Methods and Developments in Zinc-Based Anticorrosion Coatings

M. Gore and S. Smith, *Greenkote PLC, Brook Park, Ohio*

Corrosion, particularly on iron and steel components and structures, represents a very significant cost to society. Corrosion-resistant coatings have become vital for helping to mitigate the impact of corrosion in many industries, including water systems, oil and gas, construction, military, automotive, and aircraft. Today, the issues and concerns extend well beyond corrosion. As users seek improved corrosion protection, now they are also looking for metal coatings that can provide enhanced properties such as resistance to wear and galling, better thickness uniformity, stronger surface adhesion, greater affordability, and resistance to hydrogen embrittlement of high-strength steel, all while being eco-friendly.

Zinc-based coatings, one of the oldest anticorrosion methods, is still among the most commonly used. Hot-dip galvanizing (HDG) is one of the most widely used corrosion-resistant coatings. It involves dipping a fabricated steel part into a pool of molten zinc (Figure 1). HDG was developed in the 1700s and continues to be used in many industries. It is cost effective and provides a thick coating to all exposed surfaces. The molten zinc metallurgically bonds to the surface of the part and provides good adhesion. The HDG process can accommodate a very wide range of part sizes—from construction beams and angle irons to nuts and bolts. Complicated shapes such as fastener threads, however, can suffer from nonuniform coating, and require rework on precision features. Another issue is that small components are often cleaned by pickling in preparation for HDG, and this can introduce the risk of hydrogen embrittlement (HE) to the part. Recent innovations, such as specialized alloying additives, can be utilized to enhance HDG's corrosion resistance, and techniques such as spin galvanizing can improve the thickness uniformity. Overall, HDG remains a capital-intensive and heavily regulated process because of its use of acids during pickling, zinc vaporizing from the molten pool, and leaching of lead.

Zinc Electroplating

Another widely used coating process is zinc electroplating, or electrogalvanizing. Electroplating involves placing a steel part and a zinc anode in an alkaline or acidic zinc bath through which a current is passed (Figure 2). Zinc from the anode then deposits onto the surface of the steel part (cathode) and builds a continuous layer. The thickness can be precisely controlled by the magnitude and duration of applied current, but the deposition is generally thinner than HDG because it is a slower process. Uniform coatings can be applied to complicated shapes, but features such as recesses and sharp corners can enhance or limit coating thickness as the coating grows, leading to nonuniform or limited coverage. This is due to nonuniform current density at such features—often referred to as the Faraday effect. Because the bonding mechanism is chemical in nature, the adhesion can be limited under some conditions. However, the bright, shiny appearance of zinc electroplating is sometimes considered more appealing than HDG. Zinc electroplating is often less expensive than HDG; however, it generally does not offer the same level of corrosion protection because of the thinner coating. Also, the electrolysis reactions during cleaning and plating often generate hydrogen in high-strength steels, which can be a risk or additional cost to mitigate.

Various passivation chemistries may be added after electrogalvanizing to improve corrosion resistance, appearance, or other properties of the coated part. Zinc alloys, including those with Ni, Co, and Fe, can also be used to enhance anticorrosion properties. Proprietary combinations of alloy chemistry, combined with passivation treatments, can provide good corrosion protection and visual appearance. However, as with HDG, the electrogalvanizing industry is heavily regulated because of its use of acid/alkaline chemicals, the large amounts of water consumed or treated, and the heavy metals used in alloying and passivation treatments. The overall environmental concerns associated with plating operations are potentially very severe.

FIGURE 1 HDG of fabricated steel parts.

Zinc Powder Methods

Zinc powder can be applied directly to metal parts through mechanical plating or spray metallization. In the mechanical plating process, parts are tumbled in a rotating drum with proprietary activation chemicals and a tumbling medium such as glass beads. In many instances, the components are given a prior flash plating layer as part of the overall cleaning and preparation process. The zinc powder, which is mechanically peened onto the surface of the part, forms a protective layer of zinc; but at a much lower density (typically 65 to 70% compared to HDG or electrogalvanizing). Coating uniformity can be an issue as well. High spots tend to wear in the mechanical tumbling action, and areas that cannot receive the mechanical peening action, such as holes, have limited opportunity to receive a zinc layer. Mechanical zinc is still used on high-strength steels, as it can be applied with no exposure to hydrogen and no risk of embrittlement.

In spray metallization, zinc powder or wire is melted with some type of heat source, such as an electrical arc, gas plasma, or oxyacetylene flame, and sprayed directly onto a metal component at high velocity (Figure 3). The partially or fully molten zinc particles impact the part surface and solidify into a coating that is denser than mechanically peened zinc and can approach 90% density. However, it still is not as dense as HDG or plating, and its adhesion is primarily mechanical in nature. One advantage of spray metallizing is that it can be applied in the field to coat welded or assembled structures or repair other galvanized coatings.

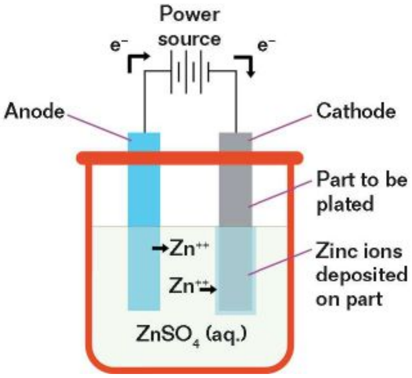

FIGURE 2 Zinc electroplating diagram.

Zinc Flake and Paint Coatings

Processes such as zinc flake or zinc paint represent a hybrid type of coating that bridges the gap between metallic and organic coatings. Zinc dust can be mixed with an organic or inorganic binder and, similar to paint, be brushed onto the surface of a part or structure to yield a zinc-rich surface layer when dried or cured. The resulting low-density coating provides some degree of barrier and sacrificial protection to the substrate. However, like paint, the zinc coating's corrosion protection and adhesion will depend on how well the substrate's surface is cleaned and prepared. A technically advanced form of this hybrid coating, often referred to as zinc or metal flake coating, is comprised of

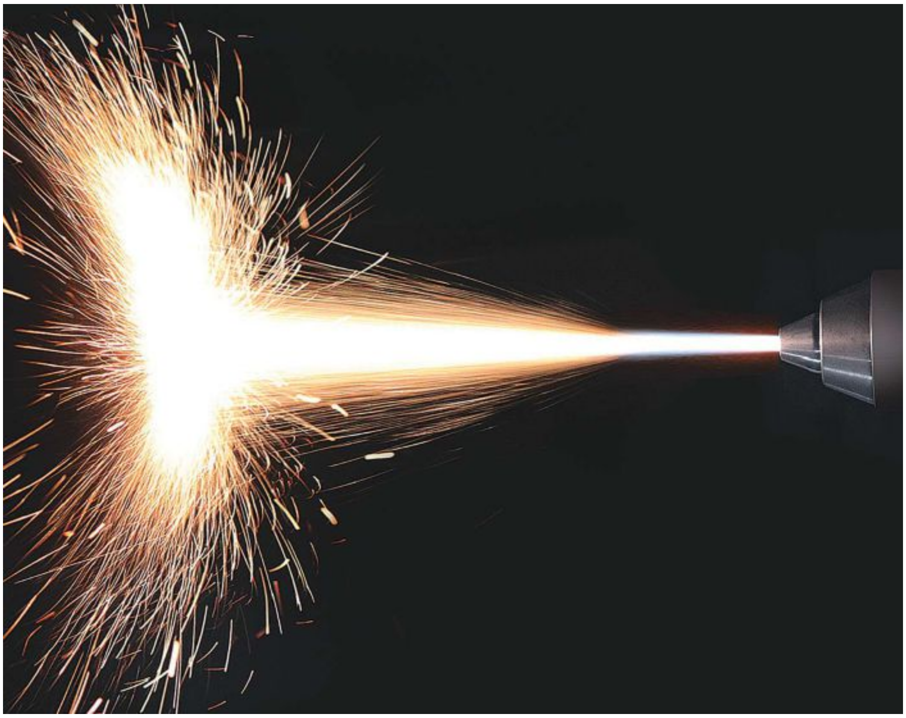

FIGURE 3 Thermal spray coating.

FIGURE 4 Comparison of zinc coatings after 500 h of salt spray testing.

proprietary formulations with zinc powder materials in combination with organic and inorganic binders and sometimes metal powders such as aluminum. These zinc flake coatings are applied using dip-spin or precision spray techniques to create a uniform coating, and they often employ specialized base layer and topcoat combinations to address specific applications and environments. The resulting coatings can provide high levels of corrosion protection with the added advantage that binders can be colored to provide a range of decorative finishes. As with all barrier-type coatings, zinc flake coatings can be vulnerable to mechanical damage and breakdown from extended exposure to ultraviolet light and weather. The solvents and other carriers used to apply these coatings also create environmental issues during the curing process, although there is an increasing push toward water-based carrier systems.

Zinc Thermal Diffusion Coating

A zinc thermal diffusion (TD) coating represents a newer, more technically advanced version of an older process called diffusion coating or Sherardizing, invented in the early 1900s by Sherard Cowper-Coles. In the original diffusion coating process, finished metal components were placed into an enclosed cylindrical drum containing a filler medium, typically sand, to which zinc dust was added. The drum was sealed, mechanically rotated, and placed into a kiln to heat the mixture to approach the melting point of zinc (419 °C). At this temperature, the zinc dust vaporized and diffused into the steel parts, building a layer of zinc-iron intermetallics across all exposed surfaces.

The Sherardizing process yielded satisfactory corrosion protection for certain applications, but the coating systems were complex and expensive and the coatings' thickness, uniformity, and density were difficult to control. Continuous charging of the zinc raw material tended to result in inclusions or regions in the coating with high iron content as well as sand entrapment, which led to inconsistent corrosion protection properties.

Modern furnace designs, often with radiant heating as well as simplification of the drum loading and charging process, have improved efficiency and ease of use for the zinc TD coating process while dramatically reducing capital costs. Companies such as Greenkote, PLC are supplying this newer generation of zinc TD coating worldwide.

Modern Zinc Thermal Diffusion Coatings

Consistent, predictable zinc TD coatings in the range of 10 to 50 µm currently can be applied with a combination of very good uniformity and density, even on parts with complex geometries. With proper drum/retort design, parts of many shapes and sizes, from a few millimeters to several meters in length, can be coated with zinc TD. Batch sizes can range from 100 to over 5,000 kg. Finely tuned control of the temperature profile, coating material charge, retort rotation, and process times can efficiently process many different ferrous materials in wrought, cast, or powder metal formats. Further innovations in equipment design have eliminated the need for sand or other filler media, so the batch size is maximized and coating inclusions are minimized. Specialized zinc-alloy chemistries also have been developed to accelerate the reaction, promote full density, and enhance corrosion resistance of the coating by generating a more robust alloyed surface oxide layer.

Modern zinc TD processing can provide excellent corrosion resistance for steel, in part because zinc-iron intermetallic structures intrinsically have better corrosion resistance than pure zinc or metallic zinc layers (Figure 4). However, the advantages of a TD coating go well beyond basic corrosion resistance: since the coating is integrally diffused into the surface of the part and provides a true metallurgical bond, coated parts can withstand deformation and still maintain corrosion protection. In addition, the Zn-Fe intermetallic structure is inherently harder than traditional metallic zinc coatings, in the range of HRC 40, which provides enhanced wear and abrasion resistance and makes the coated part significantly more damage-tolerant in the field. This increased surface hardness also reduces the potential for galling.

Since the surface coating fully reacts with the steel surface metallurgically, the coating is thermally stable up to the range of 600 °C. Because the coating is created by continued evaporation of zinc in close proximity, even complex surface geometries can be uniformly coated, including recesses and even internal diameters. The TD process also allows assembled components, such as chains or hinges, to be effectively coated while fully assembled. In addition, the zinc TD coating surface features a unique, natural microroughness (Greenkote[†], Figure 5) that enhances the adhesion of subsequent surface layers. Paints or other organic and inorganic layers can be applied to the TD surface with little or no special surface preparation. For the same reason, zinc TD surfaces are well suited for rubber overmolding and other subsequent bonding applications.

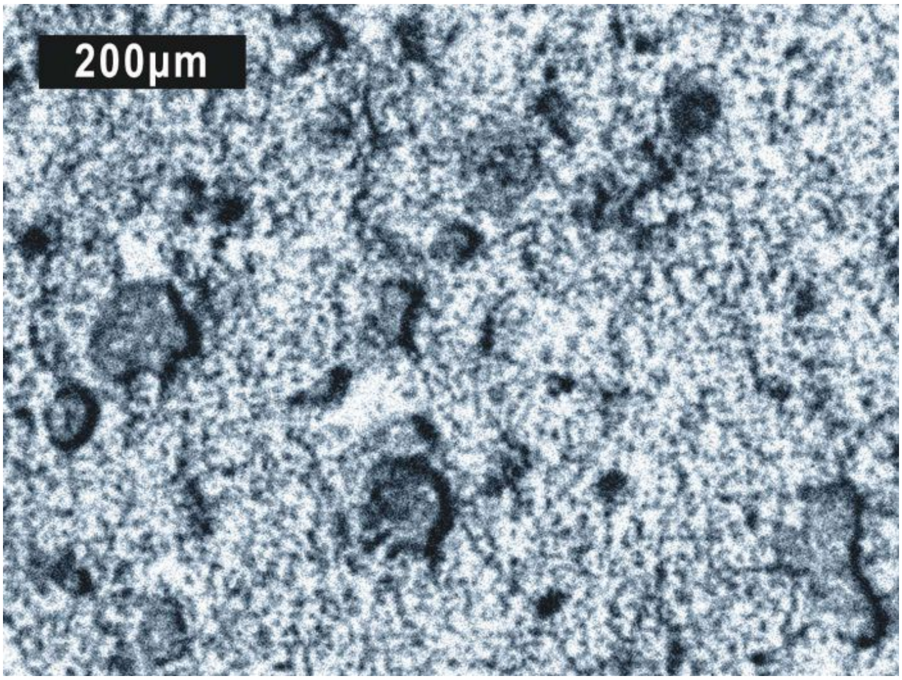

FIGURE 5 Surface of a zinc TD coating showing its characteristic microroughness.

Environmental Issues

In contrast to most of the other zinc coating processes, zinc TD is inherently clean and environmentally benign. The process uses no solvents, acids, or complex gases and requires very little process water except for post-cleaning, and even that water can be cleaned and reused. The process does not involve any dangerous chemicals and contains no heavy metals such as Cr, Ni, Cd, or Co, which are experiencing increased regulatory scrutiny. The only process waste is a minimal amount of zinc oxide (ZnO) dust, which can be collected and recycled or sold as a raw material to other industries.

Conclusions

Because of its strength, ductility, and toughness, as well as recyclability, steel is likely to remain the material of choice for a great many applications for years to come. While corrosion is still a significant vulnerability for steel, modern zinc-based coatings continue to mitigate the problem and extend the life of this very useful metal. Developments in zinc-based protective coatings are ongoing, and advances for the zinc TD coating in particular have positioned it to play an even stronger role in the future. This new generation of coating is bringing superior corrosion protection along with increased wear and galling resistance, excellent adhesion, conformal coverage of complex shapes, and elimination of HE—all while remaining eco-friendly.

MARK J. GORE is president and chief executive officer of Greenkote Plc, 6435 Eastland Rd., Brook Park, OH 44142, e-mail: mark.gore@greenkote.com. He has 30 years of experience in the areas of coatings and surface modification technologies in the steel, battery, synthetic diamond, semiconductor, oil and gas, and anticorrosion industries. He has a B.S. degree in metallurgical engineering from the University of Cincinnati and a Ph.D. in metallurgy from the Massachusetts Institute of Technology. A member of NACE International, Gore is a member of the ASTM Metallic-Coated Iron and Steel Products A.05 Technical Committee.

SEAN SMITH is the engineering manager at Greenkote Plc, e-mail: sean.smith@greenkote.com. He has worked in the foundry industry for 10 years as a metallurgist and operations manager. He joined Greenkote in early 2015. He has a B.S. degree in materials science and engineering from The Ohio State University. He is a member of NACE International. MP

[†]Trade name.