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Atmospheric Corrosion Behavior of Aluminum-Zinc Alloy-Coated Steel*


ABSTRACT: The influence of the aluminum content of hot-dip aluminum-zinc alloy coatings on their corrosion behavior was studied by means of salt-spray and atmospheric corrosion tests. The objective was to develop an improved aluminum-zinc alloy coating on steel that would be more durable than galvanized coatings and that would be more protective to cut edges and areas of mechanical damage than hot-dip aluminum coatings. The optimum alloy was found to be 55 weight percent aluminum-zinc. This new alloy coating is two to four times as corrosion-resistant as a galvanized coating of similar thickness. Furthermore, for the galvanic protection of cut edges of sheet in some environments, this coating proved to be superior to aluminum coatings.

KEY WORDS: coatings, hot-dip coating, zinc-containing alloys, aluminum-containing alloys, atmospheric corrosion, salt-spray tests, zinc-aluminum alloys

A brief look at the status of the two major metallic coatings for sheet steel—with their important advantages as well as certain shortcomings—will be useful in showing why there was a need to develop an aluminum-zinc alloy coating.

Zinc has been used as a coating for steel products for the past 135 years. Galvanized coatings today occupy a major place among the most successful coatings for steel. Some 4.5 Gkg (5 million tons) of sheet and strip are galvanized for corrosion protection each year. Galvanized coatings have a good initial appearance, a fair-to-good resistance to corrosion in the atmo-

*Original experimental data were measured in U.S. customary units.

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sphere, fresh water and soil, and provide excellent galvanic protection to cut edges, thus preventing rust staining. Galvanized steel has, of course, a better, more acceptable corroded appearance than ordinary uncoated steel. Galvanized coatings also tend to suppress pitting of the steel base until the coating has been mostly consumed by corrosion. The chief drawbacks of zinc coatings are inadequate resistance to high temperatures and limited life in severely corrosive environments. As an example of the latter, data have been published [1] that indicate steel coated with 0.3 kg (1 oz) of zinc per m² (ft²) of sheet would last less than 6 years before the onset of rust in the marine environment of Sandy Hook, New Jersey, and less than 3 years in the industrial environments of Brunot Island and Altoona, Pennsylvania.

Aluminum has been used commercially as a coating for steel sheet and strip for over 30 years and on other products for shorter times. Because of the formation of a more protective oxide film on aluminum, the corrosion and oxidation rates of this metal are generally less than those of zinc. Thus, aluminum appears to solve the major drawbacks of zinc coatings, namely, the need for greater atmospheric and high-temperature durability.

However, aluminum coatings also have drawbacks. For example, aluminum coatings do not galvanically protect steel in industrial and rural atmospheres. Thus, early rust-staining occurs at cut edges and at forming and other mechanical damage to the coating. Although early rust-staining at coating defects and cut edges of sheet has little consequence structurally, it can be aesthetically objectionable and may eventually develop into rust growths, or "pox." It is also recognized that aluminum coatings must be thicker (25.4 to 50.8 μm [1 to 2 mils]) is required for hot-dip aluminum coatings as compared to about 25.4 μm [1 mil] for G90 galvanized coatings) than zinc coatings in order to have acceptable corrosion resistance in the atmosphere. Furthermore, temperatures above the melting point 660°C (1220°F) of pure aluminum cause recrystallization and appreciable softening of cold-worked steel during hot-dip coating. Thus, the maximum strength which can be attained by ordinary steel sheet is limited by hot-dip application of pure aluminum coatings. Nevertheless, some 0.27 to 0.45 Gkg (300 000 to 500 000 tons) of aluminum-coated sheet are produced for high-temperature and atmospheric applications in this country each year. Thus, there is little question that aluminum coatings are a successful coating for steel products.

As valuable as the contributions of galvanized and aluminum coatings are, their respective shortcomings underlined the need for some type of coating for steel sheet and other products that would combine the best properties of both of these traditional coatings. To meet this need, in 1958 Bethlehem Steel began a research program to develop through alloying either a more durable zinc coating or a more galvanic aluminum coating. There had been many previous studies [2–5] of the effects of alloying zinc

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2The italic number in brackets refer to the list of references appended to this paper.
or aluminum with small additions of second elements, but these efforts met with little technical or commercial success. Although Bethlehem researchers also tried many approaches, early in their program they found that combining large amounts of aluminum and zinc to form an aluminum-zinc alloy coating showed the most promise for producing a superior coating. Consequently, our program began a systematic investigation of a broad range of aluminum-zinc alloys as coatings for steel. Although many investigators had studied various combinations of zinc and aluminum in search of better die-casting alloys, there had been very little effort to develop these alloys as coatings for steel. Wehr and Mahlie [6] studied the addition of 5 to 20 weight percent aluminum to zinc to improve corrosion and heat properties but encountered severe production difficulties and apparently marginal improvements in performance. Bablik [7] showed that the aluminum-zinc alloy system could cause severe alloy growth activity on steel, a discouraging effect. Stanners [8] and Hoar et al. [9, 10] used metallizing to apply a full range of aluminum-zinc coatings on grit-blasted steel, and these coatings exhibited good corrosion performance.

Prior to Bethlehem Steel's research and development program that led to the development of the 55 weight percent aluminum-zinc hot-dip coating, however, aluminum-zinc coatings were not being applied by a continuous hot-dip method, the result being that there had simply been no opportunity to learn more about the potentialities of the aluminum-zinc coatings in terms of corrosion resistance and their properties. Our paper outlines briefly the hot-dip coating practice we developed and describes the corrosion resistance of the aluminum-zinc alloy system in the form of hot-dip coatings on steel sheet, the main emphasis being on corrosion behavior of the commercially produced 55 weight percent aluminum-zinc hot-dip-coated sheet currently being marketed in the United States under the name of Galvalume.

Corrosion Test Procedures

Preparation of Aluminum-Zinc Alloy-Coated Sheet Specimens

Aluminum-zinc alloy coating baths were made up containing 0, 1.0, 4.0, 7.4, 12.2, 16.6, 21.0, 24.9, 35.1, 44.6, 53.9, and 69.6 weight percent aluminum, about 3 weight percent silicon with respect to the aluminum content, and a balance of special high-grade zinc.

The preparation and coating of 15.2-cm (6-in.)-wide, 0.043-cm (0.017-in.)-thick, cold-rolled strip on a continuous pilot line is presented in Table 1.

Salt Spray Test

The salt spray test is that described in ASTM Specification for Salt Spray (Fog) Testing (B 117-73). Our coated panels were exposed to a salt fog of
TABLE 1—Procedure for preparation and coating of aluminum-zinc-coated specimens.

1. Alkaline cleaning.
2. Water-rinse and drying.
3. Heating to about 649°C (1200°F) in a Saelas-type annealing furnace, followed by cooling in a furnace containing hydrogen to protect the strip from oxidation.
4. Coating of strip, the temperature of the bath of each alloy being maintained above the liquidus of the alloy. Coating thicknesses were controlled at about 1 mil* on each side of the strip by using rollers on both sides of the strip upon leaving the bath.
5. Air cooling to freeze the coating followed by water quenching of the coated strip.
6. Shearing into 4 by 6-in. panels for corrosion testing in salt spray and in the atmosphere.

*1 mil = 25.4 \( \mu \)m.
*1 in. = 2.54 cm.

5 percent sodium chloride solution at 35°C (95°F). To prevent galvanic effects from exposed areas of bare steel, cut edges of the panels were covered with electroplaters' tape.

**Atmospheric Tests**

Sheet specimens 10.2 by 15.2 cm (4 by 6 in.) were weighed and exposed 30 deg from the horizontal at the International Nickel Company's Corrosion Station at Kure Beach, North Carolina, 24 and 245 m (80 and 800 ft) from the ocean surf, at Bethlehem, Pennsylvania (Homer Research Laboratories and the Coke Works of the Bethlehem Steel Corporation) and at Saylorsburg, Pennsylvania, representing four typical environments: severe marine, marine, industrial, and rural, respectively. The specimens faced south, except at the 24-m lot, where they faced east. To prevent staining, the panels were placed on stainless steel or Monel racks, and to prevent galvanic corrosion, the specimens were insulated from each other and from the racks by ceramic insulators. Testing was completed at the Bethlehem Coke Works after a 5-year exposure, and tests at the other sites are still in progress.

After a particular exposure period, the specimens were removed from the racks, cleaned in 20 percent chromic acid at 82°C (180°F), rinsed in running tap water, dried, and weighed. Cleaning continued until constant weights were obtained. Specimens were removed from test subsequent to cleaning. Weight losses \( W \) were determined, and the thickness loss \( T \) was calculated from the formula

\[
T = \frac{W}{AD}
\]

where \( A \) is the area and \( D \) the density of the coating. Thickness losses thus calculated and reported on Figs. 2 and 7 through 10 represent an average value of both skyward and groundward surfaces. Calculations employed
the density of the alloy coating in the case of coatings containing up to 22 weight percent aluminum. For calculating thickness losses of aluminum-zinc coatings in the range 22 to 70 weight percent aluminum. The density of a 22 weight percent aluminum alloy was used as an approximation to the density of the zinc-rich portion that was observed to corrode preferentially.

For the corrosion-time curves of the 53.9 weight percent aluminum-zinc coating (referred to henceforth under the collective term "55 weight percent aluminum-zinc coating"), the actual composition of the corroded phase was determined from the weights and analyses of the coatings before and after exposure. The density of this composition was used in calculating the average thickness loss of the 55 weight percent aluminum-zinc coating.

Results and Discussion

The results of the salt-spray and atmospheric tests of the 0 to 70 weight percent aluminum-zinc coatings as well as the 55 weight percent aluminum-zinc coating are summarized in the following section. These results show the effect of aluminum content on the corrosion behavior of aluminum-zinc coatings. Finally, we present data on the microstructure and atmospheric corrosion resistance of the 55 weight percent aluminum-zinc alloy-coated sheet steel.

Effect of Aluminum Content of Coatings

Figure 1 shows the effect of aluminum content on the salt-spray life of aluminum-zinc alloy coatings. Galvanized coatings lasted about 300 h per 25.4 μm (mil) to first rust in salt spray. In contrast, aluminum additions increased the life linearly up to about 5500 h for the 55 weight percent aluminum-zinc coating (the optimum composition), after which performance dropped off with a further increase of aluminum.

Figure 2 shows the effect of aluminum content on atmospheric corrosion resistance after a 5-year exposure. Starting at the zinc end, corrosion resistance increases with aluminum additions up to 4 to 7 weight percent aluminum (eutectic composition at 5 weight percent aluminum), beyond which corrosion resistance decreases, that is, corrosion losses increase with aluminum content to about 21 weight percent aluminum (the eutectoid composition being 22 weight percent aluminum). Generally, the corrosion rate of the eutectoid composition is as high as the corrosion rate of zinc and in milder environments may be even higher. Beyond 21 weight percent aluminum the corrosion decreased to 70 weight percent aluminum more or less linearly. All coatings provided galvanic protection of cut edges, except the 70 weight percent aluminum-zinc coating, which tended to behave like aluminum coatings in this respect.
On the basis of the atmospheric and salt-spray corrosion tests as well as observations of the condition of cut edges, the 55 weight percent aluminum-zinc alloy coating proved to have the best combination of corrosion resistance with galvanic protection and, therefore, was selected for commercial development as our Galvalume sheet coating.

**Microstructure of 55 Weight Percent Aluminum-Zinc Coatings**

The equilibrium phase diagram for the binary aluminum-zinc system [11], Fig. 3, predicts that alpha phase containing about 82 weight percent aluminum is the first solid to form as a 55 weight percent aluminum-zinc alloy is cooled below the liquidus temperature. With nonequilibrium cooling, alpha-phase dendrites grow and reject zinc-rich liquid until the temperature of the rejected liquid is finally sufficiently below its solidus to complete the freezing process. The resulting structure consists of about 80 percent by volume of cored alpha-phase dendrites, with zinc-rich interdendritic alloy filling in the interstices.
FIG. 2—Effect of aluminum content on corrosion performance of aluminum-zinc alloy coatings after 5-year exposure in various atmospheres. (1 mil = 25.4 \mu m; 1 ft = 0.305 m)

The cored dendritic structure of a 55 weight percent aluminum-zinc coating is most apparent when the center of an individual spangle is viewed at high magnification normal to the sheet surface (see Fig. 4). X-ray diffraction analyses indicate that the (111) plane of the light-etching aluminum-rich alpha phase is oriented parallel to the sheet surface, and the sixfold symmetry of the face-centered-cubic (111) plane is evident in Fig. 4. Dark-etching zinc-rich alloy with an average composition of about 22 weight percent aluminum fills the spaces between the secondary branches of the alpha-phase dendrites.

A cross section of steel coated with 55 weight percent aluminum-zinc, Fig. 5, again shows the alpha-phase dendrites and a network of interdendritic zinc-rich alloy. Scattered particles of silicon are also present in the overlay. The coating is bonded to the steel substrate with a thin intermetallic layer comprised of about 48 weight percent aluminum, 24 weight percent iron, 14 weight percent zinc, and 11 weight percent silicon. X-ray diffraction of the intermetallic layer gives lines which are similar to the intermetallic compound Al_12Fe_4. Based on the chemical analysis we believe that zinc atoms are substituted for about one-third of the iron atoms in the

FIG. 3—Phase diagram of aluminum-zinc system.
FIG. 4—Dendritic structure of 55 weight percent aluminum-zinc coating viewed normal to sheet surface at approximate mid-thickness of coating (×200, amyl-nital etch).

FIG. 5—Random cross section of a 55 weight percent aluminum-zinc coating (×500, amyl-nital etch).
Al\textsubscript{13}Fe\textsubscript{4} lattice. Electron probe and ion microprobe analyses indicate that most of the silicon associated with the intermetallic layer is concentrated at the overlay/intermetallic layer interface.

**Atmospheric Corrosion Resistance of 55 Weight Percent Aluminum-Zinc Alloy-Coated Sheet**

After an 11-year exposure in the four environments the 55 weight percent aluminum-zinc alloy-coated, galvanized, and aluminum-coated panels 0.43 to 0.64 cm (0.017 to 0.025 in.) thick had typically the appearance seen in Fig. 6. Before describing the condition of the surfaces in detail, we should note that the small, localized discolorations at the vertical edges of some specimens were points which contacted ceramic insulators.

*Severe Marine Atmosphere, 24-m (80-ft) lot*—The galvanized coating, which had started to rust after a 4-year exposure, is now heavily rusted. In contrast, panels with 55 weight percent aluminum-zinc and 50.8-µm (2-mil) aluminum coatings are still in good condition, although some corrosion products are starting to creep inward on the faces of panels from cut edges.

Visual inspection of the cut edges show that the 55 weight percent aluminum-zinc panels have slight rust on the cut edges, whereas the galvanized specimens and the 50.8-µm (2-mil) aluminum-coated specimens have considerably more rust.

*Marine Atmosphere, 245-m (800-ft) lot*—All three types of coatings are still in good condition. Although not visible in the photograph, the cut edges of the aluminum-coated sheets have considerable rust.

*Industrial Atmosphere*—Most of the galvanized coating has been corroded away and more than ¼ of the steel surface is rusted. The aluminum-zinc and aluminum-coated panels exhibit superficial light-brown oxide stain due to particulate fallout from nearby steelmaking operations, but are otherwise in good condition.

*Rural Atmosphere*—All three materials are in good condition, but there is some rust staining apparent along the edges of the 50.8-µm (2-mil) aluminum-coated panels.

Observations of cut edges throughout the test period showed that in all but the severe marine atmosphere the galvanized coating provides the best galvanic protection against rust staining from cut edges, followed by the 55 weight percent aluminum-zinc coating, with the aluminum coating providing little or no galvanic protection.

Figures 7 to 10 are the corrosion-time curves for these same three materials after 9 years’ exposure. In order to facilitate a comparison of the corrosion resistance of a 55 weight percent aluminum-zinc coating with that of a conventional galvanized coating, we calculated the ratio of the average corrosion rates for the two coatings as shown in Table 2. For each material, the average corrosion rate was determined by dividing the total corrosion loss by the longest exposure time shown in Fig. 7 to 10.
FIG. 6—Appearance of galvanized, aluminum-coated, and aluminum-zinc-coated steels after a 11-year exposure in the atmosphere (skyward surface). (1 mil = 25.4 μm; 1 ft ~ 0.305 m)

<table>
<thead>
<tr>
<th>Site</th>
<th>Material</th>
<th>Ratio of Average Corrosion Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kure Beach, N.C., 24-m (80-ft) lot</td>
<td>Galvanized: 55 w/o Al-Zn</td>
<td>3.5:1</td>
</tr>
<tr>
<td>Kure Beach, N.C., 245-m (800-ft) lot</td>
<td>55% Al–Zn Coated (1-Mil)</td>
<td>2.2:1</td>
</tr>
<tr>
<td>Saylorsburg, Pa.</td>
<td>Aluminum Coated (2-Mil)</td>
<td>2.9:1</td>
</tr>
<tr>
<td>Bethlehem, Pa.</td>
<td></td>
<td>5.3:1</td>
</tr>
</tbody>
</table>
FIG. 7—Corrosion performance of galvanized, aluminum-coated, and aluminum-zinc-coated steels in severe marine atmosphere (Kure Beach, 24 m [80 ft] lot). (1 mil = 25.4 μm)
FIG. 8—Corrosion performance of galvanized, aluminum-coated, and aluminum-zinc-coated steels in marine atmosphere (Kure Beach, 245-m [800-ft] lot). (1 mil = 25.4 \mu m)
FIG. 9—Corrosion performance of galvanized, aluminum-coated, and aluminum-zinc-coated steels in industrial atmosphere (Bethlehem, Pa.). (1 mil = 25.4 μm)
FIG 10—Corrosion performance of galvanized, aluminum-coated, and aluminum-zinc-coated steels in rural atmosphere (Saylorsburg, Pa.). (1 mil = 25.4 μm)
Thicknesses of commercially available coatings are typically 23 μm (0.9 mil) for G90 galvanized and 20 μm (0.8 mil) for 55 weight percent aluminum-zinc. Accordingly, we can predict that the commercially available 55 weight percent aluminum-zinc coating will outlast G90 galvanized by at least two to four times in a wide range of atmospheric environments.

The concentration of zinc in that part of the coating which has corroded (Fig. 11), is initially about 90 weight percent and decreases with time. In the rural and industrial environments, the composition of the corroded phase seems to level off after 9 years at roughly 80 weight percent zinc, while in the marine environments it continues to decrease.

Atmospheric Corrosion Mechanism

The results of the atmospheric corrosion testing, now going into the twelfth year, have demonstrated that the 55 weight percent aluminum-zinc alloy coating has excellent corrosion resistance. On the basis of these results, the commercial 20 μm (0.8-mil), 55 weight percent aluminum-zinc alloy coating is expected to last at least two to four times as long as the G90 galvanized coating (about 23 μm [0.9 mil]) in most atmospheres, and be more effective than the aluminum coating in resisting rust stain at cut edges. To account for the exceptionally good performance of the 55 weight percent aluminum-zinc coating it is useful to consider the mechanism and morphology of the corrosion process.

The time dependence of corrosion potential for 55 weight percent aluminum-zinc coatings exposed to laboratory chloride or sulfate solutions is shown schematically in Fig. 12. Subsequent to first immersion (Stage 1), the coating exhibits a corrosion potential close to that of a zinc coating exposed under identical conditions, generally about −1.0 to −1.1 V saturated calomel electrode (SCE). During Stage 1, the zinc-rich portion of the coating dissolves preferentially and the coating, like zinc, is anodic to steel. Stage 1 persists until the zinc-rich interdendritic portion of the coating is consumed, the exact time depending upon the thickness of the coating (mass of available zinc) and the severity of the environment (rate of zinc corrosion). Following depletion of the zinc-rich fraction, the corrosion potential rises and approaches that of an aluminum coating, generally about −0.7 V (SCE). During this period (Stage 2), the coating behaves like an aluminum coating, passive in sulfate environments, but anodic to steel in chloride environments.

Behavior of the 55 weight percent aluminum-zinc coating during atmospheric exposure appears to proceed in a manner analogous to that observed in laboratory solutions, although the time scale is greatly extended. We observe that the zinc-rich interdendritic portion of the coating corrodes preferentially as evidenced by the composition of the corroded phase, Fig. 11. During this period, the coating is sacrificial to steel and cut edges
FIG. 12—Schematic time dependence of corrosion potential of 55 weight percent aluminum-zinc coating in aqueous solution.

of light-gage, coated steel sheet are galvanically protected. The initial overall rate of corrosion of the aluminum-zinc coating is less than that of a galvanized coating because of the relatively small area of exposed zinc.

As the zinc-rich portion of the coating is gradually corroded, the interdendritic interstices are filled with zinc corrosion products. The coating is thus transformed into a composite comprised of an aluminum-rich matrix with zinc corrosion products mechanically keyed into the interdendritic labyrinth. The zinc corrosion products should offer continued protection as a physical barrier to the transport of corrosives. In addition, as others have reported [12], these products may act as a cathodic inhibitor by providing continued protection at cut edges, as they are gradually leached from the coating. The decreasing corrosion rates with time in the rural and industrial environments, Figs. 9 and 10, appear to reflect a gradual change from active, zinc-like to passive, aluminum-like behavior.

The intermetallic layer is generally cathodic to the steel substrate as well as to the other components of the coating. Accordingly this layer appears to function as a barrier which prevents corrosion of the steel substrate subsequent to interdendritic corrosion of the overlay.

Conclusions

1. Of the 0 to 70 weight percent aluminum-zinc alloy coatings, the 55
weight percent coating has the best combination of salt-spray and atmospheric corrosion resistance.

2. The general corrosion resistance of the 55 weight percent aluminum-zinc alloy coating is superior to that of galvanized. Specifically, the commercial 20 μm (0.8-mil) 55 weight percent aluminum-zinc alloy-coated product should last two to four times longer than conventional galvanized of about the same coating thickness—20 μm (0.9 mil).

3. In all but the severe marine atmosphere, the best galvanic protection for cut edges is provided by the galvanized, with the 55 weight percent aluminum-zinc coating following, and the aluminum coating providing little or no protection.

To sum up, since the 55 weight percent aluminum-zinc alloy coating combines some of the best properties of both galvanized and aluminum coatings, it is inherently of great commercial importance as a new type of protective metallic coating for a wide range of sheet and other steel products.

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