Coating Defects: Origins and Remedies

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Abstract

Although the science and technology of continuous galvanizing have improved significantly over the years, it is still a challenge to produce defect-free coatings. Studies indicate that poor substrate surface quality, insufficient strip cleaning, mechanical damage to the substrate surface due to handling, and inadequate process control are the main causes of coating defects. The recent introduction of high strength steels makes the production of galvanized coatings for applications such as exposed autobody panels even more challenging. To produce high quality zinc-coated strip, galvanizers need to improve quality control of the incoming strip as well as the continuous galvanizing process.
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Introduction

The surface quality of continuously galvanized coatings has improved significantly in recent years, enabling these coatings to replace electro-galvanized (EG) coatings in applications of exposed automotive body panels. However, galvanizers capable of producing such coatings are limited in number because the requirement of coating surface quality is extremely stringent. Any tiny blemish on the coating surface is objectionable for exposed automotive applications. The origins of coating defects can vary widely. The strip travels along a production line comprised of various equipment and rolls and involves a number of chemical reactions in the process. Any slight negligence in the maintenance of the line machinery and its control system can easily induce defects in the coatings. Also, the relevant chemical reactions take place mostly at elevated temperatures where reaction kinetics is hard to predict and control. Insufficient cleaning of the strip could result in poor wetting of the molten zinc alloy to the substrate, leading to bare spots. Improper atmosphere or temperature control in the in-line heat-treatment section may introduce carbon deposits or thin oxide film on the substrate surface, leading to bare spots or poor adhesion of the coating. Pot chemistry, working condition of the submerged hardware, bath skimming practices and air-knife settings all affect coating quality. It has been shown that good bath management practices can reduce coating defects. However, good bath management alone cannot eliminate all the defects. As a matter of fact, the chemistry of the steel and the substrate surface quality is of paramount importance for producing a high quality coating. In this regard, galvanizers who do not produce their own strip are at a disadvantage. While IF steels and similar grades can be easily galvanized, newly developed steel grades possess a complex chemistry, resulting in poor galvanizability. These steels contain strengthening elements, such as silicon and manganese, which are surface-active and have a strong affinity for oxygen. In an atmosphere which is reducing for iron, these elements can easily segregate toward the substrate surface and be preferentially oxidized. The galvanizability of these high-strength steels is currently the subject of intensive research. In this article, typical coating defects are presented following a chronological order of the occurrence of their origins with respect to the galvanizing process. Their remedies, if not obvious, are also discussed.

A. Defects Related to Substrate Surface Quality

It is well known that defects and imperfections pre-existing on the substrate surface can be easily duplicated and magnified in the hot-dipping stage, resulting in defective coatings. The experience of Cominco’s technical service team indicates that strip with a good surface quality is the pre-requisite for producing a good quality coating. In fact, many coating defects are caused by the poor surface quality of the incoming strip. Typical defects with this origin are discussed here.
**Rough Surface**
A rough substrate surface containing iron fines and slivers is prone to the development of outbursts in the coating. The resultant coating is rough with numerous areas of localized thick coatings. After being flattened in temper rolling, these areas reflect light differently, appearing as either dark or bright spots depending on the lighting condition. A typical sample is shown in Figure 1. Studies indicate that the density of this kind of defect decreases with increasing coating weight, suggesting that such a defect can be masked by a thick coating.

![Figure 1: A rough substrate surface results in Zn-Fe alloy outbursts in the coating.](image)

**Mechanical Damage**
Mechanical damage on the substrate surface, such as scratches and gouges, increases steel reactivity in galvanizing because iron atoms in these areas are in a high-energy state and can readily dissolve into the molten zinc alloy, resulting in an abnormally high iron solubility locally. If the bath effective aluminum level is relatively low and the extent of the damage is large, the reaction between the zinc and iron may not be inhibited. As a result, a Zn-Fe alloy layer forms at these gouges, resulting in a coating much thicker than the surrounding coating. Since the reaction kinetics is so fast, the Zn-Fe alloy layer can sometimes grow through the coating thickness and appear as dark spots. A typical sample is shown in Figure 2. Areas with a thick coating turned into so-called “abraded asperities” after skin pass and could appear as black spots as well.

![Figure 2: Coating defects induced by mechanical damage to the substrate.](image)

a. Numerous black spots exist on the coating surface; b. Localized Zn-Fe alloy layers grew through the thickness, forming black spots in the coating; c. A large number of gouges were revealed after the coating was stripped off.
Hot-Rolled Strip
The surface of hot-rolled strip is normally rougher than that of cold-rolled strip. However, the surface roughness can be mostly masked following the hot-dip process provided that the coating is thick enough. Such coated steels are mostly for construction applications. The quality requirement for these coated steels is by no means critical or stringent, and most surface imperfections can be tolerated by the users. A common defect that causes rejects is the peeling off of the coating due to poor adhesion. In addition to these factors which could also result in coating adhesion problems for cold-rolled strip, patches of residual surface oxide layer not totally removed in the de-scaling operation are a unique defect for hot-rolled substrate. The molten zinc alloy can wet the thin oxide layer well because the oxide reacts with aluminum in the molten zinc alloy to form a spinel-type product. The coating appears normal at first glance. However, the bonding between the substrate and the oxide layer is weak. The coating can be easily peeled off when subjected to forming operations. The remedy for this kind of defect is rather obvious – thorough de-scaling and pickling.

![Image](image.png)

Figure 3: Defects related to pickling and rinsing operations. Residual pickling solution reacts with aluminum in the molten zinc, releasing aluminum chloride (AlCl₃) gas and forming numerous volcano-like craters in the coating.

Hot-rolled strip is normally pickled to remove surface oxide and mill oil residue. If the pickling time is too long or the rinsing following the pickling is insufficient, residual pickling liquor can be entrapped at grain boundaries, which are always preferentially attacked in pickling. The residual pickling solution, containing mostly iron chlorides, is dried up during in-line heat-treatment. When the strip is being coated in the molten zinc pot, the iron chlorides at the grain boundaries react with aluminum in the molten zinc alloy, forming aluminum chloride (AlCl₃), which vapourizes easily because of an extremely high vapour pressure at the galvanizing temperature. Numerous volcano-like craters will form on the coating surface. A typical sample is shown in Figure 3.

B. Defects Related to Line Operation

Insufficient Cleaning
The strip must be thoroughly cleaned to remove all kinds of surface contaminants and to expose a chemically activated and metallically clean substrate surface. Failing to do so results in the formation of bare spots. It is a common practice to produce automotive-grade galvanized coatings in baths containing aluminum in excess of 0.2%. When the bath aluminum content is high, the cleanliness of the substrate surface becomes more critical to ensure a good wetting. Bare spots are frequently observed in automotive-grade coatings although these bare spots are too small to be noticed by the naked eye. A typical sample is shown in Figure 4.
Improper Heat Treatment
An improper in-line heat treatment can result in a number of problems including carbon contamination and surface oxidation.

Carbon contamination of the strip can occur in direct-flame-fired furnaces if the temperature is lower than normal and an atmosphere of carbon monoxide occurs. Although carbon contamination is hard to detect using SEM-EDS only, its impact on coating structure is unmistakable. The inhibition layer on the affected areas is thin and ill-defined. Consequently, coating adhesion is poor. If the problem is severe, wetting becomes problematic, resulting in bare spots.

For high-strength steels under development, such as dual-phase and TRIP steels with a design tensile strength higher than 600 MPa, the chemistry is so complex that a heat-treatment scheme to ensure good galvanizability has yet to be developed on existing galvanizing lines.

Poor Bath Management
Good bath management practices can not only reduce the severity of defects originated from a complex steel chemistry and inadequate substrate surface quality, but can also avoid defects originated in the hot-dipping stage, such as the entrapment of dross particles, the formation of Zn-Fe alloy crystallites in the coating, dents (localized thin coating), and line defects induced by dross growth on pot rolls.

Snout Dust If the atmosphere in the snout is too reducing, zinc evaporates quickly. The vapour condenses in the snout and the cooling section. When the zinc dust comes into contact with the substrate before it enters the molten zinc bath, it reacts with the steel to form Zn-Fe alloys. These areas appear as tiny black spots, resembling bare spots. The defect can be eliminated by introducing moisture to the snout, thereby minimizing zinc vapourization, and by periodical cleaning of the snout and the cooling section to physically remove the dust.
If the snout immersion depth is insufficient, bath surface oxide can enter into the snout. The oxide will be dragged out by the strip, resulting in defective coatings.

**Aluminum and Temperature Control**  When the bath effective aluminum level is relatively low and the strip entry temperature is relatively high, Zn-Fe alloy crystallites form in coatings. These crystallites are metastable in nature and their formation mechanism has been explained by Tang.\(^7\) Normally, if the crystallites are small and discrete, they do not negatively affect coating quality in terms of both coating ductility and adhesion. However, the defect could be severe if the bath aluminum level and the strip entry temperature are out of control, or the substrate surface quality is poor. In this case, outbursts or a continuous alloy layer form, as shown in Figure 1, resulting in low ductility and poor adhesion of the coating.

Heavy coatings produced using a slow line speed may suffer from a line defect referred to as sag-lines and/or rippled coatings. Reducing the bath effective aluminum level and adding small amounts of antimony will generally alleviate the problem.

**Sink-Roll Growth**  Growing on sink-roll grooves, intermetallic compounds can scratch the substrate, thereby inducing defects in the coating. The defects are easily recognizable because they distribute along lines with spacing matching that of the grooves. A typical sample is shown in Figure 5.

![Figure 5: Intermetallic growths in sink-roll grooves can scratch the substrate surface, resulting in line defects with spacing equal to that of grooves.](image)

**Dross Entrapment**  Top dross particles frequently coexist with the oxide film on the bath surface. These particles can enter the coating together with the oxide film picked up on the coating surface. A typical sample is shown in Figure 6. Maintaining a clean bath surface can avoid the entrapment of dross particles in coatings.
Dross entrapment in coatings occurs frequently during GA to GI production transition periods when brightener is used to speed up the transition. Due to a rapid increase in the bath aluminum level, iron solubility decreases correspondingly, resulting in the formation of dross particles. Also, bottom dross particles accumulated during the GA campaign start to convert to top dross particles, leading to a significant increase in the volume fraction of dross particles in the bath. Frequently, particles entrapped in coatings during the transition are larger in size. Such particles cause printing-through following temper rolling. A typical sample is shown in Figure 7. Recent studies carried out by Cominco indicated that a well-designed GA to GI transition practice could minimize dross formation and conversion, thereby reducing the incidence of dross entrapment in coatings.

It should be mentioned here that the problem of dross particle entrapment in coatings is, in general, exaggerated by galvanizers because a number of defects, such as high or low points and surface contamination, resemble dross pick-up. Recent studies\(^{(4)}\) carried out by Cominco in ILZRO Project ZCO-34 indicated that only less than 10% of all the defects, initially believed to be dross pick-up, were indeed dross particle entrapment in coatings. The majority of these coating defects was caused by problems of substrate surface quality.

**Air Wiping** A number of defects can be generated when the coating passes air knives. Typical defects include dents, blow lines, sag-lines and peculiar features such as so-called “caterpillars”. Localized thin spots, as shown in Figure 8, are frequently observed. This defect is referred to as white spots by one galvanizer and chip marks by another. The origin of this type of defect is not exactly known. Judging by the relatively straight edge on its topside and the associated flow lines on its flanks, the defect could be caused by the blowing away of entrapped dross particles. However, in some cases, the defect was so severe in nature and so large in size, yet no solid particles could be found in the coatings. A recent study\(^{(5)}\) indicated that the inhibition layer associated with the dents was impaired due to the existence of residuals of rolling oil. Improper air-knife settings may also cause this type of defect. Indeed, reducing air-blowing pressure and increasing bath and strip entry temperatures will reduce the severity of the defect.
A type of defect referred to as “caterpillars” according to their morphology is encountered from time to time by producers of spangled coatings. A typical sample is shown in Figure 9. “Caterpillars” appear to nucleate along the solidification front of the coating. They run upwards from the edges toward the center of the strip, outlining an apparent isothermal line on the coating. Although its cause has not been clarified, the defect can be reduced or totally eliminated by lowering the bath temperature. Another type of line defect, referred to as “snaky coating”, is shown in Figure 10. Instead of running upwards, these lines run downwards. This type of defect only occurs on heavy gauge steel with a heavy coating (>G90). Judging by its appearance, this defect is most likely caused by sagging of the coating during solidification. The sag-lines are stabilized by narrow bands of oxide film along these lines. Maintaining a clean oxide-free bath surface can alleviate this type of defect.
Mini-Spanglizer  The operation of a mini-spanglizer may introduce coating defects. Shown in Figure 11 are circular dents apparently caused by the impingement of liquid droplets from the spanglizer. If spangles are minimized through the spray of zinc dust to the coating, residual zinc dust may accumulate on rolls down the stream, causing coating defects.

Post Hot-Dipping Treatment
Defects generated in post hot-dipping treatment include scratches, stains and zinc-dust pick-up, etc. These defects are easily recognizable due to the periodicity in their distribution.

C. Defects in Galvanneal Coatings

Powdering and flaking of galvanneal coating on titanium-stabilized IF steels was a major problem at the beginning of the 1990s. Some researchers suggested that carbon-free grain boundaries serve as fast diffusion paths for zinc, resulting in outbursts at emerging grain boundaries. However, a number of studies produced evidence suggesting free titanium (titanium in solid solution) to be the main culprit. The problem has been largely resolved by partly replacing titanium with niobium, controlling the titanium/carbon ratio to reduce free titanium, increasing the bath effective aluminum level, and optimizing the in-line annealing scheme.
It has been well established that the optimum bath composition for producing galvanneal of IF steels is 0.135% Al, the knee-point of the iron solubility curve. This composition corresponds to the changeover of the $\delta$ phase (bottom dross) to the $\eta$ phase (top dross) as the equilibrium compound in the bath. Maintaining the bath aluminum at such a level can minimize the formation of bottom dross, thereby prolonging the GA campaign. The inhibition layer formed during the hot-dipping stage is thin. It becomes unstable and dissolves easily during the annealing treatment. In recent years, high-strength steels are replacing IF steels as the substrate for galvanneal coatings. Alloying elements in the steels, such as silicon and phosphorus, apparently stabilize the inhibition layer. Correspondingly, a much higher annealing temperature is employed to break down the inhibition layer. Preferably, the effective bath aluminum for producing galvanneal of high-strength steels should be lower than 0.135%. However, not all galvanizers are capable of controlling bath effective aluminum within a narrow range. From time to time, the bath aluminum level becomes too high, resulting in an inhibition layer too thick and stable. Correspondingly, galvanizers must resort to a much higher annealing temperature, producing galvanneal coatings with a thick $\Gamma$ layer. Once again, powdering and flaking become a concern of galvanizers. Shown in Figure 12 is galvanneal coating of high-strength steel. Apparently, the $\Gamma$ layer is quite thick.

Figure 12: Galvanneal coating with a relatively thick $\Gamma$ layer. Powdering resistance of the coating deteriorates with increase in the thickness of the $\Gamma$ layer.

Conclusion

Due to the increasing applications of GI and GA coatings for exposed automotive body panels, the requirement of coating surface quality has become increasingly stringent in recent years. Coated steels, considered to be good quality products for applications in the construction industry, could be objectionable from the viewpoint of the automotive industry. This article has described a number of defects, together with their origins and remedies. The experience of the authors indicates that substrate surface quality is of paramount importance for the production of high-quality coatings. If the substrate quality is poor, defects are inevitable. Good bath management practices can reduce the severity of these substrate quality-related defects, but cannot totally eliminate them. However, good bath management procedures can avoid all the defects originating from the pot area.
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