The Process Metallurgy of Zinc-Coated Steel Wire and Galfan® Bath Management

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Abstract

The physical metallurgy and related process and product performance concepts for the zinc and zinc alloy hot dip coating of steel wire are briefly reviewed, and are illustrated with a detailed model of aluminum behavior in Galfan® process technology. Applications to hot dip bath management practices are set forth.

The coating of iron and steel with zinc to improve corrosion resistance has been practiced in various forms for 260 years, and a thorough description of the numerous wire-related technologies has been compiled in the handbook Ferrous Wire.[1] In general, the basic unalloyed zinc technologies may be grouped under the headings "hot dip galvanizing" and "electrogalvanizing". Hot dip practice involves the passage of wire through a molten zinc bath, whereas electrogalvanizing involves electroplating. The galvanized steel coating may involve no further processing. Alternatively, it may be redrawn, or otherwise reworked, chromated or oiled.

It is important to note that the success of these technologies and the serviceability of the final product depend substantially on prior conditioning of the wire. Critical annealing, cleaning and fluxing (in the case of hot dip) processes precede the coating step. Moreover, hot dip coatings are optimized by the maintenance of small additions of aluminum in the zinc bath and by "wiping" and quenching practices upon emergence from the bath. Modern, in depth presentations on zinc-based steel coating systems may be found in Zinc-Based Steel Coating Systems: Production and Performance.[2] The physical metallurgical basis of zinc-coated steel has been recently reviewed in detail by Marder.[3]

It is practical and economical to apply a zinc alloy coating. Although traditional galvanized coatings with small (0.1%) aluminum compositions are the most popular, the most rapidly growing hot dip coating is made with the Galfan® process, wherein a Zn-5% Al coating is applied by hot dipping (all composition data in this paper are in % by weight). This paper

reviews this process and presents a model for management of the aluminum content in the hot dip Galfan® bath.

Galfan® Coating and Its Advantages

In 1980, researchers at Centre de Recherches Métallurgiques, Liège, Belgium, under sponsorship of International Lead Zinc Research Organization Inc., developed the Galfan® coating system, involving a Zn-5%Al coating. Most commonly this coating involves a mischmetal addition, containing lanthanum and cerium additions up to about 0.5%. The Galfan® coating system has been widely licensed, and an extensive set of ASTM Standard Specifications pertain. Galfan® ingot for preparation of the hot dip bath is addressed by ASTM Designation B 750-99, and basic Galfan® coated carbon steel wire is addressed by ASTM Designation A 856/A 856M-98. The wire may be drawn after coating, and ASTM Designation A 764 (Type C) pertains to Galfan® coated and drawn mechanical spring wire. Additional specifications exist for strand (ASTM A 855/A 855M-98 and ASTM A 925-98), for chain link fence (ASTM A 817-94 and ASTM A 824-95), for gabions (ASTM A 974-97), and for steel-reinforced aluminum conductors (ASTM B 232/B 232M-99 and ASTM B 401-99).

The Zn-Al phase diagram is shown in Figure 1, and an eutectic point exists at a composition of 5% Al and at a temperature of 381°C.[4] Thus, the Galfan® microstructure is largely that of a fine interspersion of the zinc terminal solid solution, ç, with up to 1.2 % aluminum, and the â phase, with at least 16.9% aluminum. The eutectic microstructure can be

either lamellar or of a rod type, and a mixture of the two structures is shown in Figure 2.[5] It is possible for the Galfan® microstructure to contain ç dendrites, and such dendrites may appear in conjunction with the rod type eutectic structure.[5] The Galfan® microstructure is sensitive to cooling rate, with rapid cooling refining the eutectic structure and tending to eliminate ç dendrites.

The additional of mischmetal to the Galfan® composition improves the fluidity and wetting characteristics of the molten alloy.

The Galfan® coating provides improved corrosion resistance in comparison to a conventional galvanized coating, combining, in effect, the passive corrosion inhibition of aluminum oxidation with the active and passive effects of zinc. Representative data are shown in Figure 3.[6] Beyond this, the eutectic structure is quite ductile, and Galfan® processing avoids the more brittle intermetallic phases that can exist in conventional galvanized coatings.[7] Hence, Galfan® coated steel wire can be extensively redrawn and subjected to relatively severe wire forming operations. Adriaensen has discussed the advantages of Galfan® coated wire, vis-a-vis conventional galvanized wire, for steel springs and spring manufacturing, including consistency of spring length (associated with a decreased frictional interaction with coiling tools), and the good adherence of the Galfan® coating to organic coatings.[8]

Two Galfan® Processing Issues

Molten Galfan® alloy is not compatible with the flux systems normally used with conventional galvanizing. While alternate fluxing arrangements are possible, this process limitation has led to wide usage of "double dipping" processes wherein the Galfan® hot dip simply follows a conventional galvanizing hot dip, as schematically illustrated in Figure 4.

In the double dip processing, the properly annealed, cleaned and fluxed steel acquires a galvanized coating in the first bath. This coating will generally include a series of iron-zinc intermetallic compounds at the iron-zinc interface, together with an overlay that is nearly pure zinc. The series of intermetallic compounds can be a source of coating brittleness. When the galvanized wire enters the second bath, containing molten Galfan®, the bath temperature will generally be high enough to melt or dissolve the essentially zinc galvanized overlay, and, furthermore, to transform the iron-zinc intermetallic layer into an aluminum-iron-zinc intermetallic. Upon emergence from the Galfan® bath a layer of essentially Galfan® alloy solidifies on top of the transformed aluminum-iron-zinc intermetallic layer.

The above scenario is not one of steady-state, however, and the aluminum that enters into the aluminum-iron-zinc intermetallic layer inherently lowers the aluminum concentration in the Galfan® bath. Thus, Galfan® bath management requires the monitoring and management of the aluminum concentration. This paper sets forth, below, a process model that can be used by Galfan® processors to understand and undertake such bath management.

A Model of Galfan® Bath Aluminum Concentration

Let us start with the assumption that the process line is able to add Galfan® alloy to keep the bath mass constant in the face of withdrawal of alloy from the passage of wire. In such a case, the incremental depletion of aluminum in the bath, associated with an increment of wire coating, can be expressed as follows:

$$(M)\, dC \ = \ -I\, dA \ + \ (0.05)\, G\, dA \ - \ C\, W\, dA, \qquad (1)$$

where C is the aluminum concentration in the bath, dC is the incremental change in bath aluminum concentration, dA is the increment of wire surface coated, M is the mass of the bath, I is the mass of aluminum per unit of wire surface area in the transformed intermetallic layer, G is the net mass of Galfan® melt removed per unit of wire surface area, and W is the mass of the Galfan® overlay that solidifies per unit of wire surface area.

The expression at the left in Equation (1) is simply the incremental mass of aluminum lost when an increment of wire surface area, dA, is coated in the Galfan® bath. The first expression on the right of equation (1) is the mass of aluminum that is lost to the transformed intermetallic layer when an increment of wire surface area is coated. The second expression on the right of Equation (1) is the amount of aluminum that is added to the bath per increment of wire surface area, assuming simultaneous bath replenishment with Galfan® alloy. The third expression on the right of Equation (1) is the aluminum lost per increment of wire surface area coated simply due to the solidification of the bath alloy on the emerging wire.

Equation (1) can be usefully reorganized as follows:

$$dC = -(X + YC) \, dA, \qquad\qquad (2)$$

where

$$X = [I - (0.05) G] / M \qquad\qquad (3)$$

and

$$Y = W / M. \qquad\qquad (4)$$

Further reorganization leads to the expression:

$$dC / (X + YC) = -dA. \qquad\qquad (5)$$

One can now simply integrate both sides of Equation (5). On the right side, one can integrate between the limits of zero and the total surface area coated, namely A. On the left side one integrates between the limits of the starting bath composition, C_0, and the final bath composition, C_1, arrived at after the coating of wire of surface area A. The resulting equation is:

$$(1/Y) [\ln (X + YC_1) - \ln (X + YC_0)] = -A. \qquad\qquad (6)$$

Multiplying through by (Y) and raising both sides of the equation to an exponential, one obtains:

$$(X + YC_1) / (X + YC_0) \;=\; \exp(-YA). \hspace{3cm} (7)$$

Finally, if one substitutes Z for X/Y, one obtains the relatively convenient expression:

$$C_1 \;=\; (Z + C_0) \exp(-YA) \; - \; Z. \hspace{3cm} (8)$$

Of course, Z is $[I - (0.05) G] / W$ with Y being W/M. One can see, by inspection, the trivial case of C_1 simply being C_0 when no area of wire has been coated. A practical illustrative calculation is undertaken below.

A Practical Example

Consider the Galfan® coating of 2,000 kg of 1 mm diameter steel wire. The length of this wire is 323,000 m and the surface area, A, of this amount of wire can be calculated to be roughly 1,000 m^2. Useful formulae and tables for such calculations may be found in the handbook Ferrous Wire.[9] Now, let the bath mass, M, be maintained at 10,000 kg. In such processing, the galvanized and Galfan® coating weights can be relatively insensitive to line speed, and a practical process might involve a galvanized coating of 250 g/m^2 and a overall coating weight after the Galfan® bath of 320 g/m^2. Thus, the value of G would be 70 g/m^2. Careful measurements of the intermetallic layer after passage through the Galfan® bath in such cases will reveal an intermetallic layer weight of about 20 g/m^2, with an aluminum level, I, in the intermetallic layer of about 8 g/m^2. The value of W is therefore (320 - 20) or 300 g/m^2. On this

basis, Z is 0.015, Y is 0.00003 m^{-2} and AY is 0.03. Thus, C_1 can be calculated as about 0.048, down only 4% from the C_0 value of 0.05.

At a line speed of 20 m/min, and with six lines in parallel, this wire could be processed in 45 hours or very roughly six eight-hour shifts. During this time, the Galfan® alloy to be replenished would be about 70 kg (70 g/m^2 x 1,000 m^2 1,000 g/kg), and an aluminum supplement of 20 kg would maintain the aluminum level. The supplemental aluminum addition is simply 4% of the product of 0.05 and the bath mass of 10,000 kg. Handled on a per shift basis, careful bath management can, in principle, be achieved.

More refined modeling can be done, as necessary. Among other considerations, one can adjust for the bath "overfill" constituted by the aluminum that is added on top of the Galfan® replenishment. However, this simple model offers a good start for sophisticated bath management analysis.

General Procedure

Using the Equation (8) and reasonable values of the several process descriptors and parameters involved, one can certainly plan tentative bath maintenance practices for a wide variety of Galfan® processing lines. The general approach would involve a rate of bath replenishment with Galfan® alloy together with a rate of addition of supplemental aluminum. It should be noted that the addition of aluminum requires care, lest excessive bath surface dross

result and foul the coating process. The addition of molten aluminum is advocated, where practical, although useful techniques exist for submersion en route to dissolution.

Obviously, periodic bath analysis should be undertaken to monitor and fine-tune this approach. Certainly direct observation of bath mass replenishment needs will provide a refined estimate of the value of G. Similar observations of galvanizing bath replenishing needs should provide a reasonable estimate of the galvanized coating weight, which when added to G will give the overall coating weight. The value of W can be estimated by subtracting 20 g/m^2 from the overall coating weight, and so forth.

In general, Equation (8) and the illustrative calculations above should only serve as a starting point for bath management policy development. Sophisticated bath management practices evolve from an ever-increasing evaluation of the process under scrutiny, not unlike the development of control methodology in "smart" systems.

<u>Summary</u>

The process metallurgy of the zinc wire coating technology has been reviewed with emphasis on a double dip Galfan® process. A process model has been set forth as a guide for the development of sophisticated bath management technique.

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Figure Captions

Figure 1.   The Zn-Al phase diagram.[4]

Figure 2.   Representative microstructure of a Galfan® coating, showing lamellar and

rod-shaped eutectic structure.[5]

Figure 3.   Representative data showing that a reduced rate of corrosion is sustained by

Galfan® coated wire in comparison to galvanized wire. Data were taken in an industrial

atmosphere (Amagasaki, Japan).[6]

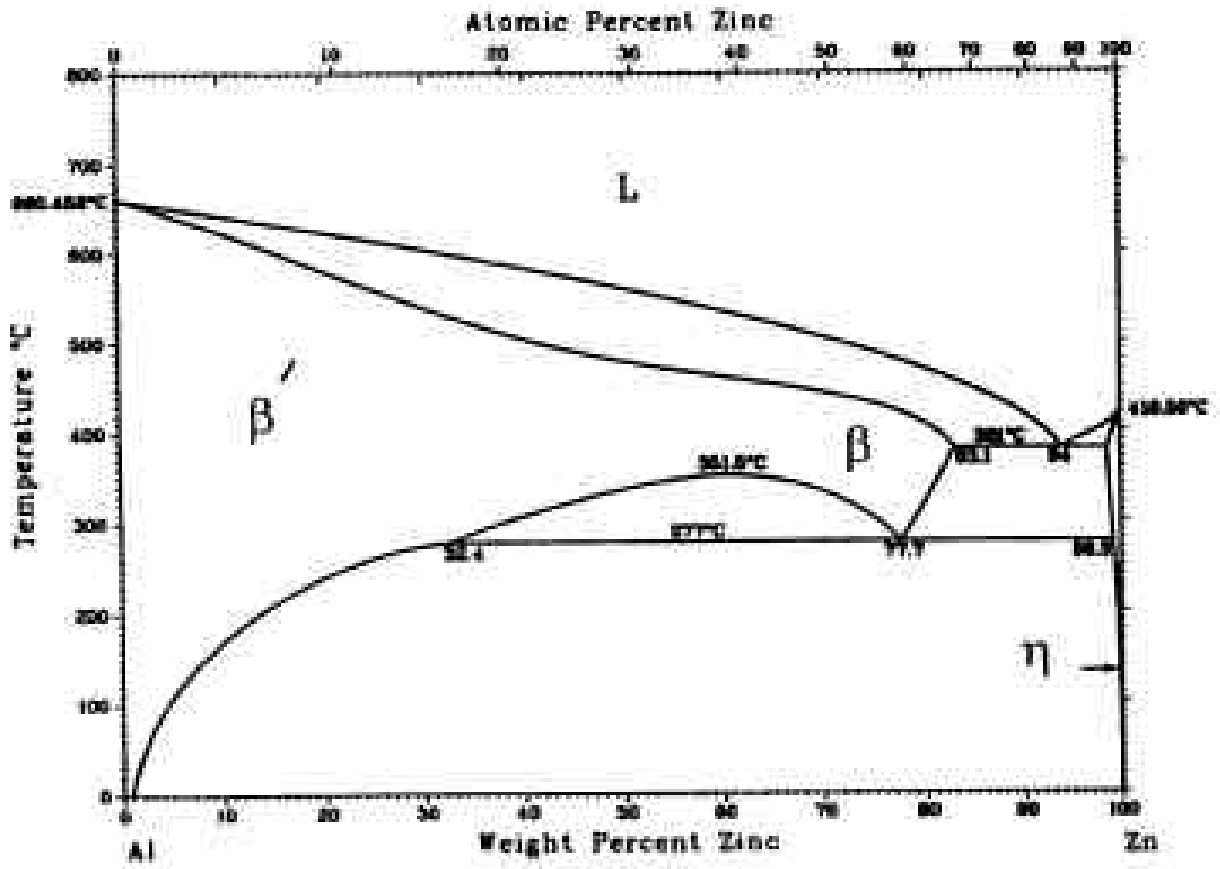Figure 4.   Schematic representation of a double-dip Galfan® processing line.
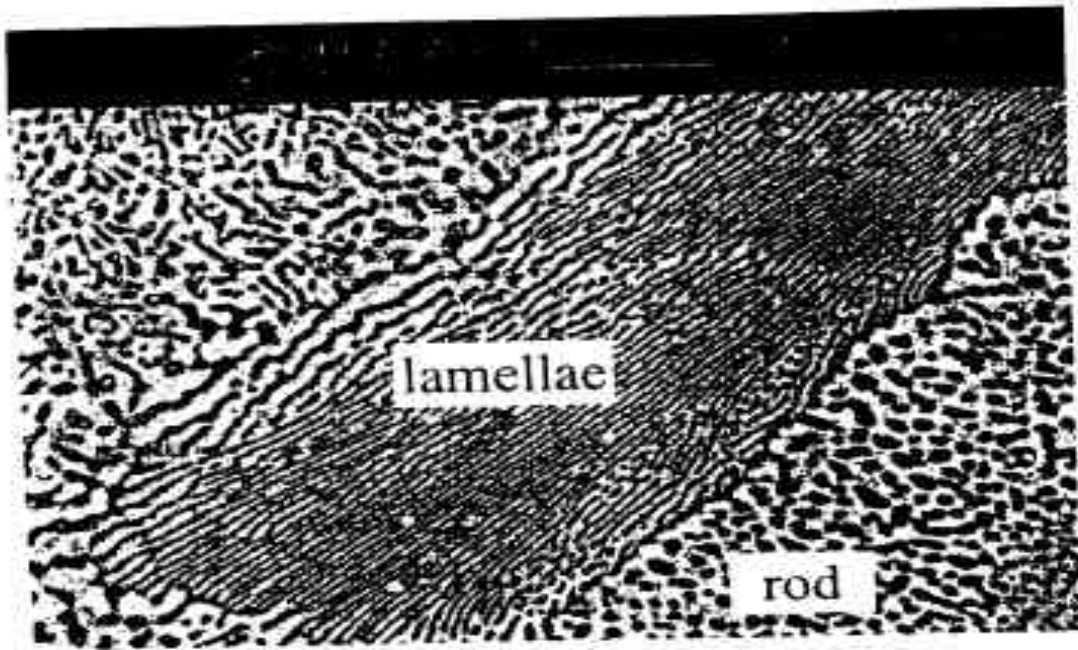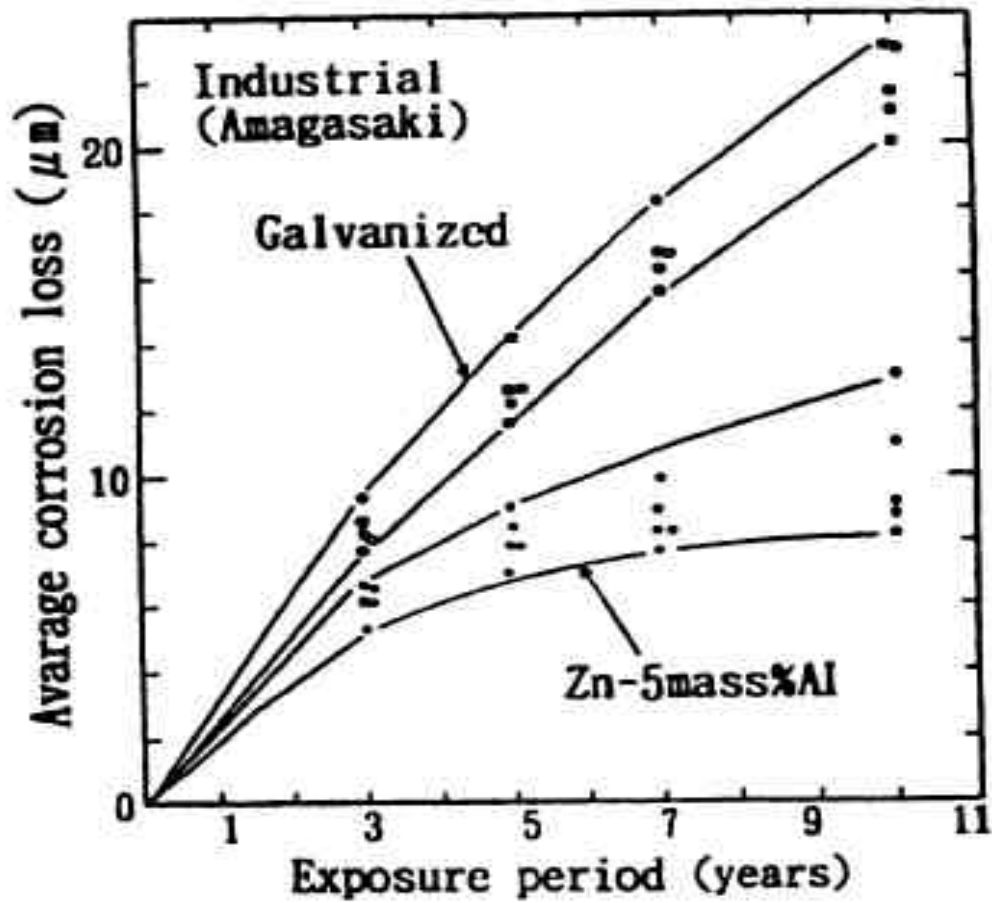
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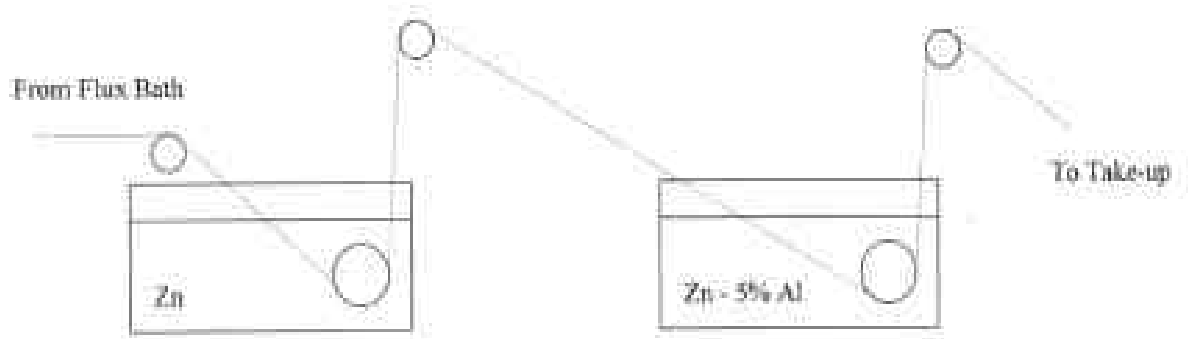
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