF heating) can promote Zn coating wettability and GA kinetics for Si bearing AHSS steels because it modifies the Si distribution near the steel surface [6]. Whereas as shown in Fig. 11, the heavy buildup can occur on the HSLA (0.084Si) steel by a combination of pre-oxidation and heating at high furnace Dew point (+5 ºC). No buildup can be reproduced on this steel by the simulator without the pre-oxidation treatment. The heavy buildup by pre-oxidation was also reported by Cleveland CGL [6].

Even though the heavy buildup can occur in typical GA and GI pots, the coating growth reduces by ~50% when the bath Al is at 0.26 wt% (Fig. 12a). Strip entry temperature has no impact on coating growth (Fig. 12b).

No heavy buildup is observed on the HR780 steel (as-hot rolled, 0.59Si) in both GA and GI pots. However, a significant coating growth (7x faster) is observed after the strip has been cold-rolled to a 50% reduction with a lab scale rolling mill (Fig. 13) due to different steel microstructure and/or surface conditions.

Post-oxidation can result in an Fe oxide layer (~1 μm) formed on top of steels (DP1180). However, the oxide layer disappears with long dipping time (≥ 30 min) and heavy coating can still be formed with time on the risky grades (see Fig. 14 a,b).



(a) (b)

Fig. 12. Effect of Bath Al and Snout-T on Coating Buildup

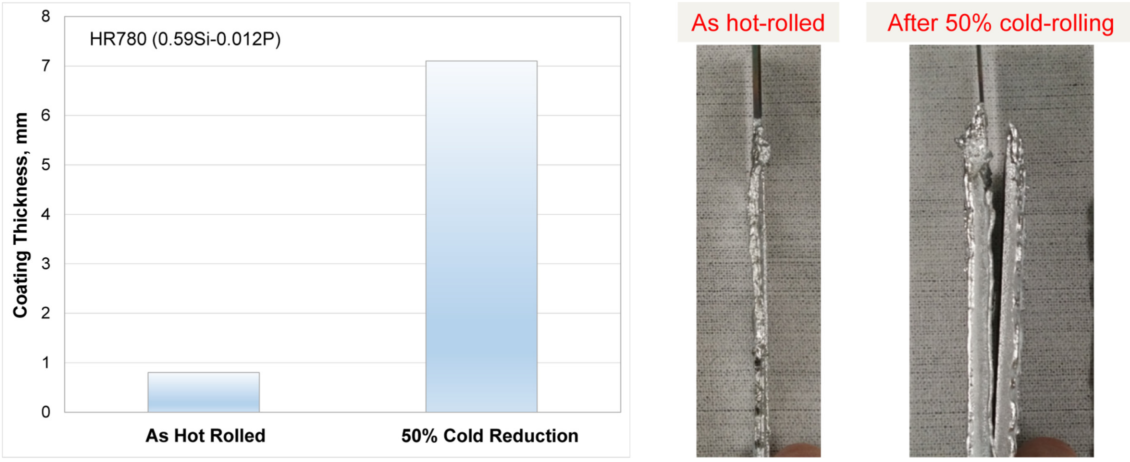
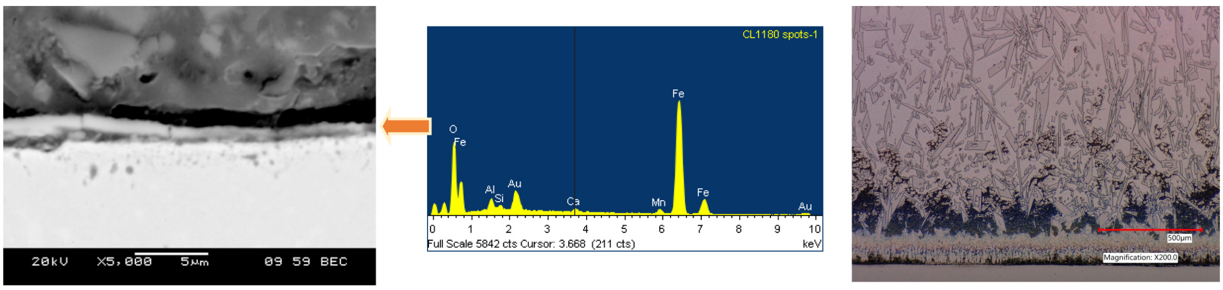


Fig. 13. Effect of Cold Rolling on Coating Buildup (HR780, GA Pot at 450 ºC, 3.5 hrs)



(a) (b)

Fig. 14. (a) Fe Oxide Layer formed on Steel Surface after Post-oxidation (DP1180, at 450 ºC, 10 s), (b) Heavy Coating Buildup after 3.5 Hours Dipping (Anneal-T: 500 ºC, Dew Point: -45 ºC)

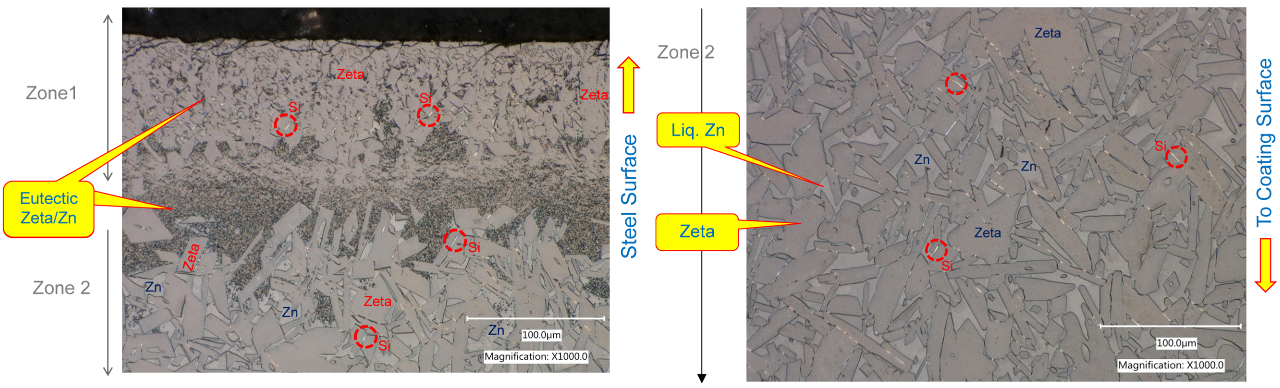
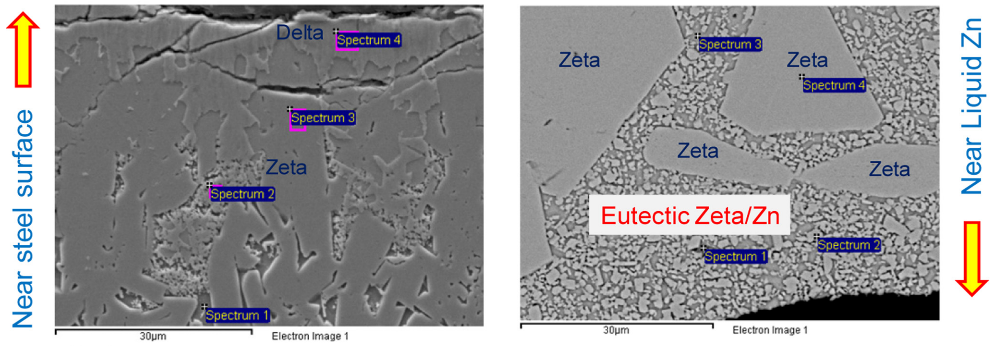


Fig. 15. Cross-section View of Buildup Coating, Showing Bulky Zeta Crystals, Liquid Zn Pockets and Eutectic Zeta/Zn Phase (HSLA: 0.33Si-0.01P, GI Pot: 459 ºC)

3.3 Coating microstructure and mechanism of heavy coating buildup

Fig. 15 shows that near the steel surface (Zone 1, ~100 μm), coating consists of many small Zeta crystals (grey) and pockets of eutectic Zeta/Zn phase (dark grey) formed after solidification. Most of the coating (Zone 2, ~99% of total thickness) consists of large bulky Zeta crystals & free Zn pockets (light grey), typical microstructure of "Sandelin growth" [3]. A thin eutectic Zeta/Zn layer (dark area) is observed between Zone 1 and Zone 2.

Some Delta phase can be detected at the coating/steel

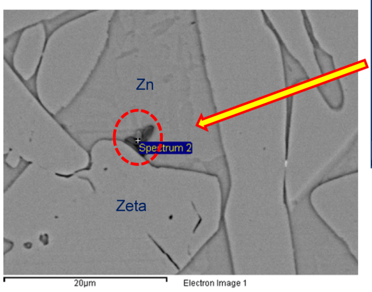


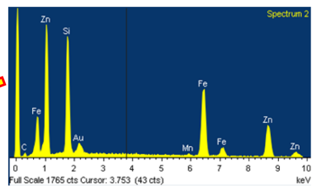
(Wt%)

Spectrum	Al	Fe	Zn	
Spectrum 1	0.00	1.40	98.60	Liq. Zn
Spectrum 2	0.47	5.99	93.54	Zeta
Spectrum 3	0.00	5.87	94.13	Zeta
Spectrum 4	0.00	8.01	91.99	Delta

Spectrum	Al	Fe	Zn	
Spectrum 1	1.02	2.89	96.09	Liq. Zn
Spectrum 2	1.69	5.99	92.32	Zeta
Spectrum 3	0.00	1.35	98.65	Liq. Zn
Spectrum 4	2.74	6.23	91.03	Zeta

Fig. 16. SEM-EDS Analyses, Showing Delta Phase at Coating/Steel Interface, Bulky Zeta Phase, and Free Zn in the Eutectic Region





(Atomic%)

Analysis #	Si	Fe	Mn	Zn
1	47.96	36.67	0.71	14.65
2	38.82	30.13	0.93	30.12

Bulk Coating Chemistry (ICP)

Sample	Fe (wt%)	Al (wt%)	Si (wt%)	Coating THK (mm/side)
DP1180 (0.8Si)	2.8	0.26	0.051	20
HSLA (0.33Si)	4.2	0.22	0.006	10
HSLA (0.1Si)	4.7	0.22	0.003	8

(a) (b)

Fig. 17. (a) SEM-EDS Analyses Show Fe-Si Phase (b) ICP Analyses Show Si% in Bulk Coating (GA Pot)

interface (Fig. 16), but no Fe-Al inhibition layer is observed. Eutectic Zeta/Zn region consists of tiny Zeta crystals and small free Zn pockets (networks) which explain the fast strip dissolution, Fe/Zn diffusion and linear coating growth rate, as observed previously.

Fe-Si particles (1~5 µm, circled in Fig.s 15 and 17a) can be seen near Zeta crystals in the free Zn pockets. Average coating Fe is 3~5 wt% (ICP results, Fig. 17b), related to coating thickness and free Zn networks. The Si level in the coating is quite low (0.003~0.05 wt%, proportional to the steel substrate Si%). It is believed that the existence of Fe-Si phase and/or solute Si in Zn coating leads to super-saturated liquid Zn networks during coating growth [3], and higher Si in steels (e.g. DP1180) can result in more free Zn networks, thus thicker (less dense) coatings.

Based on above observations and literature review [1-6], the mechanism of the heavy coating buildup (Sandelin effect or fast strip dissolution) on Si bearing steels is outlined below (Fig. 18):

- Breakdown of Fe-Al inhibition layer, dissolution of Fe and Si from steel, and early formation of Delta and Zeta Fe-Zn phases (typically within ~10 minutes dipping).
- Formation of liquid Zn networks with increasing of Si level (or Fe-Si phase) in the newly formed coating leads to fast Fe dissolution and Fe/Zn diffusion, resulting in bulky Zeta crystals and linear growth of Zn coating layer (after ~30 minutes dipping). Higher Si in steels (e.g. DP1180) can lead to a less dense and thicker coating.
- Steel microstructure and surface conditions, Zn pot conditions, and furnace atmosphere etc. can affect Fe and Si available for the coating growth, resulting in different coating structure (Fig. 19, a compact delta layer or no bulky Zeta, which limits fast coating growth).

· Too high of a Zn pot-T can lead to too fast Fe and Zn diffusion in the early stage of buildup, resulting in formation of a compact delta alloy layer, thus limiting further coating growth.
· Fully annealed steels (or as-hot rolled) lead to low Fe dissolution rate, thus only Zeta/Zn eutectic phase can be formed due to insufficient solute Fe available for formation of bulky Zeta crystals.

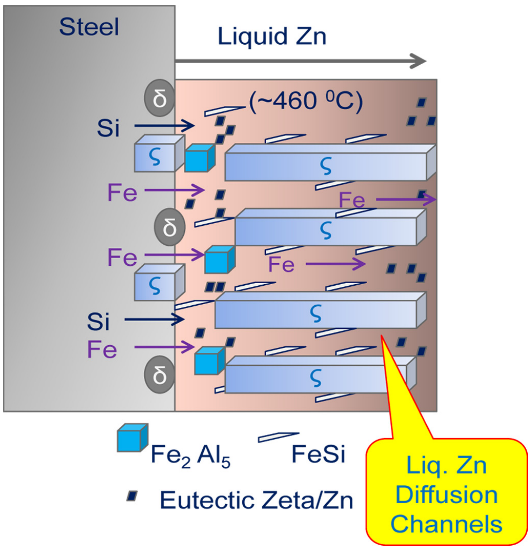


Fig. 18. Mechanism of Abnormal Zn Coating Buildup on Si-Bearing Steels

3.4 Implementation and success at arcelormittal dofasco (amd) cgls

An automatic online warning system for operators and scheduling for incoming of Si bearing steels (Si ≥ 0.04 wt%) have been implemented at AMD galvanize lines. A detailed prevention plan, regarding jogging frequency, anneal-T, and furnace Dew point etc., has also been created and is available to operators. No more heavy buildup has occurred since the solution was implemented.

4. Conclusions

The heavy coating buildup (~3 mm/h) and fast strip dissolution (~0.17 mm/h, 13x faster than typical) in the GA or GI pot can occur with the right combination of steel chemistry and processing conditions due to the unique coating microstructure being formed (mixture of bulky Zeta crystals and free Zn pockets/networks – the Sandelin effect). A summary for the conditions to avoid the heavy buildup (or fast strip dissolution) is listed below:

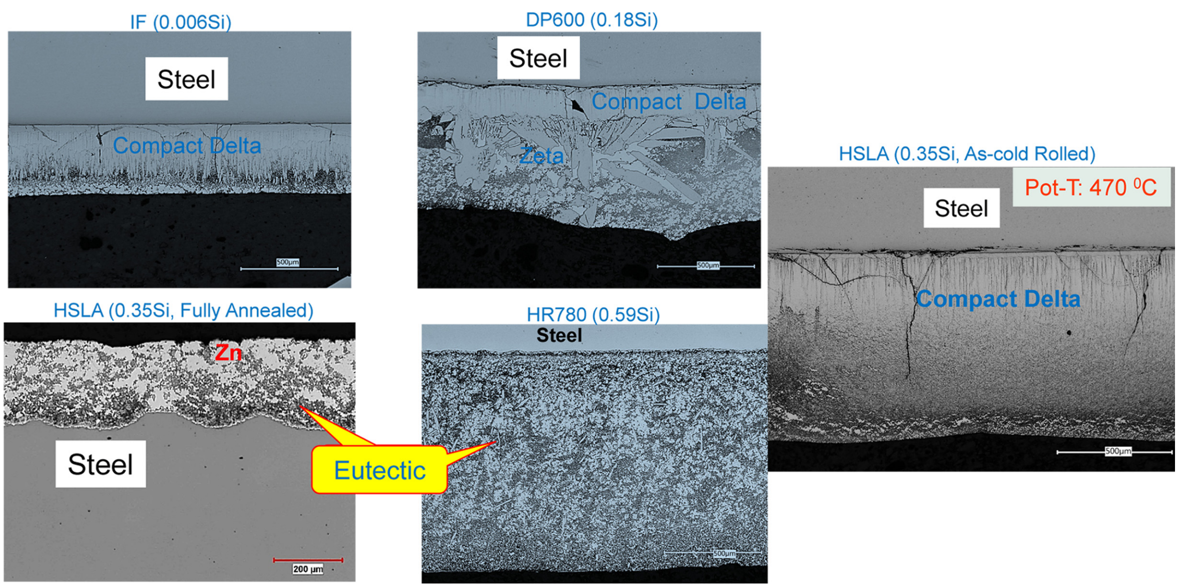


Fig. 19. Coating Microstructure on Steels without Heavy Coating Buildup

Table 1. Conditions that Can Avoid/Reduce Heavy Coating Growth (or Fast Strip Dissolution)

Steel Si%	Strip Rolling	Anneal-T	Furnace Dew Point	Bath Al%	Pot-T
< 0.04 wt%	As-hot rolled	≥ 750 °C (Fully Annealed)	≤ -35 °C (No Pre-oxidation)	> 0.25 wt%	≥ 470 °C (if Si < 0.4 wt%)

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