

# Corrosion of Zinc Coated Steel: An Atomic Force Microscopy Study of Galvanised and Galvannealed Steels

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## ABSTRACT

## 要 旨

Over the past 20 years the automotive industry has constantly improved vehicle corrosion behaviour by exploiting the benefits of zinc coated steels. The application of zinc coated steel, however, does have considerable impact on processes within the automotive industry, the choice of coating type, therefore, can differ between OEM. Using the surface sensitive technique of Atomic Force Microscopy (AFM) the local corrosion behaviour of galvanised steel (GI) and galvannealed (GA) has been compared. Three sample models have been exposed to 5 wt% sodium chloride solution, for different times, to simulate cut edge, stone chipping and galvanic coupling corrosion behaviour. AFM was used to determine the volume of material loss for each time interval which could then be related to an absolute measure of corrosion rate. By converting corrosion rate to current density values the degree of electrochemical activity of the GI and GA systems were compared. For all experimental models GA showed lower corrosion densities compared to GI. The cut edge specimens show GI to have up to 7 times the current density of GA after 256 minutes. The coupled samples magnify this difference further with almost no material loss to the GA coating but a greatly increased corrosion rate for GI. This study has confirmed that, by using the specialised technique of AFM in an innovative way, GA outperforms GI, where the zinc coating has been damaged, with its coating sacrificially corroding at a slower rate.

過去 20 年に渡り、自動車産業では亜鉛めっき鋼板を活用して自動車の腐食性能を継続的に改善してきた。しかしながら、亜鉛めっき鋼板の適用は自動車生産における各工程に大きな影響を及ぼす。それ故、めっき種の選定は自動車メーカーにより異なっている。Atomic Force Microscopy (AFM) という高感度の表面解析技術を応用し、溶融亜鉛めっき (Galvanised=GI) 鋼板及び合金化溶融亜鉛めっき (Galvannealed=GA) 鋼板の腐食挙動の比較をおこなった。端末からの腐食、チッピング傷からの腐食、GI 材と GA 材を組み合わせた場合の腐食、それぞれの腐食挙動をシミュレートするべく計 3 種類のサンプルを作成して 5 wt% 塩化ナトリウム溶液に浸漬した。AFM により各時間ごとの腐食減量を求めた後、実際の腐食速度に置き換えた。そして腐食速度から電流密度を求め、GI 材と GA 材の電気化学的挙動の比較をおこなった。その結果、全ての実験サンプルにおいて GA 材は GI 材に比べて低い腐食速度を示した。端末腐食サンプルにおいては、GI 材は GA 材に対してテスト開始 256 分後に最大 7 倍もの電流密度を示した。組み合わせサンプルの場合はこの差が更に拡大し、GA 材がほとんど腐食しないのに対し、GI 材の腐食速度は非常に増加した。本研究の結果、AFM という特殊技術を革新的手法で活用することにより、亜鉛皮膜がダメージを受けた部位において GA 材は GI 材よりも遅い速度で腐食が進行することにより優れた防食性能を有することが確認された。

## 1. Introduction

Steel has always been the major material of use in the automotive industry. In recent times, where there has been a demand for increased safety, weight reduction and reduced fuel consumption, steel has demonstrated its versatility by offering a range of high strength yet formable new products. Steel, however, is essentially

unstable and can react immediately with its environment, when exposed. The corrosion of steel in the automotive industry can have a catastrophic impact on safety critical parts and result in unwanted cosmetic defects that are unacceptable to the customer. Rust has twice the volume of steel and once the corrosion process has been initiated protective paint coatings are destroyed allowing damaged areas to grow rapidly<sup>(1)</sup>.

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In an effort to hinder the corrosion of vehicle Body In White (BIW) and closure panels zinc coated steels are being increasingly employed by the Original Equipment Manufacturer (OEMs) on a global scale. The aim is to reduce weight with no sacrifice to performance, safety and cost<sup>(2)</sup>. These targets have led to design changes allowing reduction in steel sheet thickness and growth of materials such as galvanised steel (GI) and galvanealed steel (GA). Zinc coatings offer protection to steel in two ways: firstly, zinc acts as a barrier since, being more corrosion-resistant than steel, it separates the steel from any possible aggressive environment; secondly, zinc is less noble than steel and, when coupled together in the presence of an electrolyte, will sacrificially corrode to protect the steel. The latter form of protection is particularly important where a coated substrate has been mechanically deformed and the integrity of the zinc coating broken, leaving the steel substrate exposed, as for example at a cut edge or stone chip area.

The application of a zinc coating, whilst improving corrosion resistance, can have a deleterious effect on other critical aspects of vehicle manufacturing, for example stamping, welding, painting and cost. Depending on the desired performance and quality, there are many different coating compositions and processes that can be employed by the steel mill. GI and GA have emerged over the past 10-15 years as the dominant coated substrates within the automotive sector<sup>(3)</sup>. Traditionally electro plated zinc (EG) was used, offering a class A paint finish, however, improvements in GI and GA as well as cost implications have seen a decline in the use of EG. Current trends in the automotive application of coated steel indicate that European OEMs tend to utilise GI where as Japanese OEMs favour GA.

It is fundamentally understood that the iron-zinc alloy coating of GA, provided all other factors were equal, would sacrificially corrode at a slower rate compared to the conventional pure zinc coating of GI. Previous studies have obtained average area corrosion data based on a macroscopic scale that may not be relevant to the usual forms of damage observed on BIW for example, stone chips and cut edges. This investigation seeks to rectify this deficiency by comparing the local corrosion behaviour of GI and GA on a microscopic scale using

Atomic Force Microscopy (AFM). Three experimental models, cut edge, stone chip and galvanic couple, have been developed to simulate possible on vehicle electrochemical scenarios. It is intended that the models help further the understanding of the impact of anode/cathode ratio on coating composition. AFM offers the ability to analyse surface at atomic level and, with this degree of spatial resolution, unique experiments can be carried out at the coating/substrate interface. AFM, in the contact mode, has been used to obtain quantitative corrosion data which can improve knowledge of the local corrosion at the coating/substrate interface for GI and GA.

## 2. Hot Dipped Zinc Coating of Steel

### 2.1. Advances in Coating Quality

Hot dipped galvanising of steel is by far the most common of the zinc coating processes and has existed for over 200 years<sup>(4)</sup>. Most sheet product is made on a Sendzimir type hot process continuous line, Fig. 1. After uncoiling, the strip is cleaned, to remove oils and other surface contamination, before entering the heat treatment furnace. The annealing furnace heats the strip in a reducing atmosphere, usually a Nitrogen / Hydrogen mix, above the recrystallisation temperature at about 700°C, removing further contamination from the strip. As the strip leaves the furnace it is cooled, by gas jets, to approximately 450°C, similar to the zinc pot. Next, the strip enters the zinc pot, the rate of coating tends to depend on the steel type with thickness controlled by immersion time and gas wipers at the pot exit, which remove excess material. Roller levelling, temper rolling, inspection, oiling and recoiling complete the production process.

In the automotive industry, as already discussed, GI and GA have been increasingly employed over the past couple of decades. The growing demands for these products have subsequently coincided with improved coating quality, properties and processing know how from steel suppliers. Modernisation of galvanising lines such as the implementation of automated surface control devices, greater control of temperature and atmosphere during annealing and the optimisation of strip cleaning have led to a more consistent product with tighter

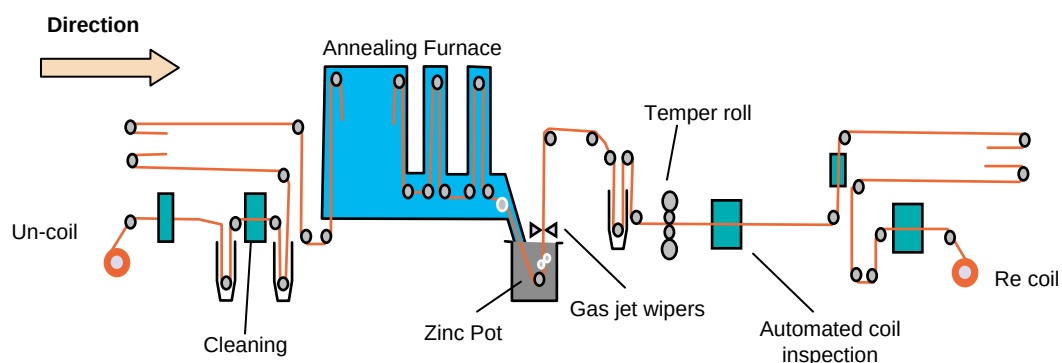


Fig. 1 Schematic of a Sendzimir continuous galvanizing line

tolerances. Zinc pot control has improved, increasing pot life and reducing costs. The wiping and solidification area is enclosed in a nitrogen atmosphere avoiding and reducing surface defects. The purpose of this review is not to detail the advances in modern hot dip galvanising but to demonstrate that zinc coated products available to the automotive industry are

constantly changing and are of a higher quality now than at any time in the past.

## 2.2. Gavanised and Galvannealed Steel

GI and GA are both hot dipped zinc coated steels. As the steel strip passes through the zinc pot several specific iron/zinc intermetallics can form. The iron/zinc system is well understood and has been reported in great detail previously. The possible phases formed by the hot dipping processes can be found by examining the zinc rich end of the iron/zinc equilibrium phase diagram, Fig. 2<sup>(5)</sup>. The composition of the coating depends on several factors; immersion time and speed, the influence of alloying elements and the application of a post annealing stage.

The processing route for GI is, essentially, the same as described in section 2.1. The microstructure of the coating is almost completely pure zinc, Fig. 3. Aluminium (0.2 wt%) is typically added to the zinc pot to prevent the formation of brittle iron-zinc intermetallics at the coating/substrate interface. The aluminium reacts preferentially with the steel forming a thin  $\text{Fe}_2\text{Al}_5(\text{Zn})$  inhibition layer, suppressing any iron/zinc alloying. In the case of GA, however, the growth of iron zinc phases is controlled and encouraged by passing the strip through an annealing tower after zinc pot exit, Fig. 4. As the freshly coated strip passes through the furnace, iron/zinc

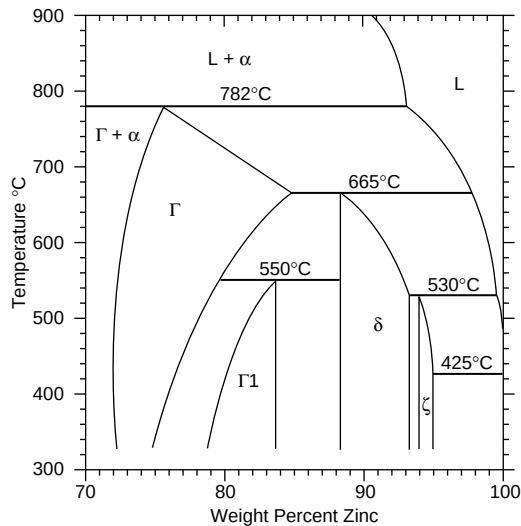
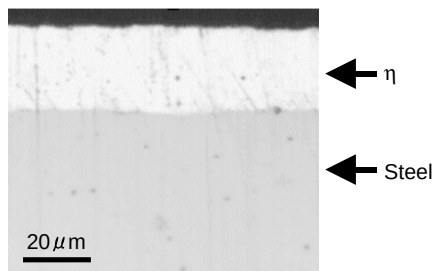
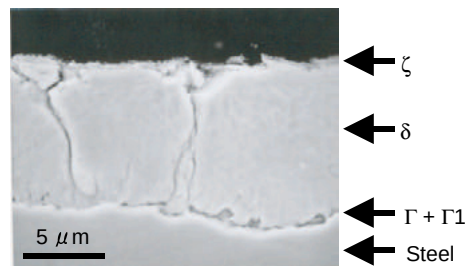


Fig. 2 Zinc rich end of Fe-Zn phase diagram

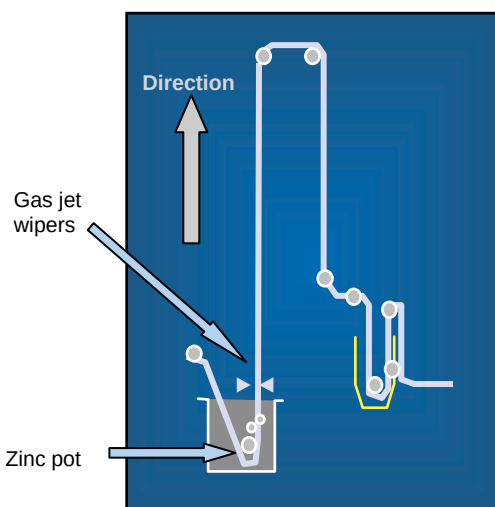


(a)

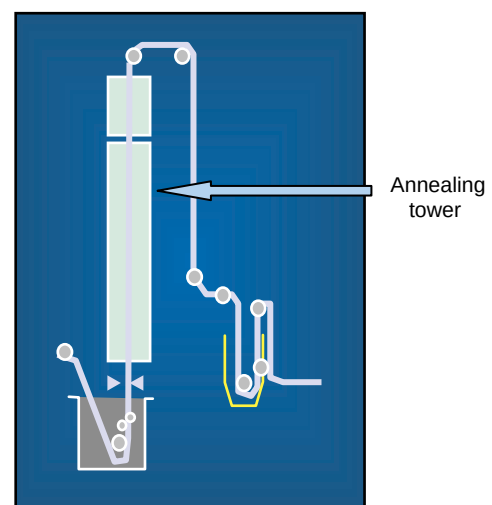


(b)

Fig. 3 Micrographs of the microstructure of (a) conventional GI and (b) typical GA found in the automotive industry



(a)



(b)

Fig. 4 Schematic highlighting process differences between (a) GI and (b) GA steel (with annealing tower)

phases grow due to thermal diffusion. A coating mainly consisting of  $\delta$ -phase is preferred by the automotive industry because of optimum weld, powdering and corrosion properties<sup>(6), (7)</sup>.

The iron/zinc alloy coating offers improved weldability and, due to a corrosion potential closer to the steel substrate than GI, enhanced corrosion protection. Traditionally GA has also offered better paintability to the automotive industry because of a higher surface roughness, although since the advent of surface texturing the paint appearance of GI has improved. The harder coating of GA however, poses powdering and drawing concerns. Finally, as steel competes more and more with the lightweight technologies offered by the use of light metals and carbon composites in the automotive industry, there have been great steps made in the development of High Strength Steel (HSS). This has been accompanied by an increase in the complexity of metallurgy, for example Transformation Induced Plasticity (TRIP) steel, which can potentially be effected by the elevated temperature of the GA annealing tower<sup>(8)</sup>.

### 3. Experimental Work

#### 3.1. Sample Preparation

##### 3.1.1. Experimental models

In galvanic protection, zinc is less noble or anodic

to steel in ambient conditions and will sacrificially corrode to protect steel. The corrosion rate, according to the Catchment Area Principle, is influenced by the proportion of the exposed zinc (anode) compared to the exposed steel (cathode). Taking into consideration different anode/cathode ratios, samples were prepared in different ways related to possible scenarios that could occur on a vehicle. Three experimental models for GI and GA were prepared, Fig. 5:

- (1) Cut Edge Simulation - Samples were mounted in cross-section resulting in a high iron exposed area (cathode) to small zinc area (anode). Estimated anode/cathode ratio = 1:1000.
- (2) Stone Chipping Simulation - A more specific laboratory developed method yielding a smaller exposed iron area compared to the exposed zinc. Stone chipping damage can be very random in its nature; however, some situations will result in a large anode to small cathode scenario. Estimated anode/cathode ratio = 24:1.
- (3) Galvanic Coupling Simulation - GI and GA were mounted together in the same epoxy and galvanically coupled (samples were touching). The resin block was then cut and polished so that their individual cut and polished edges were simultaneously exposed to the electrolyte.

To prepare the large anode to small cathode sample a specific laboratory preparation method was developed,

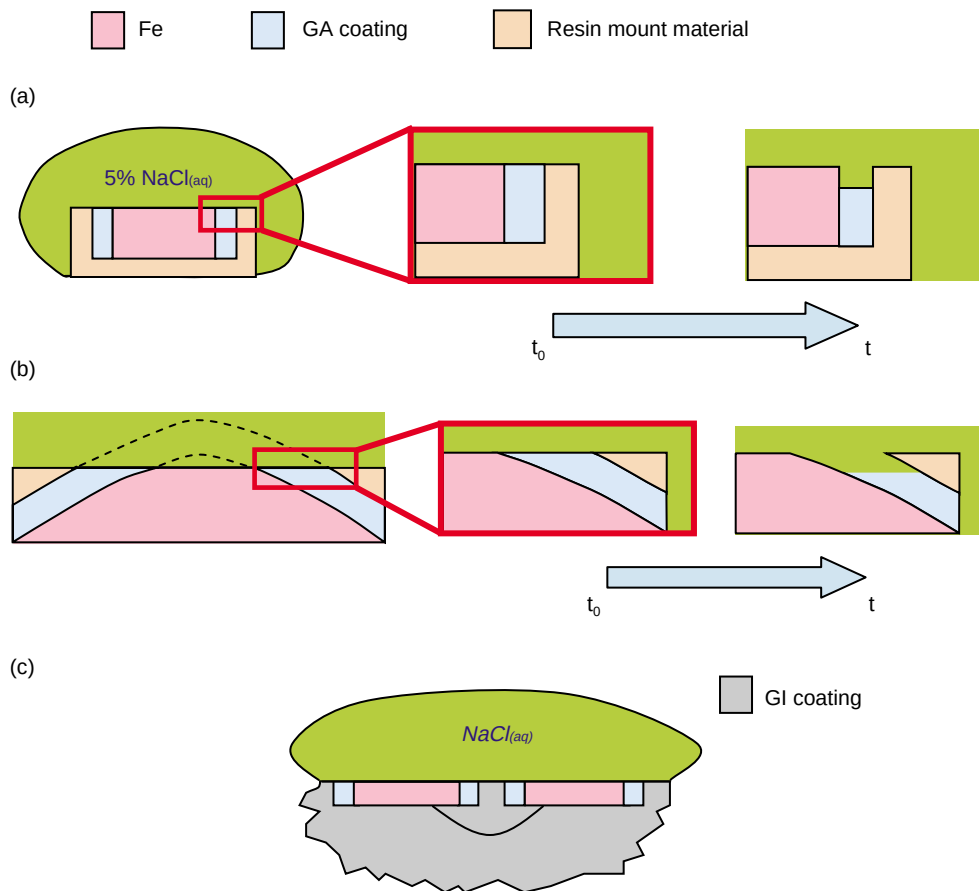


Fig. 5 Schematic diagrams of (a) the cut edge sample (b) the stone chip sample and (c) the galvanic sample. For (a) and (b) examples of the expected effect of exposure after a given time,  $t$ .

as mentioned above. 15 mm discs were cut from the steel sheet. The discs were then punched into dome shapes, described in Fig. 6. The overall aim of this work is to compare the behaviour of GI and GA, therefore reproducible sample shape was critical. A custom made tool was designed for the “dome” punch procedure, Fig. 7. Using the tool an 8 mm ball forms the disc into a dome shape to a fixed height, 0.8 mm in these experiments. The domes were then mounted in resin and ground to 4000 grit paper. The grinding process removed the top of the dome thus exposing an iron cathode surrounded by zinc, Fig. 6. The samples were polished to a 1  $\mu\text{m}$  finish and washed in a water free environment. The grinding and polishing stage was controlled for each sample to give a tolerance in the diameter of the exposed material to  $\pm 0.05$  mm.

### 3.1.2. Ex-Situ aqueous corrosion treatments

GI and GA material (0.8 mm gauge) was supplied from three industrial suppliers, samples A, B and C. Samples were cut and mounted in epoxy resin. The mounted specimens were first ground with successive silicon carbide papers, from 320 to 4000 grit, and then polished to a 1  $\mu\text{m}$  finish to give a highly smooth and

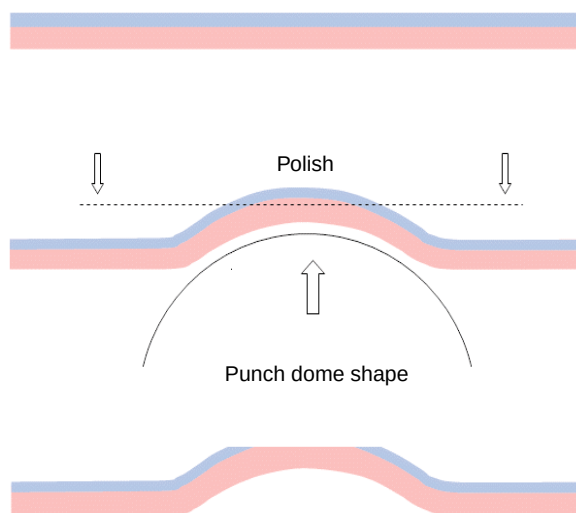


Fig. 6 Schematic diagram describing the production of the stone chip sample

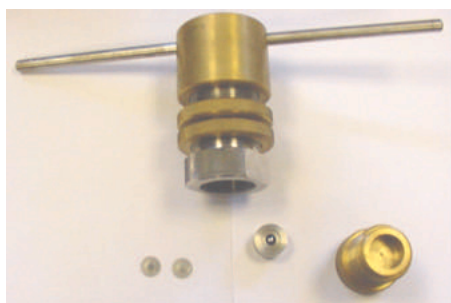


Fig. 7 Photograph of the custom made tool to make the stone chipping samples

flat surface. Specimens were usually ultrasonically cleaned in ethanol, not rinsed in water to avoid initiating corrosion. Finally the epoxy resin mount was machined to an appropriate size for AFM analysis

All samples were treated using a 5 wt% NaCl aqueous solution for test periods of 1, 4, 8, 16, 64 and 256 minutes. The treatment was carried out at room temperature and ambient pressure in plastic aerated containers. After each treatment samples were washed using six baths of de-ionised water and ultrasonically washed in ethanol.

## 3.2. Atomic Force Microscopy Analysis.

### 3.2.1. Atomic Force Microscopy

In AFM a sharp stylus, mounted on a cantilever, is scanned across the surface of the sample under investigation. The technique differs from the ‘Talysurf’ type of profilometer, widely used in industry, only in the sensitivity of the cantilever and the miniaturisation of the scanning system. In AFM the cantilever deflects towards, or away from the surface under the influence of interatomic forces and the scanning system, equally, has a resolution of atomic dimensions. The deflection of the cantilever, as it traverses the surface, is measured by a laser beam acting as an optical lever. The system provides an accurate representation of the surface with full x,y,z co-ordinates for each position and a resolution of around 1nm. The surface can be interrogated in many ways to provide measurements of roughness and other relevant surface profiles.

### 3.2.2. Analysis modes

#### (1) Height analysis

The simplest quantitative display is the height profile, which shows the elevation of the features along a line. The line need not coincide with an original scan line, but can be an arbitrary line on the image. Measurements of differences in surface elevation, horizontal distance between points, and slopes were possible with the image processing program, Nanoscope III Digital Imaging 5.12.

#### (2) Bearing analysis

The word “bearing” characterises the relative roughness of a surface in terms of high and low areas. The bearing ratio curve is the integral of the surface height histogram and plots the total percentage of the surface above a reference plane as a fraction of the depth of that plane below the highest point in the image. By utilizing bearing analysis it is possible to determine what percentage of the surface lies above or below any arbitrarily chosen height (the “bearing ratio”). For example, bearing analysis is frequently used in studies of surface wear and friction and in silicon etching procedures to observe changes in etched features over an interval of time. In qualitative terms, the bearing ratio gives a measure of how “jagged” a surface is. In this study, etching of zinc in zinc coated steel is being considered, where zinc works as a sacrificial anode. The protected iron may so be used as a height reference from which to compute the bearing volume which will then

coincide with the amount of removed zinc. In practice, the volume is measured over an area defined by a rectangle placed over the image on the screen. This area is used by the software to return the bearing volume in the form of volume per unit area. This has the units of depth and is the mean depth of the zinc removed by corrosion over the area selected. This value can be processed to give a corrosion rate in more conventional units.

### 3.2.3. Local area analysis.

To establish the rate of coating loss it was imperative that the exact same sample location was revisited after each exposure time. With small localised areas of interest,  $20 \mu\text{m}^2$ , a simple but effective method to recognise analysis areas easily was developed, Fig. 8.

### 3.3. Quantitative Electrochemical Calculation of AFM Data

Bearing analysis of the AFM data gives a measure of the removed volume of material per unit area for a given exposure time. This measure needs to be corrected by subtraction of the initial bearing volume arising from the natural roughness of the as-polished surface, Fig. 9. This correction value was determined for the reference area before exposure. The rate of material loss is an absolute measure of corrosion rate but can be related to the values often obtained by electrochemical measurements. Corrosion is essentially an electrochemical process that relies on the flow of electrons from an anode to a cathode. It is possible to convert known material loss volumes to current densities, which reflect the degree of electrochemical activity of a system, in the following manner.

The corroded mass per unit area after a time  $t$ , is given by

$$m = (V_t - V_o) \rho_{\text{Zn}} \quad (1)$$

Where  $V_t$  is the bearing volume, expressed as volume per unit area after time  $t$  and  $\rho_{\text{Zn}}$  is the density of zinc.

The mean corrosion rate is then

$$dm/dt = (V_t - V_o) \rho_{\text{Zn}} / t \quad (2)$$

at any given time  $t$ .

This corrosion rate can be converted to electrochemical current by the use of Faraday's laws. First express the rate in the form of mols of zinc per unit area per unit time

$$dM/dt = 1/M \cdot dm/dt \quad (3)$$

Where  $M$  is the atomic weight of zinc

The total electrochemical current,  $i$ , is then given by

$$i = (AnF/M) \cdot dm/dt \quad (4)$$

Where  $n$  electrons are associated with the formation of a zinc ion ( $\text{Zn}^{2+}$ ) and  $nF$  coulombs are released by the dissolution of the anodic zinc and  $A$  is the total area of zinc exposed to the electrolyte. Thus the current density is given by

$$i/A = (nF/M) \cdot (V_t - V_o) / t \rho_{\text{Zn}} \quad (5)$$

Whilst the assumption that the coating is 100% zinc is not true for the GA calculations it does not actually

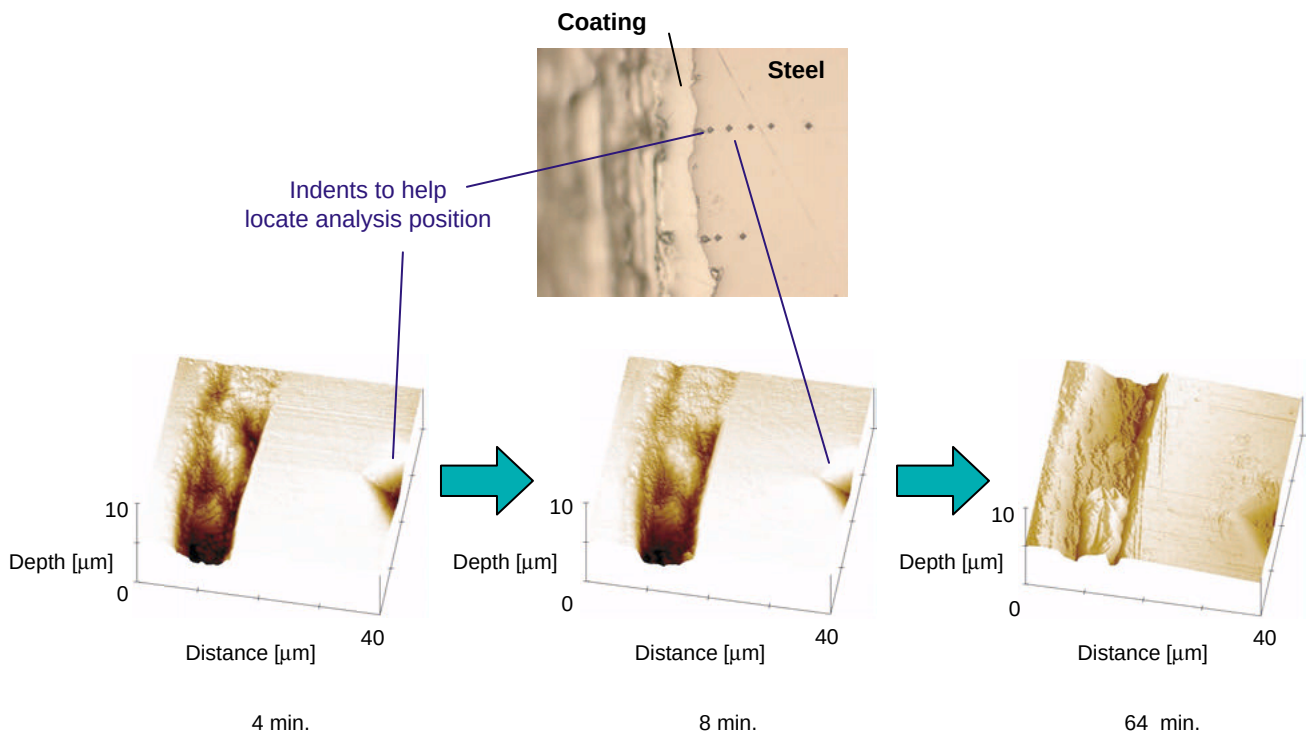


Fig. 8 AFM Images showing the use of Vickers hardness tester indents used to locate sample analysis position

change the assumption that all removed material is related to corrosion rate  $dm/dt$ . Automotive grade GA is predominantly  $\delta$ -phase which has a composition of about 90% zinc and 10% iron. The final location of the removed iron is not known, back deposited or left behind on the coating surface as mobile species are possible outcomes. In any case, the volume of material removed, as measured by AFM, relates exactly to the electrochemical current flowing. The net effect of the iron contribution in the coating on the calculation is relatively small, appearing only in the molecular mass and the density terms of Eq. (3). For the purposes of this study this small correction has been neglected.

## 4. Results

### 4.1. Cut Edge Samples

Fig. 10 shows a graph of removed volume against time for GI cut edge samples. The plot of removed volume against time is representative of corrosion rate. Following the sequence of calculations described in Section 3.3. all the removed volume values can be converted to charge, for each respective time intervals, Fig. 11. Graphs of charge against time make inferences about current density for a particular system. Using the values plotted for each time interval, however, only indicates the average current density to the respective point in time. Taking the tangent of the graph at a point in time will give the instantaneous current density, as if measured by the electrochemist using conventional methods. As can be seen the value is essentially constant after about 100 minutes. It is these values taken at 256 minutes, which are shown in Table 1 and compared against GA values.

For a GA sample the rate of loss of coating was much slower than for GI. Taking into account experimental tolerances only data at 256 minutes could be used. The data for GA values at 256 minutes, therefore, is representative of instantaneous current density values, Table 1.

Table 1 Current density values for GI and GA for cut edge samples

| Sample | Current density ( $\mu\text{A} / \text{cm}^2$ ) |      |      |
|--------|-------------------------------------------------|------|------|
|        | A                                               | B    | C    |
| GI     | 36.8                                            | 27.6 | 11.0 |
| GA     | 8.4                                             | 6.1  | 5.9  |

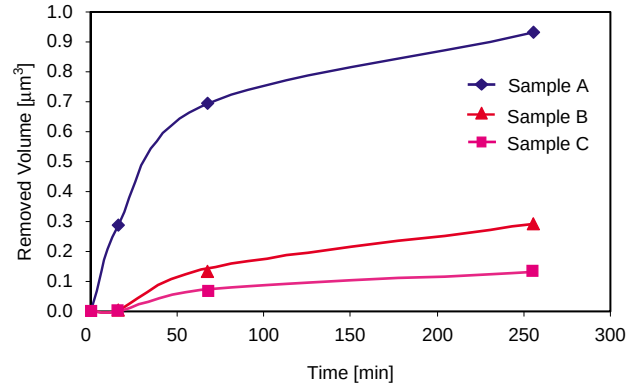


Fig. 10 Removed volume [ $\mu\text{m}^3$ ] against time [min] for cut edge GI samples

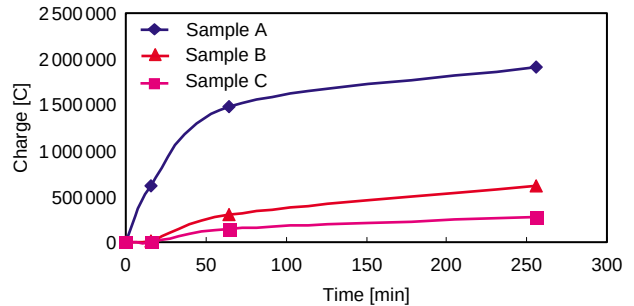


Fig. 11 Charge [C] against time [min] for cut edge GI samples

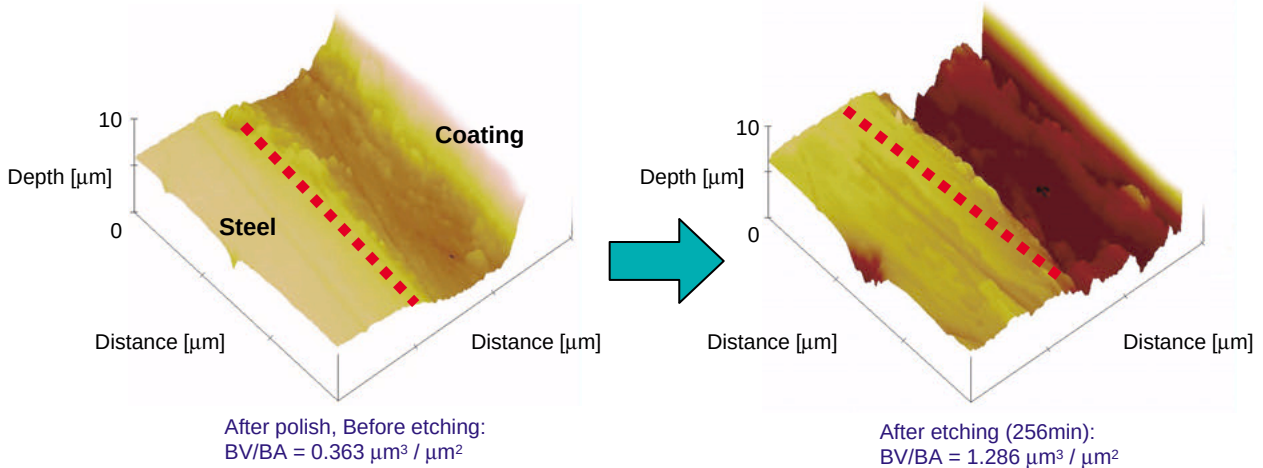


Fig. 9 AFM Images of zinc/steel coating interface at (a)  $t_0$  before exposure and (b)  $t_{256}$  after 256 minutes exposure

#### 4.2. Stone Chipping Samples

It is not the intention of this study to compare material across different suppliers and for this reason only sample B was analysed for the stone chipping (and galvanically coupled) model. Previous results have shown sample B to offer data in between the other samples and so would offer representative data for GI and GA. The calculated charge data for the stone chipping model for GI is shown in Fig. 12. In order to take into account the whole data set and reflect that the zinc coating has been sacrificially removed an average current density has been shown. The instantaneous current density at 256 minutes is so small that its value could mistakenly be thought to indicate that little or no coating loss has taken place. This was the case with the GA sample hence no data is given.

#### 4.3. Galvanic Couple Sample

No significant loss of GA coating was observed on the galvanic coupled sample. The current density values calculated for the GI coating, however, were significantly higher than previously observed. An instantaneous current density value of  $85.6 \mu\text{A}/\mu\text{m}^2$  was calculated at 256 minutes. Fig. 13 shows a graph comparing the GI values for a cut edge sample and a galvanic coupled sample.

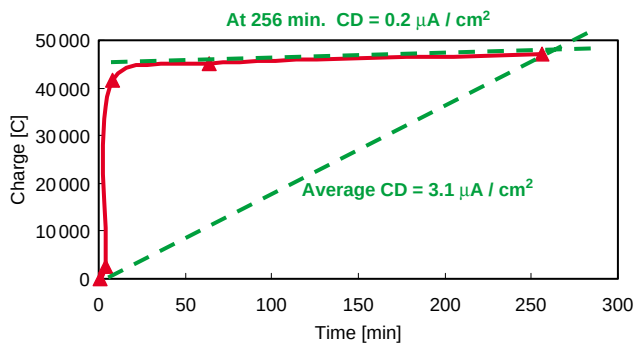


Fig. 12 Charge [C] against time [min] for stone chipping sample (Sample B only)

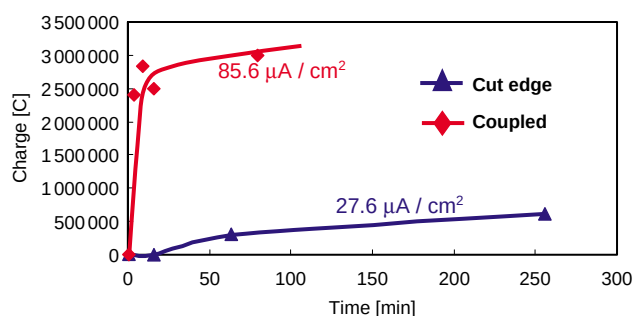


Fig. 13 Comparison of charge [C] vs time [min] curves for GI coupled and GI cut edge sample from sample B

#### 5. Discussion

The local corrosion behaviour of zinc coated steel at the coating/substrate interface has been studied. The performance of GI and GA has been compared in different situations, in the context BIW exposure, taking into consideration different anode/cathode ratios and the galvanic coupling of the different substrates. This study has taken advantage of the high spatial resolution AFM offers, to develop a novel method for the study of local corrosion activity at an interface. Current density values for the different substrates and experimental models have been calculated from raw data measured by AFM.

It is already understood that, due to its zinc/iron alloy coating, GA is expected to sacrificially corrode at a slower rate than GI. In two of the experimental models investigated corrosion of the GA coating was so small that it could not even be measured by AFM. Only analysis of the cut edge samples gave quantifiable results for both GI and GA. The GI results, shown in Fig. 10, indicate quite a large variation between samples. The GA values, whilst much lower, show less variation possibly suggesting that GA offers a more stable corrosion protection coating. One explanation, considering the process route differences, could be that the annealing furnace for GA has a stabilising effect on the coating across all suppliers.

The initial corrosion rate of the GI samples is almost linear before slowing with time. This indicates a change in the local corrosion behaviour with time due to concentration polarisation; as zinc corrodes and becomes deeper relative to the steel corrosion slows. There is also variation in the rapidity of initial corrosion of GI with sample A having much higher values than samples B and C. The instantaneous current density values of GI are considerably higher than those for GA. The current density values for GA were so low in the initial stages of corrosion that only a value at 256 minutes could be calculated. Cut edge protection is a critical area for vehicle BIW. Often paint protection at a cut edge can be at its thinnest and coupled with poor burring properties can act as site for the early onset of corrosion. From the results in this study it has been confirmed that GA offers improved substrate corrosion protection. For some OEMs, however, the cosmetic red corrosion product of GA is not acceptable, resulting in the selection of a coated substrate to be determined by performance priorities, opinions and experience.

The stone chipping model exposure tests resulted in corrosion rates and current density values that were significantly lower. For GA samples no quantifiable coating loss was measured. Even for GI the current density values were much lower; indeed the instantaneous value at 256 minutes was as low as  $0.2 \mu\text{A}/\text{cm}^2$ . The initial corrosion rate, once again, is much higher and an average value at 256 minutes is shown in Fig. 12. The lower current density values were expected, as a result of the reversal of the anode/cathode ratio from 1:1000 to 24:1. The large drop off in rapidity of corrosion was not so expected, but can be explained

by sample geometry. The stone chip sample, to all intents and purposes, is a polished dome. If a sequence of AFM height analysis curves is considered, Fig. 14, the etching of the zinc can clearly be observed on the right hand side of the figure.

After punching and grinding, the coating/substrate interface is not perpendicular to the surface but is sloped, Fig. 6. The local depth of the underlying iron determines the maximum depth to which the zinc can be etched. These geometric limitations could at some point cause a rapid drop off in the corrosion rate and explain the results shown in Fig. 12. Another reason for the drop in corrosion rate could possibly be that in the early stages of corrosion a thin oxide layer protects large areas of the coating surface, thus reducing the size of the effective anode. As this oxide dissolves so the area of exposed metallic zinc increases changing the anode/cathode ratio and slowing the rate of corrosion.

Consideration of the galvanic couple results shows no attack to the GA coating. There is, however, a relatively high current density value for the GI sample. The instantaneous current density value of  $85.6 \mu\text{A}/\text{cm}^2$  is considerably higher than the cut edge sample. The corrosion rate of the GI in the galvanic sample is due, as the name would imply, to the fact that it galvanically protects not just its own substrate but the whole of the GA sample as well. This affects the anode/cathode ratio

greatly with corrosion rate increased. Even though the GA coating is in direct contact with its respective steel substrate, the composition difference between the  $\delta$ -phase and the pure zinc of GI is sufficient for a large galvanic effect between the two substrates when connected by an electrolyte. For vehicle BIW that are predominantly GA the introduction of GI, for example for cost benefit, should be considered carefully. Other concerns such as joining methods may have been countermeasured but if galvanically connected and exposed to an aggressive environment the corrosion to the GI part would be significantly accelerated.

For the first time local current density values for a metallic coating/substrate system have been obtained. The areas analysed and volumes measured could only have been examined using AFM. The benefit of local values ensure that no external influence, such as coating defects, affect the analysis. As with any small area analysis technique a certain amount of caution must be employed when considering results as representative of a larger area. The method developed in this paper is not limited to GI and GA coatings. Metallic coatings play an important role in the automotive and other high profile industries. The measurement of coating loss and subsequent conversion to electrochemical data can help further understanding and development of other coated materials, applications and systems.

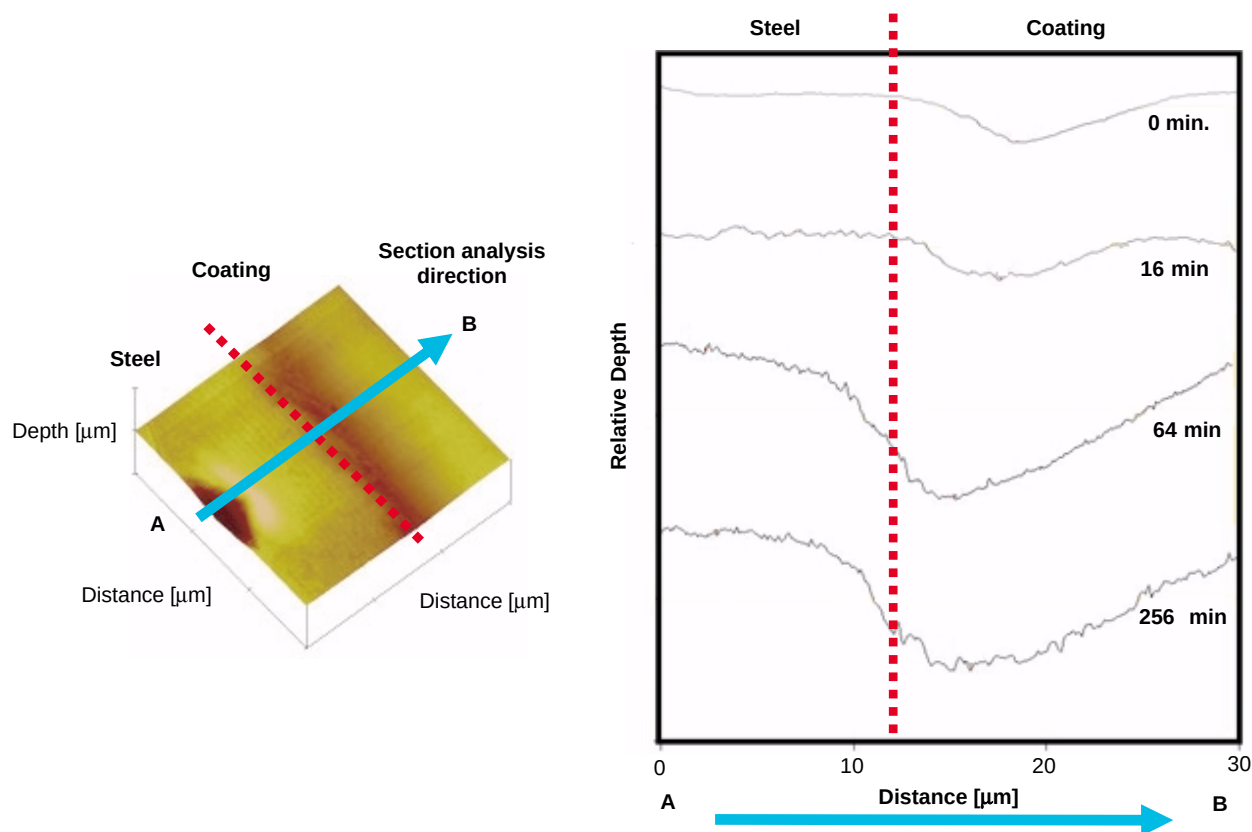


Fig. 14 AFM Height analysis curves describing the corrosion evolution of a GI sample from 0 minutes to 16, 64 and 256 minutes exposure.

## 6. Conclusion

- (1) This investigation has studied and compared the local corrosion behaviour of GA and GI at the coating/substrate interface by using AFM.
- (2) Three experimental models have been developed to simulate different possible BIW corrosion scenarios; cut edge, stone chipping and galvanically coupled.
- (3) Electrochemical activity of the different coating systems has been compared as a result of controlled corrosion experiments. Mass loss data, measured by AFM, offers an absolute corrosion rate, these values have been converted to current density values permitting conclusions to be made concerning the coating systems corrosion performance.
- (4) For each experimental model the GI coating corrodes at a faster rate than the GA coating. The initial corrosion rate for GI is greatly accelerated, and, as demonstrated by the cut edge samples exhibits a larger variation in corrosion performance compared with the more stable GA data. As expected the anode/cathode ratio has a significant effect on corrosion behaviour.
- (5) For the stone chipping model, steel remains cathodic to the coating however, corrosion is slowed significantly (for GA, material loss is almost zero).
- (6) By galvanically coupling the two systems, GI sacrificially protects all exposed metal. The change in anode/cathode ratio therefore greatly increases the GI coating corrosion rate.
- (7) For the first time a method has been developed to study the local electrochemical activity at a coating/substrate interface. The novel use of AFM has allowed the corrosion behaviour of GI and GA to be compared.
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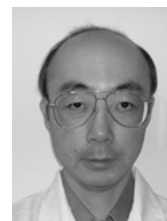
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