Indian Steel Sheet Building Group: Technical Note 2.6

Coating Processes and Surface Treatments

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The Spangle on Hot-Dip Galvanized Steel Sheet

Introduction

For many years, galvanized articles made by hot-dip coating techniques were identified by a characteristic *spangle* appearance. This is still true today to some degree. However, because of changes in the zinc refining process, in the galvanizing process, in the demands of the marketplace, and health concerns, relatively little hot-dip galvanized steel sheet made today has a visible spangle. The reasons for this are explained in this GalvInfoNote.

What is a Spangle?

The dictionary defines "spangle" as a glittering object. When the word spangle is used to describe the surface appearance of galvanized steel sheet, it means the typical snowflake-like or six-fold star pattern that is visible to the unaided eye. Figure 1 shows the details of a typical spangle pattern of a galvanize coating at a magnification of about 10X.

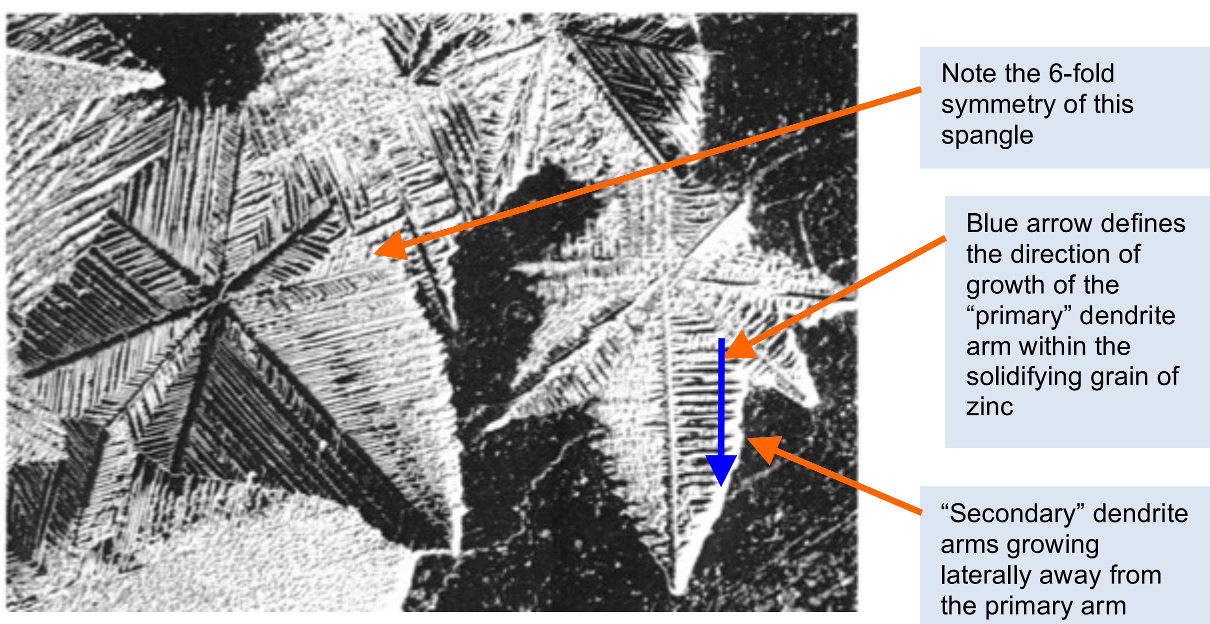

Fig. 1 The spangle structure of a hot-dip galvanize coating.

The features shown here encompass a number of quite complex metallurgical phenomena, and this GalvInfoNote explains why these features are present.

The Solidification Process

Spangles develop when the molten zinc adhering to the steel sheet is cooled below the melting point of zinc, which is approximately 787 °F [419 °C]. At this temperature, the randomly arranged atoms in the liquid zinc begin to position themselves into a very ordered arrangement. This occurs at many random locations within the molten zinc coating. Transformation from a disordered arrangement of atoms (liquid state) into an ordered crystal arrangement is known as solidification or crystallization. The small solidifying regions within the molten zinc are defined as "grains" (see sidebar). As individual atoms in the molten zinc attach themselves to a solidifying grain (causing grain growth), they do so in an ordered fashion and form into a distinct array, or crystal. In the case of zinc, the crystals form with hexagonal (six-fold) symmetry. As the solid zinc grains grow larger, individual atoms of zinc arrange themselves into the often-visible hexagonal symmetry of the final spangle. When the coating is completely solidified, individual spangles define individual grains of zinc.

Grains

Metals, like many solids in nature, have a crystal or "grain" structure. For example, the steel sheet beneath the galvanized coating consists of many small grains of iron-carbon alloy (steel). The individual grains of steel are very small compared with the grains of zinc in the zinc coating, and are "glued" to one another by atomic bonding forces. Think of this as "grains of sand" in a sandstone rock. The size of the individual grains of sand may be larger than the grains in the steel sheet, but this analogy allows the concept of grain structure to be visualized.

"Nucleation" is the transformation of randomly arranged atoms of molten metal into a small, organized array of atoms in the "seed" crystals at the initial stage of solidification. A high rate of nucleation during the freezing process tends to cause the formation of numerous small grains in the final solidified structure, while a low rate tends to favour the growth of large grains.

Dendritic Growth

There is another aspect of the solidification process that leads to the snowflake pattern in galvanize coatings, viz., "dendritic" (tree-shaped) growth. Dendritic growth causes the individual growing (solidifying) grains to grow into the melt (the molten zinc coating) with a distinct leading rounded edge. A "primary" dendrite arm is identified in Figure 1. There are secondary dendrite arms that grow laterally away from the "primary" dendrite arms.

Dendritic grain growth during the solidification of metals is very common. The reason that the dendrites are readily visible in a galvanize coating is that we are seeing a two-dimensional version of a large, as-cast, dendritic, solidified grain pattern. The coating is typically less than 0.001 in (25 μm) thick, considerably less than the diameter of a spangle. In other metals (for instance the steel substrate), the original as-cast, three-dimensional, dendritic structure of the grains is subsequently broken up into many smaller, more equiaxed grains. This is due to the effects of hot rolling (for example, rolling a 9-inch [230 mm] thick slab of steel reduced in thickness to as low as 0.050-inch [1.3 mm] thick steel sheet), cold rolling and recrystallization during the sheet annealing process.

The rate of growth of the dendrite arms during the solidification of a galvanize coating competes with the rate of nucleation of new grains within the molten zinc. This process determines the final size of the completely solidified structure. In the case of Figure 1, which is a galvanized coating with a well-defined large spangle pattern, the rate of dendrite growth dominated the solidification process leading to a small number of large spangles. One characteristic of such spangles is that they are thickest at their centers and thinnest at their edges, or grain boundaries. The grain boundaries can be said to be "depressed" and are difficult to smooth by subsequent temper (skin) passing. Galvanize coatings with small spangles generally have less depressed grain boundaries, and can be smoothed more easily by skin passing.

The Effect of Zinc Bath Chemistry

The nature and rate of dendritic growth during the solidification process is affected by the presence of other metallic elements in the molten metal. These can be either intentionally added alloying elements (aluminum) or impurities (lead). In the case of galvanize coatings on steel; the most common reason for the well-defined dendritic growth pattern was the presence of lead in the zinc. In research performed in the 1990s[1,2], it was found that the presence of lead decreases the solid/liquid interfacial energy in the solidifying coating. Lowering of the interfacial energy raises the energy barrier to heterogeneous nucleation. Lead, by inhibiting nucleation, effectively increases the spaces between neighboring nuclei, allowing larger spangles to form. It is also postulated that the presence of lead results in an increased dendrite growth velocity.

Lead, being insoluble in solid zinc, is rejected during solidification and precipitates at spangle boundaries and at the coating surface. The varying distribution of lead particles across the surface, define the optical appearance (dull vs. shiny spangles). Research[3,4] has also shown that poorly reflecting spangles contain comparatively more lead at the surface than bright spangles. The higher concentration of lead and other elements rejected from the freezing zinc to its surface contribute to early selective spangle darkening.

As solute elements are rejected from the outward-solidifying phase, the lead-rich zone ends up as the uppermost layer of the zinc coating. In fact, lead enrichment at the surface of some spangles can be as much as an order of magnitude or more greater than the bulk lead content of the liquid zinc, as is shown in Fig. 2. For example, a zinc bath containing 0.15-0.20% lead could result in a zinc coating with some spangles having a surface layer containing over 2% lead.

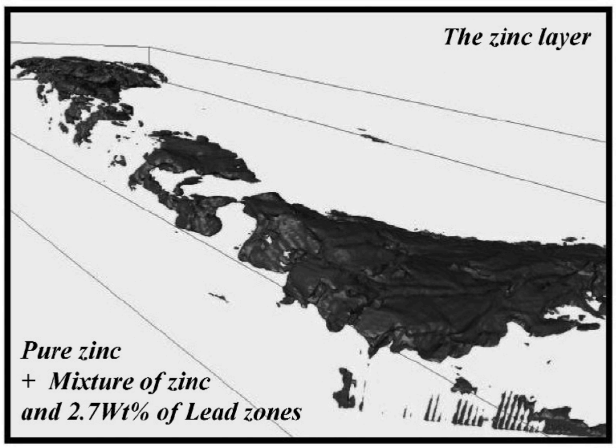

Fig. 2 Lead-rich zone of the coating is a separate volume at the surface of the zinc coating [4]

In years past, a common method of zinc refining included smelting, distillation and condensation. Lead is a metal found in most zinc-containing ores, and this refining process carried it through as an impurity in the zinc. From the early days of galvanizing its spangled appearance was therefore a natural and expected result. It easily identified steel as being galvanized, so much so that if a spangle wasn't visible, the steel was not considered to be galvanized. This was a problem in some markets when zero-spangle, hot-dip galvanize was first introduced, and even helped to reinforce the misconception by many users that spangled galvanize was “better” than non-spangled product.

The first galvanize coatings contained as much as 1% lead. Increasingly over the past 50 years, the presence of such high lead levels has become less and less common in galvanized steel sheet, at least in North America, Europe, and Japan. Typical concentrations of lead in most hot-dip galvanized sheet made up to about 25 years ago was usually less than 0.15%, and sometimes as low as 0.03 to 0.05%. Even this lower amount of lead is still sufficient to develop the dendritic growth behaviour during coating solidification that results in a spangle.

As there is now much more concern about the environmental and health hazards of lead, some galvanized sheet manufacturers that wish to market a spangled product have established practices that use lead-free zinc, but add a small amount of antimony to the zinc coating bath. Antimony influences spangle formation in a similar fashion to lead. The final result is a relatively smooth, visibly spangled coating. Typically, the amount of antimony in the coating bath is about 0.03 to 0.10%.

Years ago, to obtain smoother coatings with lead-bearing zinc, spangles were suppressed by rapidly cooling the still molten coating as the sheet exited the zinc bath. Cooling was achieved by the use of a spangle “minimizing” device above the zinc bath. These devices directed steam or zinc dust at the surface to rapidly nucleate and freeze the zinc, essentially resulting in a zero spangle. The product was known as “minimized spangle” galvanized sheet and could be easily skin passed to produce an extra smooth product for markets that did not want a spangled product, e.g., automotive. Such technology has been abandoned, as it is not required for lead-free zinc coatings for the reasons explained in the next section.

Zero Spangle Coatings

Years ago, the production of zinc from zinc-containing ores was changed to an electrolytic recovery process. In this method of zinc production, the refined zinc is very pure, with lead being excluded. This change was in place at the time many users of galvanized sheet, especially those desiring a high quality finish after painting, such as the automotive and appliance industries, needed a zero spangle coating. Removing the lead gave them the product they desired. The lead level in zinc used to produce zero spangle product is a maximum of 0.007% (70 ppm), and often less than 0.005% (50 ppm).

Lead-free coatings still have a grain pattern that is, at best, barely visible to the unaided eye. Typically, the spangles are about 0.5 mm in diameter and are clearly visible when seen at 5 to 10X magnification. However, the grains no longer grow by a dendritic mode but by a cellular growth mode. Essentially, the zinc grains nucleate heterogeneously on the steel surface, and grow outward toward the free surface. The absence of lead takes away the strong driving force for growth in the plane of the sheet, preventing the formation of large spangles. As spangles cannot grow in size, the result is the coating appears uniformly shiny. Grain boundary depressions, for all intents and purposes, do not exist in these coatings.

Zero spangle coatings, when combined with temper rolling by the galvanized sheet producer, can very easily be made extra smooth. The large grain boundary depressions and surface relief of a spangled coating are not present. The coating can then be painted to give a very smooth finish.

Lead levels of even 100 ppm in zinc coatings can result in an increased rate of spangle boundary corrosion in humid, warm environments[5], which can create a problem known as 'delayed adhesion failure of the coating. Essentially, bimetallic corrosion cells are created between lead and zinc, which progressively undermines zinc adherence. Using lead-free zinc avoids this issue. The absence of lead can only enhance corrosion resistance.

The very small spangles of lead-free coatings have an as-coated shiny metallic and very uniform appearance, unlike that of large spangle, lead-bearing zinc coatings, where the luster of each spangle differs, giving the sheet a non-uniform appearance. The above advantages of lead-free zinc coatings belie the notion held by some users that spangled galvanize is a higher quality product.

Why is Lead Still Used on Some Galvanizing Lines?

The manufacture of high quality zero spangle coatings, free of lead (or antimony), is sometimes not so easily done. The reason relates to the influence of even a small amount of these additions to the surface tension of molten zinc. The surface tension of pure zinc at 815 °F [435 °C] is 770 dynes/cm. A zinc bath containing 0.1% lead, for instance, has a surface tension of 700 dynes/cm, a decrease of about 9%[6]. The lower the surface tension the faster molten zinc drains, and the easier it can be gas-wiped off the sheet in an even manner. It is more difficult to avoid sags and ripples in the zinc coating when lead/antimony-free zinc is used, due to its higher surface tension. Also, the thicker the coating, the greater the tendency to form sags and ripples during freezing. Fortunately, the automotive and appliance industries need only relatively thin coatings (typically 60 to 80 g/m^2/side) of zinc to obtain the level of corrosion resistance their customers demand. Also, the products used by these industries are made on relatively new high-speed lines, or older lines that have been refurbished to allow production at higher speeds. The combination of high processing speeds and low coating weights allows producers to use lead-free coating baths, avoid the development of spangles, and still attain a ripple-free coating. Improved gas-wiping technology and practices have also helped in producing smoother coatings.

When producing a heavier coating mass (100 g/m^2/side and higher) using a lead/antimony-free bath with its higher surface tension, visible sags and ripples may develop, more so near the edges of the sheet. The surface is not smooth and the coating is composed of locally thick and thin regions. This tendency for sags is exacerbated at low line speeds (<50 m/minute). Older, low speed coating lines designed to process heavy-gauge sheet, and those that are used to make heavy coating weight products (heavier than 275 g/m^2 or G90), typically have the most difficulty in producing smooth and uniform coatings. Some lines do use antimony additions of between 0.03 and 0.10% (300 and 1000 ppm), as it also has a similar same effect as lead in lowering the surface tension of molten zinc. A high coating mass, zero spangle coating, free of ripples on heavy gauge sheet may be difficult to attain on some coating lines, requiring special adjustment of the gas wiping equipment.

Many coating lines that agree to produce a visible spangle pattern do so using only antimony additions. This meets with marketplace needs in that a number of industries, especially those that use bare (unpainted) galvanized sheet, still want a spangle pattern. The use of antimony mitigates the health and environmental concerns of lead, however spangle boundary corrosion can remain an issue.

ASTM B852 Specification for Continuous Galvanizing Grade (CGG) Zinc for Hot-Dip Galvanizing of Sheet Steel restricts lead to 0.007% (70 ppm) maximum in all but one of its 8 zinc grades. At this level the lead level is residual and the zinc is considered to be lead-free. A653/A653M, Specification for Steel Sheet, Zinc-Coated (Galvanized) has recently been revised to restrict the lead level of the zinc used to coat the sheet to a maximum of 0.009% (90 ppm), since the absence of lead does improve the quality of the coating, and there is wide availability of lead-free zinc. Spangled product that meets this specification must now be made using only antimony.

Specifying Spangle Size

Not withstanding the above discussion, users often ask if there is specifications that govern the size (diameter) of galvanize spangles. Unfortunately there are no quantitative specifications that regulate this feature of galvanized sheet. Spangle size can be affected not only by the zinc chemistry and cooling rate, but also by other factors such as the smoothness of the substrate. Consistently controlling spangle formation to a specified size, and then verifying compliance, would be an extremely difficult task. For this reason, spangle size terminology is qualitative. It is defined in ASTM A653/A653M, Specification for Steel Sheet, Zinc-Coated (Galvanized) as follows:

- Regular spangle – zinc-coated steel sheet with a visible multifaceted zinc crystal structure. The cooling rate is uncontrolled, which produces a variable grain size.
- Minimized spangle – zinc-coated steel sheet in which the grain pattern is visible to the unaided eye, and is typically smaller and less distinct than the pattern visible on regular spangle. The zinc crystal growth is arrested by special production techniques, or is inhibited by a combination of coating bath chemistry plus cooling.
- Spangle-free – zinc-coated steel sheet with a uniform finish in which the surface irregularities created by spangle formation are not visible to the naked eye. The finish is produced by a combination of coating bath chemistry, or cooling, or both.

In the absence of specifications for galvanized sheet spangle size, Figures 3, 4, 5, & 6 are suggested size ratings provided by the GalvInfo Center. While spangle-free products are the result of non-lead bearing requirements, and are preferred for many end uses, some users still desire galvanized sheet having a visible spangle. Keeping in mind that it is generally not possible to order by spangle size, and that spangle products are not available in all regions of the world, the photos in Figures 3 – 6 illustrate the range of spangle sizes that can still be obtained from producers in some parts of the world.

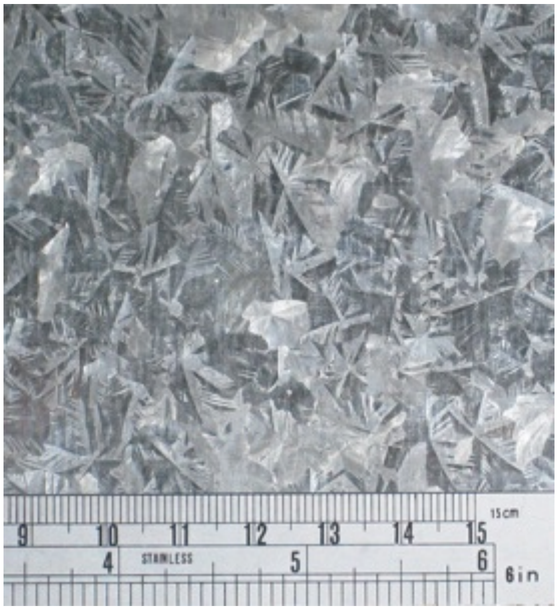

Fig. 2 Large – Spangles ≥ 15 mm across

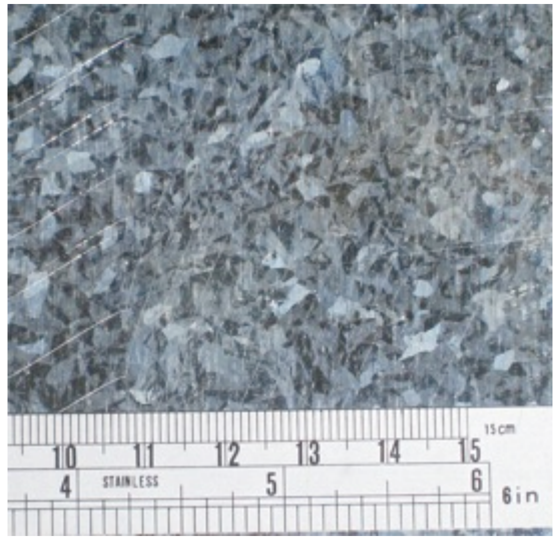

Fig. 3 Medium – Spangles up to 10 mm across

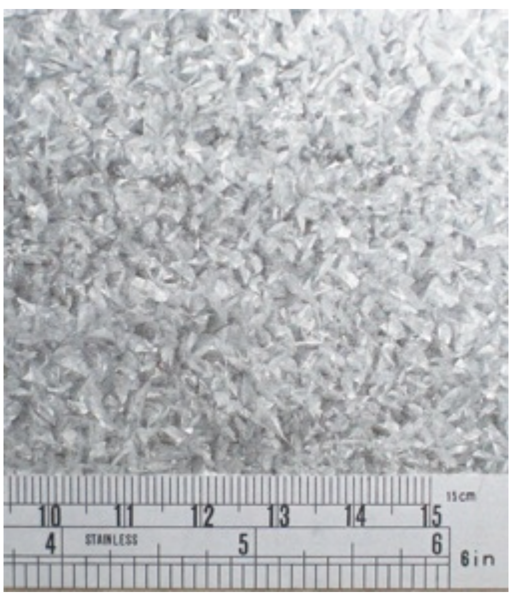

Fig. 4 Small – Spangles up to 5 mm across

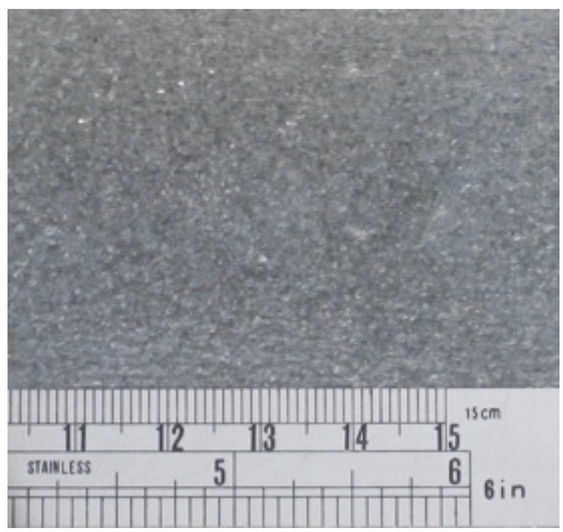

Fig. 5 Spangle-free – Spangles ≤ 0.5 mm across

Summary

The spangle on hot-dip galvanized steel sheet had been its primary identifying feature for many years. The demand for both lead-free coatings and very smooth products has resulted in spangle size being reduced by most producers until it is no longer visible to the unaided eye. This was, and to some extent still is, of concern to certain segments of the marketplace, but most users of galvanized sheet have become accustomed to a product that does not have a large, easily seen spangle. While, in the future, demand for a visible spangle may disappear, for aesthetic reasons some consumers still want to use spangled galvanize sheet for their products. There is a method of providing this without the risks of using lead-containing zinc.

[1] J. Strutzenberger, J. Federl: Metall. Trans. A, 1998, vol. 29A' pp. 631-646
[2] Fraley, Richard E., "The effects of lead on the solidification and preferred orientation of the zinc coating on continuously hot dipped galvanized steel sheet" (1994). Theses and Dissertations. Paper 257. Lehigh University.
[3] A.K. Singh, et al, Surface & Coatings Technology 200 (2006) 4897 – 4903
[4] A. Chirazi, et al, Iron & Steel Technology, Vol. 4, No. 4, April 2005, pp. 193-207
[5] Zhang, X.G., "Corrosion and Electrochemistry of Zinc", Plenum, 1996, p.231
[6] Fraley, Op. Cit.