

Some Failure Analysis Case Histories in Galvanized Steel Products

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Abstract: The three case histories presented in this paper concern defects and causes of failure associated with galvanized steel sheet material. Optical metallography and microindentation hardness testing were the principal methods employed in determining the causes of failure but were supplemented as necessary by scanning electron microscopy and energy-dispersive X-ray spectrometry.

One of the case histories presents defects associated with the actual hot-dip galvanizing process itself. In one instance, tiny hydrogen blisters were observed to have occurred at oxide scale deposits at the interface between the steel and galvanized coatings.

When galvanized sheet steel cracks in bending during forming operations, most end users tend to place the blame on the galvanized material. However, several separate investigations of formed and cracked galvanized steel parts have revealed that the cracking often initiates at the sheared edges of the part where plastic deformation has produced a local increase in hardness and a corresponding decrease in ductility. Ductility is the property of steel required to successfully withstand forming operations.

The final case history present some observations made during failure analysis of corroded galvanized and painted panels at a utility plant. The coating system was composed of a galvanizing layer, a thin primer, and a final top coat. The problem was identified as localized development of white rust. The problem was found to be caused by the presence of a second-phase precipitate in the galvanizing layer that adversely affected its ductility allowing it to crack during forming. This produced localized stress in the paint layer that then cracked, permitting moisture to come into direct contact with the zinc, resulting in white rust formation.

Keywords: galvanized steel, failures (materials), intergranular precipitation, hydrogen blisters, forming problems, metallography, metallurgical specimens, microstructure, metallographic techniques.

Historical Background

Centuries before zinc was discovered in the metallic form, its ores were used for making brass. Ancient metallurgists probably lost this volatile metal as vapor because their apparatus was not designed for condensing it. Metallic zinc is not an easy metal to produce. Zinc oxide cannot be reduced by charcoal at temperatures below 1000°C. However, zinc boils at 923°C and the metal is, therefore, produced as a vapor that must be collected and condensed.

It is claimed that China first produced zinc in the period 200 B.C. to 100 A.D. As far as China is concerned, there is a reference in a textbook on metallurgy, dated to 1637, for the production of zinc in sealed crucibles. Zinc was even used for coinage during the Ming dynasty (1368 to 1644).

There is considerable evidence of the production of zinc in India between the tenth and sixteenth centuries. At Zavar, near Udiapur in Rajasthan, great heaps and walls of small retorts have been

found recently. It is estimated that the elliptical retorts found at Zawar represent the extraction of 100,000 tons of metallic zinc.

Long before zinc was smelted in Europe, it was being sold there by Portuguese and English traders who brought it from the Orient. Zinc was being imported by the East India Company from about 1605 onwards. At this time, the zinc was added to copper to make brass.

Lead ores are often contaminated with zinc because the two metals occur together. Small amounts of metallic zinc were obtained as a by-product of the lead industry and Agricola mentioned the formation of "zincum" in the furnaces of Silesia. This is probably the first indication we have in the West of any attempt to recover metallic zinc. The credit for the first intentional production of metallic zinc in the West is given usually to William Champion who developed a vertical retort method in 1718. Rows of horizontal retorts, which are more thermally efficient and, therefore, more economical, were installed by the Abbe Dony at Liege, Belgium in 1807.

The first recorded experiments for producing zinc coatings by the dipping process are those of a French chemist, Melouin, in 1741. Tinned iron was already known at that time and Melouin attempted to zinc coat iron sheets in a similar manner by immersion in a bath of molten zinc. The results of his experiments formed the basis of a report to the Academie Royale in 1742. Interest in Melouin's discovery spread through the scientific circles in Paris. The first application that was attempted was to use molten zinc as a cheap protective coating for household utensils. Zinc was used to replace tin, which had become too expensive for the poor. In 1742, Jean-Baptiste Kemerlin applied this process for coating iron kitchen utensils and these products were fairly well known in parts of France during the second half of the eighteenth century. In 1778, however, it was discovered that the zinc became corroded by organic acids and that the salts found on the zinc were poisonous. Interest in hot dipped zinc coatings then declined.

In 1780, the Italian, Luigi Galvani, discovered the electrical phenomenon of the twitching of a frog's leg muscles when contacted by two dissimilar metals, namely, copper and iron. Galvani incorrectly concluded that the source of the electricity was in the frog's leg. Experiments with dissimilar metals were further pursued by another Italian, Alessandro Volta, who came to believe that the flow of electrical current was caused by the contact of the dissimilar metals themselves. In 1800, Volta was able to prove this by constructing a stack of alternating zinc and silver plates with a piece of cloth soaked in a salt solution between the individual plates. This device, known as Voltaic pile, was the world's first battery.

Electrodeposition of zinc in the laboratory occurred in 1800, the same year that Volta developed the voltaic pile. In September of that year, The German physicist, Johann Ritter, used Volta's battery to deposit zinc on iron. In 1805, an early British patent was issued to Charles Hobson, Charles Sylvester, and John Moorhouse for a method of coating nails and bolts by placing them in a galvanic pile with zinc and seawater. Full commercial utilization of zinc plating processes had to wait until the end of the nineteenth century until electric dynamos and generators became available.

In 1824, Sir Humphrey Davy showed that when two dissimilar metals were connected electrically and immersed in water, the corrosion of one was accelerated while the other received a degree of protection. From this work he suggested that attaching iron or zinc plates to them, the earliest example of practical cathodic protection, could protect the copper bottoms of wooden naval ships. When wooden hulls were superseded by iron and steel, zinc anodes were still used. In 1836, Sorel in France took out the first of numerous patents for a process of coating steel by dipping it in molten zinc after first cleaning it with 9% sulfuric acid and fluxing it with ammonium chloride. He provided the process with its name "galvanizing". It is interesting to note that Sorel was aware of the electrochemical nature of corrosion and the sacrificial role of the zinc coating on the iron. Originally, the word galvanizing did not refer to the process of coating but to the fundamental property offered by this coating.

In addition to Sorel's patent of 1836, A British patent for a similar process was granted in 1837 to William Crawford. By 1850, the British galvanizing industry was using 10,000 tons of zinc a year for the protection of steel. Early corrugated galvanized steel used a roofing material, found its way to both Australia and California during the gold rush of 1849.

In the beginning, individual sheets of iron had to be hot-dipped by hand. The Sendzimir coating process was the first to attain commercial success by fulfilling the basic coating requirements in a continuous galvanizing operation. A coating line was installed by the Armco Steel Corporation at Butler, Pennsylvania in 1936 and proved the soundness of the process. Metallurgically, this process suppresses the formation of the brittle iron-zinc alloy layers at the steel-coating interface by the addition of 0.2 aluminum to the bath. By minimizing the thickness of the brittle iron-zinc alloy layers, the ductility of the coating is improved. The beneficial effects of aluminum alloy additions to the zinc bath were first discovered in the early twentieth century, and research in this area was later performed by Bablik and others.

Case History 1

Several pieces of galvanized steel strip were experiencing a problem with the galvanized coating. Small blisters were observed on both sides of the sheet. The strip was first passed through a furnace to oxidize and remove any oil residues. The strip was then annealed in a furnace containing a hydrogen atmosphere and finally hot-dip galvanized.

Visual Inspection

The hot-dipped galvanized coating on both sides of the steel strip possessed numerous very small blisters. The blisters were distinguishable by an increase in reflectivity caused by their raised surfaces. It was found that rubbing the blisters with a fingernail or other object would flatten the zinc coating over the blister and so eliminate it.

Metallographic Inspection

Transverse sections through the galvanized steel in the blistered areas were prepared for subsequent metallographic inspection. In the as-polished condition, the blisters were observed as small arches in the coating with complete separation occurring at the zinc-steel interface (Fig. 1). At high magnifications, small gray inclusions were observed on the steel surface within the cavity (Fig. 2). The inclusions were examined using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. Only iron was observed. The equipment cannot detect the presence of elements in the first row of the periodic table such as carbon, oxygen, nitrogen, etc. Based upon the appearance of the inclusions, and the absence of any elements other than iron, the inclusions are most likely iron oxide.

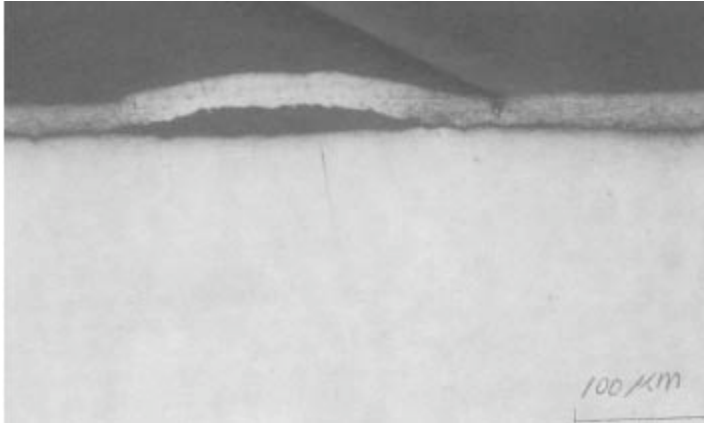


Figure 1: Photograph at 200x showing a blister under the galvanized coating as polished.

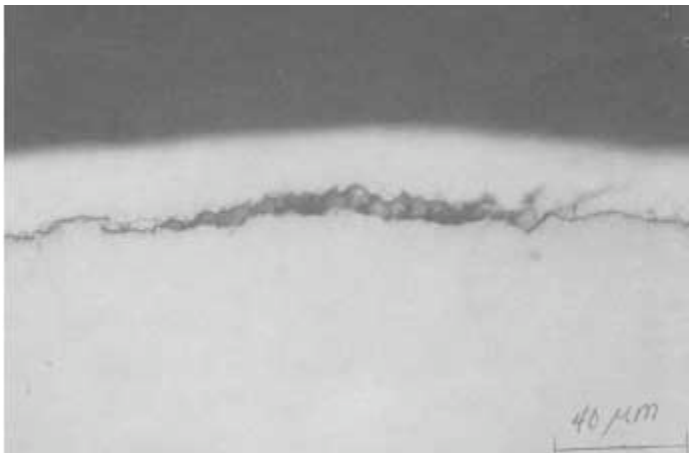


Figure 2: Photograph at 500x showing scale particles within a blister as polished.

Results

The blisters in the galvanized coating appear to have been caused by gas accumulation at the interface between the steel and the zinc coating. Iron oxide inclusions were observed within the blister cavities. The following mechanism is responsible for the blistering problem: (1) the as-received steel strip probably was incompletely pickled, which left iron-oxide scale at small isolated locations; (2) during pickling and later annealing, hydrogen was absorbed by the steel; (3) during galvanizing, the heat from the molten zinc caused the hydrogen to diffuse out of the steel; (4) at locations where surface oxides existed, the atomic hydrogen was able to recombine to form diatomic molecular hydrogen gas that raised the surface of the coating, forming the observed blisters.

To eliminate this problem, it was suggested that the surface oxides be eliminated completely. This will not prevent hydrogen absorption but should prevent the formation of gas blisters when the hydrogen diffuses out of the steel during galvanizing.

Case History 2

One section of a formed (bent) galvanized steel sheet cracked during bending. The objective of the investigation was to determine the cause of the cracking.

Visual Examination

The cracked part was observed to have been bent in two perpendicular directions as indicated by arrows (Fig. 3). A large crack is visible that had initiated at the thin edge (steel sheet thickness). The crack occurred at the outside diameter surface of the second bend where tensile stresses during forming would be expected to be greatest. The fracture surfaces of the large crack were examined with the aid of a scanning electron microscope and were observed to possess a dimpled structure that is indicative of a ductile mode of failure resulting from a tensile overload (Fig. 4).

Numerous small cracks, parallel to the primary crack, were also observed along the thin edge of the sheet (Fig. 5). This edge of the steel sheet appears to have been produced by shearing.

Transverse and longitudinal sections through the galvanized steel sheet were prepared for subsequent metallographic examination. In the as-polished condition, some sulfide inclusions were observed. Most of the cracks appear to have initiated at the surface of the material (Fig. 6), but a few small cracks were observed to have originated at subsurface sulfide inclusions (Fig. 7).

Etching with a 2% nital solution revealed the existing microstructure of the steel sheet that was found to consist of spheroidized carbide particles in a matrix of equiaxed grains of white etching ferrite. The microstructure adjacent to the edge where the cracking initiated was observed to possess highly elongated ferrite grains, indicative of the plastic tensile deformation that was produced during the shearing operation (Fig. 8).

Microindentation Hardness

A Knoop microindentation hardness survey, using a 200-g load, was performed on one of the metallographic specimens and the results are presented in Table 1. The hardness of the sheared surface was found to be significantly higher than the material at an undeformed location.

Results

The formed galvanized steel part was found to have failed as a result of cracking that had initiated at the thin edge (sheet thickness) of the sheet that was located at the outside diameter surface of a bend. The edge where the cracking initiated had been produced by shearing and possessed a plastically deformed microstructure with a hardness significantly greater than that of the undeformed base metal. The fracture surface of the large primary crack indicated that failure occurred as a result of a tensile overload.

For a ferritic steel to successfully withstand forming operations, good ductility is required.

TABLE 1 – Microindentation hardness of sheared edge

Location (millimeters from surface)	HK	Approximate HRB
Sheared Edge 0.05	253	100.4
Sheared Edge 0.10	253	100.4
Sheared Edge 0.15	234	96.6
Sheared Edge 0.20	228	95.4
Sheared Edge 0.25	203	90.4
Sheared Edge 0.30	198	89.4
Sheared Edge 0.35	186	86.5
Sheared Edge 0.40	171	82.3
Sheared Edge 0.45	161	79.0
Sheared Edge 0.50	147	74.0
Base metal	111	54.0
Base metal	111	54.0
Base metal	107	50.0

Good ductility occurs in the softer tempers of steel. The shearing, which was performed to produce the edge of the sheet, had locally cold-worked and hardened the steel. This harder material at the surface did not possess sufficient ductility to withstand the subsequent forming operations and therefore cracked.

Case History 3

Sections of two corrugated, galvanized, and painted sheet steel panels were examined. One of the panels had deteriorated in service developing both white and red rust under the paint primarily at the locations of the bends in the corrugation. The second panel was reported to be a spare panel from the original project that had never been placed in service and had been kept in an indoor environment. The material was used in an outdoor environment as roofing material for a building. The material was designed to give 20 years of service life but had begun to deteriorate after only one year.

Visual Inspection

The deterioration of the paint on the exposed panel was found to have occurred on the exterior side of the panels only at the locations of the bends in the corrugation. Furthermore, the corrosion occurred only where the bends in the corrugation placed the coating system in tension. No deterioration was observed along the flat portions of the steel sheet or where the bends in the corrugation placed the system in compression. The deterioration of the exposed panels consisted mostly, at this time, of white rust that caused the overlying paint to peel and have a blistered appearance (Fig. 9). Red rusting of the steel was observed at a few locations (Fig. 10).

The angle of the corrugation was found to be approximately 120° and the angles were not sharp.

The surfaces of the paint, at the location of the bends, were further examined using a scanning electron microscope. The surface of the paint in nonblistered areas was observed to possess a wrinkled appearance with numerous shallow, parallel furrows (Fig. 11). At locations close to where white rusting had occurred, numerous small cracks in the paint were found (Fig. 12).

Metallographic Examination

Cross sections through both the exposed and unexposed panels at the location of the bends and at undeformed areas of the panels were prepared for metallographic examination. For both panels, the steel substrate thickness was measured to be 0.864 mm (0.034 in.) with a galvanized coating 0.020 mm (0.0008 in.) thick. The primer coating was measured to be 0.005 mm (0.0002 in.) thick and the polyvinylidene fluoride (PVDF) top coat was measured to be 0.028 mm (.0011 in.) thick. Energy dispersive spectrometer (EDS) analysis of a delaminated section of the paint indicated that a chromate wash primer had been applied to the zinc prior to painting.

Etching with a 1% nital solution revealed the presence of a very thin iron-zinc alloy layer. The remainder of the galvanized coating consisted of free zinc with a hardness of approximately 54 HV. However, at all locations within the galvanized layer of the two panels, dark grain boundary precipitates were observed (Fig. 13). Away from the bend areas, the intergranular precipitates were very thin in appearance while close to the bend areas, these precipitates have a wider appearance that is attributed to internal cracking along these grain boundary films.

Immediately above some of the cracks in the galvanizing, localized plastic deformation of the paint layer was observed (Fig. 14). This localized deformation of the paint was responsible for the observed wrinkling. At other locations, cracking of the paint and intergranular cracking of the zinc was observed (Fig. 15). Uniform white rust formation was observed to be spreading away from the bend areas underneath the paint layer (Fig. 16).

The precipitates were further examined using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The intergranular precipitate in the zinc coating were found to contain iron, silicon, and calcium. Based upon the EDS analysis and the gray color of the precipitate under an optical microscope, we believe the material is an oxide impurity in the molten zinc bath that segregated to the grain boundaries during solidification. No aluminum, tin, lead, or cadmium were found within these precipitates.

Results

The white rusting of the galvanized layer and red rusting of the steel substrate appears to have been caused by a rupture of the paint film at the location of the bends in the corrugation. However, it appears that intergranular precipitates in the galvanized layer have reduced its ductility and it is the galvanized coating that cracked first and then placed stress on the paint film.

Conclusion

The art and science of galvanizing is now 150 years old. Modern improvements include continuous coating and painting of steel sheet and alloying additions, such as aluminum to improve ductility of the coating by suppressing iron-zinc layer formation. However, as with any human endeavor, actual practice can deviate from theory and produce a less than ideal product. Two of our case histories deal with such defects. Sometimes an end user of a product will erroneously blame the material for any difficulties encountered during subsequent manufacturing

operations as illustrated by our second case history. In this paper, we have shown how metallography can be used to determine the mechanism of failure of zinc-coated steel products



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