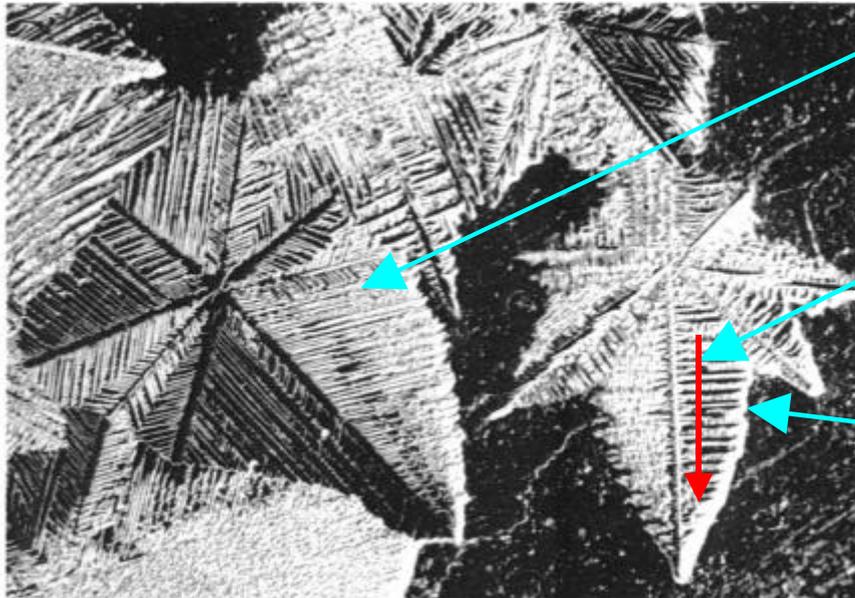


Introduction

For years, galvanized articles made by hot-dip coating techniques were identified by the characteristic *spangled* appearance. In many cases, this is still true today. However, because of some changes in the manufacturing processes associated with zinc production and the galvanizing process, not all hot-dip galvanized steel sheet made today has a visible spangle. This explanation for this is given later in this GalvInfoNote.

What is a Spangle?

The dictionary defines “spangle” as a glittering object. When spangle is used to define the surface appearance of galvanized steel sheet, it includes the typical snowflake-like or six-fold star pattern that is visible to the unaided eye. The following photograph shows the details of this pattern. This photograph shows the typical spangle pattern of a galvanized coating. The surface is magnified about 10X.



Note the 6-fold symmetry of this spangle.

Red arrow defines the direction of growth of the “primary” dendrite arm within the solidifying grain of

“Secondary” dendrite arms growing laterally away from the primary arm.

The spangled structure of a hot-dip galvanized coating.

The features shown here encompass a number of quite complex metallurgical phenomena. In this GalvInfo Note, we will attempt to explain why these features are present.

The Solidification Process

First, one needs to understand that the development of spangles occurs when the molten zinc adhering to the steel sheet is cooled below the melting point of zinc. The freezing point is approximately 419°C (787°F). At this temperature, the randomly-arranged atoms in the liquid zinc begin to position themselves into a very orderly arrangement. This occurs at many random locations within the molten zinc layer. This transformation from a disordered arrangement of the atoms into an orderly arrangement defines the “solidification” or “crystallization” process. The small solidifying areas within the molten zinc are defined as “grains”¹. As the individual atoms of molten zinc attach themselves to a solidifying grain (causing grain growth), they form into a distinct array, or crystal. In the case of zinc, the crystals form with hexagonal (six-fold) symmetry. It is this fundamental way in which the individual atoms of zinc arrange themselves as the solid zinc grains grow larger that leads to the often-visible hexagonal symmetry of the final spangle. When the coating is finally completely solidified, the individual spangles define specific individual grains of zinc.

“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 would tend to cause the formation of numerous small grains in the final solidified structure, while a low rate of nucleation would tend to favour the growth of large grains.

Dendritic Growth

There is another aspect of the solidification process that leads to the snowflake pattern in galvanized 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 the photograph above. 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 galvanized 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 in 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 related 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 galvanized 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 the above photograph, 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.

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 galvanized

¹ Metals, like many solids in nature, have a “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 these small steel grains are essentially “glued” to one another by atomic bonding forces. One can think of this as “grains of sand in a sandstone rock”. In the case of the sandstone rock, the size of the individual grains of sand are often larger than the grains in the steel sheet, but one can visualize the concept of grains using this analogy.

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 has the effect of reducing the number of nucleation sites. In recent work¹, 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 form 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. Therefore, in the early days of galvanizing, lead was almost always present in the zinc, and it was common to see the spangle pattern. Galvanized coatings on steel became identified by the characteristic spangle. Essentially, all hot-dip galvanized coatings had a spangled appearance. *If the spangle wasn't visible, the users "knew" that the steel had not been galvanized.*

The first galvanized coatings contained as much as 1% lead. During the past 25 years, the presence of such high lead levels has not been common in the galvanized coatings on steel sheet, at least not in North America, Europe, and Japan. Typical concentrations of lead in most galvanized sheet made during the past 25 years are less than 0.15%, often as low as 0.03 to 0.05%. However, this 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 primary product has a well-developed spangle pattern is in the range of 0.05 to 0.15% lead.

Non-Spangled 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-spangled 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%.

Lead-free coatings still have a grain pattern that is 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. However, the grains no longer grow by a dendritic mode but by a cellular mode of growth. Essentially, the grains of zinc 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.

This non-spangled 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 spangled coating are not present. The coating can be painted to give a very smooth, reflective finish.

An added advantage of producing a lead-free galvanized coating is that it is not susceptible to a problem known as intergranular corrosion. This is a coating failure mechanism in damp environments caused by the lead concentrating at the spangle boundaries.

Why is Lead Still Used on Many Galvanizing Lines?

The manufacture of non-spangled coatings, or lead-free coatings, is not easily done. The reason relates to the influence of even a small amount of impurities, such as lead, on the viscosity of the molten zinc. It is difficult to avoid small sags and ripples in the coating when the lead is totally removed. The thicker the coating, the greater the tendency to form sags and ripples. Fortunately, the automotive and appliance industries need only relatively thin coatings (typically 60 to 80 g/m²/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 the producer to use lead-free coating baths, avoid the development of spangles, and still attain a smooth coating.

If the end user requires a heavier coating mass (100 g/m²/side and higher), there is a distinct 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 locally is composed of thick and thin regions. This tendency for sags is exacerbated at low line speeds (<75 meters/minute). Thus, older, low speed coating lines, lines designed to process heavy-gauge sheet, and those that are used to make heavy coating weight products (275 g/m² meter or G90 and heavier) typically still have some amount of lead in the coating bath to improve the final coating uniformity. Often, the concentration of lead in the coating bath is between 0.05 and 0.15%.

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.

Some galvanized-sheet manufacturers have established practices on their older or low-speed lines where they use essentially lead-free zinc, but add a small amount of antimony to the zinc coating bath. The antimony addition accomplishes the same influence on viscosity and spangle formation as lead. The final result is a smooth, visible spangle coating. Typically, the amount of antimony in the coating bath is about 0.03 to 0.10%.

Reference:

- 1) J. Strutzenberger, J. Federl: Metall. Trans. A, 1998, vol. 29A' pp. 631-646

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