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Effect of Chemical Composition and Microstructure of Zn and Al-based Coatings on Electrochemical Response in Corrosive Environments

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PREFACE

This work has been carried out as a Master's thesis project at the Research, Development and Technology department of Tata Steel at Ijmuiden, Netherlands, during the period from 19th November 2014 to 21st August 2015. The study was part of an on-going project to investigate different coating systems for hot press forming in order to understand the inherent advantages and limitations of the existing commercially available coatings.

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At each stage of life, we come across a unique set of challenges that enables us to evolve and mature as both an individual and a professional. A large part of an individual's success in life is attributed to the mentors that we encounter, who help nurture our skills and guide us to consistently become better than what we were yesterday. In my case, I was fortunate enough to find three such impeccable mentors in Dr. Arnoud de Vooys, Dr. Peter Beentjes and Dr. Arjan Mol. Their loving guidance and invaluable expertise motivated me to keep pushing myself beyond my limits and helped me bring my graduation thesis to fruition. They always emphasized on the importance of setting realistic goals and paying attention to detail, which aided me in perfecting my technical and presentation skills. I would thus like to express my heartfelt gratitude for providing me the opportunity to work under their guidance.

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ABSTRACT

Hot formed steels are witnessing an increasing use in safety critical and structural parts for automobiles due to their high strength, light weight and absence of springback, due to which understanding the corrosion behaviour of coated products for hot forming is crucial to increase their stronghold in Body-In-White (BIW) applications for automobiles. Currently, aluminium alloy coatings are the preferred choice due to their high temperature stability and low density. However, with OEM's increasing interest in endowing sacrificial protection to hot formed components, zinc coatings are also making a foray into the product portfolio of steel solution providers.

In this study, the corrosion performance of Galvanized Iron (GI), MagiZinc[®] and Usibor[®] AlSi coatings for hot press forming was investigated with the help of electrochemical techniques. Galvanostatic testing was used to analyze the response of the coatings to austenitization. The corrosion performance and resistance to pitting was assessed using Cyclic Voltammetry and the corrosion mechanism was characterized through Scanning Electron Microscopy (SEM) and Glow Discharge Optical Emission Spectroscopy (GDOES).

The results indicated up to a five-fold improvement in coating thickness for the Zn coatings after hot forming. MagiZinc[®] containing Mg and Al 1.6 wt. % each was found to have better corrosion resistant properties, as the alloying additions rendered it a better passivation ability compared to conventional GI. Usibor[®] AlSi developed an aluminium alloy coating layer after hot forming, that possessed only limited sacrificial ability and displayed a vulnerability to pitting. Thus, in terms of the quality of cathodic protection offered to the substrate, the Zn coatings were found to have an upper hand compared to the AlSi coating.

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1. INTRODUCTION

The automobile industry is a market characterized by perpetual change in terms of design, materials and manufacturing processes employed. When viewed from a macro scale, this change is fuelled by a combination of three factors. These include – (a) the consumer's expectation to possess a technologically advanced, safe and eco-friendly car, (b) the legal and environmental guidelines that are being imposed on car manufacturers and (c) the competition between manufacturers that drives them to evolve and grow their market share. The latter two factors are critical from an OEM's perspective so as to promote economic growth and maintain high levels of customer satisfaction.

There is currently a need to usher in a new generation of light-weight cars that have a reduced carbon footprint, especially in developing Asian countries, where automobile markets are seeing surging growth [1]–[4]. With emission standards for automobiles getting more stringent due to growing environmental concerns, automobile manufacturers are being challenged to undertake light-weighting of automobile structures by adopting light weight alloys and thermo-mechanical processing. Hot press forming or press hardening belongs to the latter approach, wherein steel blanks are heated to high temperatures prior to a simultaneous forming and quenching operation. This presents a viable solution to obtain ultra high strength steel (UHSS) components with ultimate tensile strength (UTS) greater than 1500 MPa for BIW (Body-in-White) construction [5].

As with all low carbon steels, hot formed components also show high propensity for red rust formation and thus require protective metallic coatings to increase their effective service lifetime. The metallic coatings help ensure that the substrate is insulated from corrosive environments and also provide galvanic corrosion protection to it. Thus, coated steel products for hot press forming have begun to gain importance and increasing adoption among OEMs, as their performance and service lifetime are proving to be at par with galvanized cold stamped components.

1

The objective of this study was to evaluate the corrosion performance of Galvanized Iron (GI), MagiZinc[®] (ZnAl1.6Mg1.6) and Usibor[®] AlSi (AlSi10) using electrochemical methods, so as to unravel their corrosion mechanism and compare the sacrificial protection offered by hot dipped Zn coatings versus hot dipped Al coatings for hot press forming. In order to completely elucidate the effect of alloying and processing stages that the products are subjected to, a combination of electrochemical and characterization techniques was used in order to obtain a sound insight into the corrosion protection ability of the different coatings. Special importance was given to identify effect of austenitization on coating morphology and chemistry; ability to provide sacrificial (cathodic) protection and the inherent mechanism; rate limiting mechanisms during corrosion and passivation ability of the coatings.

Chapter 2 presents a background to hot press forming and the application of coated products for this technology. Earlier investigations carried out in this field at TATA Steel and in literature are reviewed and the metrics determining the corrosion performance of coated hot formed products is discussed. A brief description is also provided on the electrochemical techniques and characterization methods used in this study.

In Chapter 3, details on the experimental procedure and materials adopted for this study are presented. Chapter 4 discusses the electrochemical response of the different hot press formed coated substrates in a corrosive environment containing chloride ions and the results obtained from galvanostatic testing, SEM/EDX, GDOES and cyclic voltammetry are analyzed. Finally, in Chapter 5, the conclusions derived from this study and further recommendations for TATA Steel are presented.

2. BACKGROUND

An important consideration while designing light-weight automobiles is the crashworthiness of the Body-In-White (BIW), which is the ability to absorb the energy of the impact in case of a collision. What is desired is that the reduction in weight does not translate to a reduction in strength of the overall structure. It is at this juncture that hot press forming renders its benefits in order to develop ultra high strength BIW parts with reduced gauge thickness, tailored specifically for weight reduction purposes without compromising on crashworthiness.

2.1 Hot Press Forming

Hot press forming was first developed and patented a Swedish company called Planja, who used the process to manufacture saw blades and lawn mower blades [6]. Saab Automobile AB was the first automobile manufacturer to adopt press hardenable boron steel for the Saab 9000 in the year 1984 [7]. Currently, ultra high strength hot stamped boron steel is being increasingly utilized in the body structure of European vehicles. Over the past decade, automobile manufacturers like Volvo, Porsche and VW Group in particular have made significant investments in hot stamping technology. Outside Europe, manufacturers like Ford, GM and Honda have also shown strong interest in this technology [8].



Figure 2.1 Position of press hardened steels versus other steel grades in terms of ultimate tensile strength

The most widely used steel grade for hot press forming is boron-alloyed low-carbon steel (22MnB5), which belongs to the UHSS product group. These steels are well suited to hot forming due to the small amount of boron addition (~0.0025 wt. %) that improves the hardenability of the steel and facilitates rapid transformation of austenite to martensite during the hot forming stage [9]. This forms the key to achieving UTS greater than 1500 MPa, due to the predominantly martensitic microstructure of the steel. In addition, the hot formed products are devoid of springback and gauge thickness can be reduced to facilitate light-weighting, due to the high UTS of the components [10]. In the last decade, the use of boron steels has increased enormously, although the number of OEM's using hot stamped boron steel outside Europe is still limited. Nonetheless, the market share of these steels is expected grow strongly. It is estimated that the demand for press-hardened steel parts will increase up to the year 2015 to more than 600 million parts per year [11]

During hot press forming, the steel blanks are heated up to a temperature of 950°C to obtain an austenitic microstructure. The blanks are then immediately transferred to a press forming station with water-cooled dies, where they are deformed while still in austenitic condition and subsequently cooled to temperatures of around 200°C at a rate higher than 25°C/s. This results in the formation of an ultra-high strength martensitic microstructure with improved mechanical properties, as shown in Fig. 2.2. Thus, by press hardening, a significantly higher strength can be obtained than the conventional cold-forming processes [12].



Figure 2.2 Transformation from austenite to martensite during hot press forming

The aforementioned way of processing is known as the direct method, as shown in Fig. 2.3 (a). An alternative method for more complex parts, known as the indirect method, is shown in Fig. 2.3 (b). In this process, the components are initially cold press to the near-final shape, which is then heated followed by heating and press forming. An additional sandblasting stage is usually carried out to remove the surface oxide layer forming during hot press forming.



Figure 2.3 Schematic representation of the hot forming process by (a) direct method (b) indirect method [12]

Hot press forming is currently being used in the production of safety-critical parts and antiintrusion reinforcement panels for automobiles, as shown in Fig. 2.4, where UHSS play a crucial role due to their high energy absorbing attribute in the event of a collision.



Figure 2.4 Typical automobile components produced using hot press forming [5]

2.2 Coated Products for Hot Press Forming

The need for coated products arose from the susceptibility of bare hot formed products to corrosion and severe red rust appearance, as observed from the cyclic corrosion tests performed on non-coated hot formed boron steel (Fig. 2.5). As hot formed products will lose strength if galvanized after hot forming due to tempering of the martensite, steel manufacturers are keen on the proposition of developing coated products for hot forming to incite the OEMs interest for greater adoption of hot formed steel products into their BIW construction.



Figure 2.5 Comparison between press hardened steel versus unhardened steel subjected to cyclic corrosion testing [13]

Currently, boron steels are being coated either with a barrier-type AlSi coating or sacrificial Zn coatings like GI and GA [10]. As the components undergo deformation at high temperatures, the thermo-mechanical nature of the process leads to formation of microcracks on the heavily deformed sides. Thus it becomes imperative that the coatings protect the substrate sacrificially even in the presence of cracks, as illustrated in Fig. 2.6 (a), and prevent pitting of the substrate at the oxygen deficient regions near cracks, as depicted in Fig. 2.6 (b).



Figure 2.6 Schematic representation of (a) sacrificial protection offered by coatings to hot formed components [14] (b) threat of pitting near oxygen deficient cracks

Hot-dip galvanized coatings

Hot-dip Zn coatings have been used for decades as the popular choice for providing sacrificial protection to steel components, due to zinc's high driving force for providing cathodic protection to iron and the ability to form protective corrosion products [10]. Thus, when considering coatings for hot forming, hot dip galvanized products were one of the primary coating types to be employed.

The microstructure of hot-dip galvanized steel before and after hot forming at 900°C is depicted in Fig. 2.7 (a) and (b) respectively. After hot forming, the Zn layer deposited by hot-dip galvanizing undergoes substitutional alloying with the iron that diffuses into the coating layer during austenitization. This results in the formation of a metallic coating layer comprising of two predominant phases. The Zn-rich phase, Γ -Zn(Fe) contains iron in solid solution, whereas the Ferich, α -Fe(Zn) phase contains Zn in solid solution, as shown in the phase diagram in Fig. 2.8. Corrosion products of ZnO and Zinc hydroxychloride [ZnCl₂.4Zn(OH)₂] formed by these phases during corrosion help inhibit the formation of crystalline iron rust [15].



Figure 2.7 (a) Hot dip galvanized 22MnB5 (b) Coating layer developed after austenitization at 900°C [16]



Figure 2.8 Phase diagram showing the different phases formed by the Fe-Zn alloy system [17]

Autengruber et. al [13] investigated the response of hot dip galvanized GI on 22MnB5 when subjected to cyclic corrosion tests after hot forming. The authors observed that the metallic coating formed after austenitization maintains its galvanic protection ability and protects the substrate without the occurrence of pitting, as shown in Fig. 2.9. They noted that the Zn-rich Γ phase is the first to corrode, followed by the Fe-rich α phase and substrate attack commenced only after these two phases were completely corroded. However, since a considerable amount of Fe is present in the coating layer, the appearance of red rust is a matter of concern, even though the substrate is safe from corrosive attack.



Figure 2.9 Results of cyclic corrosion tests performed for 10 weeks on GI coated 22MnB5 after hot forming [13]

Another category of Zn coatings that have risen to prominence over the recent years are ZnMgAl coatings, due to their improved corrosion resistance and weight-saving benefits. Life cycle analysis showed that replacing a GI-coating with a thinner ZnMgAl-based coating results in a

weight saving between 1-3 kg per vehicle for an average C-class car without compromising corrosion performance [10]. The microstructure of ZnMgAl coatings is depicted in Fig. 2.10, which highlights the difference of this coating system versus the GI coating. These coatings owe their superior corrosion resistance to the cumulative action of formation of a surface aluminium oxide layer and deposition of Zn corrosion products such as simonkolleite and hydrozincite combined with Mg and Al hydroxides formed by co-deposition [18]–[21].



Figure 2.10 Microstructure of hot dip galvanized ZnMgAl [18]

In cyclic corrosion tests performed on hot dip galvanized ZnMgAl coated substrates by Uranaka et al [20] (Fig. 2.11), it was observed that when compared to a conventional Zn coated material, the former showed a superior tendency to resist red rust formation, owing to the passivation effect of corrosion products formed on the surface. This was indicated by a drop in measured corrosion currents on the samples subjected to cyclic corrosion tests, when they were analyzed using cathodic polarization testing (Fig. 2.11).

Considering this aspect, Tata Steel's MagiZinc product offering was adopted for investigation in this work, due to the limited knowledge available on their behavior after hot forming. As new products require a thorough investigation before commercialization, the performance of hot formed ZnMgAl versus hot formed GI was one of the main goals of this study.



Figure 2.11 Left - Cyclic corrosion testing of Zn coated versus ZnAlMg coated steel; Right – cathodic polarization curves obtained from samples after cyclic corrosion tests [20]

Hot-dip aluminized coatings

When considering coatings for protecting automotive components, hot dip aluminizing is an attractive alternative to hot dip galvanizing, due to the comparatively lower density of Al. Aluminium alloy coatings thus have the upper hand in helping reduce weight, provide better mechanical properties and yield high temperature oxidation resistance compared to hot dip zinc coatings [22]. These coatings owe their corrosion resistant characteristics to the formation of a stable thin film of Al₂O₃, whereas Zn coatings provide protection through a high driving force for galvanic corrosion, thereby safeguarding the substrate sacrificially.

The microstructure of Usibor AlSi before and after hot forming is shown in Fig. 2.12 (a) and (b) respectively. Aluminized coatings form by the process of interdiffusion during hot dipping. In the as-hot dip aluminized condition, the coating layer is comprised of a free Al layer, followed by diffusion layers of Al-Fe-Si intermetallics and a final inhibition layer of Fe_2Al_5 . After austenitization at 900°C for 6 min, further interdiffusion transforms the coating and it now comprises primarily of Fe-rich intermetallics FeAl, FeAl₃ and Fe-Al-Si. The long austenitization times are chosen to ensure completion of the alloying process through interdiffusion.



Figure 2.12 (a) Hot dip aluminized AlSi10 [23] (b) metallic coating layer formed after austenitization at 900°C for 6 min [24]

A concerning phenomenon was noticed when salt spray tests were conducted at Tata Steel to compare the corrosion performance of Zn and Al coatings for hot forming. The aim of the tests was to investigate whether or not the cracks formed during hot forming compromise the protective ability of the coating by making it vulnerable to pitting. As shown in Fig. 2.13, substrate attack on the galvannealed (GA) coating did not commence until all the Γ and α phase was consumed. In contrast, the AlSi coating showed a clear indication of pitting, which was already quite severe after 60 hr compared to GA. With increasing testing time, the pitting aggravated and continued to grow into the substrate, while bulk of the coating was still left intact and corrosion products deposited between the substrate and the intact layers of the coating. This phenomenon is attributed to the formation of noble Fe-rich intermetallics that do not provide adequate sacrificial protection to the substrate in case it is exposed to the electrolyte. Red rust formation was also found to be quite severe in case of the AlSi coating when compared to the Zn coatings. Thus, the AlSi coating after hot forming primarily displays barrier protection abilities in comparison to the sacrificial Zn coatings, as was also noted by Allely et al. [25].



Figure 2.13 Comparison between salt spray tests conducted on galvannealed (GA) and AlSi coated 22MnB5 after hot press forming [Ref Source 155984]

2.3 Corrosion Performance Metrics of Hot Formed Components

There are two challenges in the use of zinc coated boron steel in the direct hot forming process. Firstly, the formation of zinc oxides that result in Zn loss and reduce the weldability and secondly, the occurrence of micro cracks that propagate up to the substrate. The former is commonly dealt with by sandblasting the surface and it is the microcracking that is currently a major concern for hot formed products.

2.3.1 Oxide formation

The formation of oxides on the surface of Zn coated products for hot forming is an inevitable consequence due to the nature of the process. After austenitization and hot forming, this surface ZnO layer needs to be sandblasted to ensure low contact resistance during welding.



Figure 2.14 Formation of surface oxides during austenitization ((900°C-3min) of galvanized coatings (a) GA [26] (b) MagiZinc [Ref source 159431]

In Fig. 2.14, formation of the oxide layer on the surface of GA and MagiZinc is shown for an austenitizing treatment of 900°C-3 min. It is observed in Fig. 2.14 (a) that after austenitization, GA develops a ZnO layer coverage on its surface due to Zn oxidation in the furnace. In comparison, a 313 nm thick layer of MgO is formed on the surface of austenitized MagiZinc (Fig. 2.14 b). This difference arises due to the higher affinity of Mg to oxidize when compared to Zn. Thus, during austenitization, the Mg in the coating diffuses to the top and forms a dense MgO layer, which contains the amount of Zn lost due to oxidation. Limiting Zn loss by oxidation is crucial to ensure the presence of greater amounts of sacrificial Zn in the metallic coating. Hence in this regard, MagiZinc with its 1.6 wt. % Mg addition seems to offer an effective solution to safeguard against excessive Zn loss through oxidation. The GA coating on the other hand loses a significant amount of Zn through oxidation. When compared with GI, the oxidation was still greater with GA, even though the two differ only slightly in terms of initial microstructure (GA begins with some amount of Γ and α phases due to the annealing pretreatment given to it after hot dipping, whereas GI is just pure Zn) [Ref source 159146]. Considering this factor, GI and MagiZinc coated 22MnB5 were used as the Zn coating choices for the study.

With the AlSi coating, there is no excessive oxide layer formation as the thin Al_2O_3 layer which forms initially possesses high thermal stability and protects the underlying coating from undesired oxidation in the furnace. This eliminates the need to sandblast AlSi coated products for hot forming.

2.3.2 Microcracking

Another major issue with coated products for hot forming is the cracking of the heavily deformed sides of components. As both the coatings are inherently brittle after hot forming, they are prone to cracking that gets further attenuated by the thermo-mechanical nature of the hot forming process.

In case of the Zn coatings, two mechanisms for substrate crack formation have been well identified [14]. First, cracking due to liquid metal induced embrittlement (LMIE) can occur if low melting point (782°C) Γ -Zn(Fe) phase is present in its molten state on the steel surface during the forming step of press hardening. This results in nucleation of cracks at α -Fe(Zn)/liquid interface in the coating and their subsequent propagation into the substrate. Secondly, Zn penetration at the austenite grain boundaries during heat treatment in combination with certain specific mechanical deformation of the FeZn coating during forming can lead to micro cracks of several microns depth in the substrate. The depth of these cracks is strongly related to the type and amount of deformation applied and can be prevented among others by the use of die lubrication [10].

An incidence of this phenomenon is shown in Fig. 2.15 for the hot formed GI coating, where it can be clearly seen that the cracks penetrate the through thickness of the coating as well as grow into the substrate. It was found that the crack size and depth was found to increase with rise in forming temperatures [27]. Thus, in order to reduce the propensity for cracking by LMIE, the proportion of gamma phase must be kept to a minimum. By increasing the austenitization time, the proportion of low melting phases can be reduced, which helps reduce the occurrence and depth of cracks [28]. However, longer austenitization times also lead to greater loss of Zn through oxidation, which then consequentially reduces the amount of metallic Zn remaining to protect the substrate.



Figure 2.15 Microcrack formation in hot formed GI due to the combination of LMIE and mechanical deformation [27]

The AlSi coating also displays a tendency to form microcracks, due to formation of brittle intermetallics, as shown in Fig. 2.16. However, it was observed that in this case, the cracks always terminated at either the last intermetallic layer, or at the interface between the metallic coating and the substrate [27]. The cracks were found to become wider with increasing strain rates used for deformation. Thus in terms of microcracking, both Zn and Al coatings display a vulnerability to microcrack formation, though the severity in case of AlSi was comparatively lower as the structural integrity of the substrate was not compromised.



Figure 2.16 Microcrack formation in hot formed AlSi [27]

2.4 Electrochemical Analysis Methods

2.4.1 Galvanostatic Testing

A galvanostatic test is an electrochemical testing method in which a pre-defined current is applied to the working electrode and the resulting potential is measured, so as to obtain information on the corrosion potentials of the material under investigation. By maintaining a constant current and measuring the potential change versus time, the technique can be applied to obtain electrochemical depth profiles of coatings and measure the degree of cathodic protection offered by them.

In this study, the different metallic coating systems were subjected to Galvanostatic testing in order to examine the dissolution of the constituent phases or intermetallics in the metallic coating layer and compare the thickness of the coating developed after austenitization. In the former case, the aim is to qualitatively examine the electrochemical hierarchy exhibited by the different constituents of the coating during galvanic corrosion. The latter sheds light on the amount of interdiffusion that occurs during austenitization with increasing soaking times.

The technique was also utilized to galvanostatically etch samples for different dissolution times, after which the corroded surfaces were investigated through SEM/EDX. To obtain an insight into the underlying corrosion mechanism, the etched samples were analyzed in both top-down and cross-sectional view. The former provides an insight into the spatial distribution of corrosion, while the latter gives information on progression of corrosion through the different layers of the metallic coating.

As several previous authors were able to successfully confirm the galvanic protection ability of hot formed GI and GA using galvanostatic testing [13][26][29], the investigation was extended to analyze the electrochemical behaviour of MagiZinc and AlSi in comparison with that of GI. The aim here was to observe the effect of austenitization on the electrochemical behaviour of the coatings and compare the relative galvanic protection offered in each case.

2.4.2 Cyclic Voltammetry

Cyclic voltammetry is a potentiodynamic electrochemical technique, in which the potential is varied linearly versus time using a fixed scan rate and the resulting corrosion currents during the cathodic and anodic polarization cycles are measured as a function of the applied potential. The number of cycles is adjusted based on the corrosion phenomenon being investigated. Investigations by cyclic voltammetry are generally used to examine relative susceptibility to localized corrosion (ASTM G 61), study passivation mechanisms and analyze the protective effect of inhibitors [30]. A typical example of a cyclic voltammogram is shown in Fig. 2.17.



Figure 2.17 Typical example of a cyclic voltammogram for a reversible reaction

In this study, cyclic voltammetry was made use of considering the fact that corrosion reactions occurring on metallic coating systems of galvanic nature are easily reversible processes with low hysteresis loss. Thus the behaviour of the surface in consequent cycles of corrosion can be easily investigated as the results fall within 95% confidence limits, indicating that the bias from external factors is minimal. Hysteresis usually occurs due capacitive currents that arise during the reverse scan going from anodic to cathodic potentials. Positive hysteresis is characterized by relatively higher corrosion currents during the reverse scan as compared with the forward scan, whereas negative hysteresis involves lower corrosion currents in the reverse scan. If a thin oxide layer forms on the surface during the reverse scan, then the additional capacitance of this layer results in a reduction in corrosion currents during the reverse scan leading to negative hysteresis.

On the other hand, if no oxide layer is formed and the metal surface continues to dissolve until the voltage reverts to more cathodic potentials, then the currents in the reverse scan are relatively larger leading to positive hysteresis [30].

The hot formed samples were subjected to 3 cycles of cyclic voltammetry to analyze the progression of corrosion from the initial state to steady state when exposed to a still chloride containing environment, in order to determine the effect of preceding cycles of corrosion on subsequent cycles. The aim was to electrochemically investigate the wet corrosion characteristics and efficacy of the coatings in terms of providing galvanic protection, passivation ability and preventing pitting on the cracked deformed sides. While all previous investigations on hot formed substrates relied on the highly aggressive CCT tests, where the corrosive and reducible species are supplied to the substrate in abundance, the current investigation presents an insight into the behaviour in still aerated 0.1M NaCl. The parameters that were investigated included rate limiting mechanisms (i.e. oxygen diffusion-controlled reduction, hydrogen reduction-controlled or a mixed anodic-cathodic control) and metal dissolution in terms of - (a) shifts in corrosion potential, (b) linear polarization resistance (R_p) fitted +/-10 mV near the corrosion potential to determine corrosion currents and (c) behaviour at higher anodic potentials.

2.5 Characterization Methods

2.5.1 Glow Discharge Optical Emission Spectroscopy (GDOES)

GDOES is an optical emission spectroscopy technique that is used to obtain composition-depth profiles to analyze segregation and alloying effects in metallic systems. In this process (see Fig. 2.18), the surface of the sample is sputtered by impinging it with Argon ions accelerated by an electric field. The sputtered atoms undergo collision with the flux of Argon ions and in the process emit characteristic wavelengths that are detected and analyzed using a polychromator. An advantage of GDOES is that the polychromator can simultaneously detect spectral lines of 40 elements between 110 - 800 nm, thus making it more sensitive to the detection of elements present in low concentrations.



Figure 2.18 Schematic illustration of GDOES principle; Left- Sputtering process in vacuum using argon ions; Right- Detection Process in the polychromator

In the current study, investigation by GDOES was employed to obtain composition depth profiles of the alloying elements in the coatings after austenitization, so as to investigate the effect of process parameters on the distribution of sacrificial elements in the coating thickness. The information obtained from GDOES is complementary to the galvanostatic measurements, as both techniques give an indication of the layer build up. However, GDOES gives positive identification of each phase and can measure minority elements as well (like B, C and Mn).

3. EXPERIMENTAL WORK

This section presents the details of the substrate and coating systems selected for the experimental analysis and sheds light on the methodology adopted in preparing the samples for electrochemical investigation.

3.1 Material Specifications

The steel samples were received as cold rolled blanks that had been hot dip coated. GI140 and MZ140 were obtained from the automotive coating line at Tata Steel Ijmuiden, and the Usibor AlSi[®] steel samples were provided by Arcelor Mittal. All coating systems were applied via hotdip immersion of 22MnB5 steel and the compositions of the same, in weight percentage of the elements, are as shown in Table 4.1.

Steel substrate									
	С	Mn	Si	Cr	Al	В	Ti	Fe	
22MnB5	0.23	1.2	0.2	0.2	0.02	0.0025	0.02	Balance	
Zn-coatings									
	Zn	Al	Mg	Coating Weight					
GI140	99.6	0.4		140 g/m ²					
MZ140	96.2	1.6	1.6	140 g/m ²					
Al-coatings									
	Al	Si		Coating Weight					
AlSi	90	10		150 g/m ²					

Table 3.1 Steel grade and coating compositions used for the study in weight percentages

The MZ140 coated 22MnB5 was provided an additional phosphate passivation of 1.1 g/m^2 by Zinc phosphating with Granodine 5893 through a no-rinse phosphating procedure (i.e. the immersion was not followed by rinsing before drying). From previous investigations performed at Tata Steel Ijmuiden, this procedure was found to help contain Zn oxidation and reduce Zn outbursts and flaking of the surface after hot forming. For this reason, MZ140 will be henceforth referred to as MZ+ to distinguish it from the standard MZ140.

3.2 Experimental Methodology





The experimental testing methodology adopted in this study in shown in Fig. 3.1. Since top hats were available only for GI and AlSi, the MZ+ samples were hot formed using a flat press quench method, as is discussed in the following section.

3.3 Sample Preparation

Hot dip coated 22MnB5 samples were subjected to an austenitization treatment in a Gemco[®] furnace, as shown in Fig 3.2. The furnace was pre-heated to 900°C after which the different coated samples were heated in the furnace. GI and MZ+ were austenitized for 3, 4 and 5 min, while AlSi was austenitized for 6 min.



Figure 3.2 Austenitization treatment during hot press forming

In order to obtain top heads for GI and AlSi, the heated blanks were subjected to hot press forming to obtain omega-shaped blanks as shown in Fig. 3.3. The top surface of the component remains relatively undeformed with the absence of major cracks and is henceforth referred to as the *undeformed* surface in the remainder of the report. On the other hand, the side walls of the component are subjected to considerable deformation during this process, thus developing micro cracks and are referred to as the *deformed* surface in this report.

The samples for MZ+ were prepared by using a flat press. After austenitization, the samples were instantly transferred and quenched between two aluminium blocks, thereby representing the conditions encountered by the top surface of the omega blanks. Thus the discussions on MZ+ are based on electrochemical investigation of this undeformed surface (i.e. without micro cracks).



Figure 3.3 Schematic representation of the hot stamping process and the top heads obtained [25]

After the processing stages, the blanks were cut to obtain samples of dimension 200 x 200 x 1.5 mm. Where sandblasting was required, the oxide layer on the hot formed surfaces was removed by impinging with pressurized sand particles. In order to prepare the samples for electrochemical testing, the procedure prescribed by ASTM G 61 standards were followed, which involved an initial cleaning with demineralised water and then an ultrasonic degreasing with analytical grade acetone.

3.4 Corrosion Testing

The electrochemical investigations were performed with a three electrode flat cell setup, using a Saturated Calomel Electrode (SCE) as the reference electrode and a Pt counter electrode. All electrochemical tests were carried out at room temperature using a Solartron analytical 1280C potentiostat/galvanostat and the results were analyzed and interpreted using CorrWare[®].

Open Circuit Potential (OCP) Evaluation

The preliminary OCP tests were carried out in aerated 0.1M NaCl with a pH of 6-7 to evaluate the surface electrochemical activity before and after hot forming. Tests were carried out for 10-15 min to allow the samples to equilibrate in solution until a state of quasi-static equilibrium was reached.

Galvanostatic Testing

The galvanostatic tests were carried out in 100 gl⁻¹ ZnSO₄.7H₂O + 200 gl⁻¹ NaCl electrolyte (pH 6-7) in aerated condition and at room temperature. This solution is known as the 'stripping solution' due to its ability to facilitate selective dissolution of Zn-rich phases [31]. A current density of 11.76 mA/cm² was employed for all tests, as this value was found to provide the best balance between the accuracy of the electrochemical response and testing time [13][31]. The exposed spot size in all cases was 0.95 cm², which considering the current density used, corresponds to a current of 0.0112 mA applied to the working electrode. All tests were repeated several times so as to ensure repeatability of the acquired data.

Cyclic Voltammetry

The investigation of wet corrosion performance of the coatings was investigated by cyclic voltammetry, using aerated 0.1M NaCl electrolyte. After analyzing the response of the coatings over different potential ranges to ensure their repeatability and reversibility, a potential range of - 0.4 to + 0.4 V was selected for the tests. Cyclic polarization was carried out over 3 cycles with a scan rate of 1 mV/s. The linear polarization resistance was determined +/- 10 mV near the corrosion potentials by computerized Tafel fit method using CorrWare[®].

3.5 Characterization

GDOES

In order to obtain composition depth profiles of the alloying elements in the austenitized coatings, a Jobin Yvon JY 5000 RF glow discharge profiler was used. The sputtering was carried out using Ar under a pressure of 3 mbar and a power setting of 30 W.

<u>SEM/EDX</u>

For the SEM analysis, a Zeiss UltraPlus scanning electron microscope combined with an EDX detector was used. The electron beam energy used in the investigations was 15 keV. SEM analysis of the galvanostatically etched samples was carried out in both top-down and cross-sectional view, so as to obtain an overview of the progression of corrosion. In both cases the back-scattered electron detector was used in order to emphasize the contrast between the different metallic phases.
3.6 Test Matrix

Material	Treatment	Surface Condition	ОСР	GS	CV	SEM/EDX	GDOES
GI		As received	x	x			
	900°C–3m	Undeformed	х	х	x	x	x
	900°C–3m	Deformed	х	x	х	x	
	900°C–3m	Sandblasted	x		x		
GI	900 [°] C–5m	Undeformed	x	х	x	x	x
	900°C–5m	Deformed	x	x	х	x	
	900°C–5m	Sandblasted	x		x		
MZ+		As received	x	x			
	900°C–3m	Undeformed	x	x	x	x	x
	900°C–3m	Sandblasted	x		x		
MZ+	900°C–5m	Undeformed	х	x	x	x	x
	900 [°] C–5m	Sandblasted	x		x		
AlSi		As received	х	x			
	900°C–6m	Undeformed	x	x	x	x	х
	900°C–6m	Deformed	x	х	х	x	
22MnB5	900°C–5m	Sandblasted	x		x		

Table 3.2 Testing methodology adopted during experimental analysis of the coatings

4. RESULTS AND DISCUSSION

While investigating the corrosion performance of coated substrates for hot press forming, the following parameters have a direct consequence on the corrosion protection life cycle of metallic coatings.

- Coating thickness developed as a result of the austenitization treatment.
- Distribution of sacrificial species through the coating thickness.
- Loss of element offering active corrosion protection by oxidation.
- Cracks penetrating through thickness and those reaching the coating-substrate interface.

The above considerations have been used as the basis to judge the quality of cathodic corrosion protection offered by the different coatings, in correlation with the results of the electrochemical analysis. The latter results have also been used to elucidate the corrosion protection mechanism offered in case of Zn and Al-based coatings.

4.1 Preliminary OCP Testing

The starting point of most electrochemical measurements is the OCP, which provides information on the nobility (value of the potential relative to the other materials) and reactivity of the surface (changes of the potential in time). Hence, initial OCP testing was carried out in 0.1M NaCl solution to examine the surface activity of the samples before and after hot press forming. The samples were allowed to equilibrate in solution for 10-15 minutes, until a state of quasi-static equilibrium (indicated by the OCP signal having a constant value) was reached.



Figure 4.1 OCP of the coatings in 0.1M NaCl before hot forming

The results of the OCP tests on samples *before* hot forming [henceforth referred to as non heattreated (Non HT)] are as shown in Fig. 4.1. These correspond to the surface activity of the as received hot dip coated substrates. From the figure, it can be observed that the GI and MZ+ are more active compared to AlSi and the 22MnB5 substrate, as they exhibit more negative potentials compared to the latter two. This indicates that while the Zn-coatings have a high driving force for cathodic protection, the AlSi coating has a more passive nature due to the close proximity of its OCP with 22MnB5. The steady state OCP recorded for GI, MZ+ and AlSi were -0.95, -0.97 and -0.6V respectively, and the OCP of the substrate was found to be -0.6V. The fluctuations in the OCP of AlSi occur due to the repeated formation and breakdown of the surface aluminium oxide layer, meaning that the potential is determined by any exposed steel rather than the AlSi coating.

GI coating after hot press forming:

The surface activities of the GI coated samples after austenitization at 900°C and hot forming is depicted in Fig. 4.2. From the graph, it is observed that austenitization results in the OCP of *Non HT* GI to rise to less negative potentials, i.e. the coating becomes comparatively more passive.

This is due to the fact that Fe and Zn undergo substitutional alloying during austenitization as described in Section 2.2. The formation of the Γ -Zn(Fe) and α -Fe(Zn) phases render the metallic coating a potential intermediate between *Non HT* GI and 22MnB5. Increasing soaking time in the oven does not have a pronounced effect on the OCP and the potentials for 3, 4 and 5 min differ consecutively by 20mV. The OCPs of the deformed sides were also found to be similar to their undeformed counterparts.



Figure 4.2 Open circuit potentials of GI coating in 0.1M NaCl after hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus}=3, 4, 5min$)

MZ+ coating after hot press forming:

The effect of hot forming on the surface activities of MZ+ coated samples is shown in Fig.4.3. As observed with GI, the MZ+ coated samples also assume less negative potentials, indicating the formation of a more passive coating due to austenitization. The OCPs for 3, 4 and 5 min differ consecutively by about 40mV from each other. When compared with the OCPs of austenitized GI coated samples that lie between 800 to 850 mV, it is observed that the MZ+ coated samples are slightly more passive and lie between 750 to 800 mV. The slight difference is due to the difference in coating chemistry and it should be noted that the predominant constituent



Figure 4.3 Open circuit potentials of MZ+ coating in 0.1M NaCl after 3 hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus}=3, 4, 5min$)

phases in both GI and MZ+ coatings after austenitization is the Γ -Zn(Fe) and α -Fe(Zn) phases, as will be described in the sections to follow.

AlSi coating after hot press forming:

In case of AlSi coated samples, the surface activities after hot press forming were closely similar to the OCP before austenitization as shown in Fig. 4.4. The deformed side was observed to be slightly more active than the undeformed side, and in both cases the OCP coincides with that of the 22MnB5 substrate. This is due to the fact that the intermetallics in the AlSi coating have corrosion potentials closely similar to the substrate, which is discussed in detail in Section 4.2.3. Thus, it can be inferred that the AlSi coating is essentially a passive barrier coating that possesses limited sacrificial character. In addition, due to the close proximity of corrosion potentials of the intermetallics with that of the substrate, the metallic coating and the substrate will corrode simultaneously in the event that the substrate is exposed.



Figure 4.4 Open circuit potentials of AlSi in 0.1M NaCl after hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus}=6min$)

4.2 Galvanostatic Testing

The layer thickness and composition can be determined with a galvanostatic measurement by dissolving each phase (alloy) subsequently. The potential is specific to each alloy and the time until a different potential is reached can be used to calculate the thickness of each layer. As mentioned in Section 3.4, all the galvanostatic measurements discussed in this subsection were performed using 100g/l ZnSO₄ + 200g/l NaCl electrolyte in aerated condition. The pH of this electrolyte ranges from 6-7. A current density of 11.76 mA/cm² was employed and all tests were carried out at room temperature. The potentials stated are versus SCE (Saturated Calomel Electrode).

4.2.1 Galvanostatic Testing of GI coated 22MnB5

The galvanostatic curves of *Non HT* GI versus those obtained after austenitization for 3, 4 and 5 minutes, followed by hot forming, are shown in Fig. 4.5. Galvanostatic dissolution of *Non HT* GI, indicated by the black curve, is quite straightforward. The Zn layer deposited by hot dip galvanizing dissolves first at a potential of -0.96 V (SCE), after which a sharp transition to -0.42 V (SCE) is observed that corresponds to the potential of 22MnB5.

After hot forming, the galvanostatic curves exhibit modified characteristics. The most apparent observations are the shifting of the curves to less negative (more noble) potentials, appearance of two characteristic potential plateaus and a progressive increase in coating thickness due to substitutional alloying caused by the interdiffusion of Fe and Zn.



Figure 4.5 Galvanostatic measurement of GI coated 22MnB5 before and after hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus} = 3, 4$ and 5 min)

From the galvanostatic measurement for 3 min austenitization, indicated by the red curve, it is observed that the initial dissolution commences at a potential of -0.76 V(SCE). This value is representative of the Γ -Zn(Fe) phase, as also observed by Autengruber et al [13]. As it is a Zn rich phase, its potential is closer to pure Zn and is the first phase to dissolve. After 21 min, the Γ -Zn(Fe) phase is completely dissolved and the α -Fe(Zn) phase begins to dissolve at a potential of -0.6 V(SCE). This phase, being rich in Fe, has a potential closer to the martensitic 22MnB5 substrate. The α -Fe(Zn) phase is completely consumed after a measurement time of 52 min and the potential rises to -0.4 V(SCE), corresponding to the martensitic 22MnB5. Coating thickness has increase by 1.5 times after a 3 min austenitization.

The curve for 4 min austenitization, indicated by the blue curve, is only slightly different from the one for 3 min. In this case, less Γ -Zn(Fe) and more α -Fe(Zn) is observed, as can be seen from the difference in dissolution times of the phases in the two curves. This is due to the larger austenitization time, which results in the growth of the α -Fe(Zn) phase. As there is more Fe than Zn available during the formation of the metallic coating by interdiffusion, the α -Fe(Zn) phase grows preferentially compared to the Γ -Zn(Fe) phase, by incorporating the Zn in the Γ -Zn(Fe) phase into the growing α grains. This segregation was also observed in the EDX analysis of the galvanostatically etched samples, which is described in Section 4.3.1. The coating thickness has also increased two fold after a 4 min austenitization, as the longer soaking enables more Fe to diffuse into the hot dip galvanized layer.

For an austenitization of 5 min (green curve), only a small amount of Γ -Zn(Fe) phase is present and the metallic coating consists primarily of the α -Fe(Zn). The coating thickness has stabilized for most part and is only marginally greater than that for 4 min austenitization. As stated in the Section 2.3.2 on microcracking, longer austenitization times are necessary for the GI coating so as to minimize the fraction of the Γ -Zn(Fe) in the metallic coating layer and thus the propensity for cracking by Liquid Metal Induced Embrittlement (LMIE).

Thus, also observed in the OCP tests, austenitization minimizes the potential difference between the metallic coating and the substrate as a result of the alloying with iron. However, the cathodic corrosion protection ability is still intact after all austenitization times, as observed from the potential difference between Γ -Zn(Fe) and α -Fe(Zn) versus the 22MnB5 substrate, albeit with a lower driving force that indicates a decrease in the corrosion rate of the samples after hot forming.

4.2.2 Galvanostatic Testing of MZ+ coated 22MnB5

The response of the hot formed MZ+ coating to galvanostatic measurements after different austenitization times is depicted in Fig. 4.6. Prior to hot forming, the dissolution progresses similarly to GI as indicated by the black curve. Despite possessing a different microstructure than GI in its Non HT condition, in a galvanostatic measurement dissolution always progresses

according to the electrochemical hierarchy of activity. Thus, the Zn in the coating dissolves first at a potential of -0.96 V(SCE), followed by dissolution of other eutectics as observed in the small dip in potential before the martensite potential of -0.42 V(SCE).



Figure 4.6 Galvanostatic measurement of MZ+ coated 22MnB5 before and after hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus} = 3, 4$ and 5 min)

Post hot forming, the galvanostatic curves for all austenitization times are similar to each other, with differences observed only in terms of coating thickness. The curves resemble the GI coating austenitized for 4 min with the α -Fe(Zn) phase dissolving at -0.6 V(SCE). The reason for the similarity with hot formed GI is that when austenitized, the chemistry of the phases in the MZ+ coating is reset at this high temperature. Most of the Mg and Al diffuses to the surface and gets oxidized, while the Zn alloys with Fe during the interdiffusion process. The surface MgO did not dissolve during this process and was present as a black deposit on the electrochemically etched spot.

At all austenitization times, there exists only a small fraction of Γ -Zn(Fe), which progressively decreases with increasing austenitization time. This may be due to the higher Al content in the MZ+ coating, which retards the Zn-Fe interdiffusion, thereby promoting preferential growth of the Fe-rich α -Fe(Zn) phase. The α -phase then grows into the substrate by incorporating more Zn,

resulting in increasing coating thickness with increasing oven soaking time. This portrays that for MZ+ the low-melting point gamma phase can be avoided even at short austenitization times.

What is also interesting is that for the same coating weight (140 g/m^2) and austenitization times, the MZ+ coatings have longer dissolution times than their GI counterparts, indicating that larger coating thickness can be obtained in the former case. While the dissolution time increases from 20 min to a maximum of 62 min for GI and 110 min for MZ+ going from 3 to 5 min of austenitization. Thus, the peak coating thickness increases by a factor of 3 and 5 for GI and MZ+ respectively, when compared to their Non HT condition. Since a larger coating thickness directly translates to longer corrosion protection lifetime, the MZ+ coating has an upper hand over GI in this regard.

4.2.3 Galvanostatic Testing of AlSi coated 22MnB5



Figure 4.7 Galvanostatic measurement of AlSi coated 22MnB5 before and after hot forming ($T_{aus} = 900^{\circ}C$ and $t_{aus} = 6$ min)

The results of the galvanostatic test on AlSi are shown in Fig 4.7. Dissolution of *Non HT* AlSi (black curve) commences at a potential of -0.7 V(SCE), due to the greater proportion of free Al and Al-rich intermetallics with Si in the upper layer of the coating before austenitization. A transition is then observed to potentials more noble than martensite and as dissolution progresses,

the potential gradually drops to that of martensite. These noble potentials are registered due to the presence of Fe- rich intermetallics (FeAl, FeAl₃ and Fe₂Al₅) in the layers preceding martensite.

In the red curve, indicative of the hot formed AlSi ($T_{aus} = 900^{\circ}C$ and $t_{aus} = 6$ min), the initial dissolution potential (-0.48 V) has become more noble due to the alloying with Fe during austenitization. As a result, the proportion of Al-rich intermetallics has reduced, while that of Ferich intermetallics has increased. The former type of intermetallics dissolve first at a potential slightly lower than the martensitic 22MnB5 and the latter type dissolves at a potential very close to that of the substrate. De Graeve et al. [23] also observed the proximity of potentials of the intermetallics formed after aluminizing with that of the substrate in Volta potential map of *Non HT* AlSi and as is seen from the galvanostatic curves, the potentials are even more similar after austenitization. This clearly indicates the risk of pitting initiation after dissolution of the more active intermetallics.



Figure 4.8 Volta potential map of Non HT AlSi [23]

In terms of coating thickness, the *Non HT* AlSi coating starts off with a thickness of 25 μ m, which is greater than the 10 μ m thick Zn coatings so as to increase its passive barrier functionality. Correspondingly longer austenitization times are thus necessary for completion of alloying process in the oven. However after austenitization, the coating thickness only increases

to 30 μ m as was observed in the SEM images of crosscuts, indicating that the formation of intermetallics is not accompanied by a significant increase in coating thickness. Hence, the long dissolution times in Fig. 4.7 do not correlate to an increased coating thickness for AlSi, as the noble intermetallics take time to completely dissolve, during which time pitting occurs for a considerable duration before the actual martensite potential is reached.

4.3 SEM-EDX Analysis of Coatings

In order to characterize the stages of cathodic corrosion protection offered by the phases and intermetallics in metallic coatings of Zn and Al respectively, the samples were characterised using SEM/EDX. The analysis was done at both the uncorroded and partially etched coatings by interrupting the galvanostatic measurement at specific points where one phase is removed and the other phase is still present. Furthermore, the characterisation was done in both cross sectional view (depicting the build-up of the layers) and top-down (which gives an idea of the spatial distribution of corrosion).

The samples were galvanostatically etched for two separate intervals, for austenitization times of 3 min for GI & MZ+ and 6 min for AlSi. The results give an insight into the capability of the metallic coatings to sacrificially protect the substrate in an anodically polarized corrosive environment containing chloride ions at neutral pH.

4.3.1 SEM analysis of GI coated 22MnB5

The surface morphology of GI coated 22MnB5 on the undeformed and deformed sides after hot forming is depicted in Fig. 4.9 (a) and (b) respectively. It can be seen that the undeformed surface has an extensive coverage of thermally formed ZnO over α and Γ grains, due to austenitization. This oxide needs to be removed by sandblasting to reduce the contact resistance while welding. On the deformed sides, the ZnO coverage is comparatively less as the sides of the die scrape away some of it away, leaving a thin oxide layer covering the α grains. An important feature on the deformed sides is the cracks formed during the hot forming due to a combination of deformation with LMIE, which are present all across the surface and facilitate ingress of electrolyte into the metallic coating layer.



Figure 4.9 BSE surface image of hot formed GI (900C-3m) (a) Undeformed side (b) Deformed side

To observe the action of the electrolyte cathodically consuming the phases, SEM images were recorded in top down and cross section view. The progression of corrosion in top down view is as shown in Fig. 4.10. In Fig. 4.10 (a) and (b), the undeformed side was galvanostatically dissolved for 10 and 30 min respectively, and in Fig. 4.10 (c) the deformed side was dissolved for 30 min.

The investigation clearly displayed the cathodic corrosion protection ability of the phases in the metallic GI coating. In Fig. 4.10 (a), it is observed that uniform galvanic dissolution initiates by consuming the interspersed Γ -Zn(Fe) phase first, forming a honeycomb-like morphology. This then allows the electrolyte to permeate those cavities and dissolution progresses by consuming the α -Fe(Zn) phase, as seen in Fig. 4.10 (b). Attack begins at α grain boundaries and ultimately consumes the entire grain. On the deformed side (Fig. 4.10 c), a similar process was observed as well, as is seen from the honeycomb-like morphology in the region between the cracks. The fine needle shaped crystals seen in the figure are the salt deposits from the stripping solution.



Figure 4.10 BSE surface images of hot formed GI (900C-3m) (a) undeformed side (10min dissolution) (b) undeformed side (30min dissolution) (c) deformed side (30min dissolution)

In order to confirm the absence of corrosive attack on the substrate, images of the crosscut were also obtained as shown in Fig. 4.11. The cross section of as hot-formed GI is shown in Fig. 4.11 (a). In the adjacent figure of the undeformed side dissolved for 10 min (Fig. 4.11 b), the commencement of galvanic corrosion is seen from the dissolution of the Γ phase, while the α phase is still intact. After 30 min of dissolution on the undeformed side (Fig. 4.11 c), all the Γ and a large portion of the α phase has corroded, while the substrate is still untouched. As a comparison, Fig. 4.11 (d) shows the deformed side after 30 min dissolution, where a lesser proportion α phase is still remaining as compared to its undeformed counterpart. This is expected, as the electrolyte has easy access to the α grains through the cracks, but since this a

galvanostatic dissolution, it is *not* indicative of the corrosion rate. The important thing to note here is that despite the presence of cracks, the martensite corrodes only after all the α phase is eaten away.



Figure 4.11 BSE images of crosscuts of hot formed GI (900C-3m) (a) after hot forming (b) undeformed side (10min dissolution) (c) undeformed side (30min dissolution) (d) deformed side (30min dissolution)

A line scan performed across the α and Γ phases, shown in Fig 4.12, reveals the alloying in the two phases. The Γ -Zn(Fe) was found to have a composition of Zn 70 at. % and Fe 30 at. % and α -Fe(Zn) contained Fe 60 at. % and Zn 40 at. %. The composition of α phase increases to Fe 70 at. % and Zn 30 at. % for 5 min austenitization, which is the stable composition beyond which there is no further alloying. Consequently, beyond 5 min austenitization there is limited growth

of the metallic coating layer as seen in the galvanostatic curves, and this seems to be the upper limit for austenitization time for GI.



Figure 4.12 EDX line scan across α and Γ phase in the metallic GI coating after hot forming

4.3.2 SEM analysis of MZ+ coated 22MnB5

The surface of MZ+ coated 22MnB5 after hot forming at 900°C for 3 min is illustrated in Fig. 4.13. In this case, the surface displays an extensive coverage of dense MgO, interrupted by small islands of α -Fe(Zn) that have a thin layer of ZnO on them, as is shown in Fig. 4.13 (a). As Mg has a greater affinity for oxygen than Zn, it diffuses to the surface during austenitization and gets oxidized. This insulates Zn from oxidation in the oven, enabling it to alloy rapidly with Fe by interdiffusion. As a result, a thicker coating is developed in a shorter time when compared with GI. On close observation of the MgO layer (Fig. 4.13 b), small white spots were observed at pores present in this highly compact layer. These were found to be ZnO globules, which form when some Zn atoms manage to force their way through the pores in the MgO. In this way, MZ+ was found be efficient in terms of minimizing Zn loss via oxidation.



Figure 4.13 BSE surface image of hot formed MZ+ (900C-3m) (a) Undeformed side (b) thermally formed MgO layer

As was also observed in the galvanostatic measurements, the MZ+ metallic coating is similar in microstructure to the GI metallic coating (Fig. 4.14 a), as the predominant phase in both cases is α -Fe(Zn). Thus the corrosion mechanism of hot formed MZ+ is similar to what happens with GI, where the Γ and α phases dissolve consecutively, as shown in Fig. 4.14 (b). In terms of composition of the α phase, consistency was observed with all austenitization times resulting in a composition of 70 at. % Fe and 30 at. % Zn. This indicates a faster alloying process with MZ+ when compared to GI.



Figure 4.14 BSE images of crosscuts of hot formed MZ+ (900C-3m) (a) after hot forming (b) after 30min dissolution



Figure 4.15 (a) BSE surface image of galvanostatically etched spot after 30 min; EDX spot scan with stronger Mg signal at (b) grain boundaries than at (c) grain interiors.

A similar phenomenon was observed by Uranaka et al. [20] in their investigation of cut edge corrosion of ZnAl6Mg3, as shown in Fig. 4.16. The authors were examining the corrosion resistance of hot dip galvanized Zn-Al-Mg through cyclic corrosion testing (CCT) and found that Mg and Zn eluted from the coating layer to the cut edges by galvanic action and helped improve corrosion resistance through the formation of Zn corrosion products enriched with Mg and Al. Thus, in case of hot formed MZ+, it can be inferred that some elemental Mg is present in the metallic coating layer even after austenitization, which segregates to the α grain boundaries through galvanic action and offers additional cathodic protection. To confirm the presence of elemental Mg in the coating, a GDOES test was performed on the cross section to obtain a composition depth profile, which is discussed in the following subsection.



Figure 4.16 Surface morphology of corrosion products formed on cut edges of hot dip galvanized ZnAl6Mg3 after 40 cycles of CCT [20]

4.3.3 GDOES comparison between GI and MZ+

Investigation by GDOES was employed to obtain composition depth profiles of the alloying elements in GI and MZ+ metallic coatings, so as to analyze differences in their response to austenitization. In particular, as the two coatings possess similar microstructures post austenitization, GDOES was used to examine the distribution of Al and Mg in MZ+ to ascertain whether the entirety of Mg and Al oxidizes during austenitization, or if some percentage of it distributed through the coating thickness.

The information obtained from GDOES is complementary to the galvanostatic measurements, as both techniques give an indication of the layer build up. However, GDOES gives positive identification of each phase and can measure minority elements as well (like B, C and Mn), whereas galvanostatic measurements is less sensitive to spatial mixing of the phases (a pocket of Γ phase in α -matrix is selectively etched, whereas GDOES would measure a mixture).

The GI coating contains a small amount of Al, which is added to galvanizing baths so as to promote better adhesion of Zn to the substrate. This Al combines with Fe from the substrate to form very thin Fe_2Al_5 inhibition layer after galvanizing. As a result of austenitization, Al diffuses to the surface and gets oxidized and is present as a surface oxide along with ZnO, as shown in Fig. 4.17.



Figure 4.17 GDOES composition-depth profile of Al in hot formed GI

In case of MZ+, which contains a higher Mg and Al content compared to GI, the Mg fulfils its intended role during austenitization and diffuses to the surface forming a dense oxide layer about 2.5 μ m in thickness, as shown in Fig. 4.18 (a). Interestingly, a small proportion of elemental Mg was found to be present up to a depth of 5 μ m and 7.5 μ m for 3 and 5 min austenitization respectively, which could explain why eluting of Mg to grain boundaries was observed in the top-down SEM image that was also galvanostatically etched to a depth of around 10 μ m. Whether this phenomenon offers any passivation benefits before and after sandblasting was investigated through cyclic voltammetry and is elaborated further on in detail in Section 4.4.2.

The composition-depth profile of Al (Fig. 4.18 b) also indicated distribution of Al in the metallic coating layer. As seen from the scale bars, the percentage of Al present in the α -Fe(Zn) layer is lesser than that of Mg. However, Al is distributed more uniformly throughout the coating thickness, whereas Mg is only found in the beginning one third of the coating thickness. One would then expect this Al to render some passivation ability through the formation of a passive Al₂O₃ layer covering the α grains. Indications of such behaviour were observed during investigation by cyclic voltammetry and have been dealt with in Section 4.4.2. The presence of small amount of elemental Mg and Al across the thickness of the metallic coating layer seems to be the subtle difference between GI and MZ+ after hot forming.



Figure 4.18 GDOES composition-depth profile of (a) Mg and (b) Al in hot formed MZ+

An important occurrence was observed with regard to the GDOES profile of boron and manganese in GI, which are the elements that affect hardenability of boron steels. It was noticed that for an austenitization time greater than 3 min, a significant amount of boron and manganese had diffused to the upper layer of the metallic coating, as shown in Fig. 4.19 (a) and 4.20 (a) respectively. This was exclusive to GI and was not noticed in MZ+ (Fig. 4.19 b and 4.20 b), indicating that the latter has a larger processing window, as hardenability is not compromised even after 5 min of austenitization.



Figure 4.19 GDOES composition-depth profile of boron in (a) hot formed GI and (b) hot formed MZ+



Figure 4.20 GDOES composition-depth profile of manganese in (a) hot formed GI and (b) hot formed MZ+

Thus, it appears that reducing the rate of Zn oxidation also suppresses depletion of the substrate of its alloying additions to facilitate increased hardenability. In MZ+ Mg helps in suppressing Zn oxidation. However in GI, the Zn is free to oxidize and once a substantial amount of Zn gets oxidized, boron and manganese also make their way to the surface layers where they get oxidized. Hence, the processing window for GI is only up to 3-4 min, whereas for MZ+ it is possible to go up to 5 min.

4.3.4 SEM analysis of AlSi coated 22MnB5



Figure 4.21 BSE surface image of hot formed AlSi (900C-6m) (a) Undeformed side (b) Deformed side

The surface morphology of hot formed AlSi (900°C-6min) on the undeformed and deformed sides is shown in Fig. 4.21. From the images it is observed that unlike Zn coatings there is no extensive coverage with surface oxide, as Al_2O_3 forms a thin oxide layer on the surface during austenitization, which serves as a thermal barrier to further oxidation due to the stability of the oxide at the ambient over temperature. This is why shot blasting is not a primary concern for hot formed AlSi coated 22MnB5. On the deformed side, cracking is observed due to the thermomechanical nature of the process. However as mentioned in Section 2.3.2, the cracks do not penetrate into the substrate and terminate at the last intermetallic layer.

After galvanostatic dissolution for 10 min, the surface SEM images revealed initiation of corrosion through the uniform dissolution of Fe-rich intermetallics as is shown in Fig 4.22 (a) for both the undeformed and deformed sides. However, when the dissolution was carried out for 100 min, pitting was already visible on the surface of the deformed side as shown in Fig. 4.22 (b), where an EDX scan (Fig. 4.22 c) revealed a strong Fe signal indicating that the martensite had been exposed.



Figure 4.22 BSE surface image of hot formed AlSi (900C-6m) (a) Undeformed side (10 min dissolution) (b) Deformed side (100 min dissolution); (c) EDX spot scan at exposed martensite

When the cross-cuts of the hot-formed samples were examined the threat of pitting was evident even clearly. The composition of the AlSi coating after hot forming is described in Fig. 4.23 (a), which shows how the different intermetallics (Fe₂Al₃, FeAl and Fe-Al-Si) are stacked upon each other. Small Kirkendall voids are formed in the layers of the metallic coating during the formation of the intermetallic layer by diffusion, as was also observed in the investigations by Fan et al. [32] and in References [22] & [33].



Figure 4.23 BSE images of crosscuts of hot formed AlSi (900C-6m) (a) after hot forming [24] (b) undeformed side (30min dissolution) (c) undeformed side (100 min dissolution)

To test the vulnerability to pitting, the undeformed side was examined at intervals of 30 and 100 min of dissolution as shown in Fig. 4.23 (b) and (c). Surprisingly, a clear indication of pitting was indeed evident. After the short dissolution, it was observed that FeAl and Fe₂Al₃ had preferentially dissolved and the substrate was untouched at this stage. However, at longer

dissolution times, the Fe-Al-Si intermetallic layer seems to have completely dissolved, while a considerable amount of FeAl and Fe₂Al₃ is still intact. In addition, dissolution progressed by the attack of both the substrate as well as the metallic coating, which was witnessed through the initiation of pit formation and propagation. Thus the gaps left from corrosion allow access of electrolyte to the martensite, due to which substrate attack then commences as a result of the proximity of the substrate's corrosion potential with that of the bulk of the coating. These observations were consistent with the data obtained from the galvanostatic curves and VDA testing. Thus, at longer exposure times, pitting and creepback of the substrate are a concern for AlSi coatings, as once the electrolyte gains access to the substrate through the cracks and gaps in between the corroded intermetallics, the remainder of the coating does not provide sufficient sacrificial protection, and pitting progresses in an autocatalytic manner accelerated by the increasing pH and concentration of chloride ions near the substrate.

4.4 Investigation by Cyclic Voltammetry

The hot formed samples were subjected to 3 cycles of cyclic voltammetry to analyze the progression of corrosion from the initial state to steady state when exposed to a still chloride containing environment, in order to determine the effect of preceding cycles of corrosion on subsequent cycles. The aim was to electrochemically investigate the wet corrosion characteristics and efficacy of the coatings in terms of providing galvanic protection and preventing pitting on the cracked deformed sides.

Whereas all previous investigations on hot formed substrates relied on the highly aggressive CCT tests, where the corrosive and reducible species are supplied to the substrate in abundance, the current investigation presents an insight into the behaviour in still aerated 0.1M NaCl to investigate rate limiting mechanisms and metal dissolution in terms of shifts in (a) corrosion potential (E_{corr}), (b) corrosion currents (i_{corr}) at corrosion potential and (c) response to increasing anodic potentials. The former two were obtained via linear polarization resistance at +/- 10 mV near the corrosion potential, while the latter was analyzed based on the cyclic polarization curves in linear and logarithmic mode. All tests were conducted over the range of -0.4 to +0.4 V with a scan rate of 1 mV/s.

4.4.1 Cyclic Voltammetry testing of GI coated 22MnB5

A summary of the results for hot formed GI is presented in Table 4.1. The results are indicative of linear polarization resistance analysis performed to determine shifts in E_{corr} and i_{corr} . Tests were performed on the undeformed and deformed sides after initial hot forming and subsequent sandblasting (SB), post austenitization times of 3 and 5 min, so as to investigate differences in the electrochemical response after different processing stages.

Table 4.1 Summary of corrosion potentials and corrosion current density for hot formed GI obtained through cyclic voltammetry

Material	Treatment	Surface Condition	Cycle 1		Cycle 2		Cycle 3	
			E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)
GI	900°C–3m	Undeformed	-0.74	90.7	-0.86	16.6	-0.92	6.5
		Deformed	-0.81	6.5	-0.95	3.7	-1.00	11.9
	900°C–3m SB	Undeformed	-0.74	30.5	-0.96	5.3	-0.98	13.54
		Deformed	-0.74	24.4	-0.98	6.7	-1.00	12.9
	900 [°] C–5m	Undeformed	-0.74	73.8	-0.80	15.8	-0.80	4.3
		Deformed	-0.78	19.9	-1.00	15.6	-0.97	8.6
	900°C–5m SB	Undeformed	-0.59	20.2	-1.00	15.6	-0.97	8.6
		Deformed	-0.56	13.4	-0.84	2.42	-0.89	5.24

Hot formed GI (900°C-3 min)

The results of the polarization tests conducted on the undeformed and deformed sides of GI after a 3 min austenitization is shown in Fig. 4.24 (a) and (b). In the figure, only the forward scans are represented as the reverse scans, which indicate the deactivation process, demonstrated similar behaviour due to the reversible nature of metallic systems. From initial observations, it is seen that the curves indicate diffusion controlled oxygen reduction in the cathodic regime and dissolution of the metallic phases in the anodic regime. The curves also show the ability of hot formed GI to sacrificially protect 22MnB5, as in each cycle the coating is more active than the substrate.



Figure 4.24 Cyclic polarization curves of hot formed GI (900C-3min) (a) Undeformed side (b) Deformed side

From Table 4.1, it is observed that with progressing cycles of corrosion, the corrosion potential shifts to more active potentials, which is due the galvanic nature of the process that causes dissolution of Γ -Zn(Fe) phase to dominate. This occurrence is indicated by the shift in the position of the curves to more negative (active) potentials as seen in Fig. 4.24 (a) and (b). The corrosion potentials on the undeformed and deformed side differed by 80 mV in each cycle, which is a consequence of more Γ -Zn(Fe) exposed on the deformed side.

The corrosion currents on the undeformed surface near E_0 indicated a decreasing trend, going from 90.7 μ A/cm² to 6.5 μ A/cm². Decreasing corrosion currents after the initial corrosion cycle convey that there is formation of corrosion products such as Zn(OH)₂ and simonkolleite (Zn₅(OH)₈Cl₂) [1,5] on the surface due to the increasing availability of Zn metal ions from the dissolving metallic phases after each corrosion cycle. This helps in reducing the corrosion currents while transitioning to anodic potentials. However, the hydroxide layer breaks down rapidly with increasing anodic potentials, as seen from the lack of passivation in Fig. 4.24 (a).

In contrast, the deformed side started with a much lower initial corrosion current of $6.5 \,\mu\text{A/cm}^2$ that decreased further to $3.7 \,\mu\text{A/cm}^2$ in cycle 2 and finally rose to $11.9 \,\mu\text{A/cm}^2$ in cycle 3. When compared to the undeformed surface, an active-passive transient was observed as potentials rose to more anodic values in cycle 2 and 3. Thus, it follows that the after initial dissolution, the cracks on the deformed side facilitates better accumulation of corrosion products, causing corrosion currents to reduce. A similar phenomenon was also observed on deformed hot dip galvanized steel sheets by Vagge et al. [34] and Raja et al [35]. However, since the aforementioned corrosion products are easily soluble, their passivation effect is not very pronounced.



Figure 4.25 Cyclic voltammogram of hot formed GI (900C-3m) (a) undeformed side (b) comparison between undeformed and deformed side.

The response of the coating to higher anodic potentials is indicated in Fig. 4.25. In Fig. 4.25 (a), the behaviour of the undeformed side is depicted, which revealed characteristics of an activating system (indicated by the red arrow) due to progressively increasing corrosion currents. However, the peak anodic currents do not differ significantly. A small amount of positive hysteresis (indicated by direction of blue arrows) was observed during the reverse scan, which represents that there is no hydroxide barrier layer formed as the potential drops and metal dissolution continues until the voltage transitions to cathodic potentials. The same mechanism was also observed when the deformed side was subjected to higher anodic potentials, as shown in Fig 4.25 (b). Peak anodic currents were observed to be quite consistent, but the corrosion rate was comparatively higher than the undeformed side owing to the presence of cracks, as seen from the difference in slopes of the two curves at high anodic potentials. Thus, despite indication of some feeble passivation at low anodic potentials, metal dissolution of the as hot formed surface at higher anodic potentials progressively increased with increasing cycles of corrosion.

Hot formed GI (900°C-3 min) after sandblasting



Figure 4.26 Cyclic polarization curves of hot formed GI (900C-3min) after sandblasting (a) Undeformed side (b) Deformed side

The polarization curves of hot formed GI (900°C-3min) after sandblasting the oxide layer, is shown in Fig. 4.26. As observed with the surfaces after hot forming, E_0 shifts to more active potentials with increasing cycles of corrosion. The steady state E_0 for sandblasted surfaces is identical to that recorded for the surfaces after hot forming.

When corrosion currents at the commencement of each anodic cycle were measured (Table 4.1), it was found that in the first two cycles, the sandblasted undeformed surface registered values 3 times lower than the as-hot formed samples. Furthermore, a more pronounced active-passive transient spanning a potential range of 150 mV was recorded while transitioning to higher anodic potentials, which indicates that the sandblasted surface forms a more homogenous coverage of Zn corrosion products after removal of the oxide layer. The sandblasted deformed surface also yielded identical corrosion currents versus its undeformed counterpart. In this case, a higher initial i_o was registered in the first cycle due to more exposed surface area after removal of oxides, but the values subsided to become similar to that on the sandblasted undeformed surface. An active-passive transient spanning a 200 mV potential range was observed with increasing anodic polarization, indicating that the corrosion products cover more surface area due to the presence of cracks.



Figure 4.27 Cyclic voltammogram of hot formed GI (900C-3m) after sandblasting (a) undeformed side (b) deformed side.

Behaviour of the sandblasted surfaces at high anodic potentials is shown in Fig 4.27. In the cyclic voltammogram of the sandblasted undeformed side (Fig. 4.27 a) it is observed that the peak anodic current reduces in consecutive cycles (indicated by the green arrow) and a drop of 1.5 mA/cm² was recorded going from cycle 1 to 3. This is an indication that the system passivates on progression of corrosion from an initial to a steady state. The sandblasted deformed side (Fig. 4.27 b) also displayed the trend of a passivating system and registered a drop in peak anodic currents. However, the corrosion rate of the sandblasted deformed side was lower than its undeformed counterpart during metal dissolution at high anodic potentials, as seen from the slopes of the curves versus their as-hot formed condition. As opposed to the hot formed surfaces, the sandblasted surfaces show a small amount of negative hysteresis (indicated by the direction of blue arrows) which means that the latter develops a thin oxide or hydroxide layer during the reverse scan. Thus, sandblasting improves the ability of the hot formed components to develop a uniform coverage of hydroxides, which impedes anodic dissolution during the initial stages of corrosion.

Hot formed GI (900°C-5 min)

The response of as-hot formed GI subjected to a 5 min austenitization is shown in Fig. 4.28 (a) and (b). As the metallic coating layer is by now predominantly the α -Fe(Zn) phase, the results shed light on the behaviour of hot formed GI with higher proportion of α phase, as compared to a 3 min austenitization where the coating also has a significant amount of Γ -Zn(Fe).



Figure 4.28 Cyclic polarization curves of hot formed GI (900C-5min) (a) Undeformed side (b) Deformed side

The E_{corr} values of hot formed GI after 5 min austenitization (Table 4.1) indicated more noble potentials as compared to the 3 min austenitization, owing to the lower amount of Zn-rich Γ phase. Starting from -0.74 V in cycle 1, the E_{corr} shifted to -0.8 V in cycle 2 and 3. Corrosion currents near E_{corr} indicated a decreasing trend going from 73.8 μ A/cm² to 4.3 μ A/cm² and a lack of passivation was observed in the initial stages of anodic polarization in all cycles.

On the deformed side the E_{corr} values were relatively more active than the undeformed side and increased from -0.78 V to -0.97 V. However i_{corr} near E_{corr} decreased from 19.9 μ A/cm² to 8.6 μ A/cm². In addition, a pronounced passivation effect was observed at low anodic polarization, which spanned a potential range of 150 mV and 100 mV in cycle 2 and 3 respectively. The decreasing i_{corr} in both cases is due to combination of Zn and Fe corrosion products formed due to the dissolution of the α -Fe(Zn). While the corrosion products from the Γ -Zn(Fe) phase are mainly composed of simonkolleite (Zn₅OH₈Cl₂), the α phase forms a larger amount of akaganeite (β -FeOOH) along with small amounts of simonkolleite [13]. This mixture of corrosion products provides a better resistance against metal oxidation, as seen in the strong passivation on the deformed side due to accumulation of corrosion products in the cracks.



Figure 4.29 Cyclic voltammogram of hot formed GI (900C-5m) (a) undeformed side (b) comparison between undeformed and deformed side.

When the behaviour at higher anodic potentials was analyzed (Fig 4.29), a drop in peak anodic currents (indicated by the green arrow) was observed in each cycle for both the undeformed and deformed surfaces. The values dropped by 1.5 mA/cm² for the undeformed side and 0.5 mA/cm² for the deformed side going from cycle 1 to 3. Negative hysteresis (indicated by the direction of blue arrows) was observed during the reverse scans for both surfaces, indicating that a protective hydroxide layer forms while drifting to more cathodic potentials. From these observations, it follows that the coating containing more proportion of α -phase is a better passivating system than the coating with a combination of Γ and α , when going from an initial state of corrosion to a steady state.

Hot formed GI (900°C-5 min) after sandblasting



Figure 4.30 Cyclic polarization curves of hot formed GI (900C-5min) after sandblasting (a) Undeformed side (b) Deformed side

The response of the hot formed (900°C-5min) surfaces to cyclic polarization after sandblasting is shown in Fig. 4.30. In this case, an E_{corr} value of -0.59 V and -0.56 V was recorded in the first cycle on the undeformed and deformed surfaces respectively, which was the most noble value compared to all previous treatments. With progressing cycles, E_{corr} values rose to more active potentials. Corrosion currents near E_{corr} for the sandblasted undeformed surface were about 3 times lower than the as-hot formed surface in the first cycle, though in consequent cycles no significant difference was observed. The sandblasted deformed surface, however, registered the lowest i_{corr} value compared to all previous treatments. On inspection of the behaviour at low anodic polarizations, it was observed that the sandblasted undeformed surface (Fig. 4.30 a) showed strong passivation spanning 150 mV in cycle 2 and an active-passive transient in cycle 3. On the other hand the sandblasted deformed surface (Fig. 4.30 b) showed an active-passive transient in cycle 2 and 3. Hence, the combination of akaganeite and simonkolleite yields better passivation after sandblasting. While they form a homogenous coverage that is hard to dissolve on the undeformed surface, on the deformed surface they help slowing down metal dissolution by depositing in the cracks.

The behaviour of the sandblasted surfaces at high anodic polarization is represented is Fig. 4.31. At these potentials, it is observed that after a 5 min austenitization both the sandblasted surfaces are passivating systems, similar to their as-hot formed counterparts. The peak anodic currents are decreased by 0.5 mA/cm^2 and 1 mA/cm^2 on the on the sandblasted undeformed and deformed surface respectively. Post sandblasting, a decrease in corrosion rate on the deformed side was observed from the reduction in slope of the curves with progressing cycles.



Figure 4.31 Cyclic voltammogram of hot formed GI (900C-5m) after sandblasting (a) undeformed side (b) deformed side.

To highlight the difference between a coating containing a mixture of Γ and α and that containing mostly α , the cyclic voltammograms of hot formed and sandblasted GI after 3 and 5 min of austenitization is compared in Fig. 4.32. From the figure it is observed that even though both treatments yielded passivating systems, the samples hot formed for 900°C-5 min have reduced corrosion rates, apparent from their lower slopes for metal dissolution in the anodic regime. Thus, it can be concluded that the α phase has a lower corrosion rate than the Γ phase and also provides better passivation owing to the formation of a mixture of simonkolleite and akaganeite.



Figure 4.32 Cyclic voltammograms of hot formed and sandblasted GI after 3 and 5 min austenitization

4.4.2 Cyclic Voltammetry testing of MZ+ coated 22MnB5

The summary of the results of linear polarization resistance of hot formed MZ+ is presented in Table 4.2. Tests were performed on the undeformed side after initial hot forming and subsequent sandblasting (SB), post austenitization times of 3 and 5 min.

Table 4.2 Summary of corrosion potentials and corrosion	n current density for	hot formed MZ+	obtained through
cyclic voltammetry			

Material	Treatment	Surface Condition	Cycle 1		Cycle 2		Cycle 3	
			E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)
MZ+	900 [°] C–3m	Undeformed	-0.78	20.8	-0.92	3.6	-0.94	7.6
	900 [°] C–3m SB	Undeformed	-0.68	17.5	-0.88	4.03	-0.88	3.99
	900 [°] C–5m	Undeformed	-0.65	37.7	-0.69	2.16	-0.73	3.09
	900°C–5m SB	Undeformed	-0.55	36.5	-0.81	6.7	-0.83	6.3

Hot formed MZ+ (900°C-3min) before and after sandblasting

An initial investigation of the cyclic polarization curves reveals that MZ+ also favours diffusion controlled oxygen reduction in the cathodic regime and dissolution of the metallic phases in the anodic regime. The curves also show the ability of hot formed MZ+ to sacrificially protect 22MnB5, as in each cycle the coating is more active than the substrate.

The E_{corr} values for the as-hot formed (Fig. 4.33 a) and sandblasted surface (Fig. 4.33 b) rise to more active potentials with increasing cycles of corrosion, representing that the surface is becoming more anodic. While the hot formed surfaces went from -0.78 V to -0.94V, the sandblasted surfaces changed from -0.68 V to -0.88 V, indicating that the sandblasted surface is
more noble. The E_{corr} values of MZ+ when compared with GI were all within 100 mV of each other, which follows from the similarity in microstructural constituent of the two coatings.



Figure 4.33 Cyclic polarization curves of hot formed MZ+ (900C-3min) (a) as hot formed (b) after sandblasting

As also observed with GI, the i_{corr} values of MZ+ also showed a decreasing pattern, going from 20.8 to 7.6 μ A/cm² and from 17.5 to 3.99 μ A/cm² on the as-hot formed and sandblasted surface respectively. The values recorded were found to be 4 times lower than GI for the as hot formed surface and 2 times lower than GI for the sandblasted surface. Furthermore, both conditions displayed active-passive transients in the steady state condition (Fig. 4.33 a and b) after a 3 min austenitization itself, owing to the lower Γ content of the coating. On the as hot formed surface that is covered by MgO, the transient over a 200 mV potential range was a one-time event. However, on the sandblasted surface, metal dissolution was frequently interrupted by the active-passive transients, possibly due to the better coverage of akaganeite and simonkolleite enriched with Al and Mg hydroxides, as was observed from SEM and GDOES investigations. This displays the strength of MZ+ in keeping i_{corr} values low, which alongside the formation of insoluble hydroxides, helps impede metal dissolution at low anodic polarizations.

In the range of high anodic polarization, as shown in Fig. 4.34 (a) and (b), both treatments indicated characteristics of a passivating system, revealed by a drop of 1.5 mA/cm^2 in peak anodic currents (indicated by the green arrow). Negative hysteresis was observed during the

reverse scans (indicated by the blue arrows), which hints that a hydroxide layer develops on the surface during the return scan. This combined with the increased passivation during low anodic polarization results in a drop in corrosion rates, observed from the decreasing slopes of the curves in the metal dissolution regime. Thus the α phase of MZ+ after a 3 min austenitization is indeed more passive than that in GI.



Figure 4.34 Cyclic voltammogram of hot formed MZ+ (900C-3min) (a) as hot formed (b) after sandblasting

Hot formed MZ+ (900°C-5min) before and after sandblasting

In the case of a 5 min austenitization, shown in Fig. 4.35 (a) and (b), the E_{corr} values were more noble than the 3 min austenitization in all cycles, due to the higher α -Fe(Zn) content in the former case. The recorded values increased from -0.64 to -0.73 V on the as hot formed surface and from -0.55 to -0.83 V on the sandblasted surface. In this case the sandblasted surface is comparatively more active than the as hot formed surface because of the thick MgO layer coverage in case of the latter. When compared to GI, the as hot formed surface of MZ+ was more passive by 100 mV and the sandblasted surface was more passive by 200 mV.



Figure 4.35 Cyclic polarization curves of hot formed MZ+ (900C-5min) (a) as hot formed (b) after sandblasting

The i_{corr} values also dropped in this case going from 37.7 to 3.09 μ A/cm² on the as hot formed surface and from 36.5 to 6.3 μ A/cm² on the sandblasted surface, which was found to be correspondingly lower than what was observed for GI. While progressing to more anodic potentials, a feeble passivation was noticed only in cycle 1 on the as hot formed surface, whereas a strong passivation spanning a potential range of 150 mV was displayed by the sandblasted surface. The passivation exhibited on the sandblasted surface after 5 min austenitization was more pronounced than that observed for a 3 min austenitization, as was also noticed in the case of GI. Thus, the Fe-rich α -phase appears to be the source of improved passivation for both GI as well as MZ+. However, in the case of MZ+, the active elements Al and Mg also seem to be contributing to slowing down metal dissolution by forming insoluble hydroxides.

At high anodic potentials, the peak anodic currents were quite consistent for both conditions and only increased very slightly, as shown in Fig. 4.36 (a) and (b). A small amount of positive hysteresis was observed (indicated by the direction of the blue arrows), indicating continuation of metal dissolution until cathodic potentials are reached. The slopes of metal dissolution curves for the different conditions are nearly identical, conveying that long term metal dissolution progresses in the same manner for both cases.



Figure 4.36 Cyclic voltammogram of hot formed MZ+ (900C-5min) (a) as hot formed (b) after sandblasting

The behaviour of hot formed and sandblasted MZ+ after 3 and 5 min of austenitization is compared in Fig. 4.37. After a 3 min austenitization, the coating passivates over 3 cycles and then overlaps with the cyclic voltammogram of the 5 min austenitization, as in both cases it is the dissolution of the α phase that governs the anodic regime.



Figure 4.37 Cyclic voltammograms of hot formed and sandblasted MZ+ after 3 and 5 min austenitization

4.4.3 Cyclic Voltammetry testing of AlSi coated 22MnB5

The summary of the cyclic voltammetry tests performed on the undeformed and deformed surfaces of hot formed AlSi, is presented in Table 4.3

Table 4.3 Summary of corrosion potentials and corrosion current density for hot formed AlSi obtained through cyclic voltammetry

Material	Treatment	Surface Condition	Cycle 1		Cycle 2		Cycle 3	
			E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)	E _{corr} (V vs SCE)	i _{corr} (μΑ/cm²)
AlSi	900°C–6m	Undeformed	-0.63	0.72	-0.74	1.25	-0.75	1.7
	900°C–6m	Deformed	-0.68	22.5	-0.88	29.2	-0.88	15.8

Hot formed AlSi (Undeformed vs Deformed surface)

Initial observations from the cyclic polarization curves in Fig. 4.38 (a) and (b) revealed that while the Zn coatings displayed cathodic control in their corrosion mechanism, the AlSi coating displays more mixed control. This means that in the case of Zn coatings, the diffusion limited oxygen reduction process controls the rate of galvanic corrosion (cathodic control). However in case of AlSi, the cathodic reaction is not limited by diffusion of oxygen and hydrogen evolution is easily facilitated on the exposed Fe when there is a low concentration of dissolved oxygen near the surface. Thus, both reduction processes influence the rate of corrosion in case of AlSi, which explains why the substrate is vulnerable to pitting.

The E_{corr} values of AlSi also become more active with increasing cycles of corrosion. However, the difference between i_{corr} values on the undeformed and deformed sides was quite large compared to the Zn coatings. While those on the undeformed side increased from 0.72 μ A/cm² to 1.7 μ A/cm², the same on the deformed side decreased from 22.5 μ A/cm² to 15.8 μ A/cm². Thus the deformed sides have significantly larger corrosion currents due to the additional contribution

from hydrogen evolution occurring at the surface area exposed by the cracks. In comparison, the Zn coatings yielded smaller corrosion currents on their deformed surfaces at low anodic polarizations. While the i_{corr} values on the deformed surface of AlSi was found to be the largest, that on the undeformed side was found to be the lowest at low anodic potentials compared to Zn coatings, possibly due to the more passive Al_2O_3 layer that forms on the surface of hot formed AlSi. However, this oxide layer easily breaks down when transitioning to higher anodic potentials, as seen from the lack of passivation during metal dissolution on both surfaces (Fig 4.38 a and b). The proximity of the curves with that of 22MnB5 at high anodic potentials indicates that at these potentials, contribution to metal dissolution is both from the coating as well as the martensitic substrate.



Figure 4.38 Cyclic polarization curves of hot formed AlSi (900C-6min) (a) undeformed surface (b) deformed surface

At high anodic polarizations (Fig. 4.39 a and b), both surfaces displayed characteristics of an activating system, with peak anodic currents rising by 1 mA/cm^2 going from cycle 1 to 3 (indicated by the red arrow). During the return scans, positive hysteresis was observed (indicated by the direction of blue arrows), signalling that metal dissolution processes continue until the voltage switches to more cathodic potentials. From the slope of the curves in this regime it appears that metal dissolution at high anodic potentials progresses with the same rate on both the

undeformed and deformed surfaces. This was consistent with the SEM observations of the crosscuts of the undeformed surfaces subjected to galvanostatic dissolution, which displayed occurrence of pitting even on the undeformed side after dissolution of the coating exposed a region of martensite.



Figure 4.39 Cyclic voltammograms of hot formed AlSi (900C-6min) (a) undeformed surface (b) comparison between undeformed and deformed surface

4.4.4 Comparison between Zn and Al coatings for hot forming

In order to comparatively evaluate different Zn and Al coatings, the cyclic voltammograms of hot formed GI, MZ+ and AlSi for corresponding processing conditions and austenitization times are shown in Fig. 4.40. From the curves it is observed that GI and MZ+ are passivating systems (indicated by the green arrow) at high anodic potentials, which also exhibited an ability to develop a passive hydroxide barrier layer at low anodic polarization. On the other hand, the AlSi coating is an activating system (indicated by the red arrow) at high potentials and did not exhibit any tendency to develop a passive barrier layer at low anodic polarization. This portrays that over their corrosion protection lifetime, Zn coatings will effectively protect the martensitic substrate through the action of galvanic protection and self passivation by corrosion products, whereas the AlSi coating will provide galvanic protection to the substrate only until the substrate is unexposed. Once the substrate is exposed the coating cannot guarantee protection against pitting, as facilitated by increased corrosion rate through hydrogen evolution, the martensite can undergo pitting despite the absence of oxygen reduction or coverage of surface by corrosion products.



Figure 4.40 Comparison between hot formed GI, MZ+ and AlSi for corresponding processing conditions and austenitization times

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In view of cathodic (sacrificial) corrosion protection offered, Zn coatings (GI and MZ+) demonstrated superior performance compared to AlSi. The former coating types displayed confirmation of active corrosion protection until the complete metallic coating layer was dissolved. In case of AlSi, a mixture between sacrificial and passive barrier protection was observed, with the substrate indicating a vulnerability to pitting after long exposure times, due to the presence of cathodic intermetallics residing above it.

- <u>GI</u> With increasing austenitization time from 3 to 5 min, the proportion of gamma phase reduces and that of alpha phase increases. The alpha phase indicated a better ability to passivate during wet corrosion due to the combination of Zn and Fe hydroxides, thus resulting in a lower corrosion rate after 5 min than after 3 min of austenitization. Zn metal dissolution was found to predominate and protect the martensite even in the presence of cracks, with the deformed sides also showing a better ability to passivate due to accumulation of corrosion products in the cracks.
- <u>MZ+</u> A very small amount of the Zn-rich Γ -Zn(Fe) phase is formed and the metallic coating layer is constituted mainly by α -Fe(Zn) phase. By alloying more rapidly, an increase of coating thickness of up to 5 times was achieved after hot forming compared to the three fold increase for GI for equal austenitization times, which translates to improved corrosion lifetime for MZ+. It is compatible with short dwell times due to low amount of gamma phase developed. The loss of Zn by oxidation was minimized by the presence of Mg and better passivation ability was exhibited in SEM analysis and cyclic voltammetry due to the cumulative effect of protective Fe, Zn, Al and Mg hydroxides during wet corrosion.

- GDOES profiles revealed a larger processing window for hot forming for MZ+ (upto 5 min) than for GI (maximum of 4 min). Longer austenitization times compromise the hardenability of GI due to the diffusion of B and Mn into the metallic coating layer.
- <u>AlSi</u> Initial aluminized coating transforms into 6 intermetallic phases after austenitization, with the FeAl and Fe₂Al₃ intermetallic layers present penultimate to the martensite incapable of providing adequate cathodic protection, resulting in a vulnerability to pit initiation and propagation into the substrate. Cyclic voltammetry indicated that the passive Al₂O₃ layer breaks down easily and though the active Fe-rich intermetallics do provide some sacrificial protection, pitting initiates once the electrolyte gains access to the substrate though the cracks, as the Fe-Al intermetallics are more noble than the substrate.

5.2 Further Recommendations

The results from Galvanostatic testing provide electrochemical composition-depth profiles as well as a realistic measure of cathodic corrosion protection. This study indicated that it is good precursor to VDA testing to investigate and understand the wet corrosion mechanism of coatings, due to its higher throughput. The technique could thus be extended for use in accelerated corrosion testing of hot formed products in different environments and concentration of corrosive species. VDA testing can then be used to determine nature of corrosion products and the effect of drying cycles on corrosion, thereby providing a holistic approach to the corrosion performance of coated substrates for hot forming.

Zn coatings:

MZ+ appears to be a better product offering for hot press forming than conventional GI, due to lower proportions of LMIE causing low melting point Γ phase, reduced Zn loss through preferential oxidation of Mg and improved corrosion resistance owing to presence of α -Fe(Zn) enriched with Mg and Al that reinforce its sacrificial protection ability by helping to passivate the α grains by the formation of insoluble hydroxides.

- Corrosion products formed in case of corrosion of hot formed MZ+ need to be characterized so as obtain a confirmation of the passivating effect of Zn corrosion products enriched with Al and Mg.
- Mg and Al alloying additions should be focused on containing their loss through oxidation during austenitization, thereby helping to extend the range of passivation by formation of a layer of insoluble corrosion products that helps decrease the appearance of red rust. Higher Al additions could also reduce the intensity of red rust appearance by diluting the colour of corrosion products, thereby helping to mitigate the issue of cosmetic corrosion of hot formed products. In this regard, it would be interesting to see how Arcelor Mittal's Magnelis responds to corrosion after hot forming, as it does contain Al 6 wt. % and Mg 3 wt. %.

AlSi:

Since it was observed that the Fe-rich intermetallics with Al are a threat to the integrity of the substrate, it needs to be investigated whether low austenitization times can help mitigate the proportion of Fe-rich intermetallics versus Al-rich intermetallics. The sacrificial nature of AlSi thus needs to be improved by either suppressing the formation of noble intermetallics, or by alloying additions of more active elements.

Alloying additions with Si also need to be optimized, as AlSi coatings with high Si contents were susceptible to formation of Kirkendall voids during the process of interdiffusional alloying.

6. REFERENCES

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