GalvInfoNote **2.6**

The Spangle on Hot-Dip Galvanized Steel Sheet

Rev 1.1 Mar-09

Introduction

For many years, galvanized articles made by hot-dip coating techniques were identified by a characteristic *spangle* appearance. In some cases, this is still true today. However, because of changes in zinc refining processes, in the galvanizing process, and in the demands of the marketplace, not all hot-dip galvanized steel sheet made today has a visible spangle. The explanation for this is given later 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 on a galvanize coating at a magnification of about 10X.

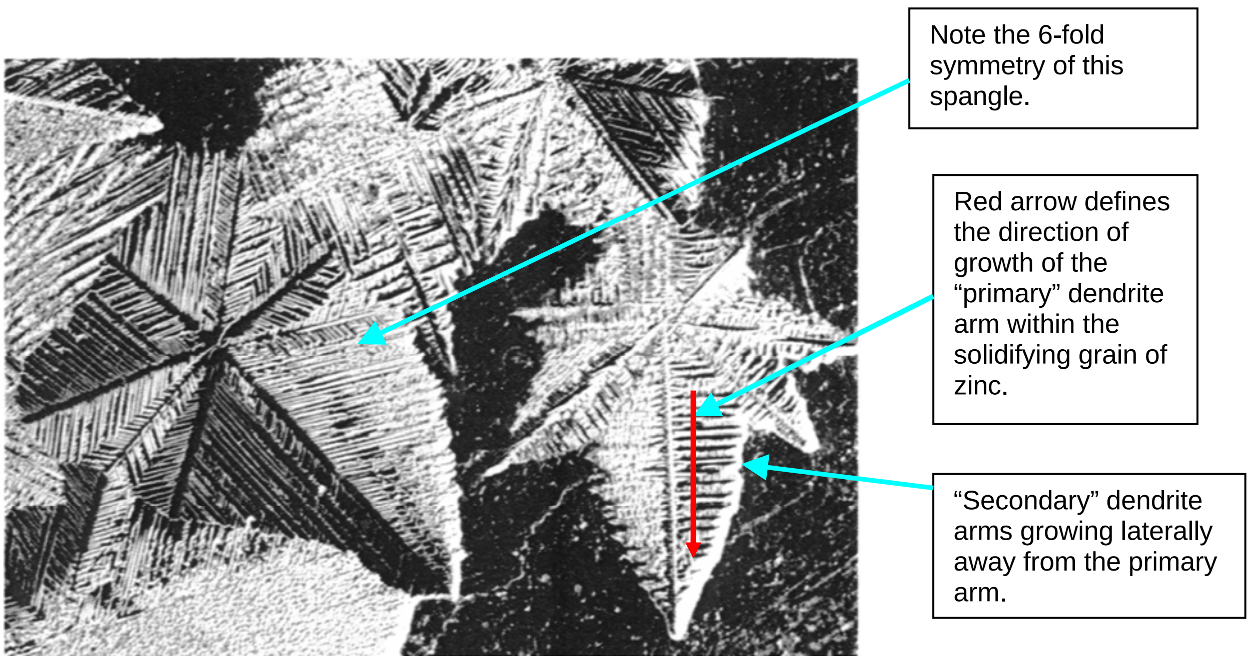

Figure 1: The spangle structure of a hot-dip galvanize coating.

The features shown here encompass a number of quite complex metallurgical phenomena. 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 419°C (787°F). 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. The transformation from a disordered arrangement of atoms (liquid state) into an ordered arrangement is the process of 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 term used to define the process of 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" (meaning 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 growth of grains during the solidifying of metals is very common. The reason that the dendrites are readily visible in a galvanize coating is that we are basically seeing a two-dimensional version of an as-cast, dendritic, solidified grain structure. Remember, the coating is 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 thick slab of steel into a 0.050-inch 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 passing. Galvanize coatings with small spangles generally have less depressed grain boundaries.

The Effect of Zinc Bath Chemistry

Dendritic growth is not the only way in which grains can grow during the solidification process. It requires one or more special conditions to be present. One of these conditions is the presence of other elements in the molten metal. These can be either intentionally added alloying elements or impurities. In the case of galvanize coatings on steel sheet; the most common reason for the well-defined dendritic growth pattern is the presence of lead in the coating. It has long been thought that the reason lead results in large spangles is that it reduces the number of nucleation sites. In recent work[i], it is proposed that the presence of lead decreases the solid/liquid interfacial energy in the solidifying coating. This leads to an increase in dendrite growth velocity, resulting in large spangles. Lead precipitates at the coating surface and the varying distribution of lead particles across the surface define the optical appearance (dull vs. shiny spangles).

Lead is a common impurity in zinc. In years gone by, the most common method of zinc metal production involved smelting, distillation and condensation. Lead is a common metal found in zinc-containing ores, and this refining process carried it through as an impurity in the zinc. In the early days of galvanizing, lead was almost always present in the zinc, and it was common to see a spangle pattern. Galvanize coatings on steel became identified by the characteristic spangle. Essentially, all hot-dip galvanized coatings had a spangle appearance. *If the spangle wasn't visible, the users "knew" that the steel had not been galvanized.*

The first galvanize coatings contained as much as 1% lead. During the past 35 years, the presence of such high lead levels has not been common in galvanize coatings on steel sheet, at least not in North America, Europe, and Japan. Typical concentrations of lead (where it is intentionally used) in most galvanized sheet made during this time has been less than 0.15%, often as low as 0.03 to 0.05%. Even this lower amount of lead is still sufficient to develop dendritic growth behaviour during the solidification process. Today, a typical level of lead in the coating bath on lines where the product requires a well-developed spangle pattern is in the range of 0.05 to 0.10% lead.

As there are now environmental concerns about the use of lead, some galvanized sheet manufacturers have established practices on their older or low speed lines that use lead-free zinc, whereby a small amount of antimony is added to the zinc coating bath. Antimony influences spangle formation in a similar fashion to lead. The final result is a smooth, visibly spangled coating. Typically, the amount of antimony in the coating bath is about 0.03 to 0.10%.

To obtain smoother coatings with lead-bearing zinc, it is possible to suppress spangle growth on the sheet by rapidly cooling the coating. This is done by using spangle "minimizing" devices above the zinc bath, that in addition to increasing the cooling rate, direct steam or zinc dust at the surface to rapidly freeze the zinc. Such technology is not required in the case of lead-free zinc for the reasons explained in the next section.

Non-Spangle Coatings

In recent times, the production of zinc from zinc-containing ores has been changed to an electrolytic recovery method. In this method of zinc production, the refined zinc is very pure, with the lead being excluded. This change occurred at a time when many users of galvanized sheet, especially those desiring a high quality finish after painting, such as the automotive and appliance industries needed a non-spangle coating. Removing the lead gave them the product they desired. The amount of lead in the coating for *lead-free coatings* is less than 0.01%, and often less than 0.005%.

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 mode of growth. Essentially, zinc grains nucleate 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. Rapid spangle growth cannot occur and the absence of lead results in the coating appearing uniformly shiny. Grain boundary depressions, for all intents and purposes, do not exist in lead free coatings.

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

An added advantage of producing a lead-free galvanize coating is that it is not susceptible to a problem known as delayed adhesion failure. This is a coating failure mechanism, occurring primarily in damp environments, related to the fact that the lead concentrates at the spangle boundaries and allows small corrosion cells to form.

Another feature of the very small spangles of lead-free coatings is that the shiny metallic appearance of the coating is very uniform, unlike the appearance of large spangle lead-bearing zinc coatings, where the luster of each spangle differs, giving the sheet a non-uniform appearance.

Why is Lead Still Used on Some Galvanizing Lines?

The manufacture of non-spangle coatings, free of lead (or antimony), is not so easily done. The reason relates to the influence of even a small amount of these additions on the viscosity of the molten zinc. Due to its lower viscosity, it is difficult to avoid small sags and ripples in the zinc coating when lead/antimony is not present. 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 high 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 has also helped in producing smoother coatings.

If the end user requires a heavier coating mass (100 g/m^2/side and higher), there is a tendency for the coating, when applied from a lead-free bath, to develop very visible sags and ripples. The result is that 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 (<75 meters/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 still have some amount of lead in the coating bath to improve the final coating uniformity. The concentration of lead in the zinc bath is typically between 0.05 and 0.10%. Antimony additions of between 0.03 and 0.10% provide the same effect.

The net result is that the final product from many lines still has a visible spangle pattern. This meets with the marketplace needs in that a number of industries, especially those that use bare (unpainted) galvanized sheet, still want the large, bright, reflective spangle pattern.

Specifying Spangle Size

Users often ask if there are 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 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 A 653/A 653M, Specification for Steel Sheet, Zinc-Coated (Galvanized) as follows:

- <u>Regular spangle</u> – zinc-coated steel sheet with a visible multifaceted zinc crystal structure. The cooling rate is uncontrolled, which produces a variable grain size.
- <u>Minimized spangle</u> – 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.
- <u>Spangle-free</u> – 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 2, 3, 4, & 5 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 2 – 5 illustrate what can still be obtained from producers in some parts of the world.

Fig. 2 Large – Spangles ≥ 15 mm across

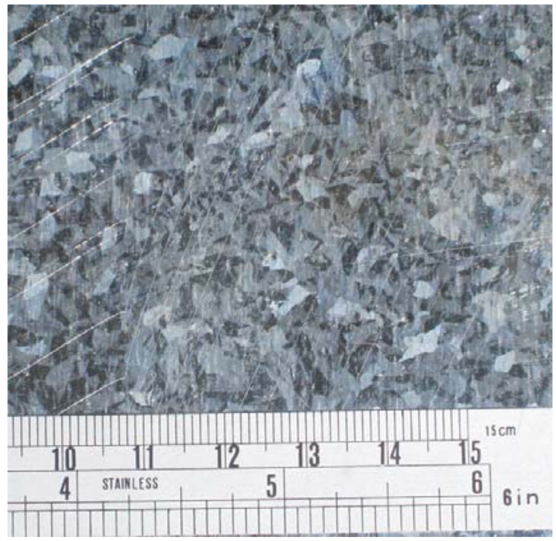

Fig. 3 Medium – Spangles up to 10 mm across

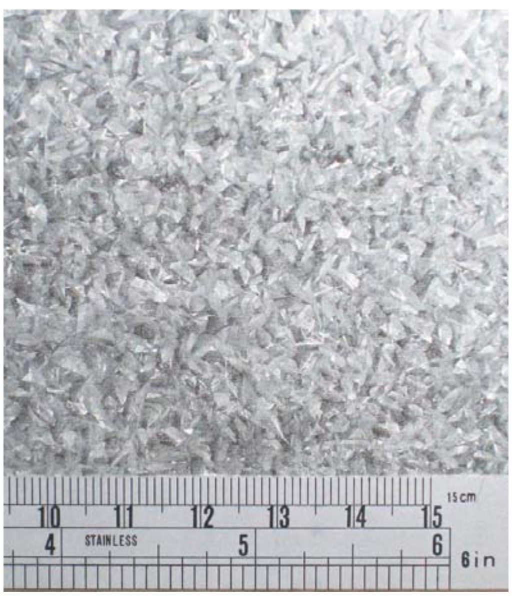

Fig. 4 Small – Spangles up to 5 mm across

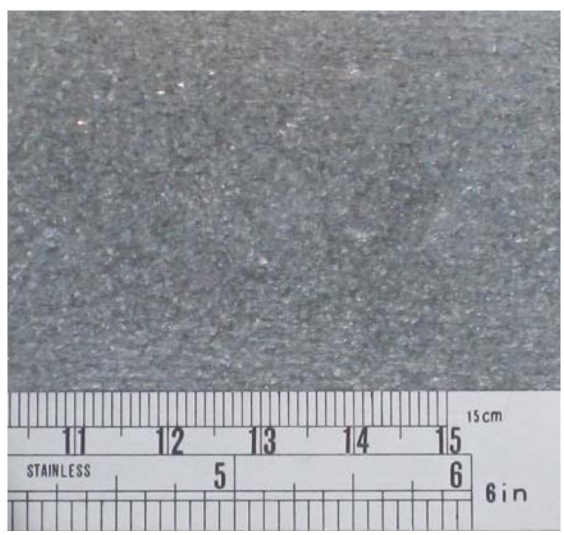

Fig. 5 Spangle-free – Spangles ≤ 0.5 mm across

Summary

The spangle on hot-dip galvanized steel sheet has 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 many 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 gradually users of galvanized sheet have become accustomed to a product that does not have a large, easily seen spangle. While in the future there may be no demand for a visible spangle, some consumers today still desire to use galvanize with a spangle for their products.

[i] J. Strutzenberger, J. Federl: Metall. Trans. A, 1998, vol. 29A' pp. 631-646