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NEXT GENERATION TECHNOLOGY FOR CORROSION PROTECTION IN GROUND SUPPORT ELEMENTS

David William Evans

ABSTRACT: Corrosion in ground support elements remains an important area for industry focus, given the immediate concern for mine safety and operational efficiencies, as well as the hidden cost of longer term rehabilitation work. This paper discusses emerging 'next generation' technology within the field of corrosion protection, providing new solutions for specific application areas of ground support product design.

Traditionally, anti-corrosion strategies have predominantly focussed upon Hot Dip Galvanising as a common industry solution. However, now complimenting this traditional solution, the more recent technology of Thermal Zinc Diffusion Galvanising is gaining interest within the Australian market, providing commercially viable solutions for a number of specific application areas that Hot Dip Galvanising cannot address.

Thermal Zinc Diffusion Galvanising is an alternative zinc based technology, which offers equivalent cathodic protection to that of Hot Dip Galvanising. Thermal Zinc Diffusion Galvanising has a comparatively deeper metallurgical bond to the steel substrate through various zinc-iron alloy layers, offering both increased adhesion and greater surface hardness. Beyond the capabilities of Hot Dip Galvanising, Thermal Zinc Diffusion Galvanising has specific applications of interest in high tensile steel grades, coating thickness consistency for threadforms, excellent torque / tension performance and greater flexibility with deformation. Thermal Zinc Diffusion Galvanising also continues to provide spark reduction properties on friction contact.

This paper provides a technical overview of the attributes of Thermal Zinc Diffusion Galvanising and its relative performance compared to that of Hot Dip Galvanising. Application of Thermal Zinc Diffusion Galvanising to ground support elements is then reviewed, relating the new technology to specific product design areas and field applications.

INTRODUCTION

Ground support failure due to corrosion mechanisms is a well-known and documented phenomenon within the mining industry globally (Villaescusa, *et al.*, 2007). Earlier efforts have been made to document the prevalence of ground collapse due to corrosive mechanisms (Potvin, *et al.*, 2001), however, it is anecdotally claimed that current industry performance more reflects the effectiveness of rehabilitation efforts, rather than actual improvements in corrosion protection technology. While specific mines will have an understanding of their strata conditions and rehabilitation needs, from an industry perspective, the impact of corrosion in ground support tends to remain a hidden cost.

As such, corrosion protection continues as an important focus area in underground roof support. Technologies are now evolving that offer new solutions within this field. Specifically, Thermal Zinc Diffusion Galvanising (TZD) is an area of technology that holds increasing interest, providing a growing number of niche solutions for strata control products. While TZD is actually a maturing technology (ASTM International, 2008) (British Standards Institution, 2003) (Roads and Maritime Services, 2012a) (Roads and Maritime Services, 2012b), specific mining industry knowledge is currently in its early stages, with further potential to explore applications in this area.

This paper provides a technical introduction to TZD, including an overview of its various properties and performance. This coating technology is then related to recently developed product applications, with the system now being applied to meet the specific demands of corrosion protection in mine site strata control.

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THERMAL ZINC DIFFUSION GALVANISING

Process history

TZD derives its technical origins from within Sherardising, also referred to as Diffusion Galvanising. The process was originally developed by the British metallurgist Sherard Cowper-Coles in 1901, based upon heating powdered zinc metal within the presence of the targeted host material and within the confines of an enclosed atmosphere (Figure 1). The zinc atoms diffuse into the surface structure of the host material, creating a specific sequence of alloyed zinc-iron layers. While the original application systems were complex and expensive, the technology has since evolved into a number of commercially viable industrial applications. TZD is the most current modern format of this technology, employing more advanced powder technologies and post application or 'top coat' treatments to provide enhanced corrosion protection performance.

Similar to sherardising, TDG involves tumbling componentry within a cylindrical drum, placed under a slow, constant axial rotation within a heated kiln. Zinc rich powders and other filler media are pre-dosed into the drum along with the targeted host material, which is then sealed to provide an air tight internal atmosphere. The zinc atoms sublimate, or vaporise on the substrate surface just below their melting temperature and progressively diffuse into the targeted host material. The kiln temperature is generally around 400°C and does not exceed the melting point of zinc. The combination of constant diffusion and drum rotation results in surface coating thicknesses that are consistent and evenly applied. Controlled parameters include the constituency of the zinc powders, the dosage quantity, the applied temperature cycles and rotation time. As such, coating thickness can be readily calibrated to suit finer product geometries as well as the grade of the targeted material.



Figure 1 - An image of an original sherardising plant, circa 1916, with processing drums and kiln visible

Beyond the capability of earlier Sherardising processes, modern TZD consumes less zinc input, permitted by improved diffusion efficiencies. The new powder technologies can be applied at lower kiln temperatures, reducing energy requirements. Coating thicknesses can be controlled through a greater range, from 20 to 120 microns, an improvement from the original 15 to 35 microns. The new technology has been used to coat products up to 12 metres in length, rather than small batch items only, as shown in Figure 2.



Figure 2 - A modern thermal zinc diffusion galvanising plant, capable of handling products up to 12 metres in length

Technical characteristics

Both Hot Dip Galvanising (HDG) and TZD result in a specific sequence of metallurgical layers that are bonded with the host material. However, there are a number of differences in the resultant chemistries between the two galvanising methods, which produce different physical attributes.

A typical microscopic cross section for HDG is shown in Figure 3. At the surface is the Eta layer, which contains pure Zinc (Zn) and no iron alloys. The second layer is the Zeta alloy layer, containing up to 6% Iron in the form of FeZn₁₃ molecules. The third layer is the Delta alloy layer, containing 7 – 11 % Iron in the form of FeZn₇ molecules. The fourth layer is the thin Gamma alloy layer, at 21 – 28 % Iron - this is a solid solution of Fe and Zn atoms about 1 micron thick. The entire coating thickness is approximately 125 microns and the base steel is visible below the Gamma alloy layer. The zinc / iron alloy layers comprise 60 to 70 % of the coating.

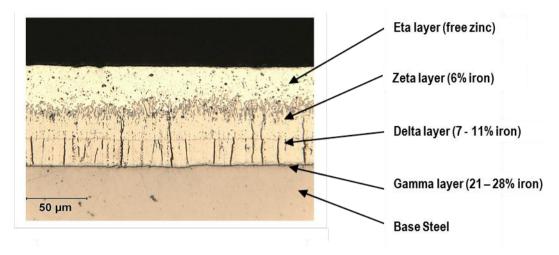


Figure 3 - A typical hot dip galvanised coating microstructure on structural steel (Industrial Galvanizers, 2006)

TZD is the only other coating where the zinc alloys with the iron in the steel substrate and forms the same three alloy layers as HDG, as shown in the micrograph of Figure 4. The predominant difference is the greater concentration of iron across the various alloy layers. There is no Eta or free Zinc layer – the first layer is actually the Zeta alloy layer with 7 – 10% Iron content in the form of FeZn₇ molecules. The second layer is the Delta alloy layer with 25% Iron content in the form of Fe₁₁Zn₄₀ molecules. The third layer is the Zn/Fe solid solution Gamma layer with 50% Iron content.

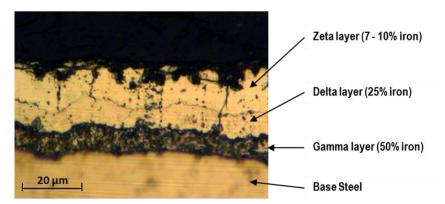


Figure 4 - A typical thermal zinc diffusion galvanised microstructure. Note the more fully alloyed microstructure and absence of the Eta free zinc layer (ArmorGalv, 2009)

A HDG coating is formed in a matter of minutes, which gives the zinc atoms only a short period of time to diffuse into the steel substrate and form the required alloy layers. This results in an almost non-existent Gamma layer of about 1 micron thickness and alloy layers with very low iron content. TZD coatings are formed over a period of 60 to 120 minutes, resulting in a 10 micron Gamma layer which is diffused into the steel substrate and a Delta and Zeta layer with much higher iron contents. The crystalline Delta and

Zeta molecules have the same hexagonal structure and form the same geometric, columnar appearance, but they have more iron atoms due to the longer diffusion process.

The more heavily alloyed the zinc is with iron, the denser and more stable the alloy structure. This provides improved performance properties – corrosion resistance and increased hardness - over a greater period of time. Table 1 shows the respective chemistry differences in the layers between HDG and TZD (Industrial Galvanizers, 2006; ArmorGalv, 2009; Kainuma and Ishida, 2007).

Table 2 shows the respective physical differences in the layers between HDG and TZD (Industrial Galvanizers, 2006; Swain, 2010).

Properties and performance

Due to the unique surface chemistry and microstructure differences, TZD has a set of physical properties that are distinctive in comparison with HDG. These differences permit TZD to offer anti-corrosion solutions in a number of niche areas of application. The following paragraphs provide a summary of these comparative differences with reference test information.

Table 1 - Comparative chemistry– HDG and TZD

Alloy Layer	Hot Dip Galvanising	Thermal Zinc Diffusion Galv.
Eta	100% Zn	None
Zeta	6% Fe (FeZn ₁₃)	7–10 % Fe (FeZn ₇)
Delta	7–11 % Fe (FeZn ₇)	25 % Fe (Fe ₁₁ Zn ₄₀)
Gamma	21–28 % Fe (Solid Solution)	50 % Fe (Solid Solution)

Table 2 - Comparative physical properties – HDG and TDG

Alloy Layer	Hot Dip Galvanising	Thermal Zinc Diffusion Galvanising
	Hardness / Microstructure	Hardness / Microstructure
Eta	70 HB / Spherical Nodes	None
Zeta	220 HB / Coarse Hexagonal Crystals	300 HB / Coarse Hexagonal Crystals
Delta	270 HB / Fine Hexagonal Crystals	350 HB / Fine Hexagonal Crystals
Gamma	Too Thin to measure	600 HB / Dense Diffusion Band

Corrosion resistance

The fundamental property of corrosion resistance for TZD coatings has been rigorously examined through laboratory tests and field trials. Neutral salt spray testing (Alvey, 2002) applied to identical base metal componentry, alternately coated in TZD and HDG, then tested in accordance with ISO9227:1990 (International Organisation for Standardisation, 1990), showed less white and red corrosion product and less corrosion overall for items coated with TDG in comparison to HDG coated items. HDG coatings had 250 hours to red rust, while TZD coatings had 1,000 hours to red rust. Salt spray testing conducted to AS2331.3.1-2001 (Standards Australia, 2001) on roof bolt material (Jeffrey, 2010) also revealed improved comparative performance for TZD, as indicated in Figure 5. The left hand image is HDG coated, while the right hand image is TZD coated - while corrosion is evident on both samples, the TZD coated roof bolt exhibited less mass loss of the original coating.



Figure 5 - Images from 1 000 hour neutral salt spray testing, conducted on the same grade of high tensile roof bolt material (Jeffrey, 2010)

Accelerated weather exposure testing conducted by the CSIRO at its Port Fairy facility has proven that the corrosion rate of pure zinc is more than double that of zinc–iron alloys (Fullston, *et al.*, 2004). Given that the TZD chemical structure has no free zinc, as well as a higher percentage of alloyed iron, TZD has a lower coating mass loss rate than of pure zinc under a given corrosive action. Correspondingly, a TZD surface will require less zinc and a lower coating thickness for equivalent performance. Based on this, a 50 micron TZD coating will typically offer equivalent anti-corrosion performance to a 100 micron HDG treatment, when subjected to equivalent environmental conditions.

Field trials conducted by the US Navy have also been recently completed, indicating that TZD has superior anti-corrosion performance to that of HDG (ArmorGalv, 2012). Comparative trials involving TZD, HDG and Zinc Electroplating were conducted on the cargo tie-down componentry of hovercraft landing vessels, being subjected to extreme salt spray operating conditions over a 22 week period. The positive outcomes from this trial resulted in TZD being formally approved for use by the US Navy for fasteners and hardware in Steel Grades up to 1,000 MPa in tensile strength (Department of the Navy, 2011).

Moderate acidic conditions

A growing body of evidence suggests that TZD may outperform HDG in moderate acidic environments. Copper Accelerated Salt Spray (CASS) Tests have been conducted under ISO 9227: 2006(E) (*International Organisation for Standardisation*, 2006) by a NATA certified laboratory (Fahey, 2013), subjecting identical parent metal componentry, alternately coated in TDG and HDG, to continuous testing in an acidic salt spray environment at pH 3.1 (acetic acid). The results of this severe testing regime appear in favour of TZD over HDG, displaying less coating mass loss. However, it must be clearly noted that both TZD and HDG do not offer any long term anti-corrosion performance in low pH environments (Galvanisers Association of Australia, 2011). Validation testing is required to test the impact of site specific acidic conditions.

Coating thickness consistency / threadforms

The process of TZD provides a uniform coating thickness that follows the contours of the componentry exactly – there is no solidifying zinc at the surface, as apparent with HDG. The consistency of the surface is produced under the diffusion action of the zinc atoms into the base metal, assisted by the slow rotation of the componentry and zinc powder within the cylindrical kiln. The coating thicknesses are governed by ASTM A1059 2008 (ASTM International, 2008). Coating classes range from 20 to 120 microns, defining the target coating thickness. For the most common coating thickness of 50 micron, thickness variance is typically between 45 and 60 micron.

Coating deformation

The depth of diffusion of zinc atoms into the steel substrate with TZD creates a Gamma layer typically 10 microns thick. This equates to extremely high adhesion in comparison to HDG and allows very fine cracking under deformation of the parent metal observed within the Gamma layer. This fine cracking permits flexibility of the TZD layers, without impacting on the adherence of the zinc – iron alloy layers to the base metal. As a result, moderate deformation of the base metal does not reduce the cathodic protection offered by TZD, and equally does not weaken the surface structure or result in loss of the bonded zinc-iron alloy content. Under extreme deformation, a low percentage of the coating will be lost via the cracks propagating to the coating surface, with some of these fissures dislodging and falling out.

Hardness and anti-abrasion

The layers of TZD typically exhibit hardness values greater than that of the parent material. Surface hardness results typically exceed 35 Rockwell C, as referenced within ASTM A 1059/A 1059M – 08 (ASTM International, 2008). A series of Vickers micro hardness tests conducted on a TZD treated high tensile steel grade produced 605 (HV) in the gamma phase and 375 (HV) in the delta phase, relative to a value of 327 (HV) in the parent steel (Swain, 2010). The increased surface hardness values from TZD result in excellent wear resistant properties.

Anti-galling

Galling is defined as localised surface deformation between two solid sliding surfaces under heavy friction contact, distinguished by microscopic, usually localised, roughening and creation of protrusions

above the original surface (ASTM International, 2006). Due to increased hardness and wear resistant properties, TZD provides good anti-galling properties, predominantly facilitated by the absence of free zinc at the outer surface. Anti-galling performance has been witnessed by the long term use of TZD treatments within the componentry of hydraulic long-wall props in the United Kingdom (Bodycote, 2006). Given the corrosive, acidic and abrasive environmental conditions of coal mining under the North Sea, TZD has been employed in the main hinge pins of longwall props as a solution to also reduce galling and seizing problems.

Torque / tension performance

The uniform surface thickness of TZD, combined with good hardness and anti-galling properties, means that TZD is highly suitable for use with thread-forms. Torque / tension ratios are a significant product performance consideration - the efficiency to induce tension in the thread-form, relative to the applied torque. Testing undertaken by the NSW Roads and Maritime Services indicates that TZD provides a better torque tension performance compared to uncoated steel (Roads and Maritime Services, 2012a) (Roads and Maritime Services, 2012b).

Anti-sparking

Sparking in ferrous metals is caused under the combined action of two mechanisms. The first mechanism is friction, creating localised heat to generate a spark – dependent upon velocity, pressure, surface roughness and levels of oxidation. The second mechanism is abrasion, generating fine particles of iron, which are small enough to self-ignite in the presence of oxygen. Zinc alloys are known to provide anti-sparking properties (International Zinc Association, 2011), acting as a surface barrier to prevent both friction and abrasion of the parent ferrous metal. TZD has been used as an anti-sparking coating within coal mining applications, to meet the risk demands of this environment. Tailored anti-sparking tests should be conducted to validate the effectiveness of the application.

Corrosive compatibility

Components from TZD and HDG surface treatments are compatible when placed in direct contact and will not result in bi-metallic preferential corrosion (British Standards Institute, 1990). Such combinations have been employed frequently in civil structural applications, taking advantage of the properties of TZD for fastener components, as well as the common application of HDG for large fabricated steel sections.

High tensile steel grades

TZD is suitable for use with high tensile steel grades, as the concern for hydrogen embrittlement is removed due to the nature of the process (Roads and Maritime Services, 2012a) (Roads and Maritime Services, 2012b). Hydrogen embrittlement is caused by the adsorption of hydrogen atoms into the steel matrix, with the trapped 'H' atoms subsequently forming 'H₂' gas molecules within the steel structure, resulting in extreme internal stresses. Steel grades at tensile strengths greater than 800 MPa are typically at risk of hydrogen embrittlement due to the acid pickling associated with surface preparation for HDG (Industrial Galvanizers, 2006). TZD does not employ acid pickling, but typically utilises shot blasting for surface preparation – permitted by the greater diffusion time and increased development of the TZD gamma layer.

Surface adhesion to topcoats

The TZD treatment has a porous, textured micro structure at the outer surface of the Zeta phase. This porous surface structure facilitates the adhesion of further applied topcoats over the TZD treatment, such as paint, powder coating and rubber lining. Given the absence of the Eta phase, applied topcoats penetrate directly into the porous TZD Zeta phase. The excellent bonding characteristics between TZD and applied topcoats are also referenced within ASTM A 1059/A 1059M - 08 (ASTM International, 2008) and BS EN13811:2003 (British Standards Institution, 2003).

APPLIED GROUND SUPPORT SOLUTIONS

The unique attributes of TZD permit solutions for anti-corrosion in mining roof support products, specifically in a number of niche areas of application. A number of specific product applications are outlined within the following section, providing working examples of use.

High tensile bolts

High tensile steel grades are commonly employed for mining roof support elements, more specifically in coal applications, where specialised steels have evolved to meet increased load bearing demands. For primary roof bolting in coal, steel grades are now employed with ultimate stress values typically at 920 MPa - exceeding the 800 MPa threshold where hydrogen induced stress corrosion cracking becomes a risk factor. The acid pickling process used for surface preparation prior to HDG is known to induce hydrogen embrittlement. Alternatively, TZD offers a galvanising solution that avoids the need for acid pickling – of particular interest for corrosion protection applications in high tensile bolts.

A further benefit arising from TZD in roof bolts is the increased surface adhesion associated with the gamma diffusion layer. Under shear and tensile action, roof bolts will deform – TZD provides greater adherence to the surface of the parent metal, compared to HDG having a thinner gamma layer. An additional benefit for roof bolts is the ability for TZD to conform to the surface dimensions of the bar – both to the threadform, as well as to the ribbed bar profile. The higher abrasion resistance of TZD also reduces coating damage during installation and rotation of the bolt within the bore hole. A typical coated bolt is shown in Figure 6.

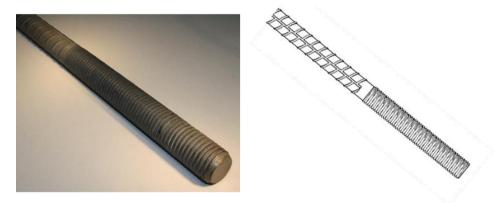


Figure 6 - TZD coated high tensile roof bolt – photographic image and product pictorial

Meshing plates

Meshing plates, as shown in Figure 7, are secondary plates used to secure mesh sheets to pre-installed roof bolts. A common form of meshing plate incorporates a threaded fastener – in this format, the plate must be rotated to engage the fastener with the threaded roof bolt. Where black steel mesh sheets and black steel meshing plates are used, it is possible to induce sparking as the rotating meshing plate contacts and bears load against the mesh surface. Within coal mining environments, incendive sparking is a major risk which must be mitigated. TZD has been utilised to provide a solution for this risk - the TZD surface provides a barrier to friction and abrasion of the parent metal of the rotating plate. Specific testing was conducted for this application to validate the level of sparking reduction at the required rotational speed and pressure. Additionally, the presence of the threaded fastener as an integral component of the meshing plate places the requirement that the thread-form cannot be fouled by the applied coating. Again, TZD provides the correct coating thickness consistency to achieve this outcome for the thread-form.

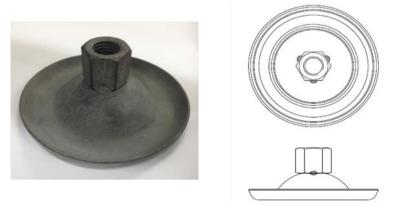


Figure 7 - TZD coated mesh express plate – photographic image and product pictorial

Nuts and couplers

Threaded devices are an integral feature of many roof support products – in the obvious form of nuts and coupling devices. TZD provides an immediate solution for corrosion protection in nuts and couplers – with the benefit of controlled, consistent coating thickness on both the inner thread profile and the outer body of the component. HDG of female thread-forms is notoriously difficult due to the build-up of excess galvanising material on the internal form. Alternatively, the dimensional consistency of TZD coatings greatly reduces the instance of interference during engagement of the male and female threads. A further benefit is the compatibility of TZD with HDG based on bi-metallic corrosion compatibility. This means that low tensile roof bolts can be treated with HDG if desired, while the corresponding nut or coupler can be treated with TZD to improve dimensional fit. A typical arrangement is shown in Figure 8.



Figure 8 - TZD coated M24 nut – photographic image and product pictorial

CONCLUSIONS

TZD is an emerging technology of great relevance and potential within the field of corrosion protection for ground support elements. Multiple test cases indicate that TZD has at least equivalent anti-corrosion performance to HDG, but also provides improved attributes in the areas of surface consistency, compatibility with high tensile steels, application with thread-forms and surface adherence under abrasion and deformation. There is some evidence to suggest that TZD may provide improved performance in mild acidic conditions, relative to HDG. However, for low pH environments, zinc based protection systems such as HDG and TZD are not suitable and will degrade rapidly.

While traditional methods of corrosion protection will continue to be employed within the industry, TZD is an area of technology that can provide solutions for a growing number of niche application areas. As knowledge of this technology is deployed across the mining industry and experience with specific product applications continues to progress, TZD has the potential to become a routine consideration within the suite of anti-corrosion solutions for mining strata control.

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