

Benchmarking of Zinc Coatings for Corrosion Protection: A Detailed Characterization of Corrosion and Electrochemical Properties of Zinc Coatings

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Due to various types of Zn coatings for many decades for various applications, it is imperative to study and compare their corrosion resistance properties of some of these. Here, we introduce a systematic methodology for evaluation and validation of corrosion protection properties of metallic coatings. According to this methodology, samples are exposed in an advanced cyclic corrosion test chamber according to ISO 14993, and removed at the end of each withdrawal for respective corrosion and electrochemical characterization to evaluate both barrier and galvanic protection properties. Corrosion protection properties of coatings were evaluated by visual examination according to ISO 10289, mass loss and subsequent corrosion rate measurements, electrochemical properties, and advanced electrochemical scanning techniques. In this study, corrosion protection properties of a commercial zinc rich coating (ZRC) on AISI 1020 mild steel substrates were evaluated and benchmarked against hot dip galvanized (HDG). Results were correlated, and corrosion protection capabilities of the two coatings were compared. The zinc rich coating performed better than hot dip galvanized coating in terms of overall corrosion protection properties, according to the exposure and experimental conditions used in this study. It proved to be a suitable candidate to replace hot dip galvanized coatings for desired applications.

Keywords: steel, zinc coatings, accelerated exposure, corrosion characterization techniques

1. Introduction

Zinc coating usually serves two functions in terms of corrosion protection.

- Barrier protection (coating acts as a barrier to the environment) thus prevents interaction of the substrate metal with the environment. While a fresh zinc surface is quite reactive when exposed to natural wet and dry cycles in the atmosphere, zinc corrosion products develop rapidly on the surface. These dense and less soluble corrosion products, act as an additional barrier between the steel and the environment.

- Galvanic protection (cathodic or active protection): Zinc will provide sacrificial protection of substrate. Underling steels exposed at scratches or cut edges are galvanically protected by the sacrificial corrosion of a zinc-bearing coating. This occurs because Zinc is more electronegative (more reactive) than steel in the galvanic series. This unique property extends the protection duration of the substrate [1,2].

There are various types of zinc based coatings used for different applications, galvanizing and zinc rich coatings / paints are the two main clusters in the market. Hot dip galvanising (HDG) is one of the oldest methods used to apply zinc based coatings on steel. Zinc is applied on the steel by continuous or batch immersion (hot dipped) of the steel in the molten zinc bath. Despite the popularity of the HDG, there are few drawbacks which limit its use for some applications, such as limitations and problems arise with the need of a plant for the coating process, losses due to transportation, potential negative environmental impacts. Zinc rich coatings/paints are mainly made out of sacrificial zinc pigments in binders. This is a class of metal rich coatings which gives both barrier and galvanic protection to the underlying metal substrates. Various zinc rich coatings with diverse modifications have been introduced and are investigated for their corrosion protection performance by different research groups [2-13]. The zinc dust (usually spherical or lamellar shape or combination of both) is dispersed in an inorganic or organic binder (usually epoxies) [6]. These zinc particles must be in electrical contact between themselves and steel sub-

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strate in order to ensure the galvanic protection. It is vital to study and validate the corrosion protection capabilities of such coatings before being used for various applications or replaced HDG. One such commercial coating is used in this study.

It is equally important to select and design corrosion characterization techniques and methods carefully for such a study to achieve a reliable correlation of coatings' real time corrosion protection performance. Although many works have been conducted on corrosion protection evaluation of zinc coatings, there is a need to establish a systematic approach based on reliable standardized exposure together with a set of comprehensive evaluation techniques and methods. Lack of recorded information on the special zinc rich coating used in this study further motivated the current work. This is because of the thriving need by Singapore industrial sector to assess and benchmark the corrosion protection properties of this particular zinc coating against HDG due to the competitive nature of two types of coatings. Therefore, a systematic methodology for evaluation and validation of corrosion protection properties of metallic coatings based on scientific principles and international standards is introduced in this work. This methodology was used to evaluate both barrier and galvanic protection properties of this commercial zinc rich coating and compare the performance with hot dip galvanized coating (HDG).

2. Experimental Procedure

2.1 Coatings and substrate

Plain carbon steel AISI1020 is selected as the substrates which has a nominal composition of ferrous 99.08 - 99.53%,

Table 1 Major elements present in the composition of ZRC and hot dip galvanised coatings (according to X-ray fluorescence spectrometer)

| Element | Content % | |
|--|-----------|-------|
| | ZRC | HDG |
| Zinc, Zn | 99.68 | 97.97 |
| Silicon, Si | 0.14 | 0.09 |
| Iron, Fe | 0.06 | 0.43 |
| Aluminium, Al | 0.52 | 0.52 |
| Chlorine, Cl | 0.03 | 0.14 |
| Lead, Pb | 0 | 0.59 |
| Other elements (Chromium, Calcium, Sulphur etc.) | Rest | Rest |

carbon 0.17 - 0.230%, manganese 0.30 - 0.60%, phosphorous $\leq 0.040\%$ and sulfur $\leq 0.050\%$. Two types of zinc coatings were selected namely hot dip galvanized (HDG) and commercial zinc rich coating from ZINGA® METALL(S) Pte Ltd (which is referred as ZRC in this manuscript hereafter). Nominal compositions of two types of coatings (as prepared) were analysed by X-ray fluorescence (XRF) spectrometer to verify the major elements present and confirm the zinc richness, major elements present are given in the Table 1 below.

Thicknesses of the coatings were measured using the thickness measurement gauge (Elcometer Coating Thickness Gauge) according to the industrial practice. Thicknesses measured for all samples for both types (initial form of coatings before any exposure) were in the range of 130 to 150 microns. Therefore, average thickness values of two types of coatings are similar. Thickness of coatings were further varied using scanning electron microscopy (ZEISS FESEM Ultra Plus) cross sectional analysis (results are not presented in this paper)

2.2 Methodology

A methodology has been introduced in this work based on international standards and scientific principles to evaluate corrosion protection properties of metallic coatings. According to this methodology, samples were exposed to a cyclic corrosion test. A set of samples has been removed at each withdrawal for a series of corrosion and electrochemical characterization to evaluate both barrier and galvanic protection capabilities of coatings. Details are given in next sections.

2.3 Accelerated exposure of samples

To assess the corrosion protection properties of two types of coatings, first those should be exposed to a reliable accelerated exposure. Accelerated cyclic corrosion test according to ISO 14993 (Accelerated testing involving cyclic exposure to salt mist, "dry" and "wet" conditions), was chosen and the Atlas CCX 2000 Advanced Cyclic Corrosion Test Chamber was used. Total 4 withdrawals were chosen to comply with the standard (Table 2). The test cycle starts with exposure to salt mist containing 5% NaCl at 35 °C for 2 hours followed by 4 hours of drying at 60 °C and finally 2 hours of high humidity at 50 °C. A set of samples has been withdrawn at each withdrawal for a series of corrosion and electrochemical characterization.

2.4 Assessment of corrosion protection by visual examination

Two sets of samples with and without scribes have been used for visual examination. Samples without scribes were used to assess the degree of substrate corrosion in accord-

Table 2 Durations of 4 withdrawals

| Withdrawal | Duration |
|------------|-------------------|
| 1 (W1) | 30 cycles (240 h) |
| 2 (W2) | 45 cycles (360 h) |
| 3 (W3) | 60 cycles (480 h) |
| 4 (W4) | 90 cycles (720 h) |

ance to ISO 10289 (Methods for corrosion testing of metallic and other inorganic coating on metallic substrates) whilst without scribes to assess the galvanic protection upon exposure. Three samples of each coating were used at each withdrawal for either assessment.

2.5 Mass loss and corrosion rate assessment

Mass loss of zinc due to formation and dissolution of its corrosion products was done by removing those products by chemical pickling using saturated glycine solution. The treatment was done in an ultrasonic bath and the total mass loss was calculated in accordance to ISO 8407 (Removal of corrosion products from corrosion test specimens). The samples were inserted vertically into the pickling solution and they were cleaned at an interval of 1 minute until no significant mass loss was observed. Corrosion rate measurements were obtained based on mass loss under above mentioned accelerated exposure conditions and used as a measure of uniform corrosion rate.

2.6 Electrochemical investigation

Electrochemical Impedance Spectroscopy (EIS) is widely used to evaluate the protective properties of coatings and the mechanism of corrosion protection. Impedance values can be used as a guide to characterise corrosion protection properties of coatings. As an example, total impedance of a system is an indication of its overall corrosion resistance [2,5].

EIS was conducted by ACM field machine using standard three electrode system; HDG or ZRC sample as the working electrode, Ag/AgCl as the reference electrode and a graphite rod as the counter electrode. Samples were gently washed before each experiment after withdrawn from the accelerated cyclic corrosion test chamber to remove any excess salt deposited on the surface. Open circuit potential was measured for 30 minutes before EIS measurement. Measurements were carried out at open circuit voltage by applying a sinusoidal voltage of 10 mV and the spectra was recorded in the frequency range of 0.1 Hz to 0.1 MHz. Experiments were done in 5 wt% NaCl. Total im-

pedance at 0.1 Hz ($Z_{0.1\text{Hz}}$) was measured against the exposure time (at each withdrawal) and used as guide to compare the corrosion protection properties of two types of coatings.

2.7 Scanning Vibrating Electrode Technique (SVET)

Scanning vibrating electrode technique (SVET) which is a non-intrusive scanning technique invented to study localized electrochemical details and corrosion activities. SVET was conducted on ZRC and HDG samples with "X" scribes to expose the plain carbon steel substrate surface on the scribed area. Scribe was made in the middle of the sample. Exposed area of the sample was around 2.8×2.8 cm and the rest of the areas were insulated. Samples were exposed to cyclic corrosion test as explained in the Section 2.3. SVET was conducted after each withdrawal on same samples repeatedly for quantifying and comparing corrosion activities along the exposure time. (One set of ZRC and HDG samples were repeatedly used, after completion of each SVET, samples were re-introduced for the rest of the cyclic corrosion exposure). Samples were gently washed by tap water before each SVET scan (after withdrawing from the chamber) to remove any salt deposited on the samples.

The SVET scans were performed at free corrosion potential with the samples immersed in tap water having the conductivity in the range of 220 - 250 μS . The amplitude of probe vibration was 30 μm , at a frequency of 80 Hz. The M370 SVET system by Uniscan Instruments was used.

Scanning electron microscope (ZEISS FESEM Ultra Plus), X-ray fluorescence (XRF) spectrometer (XRF1800) and energy dispersive X-ray spectroscopy (EDX) were used as supplementary information to support thickness, morphology and compositional details.

3. Results and Discussion

Results of each experimental technique/procedure are given in this chapter. First, three possible corrosion scenarios are explained briefly followed by results and analysis of each corrosion characterization method used in this work.

3.1 Corrosion mechanisms on zinc coatings

When zinc coated mild steel sample (in this case ZRC and HDG) is exposed to an environment, sample will interact with atmospheric constituents. Three main corrosion scenarios are illustrated briefly below as Case 1, 2 and 3. The rest of the results of this project are explained based on these three cases

Case 1: Corrosion of fresh zinc coating without defects

Fresh zinc surface is quite reactive when exposed to the atmosphere. Zinc corrosion products develop rapidly on the surface as the coating is exposed to natural wet and dry cycles in the atmosphere.

Two electrochemical reactions; anodic reaction of zinc oxidation and most probable cathodic reaction of oxygen reduction take place on the zinc coating to complete the corrosion process.

Anodic reaction:



Cathodic reaction:



Dense and less soluble corrosion products of zinc, act as an additional barrier between the steel and the environment. Under this scenario, the base mild steel substrate is protected from corrosion. The main zinc corrosion products on this case can be zinc oxide, zinc hydroxide, zinc carbonate (more protective than zinc hydroxide), zinc hydroxycarbonate complexes etc. [12-14].

Case 2: Corrosion of damaged zinc coating

When a damaged (or zinc coated sample with an artificial defect) exposed to the environment, underlying steel is galvanically protected by zinc layer. Anodic reaction which is oxidation of zinc (reaction 1 under Case 1) occurs on zinc surface whilst the cathodic reaction (e.g. oxygen reduction) occurs on the steel surface. Underlying steel is largely protected by corrosion (rusting) with the availability of sufficient amount of zinc together with good conductivity along zinc and between zinc layer and substrate. By prolong exposure, corrosion products of zinc may form along the damaged area of the coating (e.g. scribe), thus the substrate will be further protected.

Case 3: Corrosion of the underlying substrate

Corrosion of underlying substrate can be taken place mainly due to one/or both of the following reasons;

- a. If there is insufficient amount of zinc available for protection,
- b. If the conductivity among zinc layer (or zinc particles) or that between zinc layer and the substrate is lost. If the conductivity is lost, then the electron movement between zinc and substrate is prevented. Thus this may mainly cause to impede the galvanic protection ability of the coating.

Corrosion protection of mild steel by zinc coating will be diminished under this condition, mild steel will corrode and corrosion products of steel (e.g. red rust) will appear

with prolonged exposure. So corrosion protection mechanism of the zinc coating fails under this circumstance.

3.2 Assessment of corrosion protection by visual examination

Performance ratings in terms of protection ratings (R_p) and appearance ratings (R_A) of the coating can be assessed according to ISO 10289. The protection rating (R_p) is the rating number assigned to the ability of the coating to protect the base metal from corrosion and the appearance rating (R_A) is the rating assigned to describe the overall appearance of the specimen. When the zinc coated mild steel substrates exposed to atmosphere (coatings anodic to the base metal) white zinc corrosion products will form on the surface, and the appearance rating of the samples may be affected though substrate is still protected. Therefore, in this work, authors have used only the protection rating (R_p) to assess the barrier protection properties of two types of coatings. Table 3 shows the R_p rating corresponding to the area of defects (in this case substrate corrosion) according to the ISO 10289.

Fig. 1 shows photographic evidence of two types of coatings of withdrawals 1 and 4 as examples and Table 4 presents the overall R_p ranking for two types of coatings. Protection rating of ZRC remained 10 for four withdrawals therefore, no defects (substrate corrosion) are recorded. In contrast, protection rating of HDG of withdrawal 1 is recorded as 6 whilst that of withdrawal 2 onwards dropped to 2. Severe substrate corrosion is detected on HDG coated samples. ZRC samples of all 4 withdrawals behaved according to Case 1 (Section 3.1) whilst HDG samples according to Case 3. The presence of significant amount of Fe in HDG coatings (hence, corrosion products of substrate) was further verified by energy dis-

Table 3 Appearance ratings of protection corresponding to the area of defects

| Area of defects A (%) | Protection ratings (R_p) |
|-----------------------|------------------------------|
| No defects | 10 |
| $0 < A \leq 0.1$ | 9 |
| $0.1 < A \leq 0.25$ | 8 |
| $0.25 < A \leq 0.5$ | 7 |
| $0.5 < A \leq 1.0$ | 6 |
| $1.0 < A \leq 2.5$ | 5 |
| $2.5 < A \leq 5.0$ | 4 |
| $5.0 < A \leq 10$ | 3 |
| $10 < A \leq 25$ | 2 |
| $25 < A \leq 50$ | 1 |
| $50 < A$ | 0 |

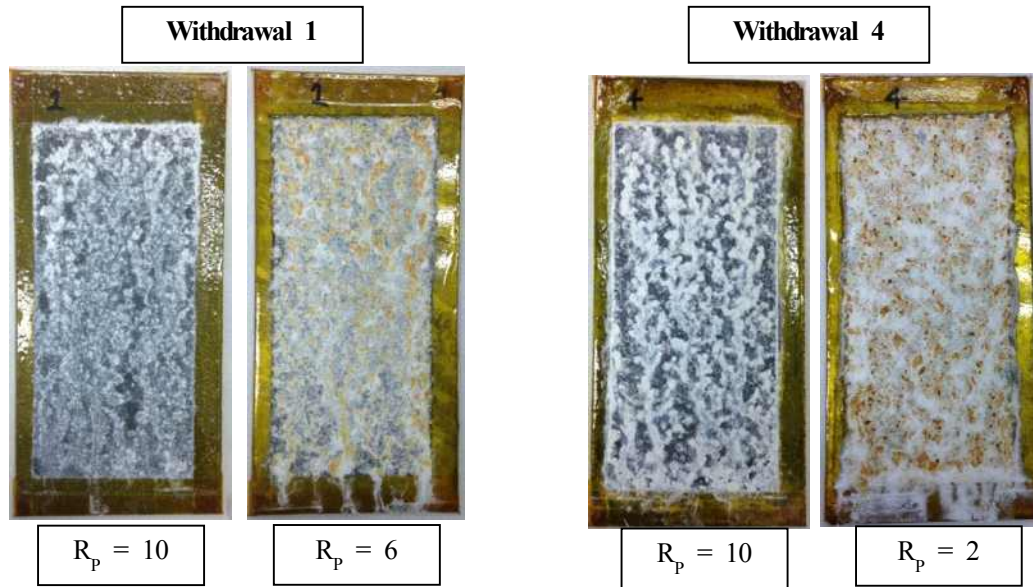


Fig. 1 Photographic comparison of ZRC (left photo under each withdrawal) vs HDG (right photo under each withdrawal) together with protection rating (R_p).

persive X-ray spectroscopy (EDS). In conclusion, based on this assessment, ZRC outperformed HDG in terms of barrier protection of substrates.

3.3 Evaluation of corrosion rate based on mass loss

Chemical pickling for ZRC samples was done for all 4 withdrawals (W1 to W4). However, that for HDG was done only for W1 as the amount of red rust was more than 10% for the subsequent withdrawals. It is a general practice in corrosion characterization (in terms of mass loss assessment) that pickling is done only if no significant amount of substrate corrosion is observed. With significant amount of red rust, the final mass loss may consist mass of the red rust as well so the mass loss of zinc will not be accurately reflected. Table 5 shows a summary of corrosion rate data for the 4 withdrawals. Note that each corrosion rate value is an average obtained from 3 similar samples and rounded off to the nearest mg and expressed as mass loss of specific area “per day” instead of “per year” to comply with exposure durations..

After the evaluation of ZRC vs HDG for withdrawal 1, corrosion rate of HDG is significantly higher than that of ZRC. This confirms the rate of corrosion of zinc is much faster in HDG than that of ZRC therefore, the higher risk of losing the amount of zinc in the coating. This implies ZRC may be able to provide longer protection for the substrate than that of HDG. Corrosion rate of ZRC decreases along the four withdrawals. This shows the zinc loss in ZRCs slows down along exposure. Note that corro-

sion rate measurements in this work were used only as a set of data to compare the coating performance at different stages of accelerated exposure. Hence, these values should not be used either to compare other corrosion rate measurements obtained under different exposure conditions or to predict the life time.

3.4 Total impedance measurements by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) spectra

Table 4 Protection rating (R_p) of ZRC vs HDG

| Withdrawal | Protection ratings (R_p) | |
|------------|------------------------------|-----|
| | ZRC | HDG |
| W1 | 10 | 6 |
| W2 | 10 | 2 |
| W3 | 10 | 2 |
| W4 | 10 | 2 |

Table 5 Average corrosion rate values of two types of coatings

| Withdrawal (W) | Coating | Corrosion rate ($\text{g/m}^2/\text{d}$) (mass loss)/(area \times time) |
|----------------|---------|--|
| W1 | HDG | 10.121 |
| | ZRC | 5.716 |
| W2 | ZRC | 5.440 |
| W3 | ZRC | 3.174 |
| W4 | ZRC | 1.255 |

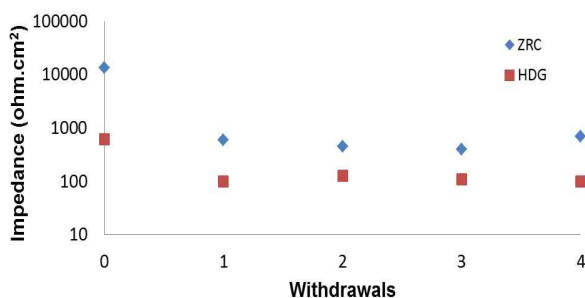


Fig. 2 Total impedance of ZRC and HDG for all withdrawals at 0.1 Hz.

were obtained from withdrawals 1 to 4. Total impedance values at 0.1Hz ($Z_{0.1Hz}$) were obtained from the bode plots for each case and plotted against the withdrawals (Fig. 2). Withdrawal “0” of Fig. 2 means the results from EIS experiments conducted on samples before exposure to the cyclic corrosion test.

Both samples showed higher impedance values initially (before exposure) however, $Z_{0.1Hz}$ of ZRC is much higher than that of HDG. This may imply higher initial impedance (hence higher resistance) of ZRC at this stage. Higher initial impedance of ZRC can be due to the pre-formed thin outer layer of zinc corrosion products having semi conducting properties. This proves higher barrier protection of ZRC than that of HDG at the initial stage before accelerated exposure. Total impedance values dropped in both types of coatings once the exposure started. Impedance drops once the zinc actively starts its oxidation, however, this does not infer any adverse effect on their corrosion protection performance of the base metal (given that no corrosion of the base metal).

This may also imply the corrosion protection at this stage is by galvanic protection [2]. Total impedance values of ZRC during all 4 withdrawals are still higher than that of HDG. This suggests higher barrier (passive) protection capabilities of ZRC than that of HDG.

However, it is noteworthy to consider the differences observed of ZRC against HDG in terms of the appearance and correlate the EIS readings with visual examinations. ZRC did not show any substrate corrosion on the surface up to four withdrawals in contrast to HDG which showed substrate corrosion from withdrawal 1 onwards. Therefore, for HDG above clarification is somewhat ambiguous as corrosion products of both zinc and substrates are observed. Hence for HDG, it is not accurate to confirm that impedance data from withdrawal 1 to 4 is solely due to zinc oxidation. It is also necessary to consider other factors as porous nature of coatings, the effect of different layers etc. if the results are used to study the coating protection

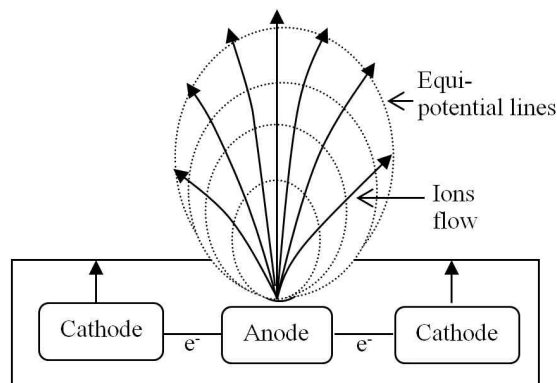


Fig. 3 Schematic diagram of electrochemical activities on zinc coated steel sample exposed to an electrolyte.

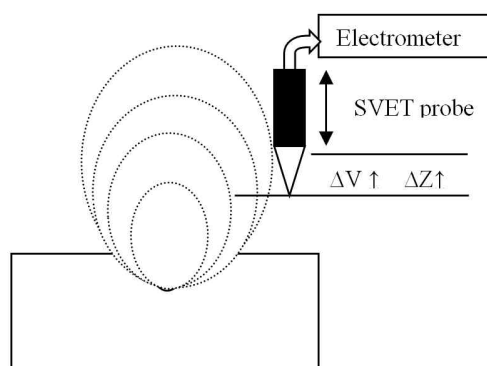


Fig. 4 Schematic diagram of the movement of scanning vibrate electrode probe across the equi-potential lines.

and failure mechanism in detail. However, the aim of this work is only to use total impedance data to compare the overall corrosion protection performance.

3.5 Evaluation of anodic and cathodic activities scanning vibrate electrode technique (SVET)

SVET is a powerful tool to study coatings, especially metallic coating for galvanic protection. The technique possesses the great advantage of detecting and quantifying the localized anodic and cathodic distribution on the surface of the metal which is a remarkable value for corrosion research [15-20]. This technique has been used in various research and development work to investigate the corrosion activities on zinc rich coatings. The effect of metallic coating thickness of Zn-Al alloy galvanizing coating on corrosion resistance properties [15], investigation on the modification of zinc dust reactivity in zinc rich coatings [17], galvanic corrosion properties of zinc and zinc rich coatings and under film corrosion of epoxy-coated galvanized steel [20] are some examples.

The technique relies on the spatial separation of anodic

Table 6 Scanning vibrat electrode technique observations on zinc rich coated sample at different exposure stages

| W | SVET map | Optical Image | Remarks |
|----|----------|---------------|--|
| W0 | | | <ol style="list-style-type: none"> 1. The scribe shows strong cathodic behaviour against the other area of the sample proving galvanic protection by the coating at the initial stage. 2. The ΔV_{map} is around 87 μV, mainly due to the cathodic activities along the scribe. |
| W1 | | | <ol style="list-style-type: none"> 1. The scribe still shows strong cathodic behaviour against the other area of the sample proving further galvanic protection. No substrate corrosion can be observed. 2. The ΔV_{map} is around 73 μV slightly lower than the sample before exposure. Higher ΔV_{map} is still due to the cathodic activities along the scribe providing galvanic protection. |
| W4 | | | <ol style="list-style-type: none"> 1. Now both anodic and cathodic activities on the scribe can be detected. According to the optical image, slight substrate corrosion can be seen at isolated areas of the scribe whilst most parts of the scribe (and the rest) are covered with zinc corrosion products. 2. The ΔV_{map} is around 55 μV mainly due to the both anodic and cathodic activities on the scribe. |

and cathodic activities on a surface which lead to small variations in potential and generation of ionic flow within the electrolyte. Potential field distribution above the active corrosion sites is given by “equi-potential lines” as presented schematically in Fig. 3. These potential fields are formed since the anodic and cathodic reactions occur on zinc coated steel system, and are characteristics of particular occasion. The vibrating probe and the SVET system detect and quantify these activities (as schematically shown in Fig. 4) and present in the form of a map.

Aggressiveness of the corrosion activity of each SVET map is quantified by potential difference gap between the maximum anodic reading and the minimum cathodic reading, which is defined in this work as the DV_{map} (rounded off to the nearest μV value).

Main scopes of using SVET for the current project are;

- Analyze the galvanic protection capabilities: Identification and quantification of anodic and cathodic activities enables to assess and prove the galvanic protection characteristics of the coatings.
- Assess the aggressiveness and propagation of corrosion activities: Change of corrosion activity along the exposure time.
- Other localized corrosion activities: Detection of other localized corrosion initiation and propagation activities of the substrate upon prolong exposure.

SVET results are explained in this section. Table 6 illustrates the SVET investigations of ZRC coatings for before exposure to cyclic corrosion test (W0) and two withdrawals (W1 and W4 as examples) whilst Table 7 illustrates those of HDG.

According to the SVET investigation on scribed sam-

Table 7 Scanning vibrat electrode technique observations on hot dip galvanized sample at different exposure stages

| W | SVET map | Optical Image | Remarks |
|----|--|---------------|---|
| W0 | <p>3D Map Analysis #2: SVP Probe</p> <p>Y-Position (millimeters)</p> <p>X-Position (millimeters)</p> <p>microvolts</p> | | <ol style="list-style-type: none"> 1. The scribe shows strong cathodic behaviour against the other area of the sample proving galvanic protection by the coating at the initial stage. 2. The ΔV_{map} is around 94 μV, mainly due to the cathodic activities along the scribe. |
| W1 | <p>SVP Probe</p> <p>Y-Position (millimeters)</p> <p>X-Position (millimeters)</p> <p>microvolts</p> | | <ol style="list-style-type: none"> 1. Most parts of the sample including the scribe show anodic behaviour. Substrate corrosion (red rust) can be seen on the sample. These observations indicate that galvanic and barrier protection capabilities of the sample are started being compromised. 2. The ΔV_{map} is around 23 μV as substrate corrosion reactions are also initiated. |
| W4 | <p>3D Map Analysis #1: SVP Probe</p> <p>Y-Position (millimeters)</p> <p>X-Position (millimeters)</p> <p>microvolts</p> | | <p>Corrosion of the substrate is extended at different locations and increased ΔV_{map} (180 μV) verifies the intense corrosion activities on the sample.</p> |

ples, both coatings showed galvanic protection at the first stage before introducing to the accelerated exposure. However, HDG did not perform well since the withdrawal 1, failed to provide corrosion protection for the substrate. Intense corrosion of the substrate hence, ferrous corrosion products were observed on the HDG sample. On the contrary, ZRC performed well proving galvanic protection to the substrate until withdrawal 3 (not given in this paper). Some substrate corrosion was detected from withdrawal 4 onwards though the majority of the substrate surface was protected. Thus ZRC outperformed HDG in terms of corrosion protection according to SVET investigations at the given experimental conditions.

This work comprised a comprehensive corrosion char-

acterization of two types of zinc coatings applied on plain carbon steel, hot dip galvanized and a commercial zinc rich coating (ZRC). Study was based on an experimental protocol established by authors using accelerated cyclic corrosion exposure and subsequent corrosion characterization techniques and methods. Samples were exposed according to ISO14993 cyclic corrosion test and a set of samples were removed at each withdrawal for a series of corrosion and electrochemical characterization in aim of evaluating barrier and galvanic protection properties of zinc coatings. Visual examination and qualitative assessment of barrier properties were done according to ISO 10289 on samples without scribes and ZRC used in this study outperformed HDG. Substrate corrosion was ob-

served on HDG samples from the withdrawal 1 onwards in contrast to ZRC there was no notable substrate corrosion.

Mass loss and corrosion rate measurements elucidate zinc sacrificial rate along exposure, direct and indirect information of coating life span. Although it is not possible to predict the life span from a short term accelerated test, comparing such values of different coatings give a clear indication of which coating performs better in long term applications. As an example in this study comparing mass loss and subsequent corrosion rates of two types of coatings at withdrawal 1, ZRC proved to be better than HDG having nearly half of the zinc loss rate compared to that of HDG. Furthermore, corrosion rate of ZRC reduces along exposure indicating that the rate of zinc loss of ZRC is getting lesser.

Electrochemical investigations can reveal useful information of metallic coatings. In this study total impedance of two types of coatings were investigated by electrochemical impedance spectroscopy which can be used to predict both barrier and galvanic protection properties. Based on total impedance evaluation together with real images of samples, ZRC behaved better than HDG in terms of overall corrosion protection of substrates.

SVET is one of the best techniques to study the localized anodic and cathodic activities of metallic coatings. Galvanic protection capabilities, aggressiveness of corrosion activities and other localized corrosion activities of two types of coatings were investigated by SVET in this work using samples with scribes. Both coating proved galvanic protection before exposure though HDG couldn't maintain that upon accelerated exposure. Substrate started corroding aggressively in HDG sample, localized corrosion activities of the substrate were observed along the scribe as well as outside the scribe. ZRC coating again behaved better than HDG according to SVET investigation without significant substrate corrosion. Correlating all results obtained in this work, ZRC has better barrier and galvanic protection properties than those of HDG.

4. Conclusion

A systematic methodology for evaluation and validation of corrosion protection properties of metallic coatings based on scientific principles and international standards is introduced in this work. Study was based on an experimental protocol using accelerated cyclic corrosion exposure and subsequent corrosion characterization techniques and methods. Samples were exposed in accelerated advanced cyclic corrosion test chamber according to ISO14993 and a set of sample was removed at each withdrawal for a series of corrosion and electrochemical

characterization. The evaluation included visual examination according to ISO10289, mass loss and subsequent corrosion rate measurements, electrochemical properties and anodic and cathodic activities by advanced electrochemical scanning technique. Barrier and galvanic protection properties of a commercial zinc rich coating were evaluated by different techniques and methods and compared with those of hot dip galvanised coating. Zinc rich coated samples used in this study performed better in terms of overall corrosion protection than those of hot dip galvanized samples.

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References

1. Denny A. Jones, *Principles and Prevention of Corrosion*, 2nd ed., Pearson Education South Asia Pte Ltd., Singapore (1996).
2. V. Barranco, S. Feliu Jr., and S. Feliu, *Corros. Sci.*, **46**, 2203 (2004).
3. S. M. A. Shibli, A. C. Jayalekshmi, and R. Remya, *Surf. Coat. Tech.*, **201**, 7560 (2007).
4. V. Barranco, S. Feliu Jr., and S. Feliu, *Corros. Sci.*, **46**, 2221 (2004).
5. S. E. Faidi, J. D. Scantlebury, P. Bullivant, N. T. Whittler, and R. Savin, *Corros. Sci.*, **35**, 1319 (1993).
6. S. Shreepathia, P. Bajajb, and B. P. Mallika, *Electrochim. Acta*, **55**, 5129 (2010).
7. M. Mouanga and P. Berçot, *Corros. Sci.*, **52**, 3993 (2010).
8. A. Meroufel and S. Touzain, *Prog. Org. Coat.*, **59**, 197 (2007).
9. C. Cachet, F. Ganne, S. Joiret, G. Maurin, J. Petitjean, V. Vivier, and R. Wiart, *Electrochim. Acta*, **47**, 3409 (2002).
10. H. Marchebois, C. Savall, J. Bernard, and S. Touzain, *Electrochim. Acta*, **49**, 2945 (2004).
11. S. M. A. Shibli, and R. Manu, *Appl. Surf. Sci.*, **252**, 3058 (2006).
12. E. Diler, S. Rioual, B. Lescop, D. Thierry, and B. Rouvellou, *Corros. Sci.*, **65**, 178 (2012).
13. J. Kasperek, D. Verchere, D. Jacquet, and N. Phillips, *Mater. Chem. Phys.*, **56**, 205 (1998).
14. D. Persson, D. Thierry, and N. LeBozec, *Corros. Sci.*, **53**, 720 (2011).

15. D. J. Penney, J. H. Sullivan, and D. A. Worsley, *Corros. Sci.*, **49**, 1321 (2007).
16. M. Yan, V. J. Gelling, B. R. Hinderliter, D. Battocchi, D. E. Tallmanand, and G. P. Bierwagen, *Corros. Sci.*, **52**, 2636 (2010).
17. A. C. Bastos, M. L. Zheludkevich, and M. G. S. Ferreira, *Prog. Org. Coat.*, **63**, 282 (2008).
18. G. A. El-Mahdy, A. Nishikata, and T. Tsuru, *Corros. Sci.*, **42**, 183 (2000).
19. R. M. Souto, L. Fernández-Mérida, S. González, and D. J. Scantlebury, *Corros. Sci.*, **48**, 1182 (2006).
20. I. M. Zin, S. B. Lyon, and A. Hussain, *Prog. Org. Coat.*, **52**, 126 (2005).