"Though achieving the possible appears, at times, improbable Overcoming the impossible, with courage and determination, Will make any dream probable"

Dedicated to Luigi & my parents.

## Surface Analysis of White Spot Formation on Industrial Electrogalvanised Automotive Steel

By

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## ABSTRACT

MSSA (Mittal Steel South Africa), which produces electrogalvanised steel for the local automobile industry, experiences a problem with white spot formation when their steel is phosphated. The addition of nickel inhibits white spot formation but produces an unacceptable discolouration of the surface layer. Furthermore the locally produced steel exhibits blister formation when heated to 300°C.

The substrates, electrogalvanised coatings, phosphated samples and annealed samples are studied with Glow Discharge Optical Emission Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectroscopy, as well as X-ray diffraction. Combining the results allows for an interpretation of the morphology, topography, composition, crystalline structure, quantitative depth profile as well as the spatial distribution of the elements

The white spot formation on the electrogalvanised surfaces is closely related to the presence of contaminants on the electrogalvanised surface and at the interface between the substrate and the electrogalvanised coatings. The accelerated phosphate reaction results in complete dissolution of the electrogalvanised surface, thereby exposing the iron substrate. The white spot consists of an anomalous protruding perimeter with elongated crystals that grow towards the centre of the spot, present inside the spot.

Partial dissolution is required in order for the phosphate process to occur. Complex phosphates deposit on the surface comprised of various cations, such as zinc, manganese and nickel. The zinc dissolution is the preferred reaction and therefore there is a slight enrichment of nickel in the sublayers of the phosphate. The manganese deposited on the surface must not be confused with the manganese present in the substrate.

The addition of other cations to the electrogalvanised layer results in a change in the structure of the phosphated layer. The presence of cobalt and copper in the electrolyte results in an increase in the deposition of manganese phosphates on the surfaces. The

manganese phosphates grow upward, away from the surface as opposed to the zinc phosphates that grow along the sample surface. The growth of the zinc phosphates only continues until the surface is covered.

The structure of the electrogalvanised deposits changes with changes in the composition of the electrolyte. The morphology changes from a well-defined rigid structure (as for the zinc electrolyte) to a complex structure consisting of both grains and a fine intricate network of small deposits as various cations such as nickel, copper and cobalt are added to the electrolyte.

The surface of the steel substrate clearly shows the rolling direction, as well as numerous dislocations. This compromises the epitaxial growth of the electrogalvanised layer. The alloy elements added to the steel are also present on the surface. These react differently compared to the steel and will therefore impact on the nature of the deposition at these sites.

The annealing of the electrogalvanised samples causes both structural and compositional changes in the samples. The movement of the zinc and possible dezincification are most likely responsible for the blister formation. This is further affected by the presence of hydrogen in the sample and the subsequent hydrogen blistering.

It is of paramount importance for all the surfaces and parameters to be controlled and monitored carefully to ensure the best coating quality. The presence of any contamination on the surfaces or in the solutions will cause adverse reactions and compromise the final product.

## **OPSOMMING**

MSSA (Mittal Steel South Africa) vervaardig tans staal vir die motor industrie. Hierdie staal is deur elektroplatering bedek met 'n laag sink. Tydens fosfatering, 'n noodsaaklike korrosie beherende behandeling, vorm wit kolletjies op die oppervlak van die staal. Nikkel word tot die elektroliet bygevoeg in 'n poging om hierdie formasie van wit kolletjies te voorkom. Alhoewel dit wel voorkomend is, veroorsaak dit 'n verkleuring van die oppervlak. Die plaaslik vervaardigde staal toon ook blaasformasie tydens hittebehandeling by 300°C.

Die substrate, elektroplateerde monsters, sowel as die gefosfateerde monsters word ondersoek met gloei ontlading spektroskopie, skandeer elektronmikroskopie, energie verstrooiende spektroskopie en x-straal diffraksie. Samevoeging van hierdie resultate bied 'n interpretasie van die morfologie, topografie, samestelling, kristallyne struktuur, kwantitatiewe diepte profiele asook inligting aangaande die verspreiding van die elemente.

Die formasie van die wit kolletjies op die elektroplateerde monsters het 'n noue verband met die teenwoordigheid van kontaminante op die oppervlak asook by die tussenvlak tussen die substraat en die elektroplateerde lae. 'n Versnelde fosfatering reaksie lei tot die algehele oplossing van die elektroplateerde lagie en sodoende word die ystersubstraat blootgestel. Die wit kolletjies bestaan uit 'n onreëlmatige buiterand en langwerpige kristalle in die kol wat na die binnekant toe groei.

Gedeeltelike oplossing van die elektroplateerde oppervlak is 'n noodsaaklike stap in die formasie van die fosfaat laag. 'n Komplekse fosfaat deponeer op die oppervlak wat bestaan uit sink, mangaan en nikkel fosfate. Aangesien die sink by voorkeur sal oplos veroorsaak dit verryking van die nikkel net onder die gedeponeerde fosfate. Die mangaan op die oppervlak, wat deponeer as 'n fosfaat, moet nie met die mangaan in die substraat verwar word nie.

Die teenwoordigheid van ander katione in die elektroplateerde laag veroorsaak veranderinge in die struktuur van die fosfaatlaag. Die teenwoordigheid van kobalt en

koper in die elektroliet lei tot 'n toename in die deponering van mangaanfosfaat op die oppervlak. Die mangaanfosfaat groei opwaarts, weg van die oppervlak, in teenstelling met die sinkfosfaat wat so groei dat dit die oppervlak bedek. Die sinkfosfaat deponeer net totdat die hele oppervlak bedek is.

Enige veranderinge in die samestelling van die elektroliet lei tot 'n verandering in die struktuur van die elektroplateerde oppervlak. Die morfologie vir die sink elektroliet is 'n goed gedefinieerde skerphoekige struktuur. Die byvoeging van katione, soos nikkel, koper of kobalt, lei tot die formasie van 'n korrelagtige omhulsel met 'n fyn netwerk van kleiner kristalle.

Die rigting waarin die staal gerol is tydens vervaardiging is duidelik sigbaar op die oppervlak. Daar is ook duidelike dislokasies teenwoordig op die oppervlak van die substraat. Die manipulasie van die oppervlak beïnvloed die epitaksiale groei van die elektroplateerde oppervlak. Daar is ook allooi elemente wat toegevoeg is tot die substraat wat op die oppervlak teenwoordig is. Hierdie punte reageer egter anders as die yster substraat.

Indien die elektroplateerde oppervlak verhit word, vind daar veranderinge in beide die struktuur en samestelling plaas. Die beweging van die sink, asook die verdamping van die sink, dra by tot die formasie van blasies op die oppervlak. Die teenwoordigheid van waterstof op die oppervlak dra by tot die blaasformasie.

Dit is uiters belangrik dat die oppervlakke en al die parameters noukeurig beheer en gemonitor word om die hoogste deklaag kwaliteit te verseker. Die teenwoordigheid van enige kontaminasie, hetsy op die oppervlak, of in die oplossings dra by tot nadelige reaksies wat die finale produk negatief beïnvloed.

## **KEYWORDS**

- 1. Sheet steel treatment
- 2. Nubbing
- 3. Phosphating
- 4. White spot
- 5. Electrogalvanised
- 6. SEM
- 7. EDS
- 8. GDS
- 9. Blistering
- 10. Automotive steel

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## Chapter 1 Preface

In this chapter, the objectives of this study and an overview of this thesis are given.

The automobile industry is constantly seeking an improved quality of electrogalvanised steel for the production of automobiles. If the zinc and zinc-alloy coated steels, used currently, are to remain in use, certain problems regarding the coatings must be addressed.

The coatings must have weldability, elasticity, be corrosion-resistant and must not have blister formation when the surface is painted or heated.

MSSA (Mittal Steel South Africa), which produces electrogalvanised steel for the local automobile industry, experiences a problem with white spot formation when their steel is phosphated. The addition of nickel inhibits white spot formation but produces an unacceptable discolouration of the surface layer. Furthermore the locally produced steel exhibits blister formation when heated to  $300^{\circ}$ C.

This study aims to examine white spot and blister formation.

## **1.1. Introduction**

Since the design of the Model T (Figure 1-1) every aspect and component of the automobile has been re-designed and improved. The materials used for the various components as well as the manufacturing and finishing techniques have been upgraded, as technology, and the understanding of alloys has grown. Currently, especially in the manufacturing of sports cars, composite materials are used alongside metal alloys.

The automotive industry is currently one of the largest consumers of coated steels. Although composite materials and polymers have recently been incorporated into the automobile design, up to 90% of the body is still constructed from steel [3]. The production of electrogalvanised steel for use as automobile panels began in 1977 in North America.



Figure 1-1: The Model T versus the Ferrari, a comparison of design [1], [2]

The primary reason for the change to electrogalvanised steel is the increased corrosion resistance of the coated steel. For several years the zinc coated steels were used exclusively, but in 1991 zinc-nickel alloy coated steels were developed. The alloy coated steel exhibited improved properties over the zinc coated steels. The addition of the nickel to the electrogalvanised layer slows the corrosion rate of this layer significantly, and thereby protects the underlying structure even more.

The continuous improvement in the coatings reflects the competitive and critical nature of the automobile manufacturers. Needless to say, the steel manufacturers are constantly streamlining production processes and improving the properties of their products to keep up with the requirements of their clients. In order to ensure the continuation in use of the zinc and zinc-alloy coated steels, the problems encountered when using these need to be addressed.

The weldability of the electrogalvanised steel is tested before the automotive manufacturers purchase a steel range. A typical weldability test involves heat treatment of the specimens at 300°C for 30 minutes. If there are no structural changes in the coating it will pass the test.



Figure 1-2: The use of various galvanising techniques in the automotive industry [4].

The elasticity of the surface coating is another important property, especially when parts are pressed out of the steel. A simple bend test is performed and any peeling or cracking of the surface will render the steel inappropriate for the specific application.

Once the electrogalvanised steel sheets have been pressed into the body parts, the assembled structure is chemically treated in a phosphate bath. The automotive industry makes use of phosphating to improve the corrosion resistance and the adhesion of the paint to the surface. The phosphating parameters differ for the various manufacturers and therefore different problems have been encountered. The most extensive of these problems is, undoubtedly, the formation of white spots on the steel surface on phosphating.

Once painted, the surface finish is carefully investigated for blister formation under the paint layers.

MSSA (Mittal Steel South Africa) currently produces an electrogalvanised steel that is used locally by several automotive manufacturers. The most common problem encountered by the manufacturers is white spot formation on phosphating. An initial study indicated that the addition of nickel to the electrogalvanised layer inhibits the white spot formation. A negative "side effect" of this addition is the discolouration of the surface layer on phosphating. The zinc-nickel coated steel appears darker in comparison to the imported or zinc coated sheets.

A secondary problem encountered with the locally produced steel is the formation of blisters upon annealing of the electrogalvanised steel. The blistering occurs in varying degrees of severity and may, in some cases, extend from the substrate interface to the surface.

## **1.2. Study objective**

The aim of this study is to investigate the white spot formation and compare the MSSA product with an unknown imported product. The formation of the blistering is also to be considered and the mechanisms at play are to be classified.

## **1.3.** Thesis overview

The theory pertaining to this study is shortly discussed in chapter 2. Electroplating of various elements is discussed including: an overview of reactions within the electrolyte, anodic dissolution of the metal surfaces and electrodeposition. The phosphating reactions and mechanisms are also discussed. Various forms of corrosion, relevant to this study, are also stated.

The most recent works, published by other researchers in this field are summarized in chapter 3. The primary consideration with regard to the use of electrogalvanising as opposed to conventional galvanising is presented along with a detailed overview of the use of co-deposition. The mechanism for the deposition of the phosphate coating is outlined and the formation of white spots on various samples is reviewed. A brief discussion on the formation of blisters on electrogalvanised samples is given.

Chapter 4 outlines the experimental work, including the sample preparations and analytical techniques applied. The use of glow discharge optical emission spectroscopy, scanning electron miscroscopy in combination with energy dispersive spectroscopy and x-ray diffraction is motivated with special mention of the benefits of these analytical techniques compared to other spectroscopic techniques.

The experimental work covers three aspects and therefore the results are given in chapters 5, white spot and phosphate analysis, 6, blister formation, and 7, immersion plated samples. The study, and suggestions for further work, is summarised in chapter 8.

# Chapter 2 Theory

This chapter discusses the theory pertaining to the processes undertaken when steel is electrogalvanised and phosphated.

Electroplating is done via electrolysis. The reactions that occur in the electrolyte, before and during electrolysis, the process of electrolysis, the anodic dissolution of metals and electrodeposition are discussed with reference to the factors affecting these processes and Faraday's laws. The industry makes use of various bath additions and the deposition of zinc, cobalt, nickel and alloys is also discussed.

Electroplated steel is phosphated to enhance corrosion-resistance. The pre-treatment, conditioning and phosphating processes are discussed. Dilute aqueous solutions are used which contain phosphate anions as well as some of the metal cations. Iron coatings and zinc coatings are discussed and the acidic dissolution of the substrate, phosphate nucleation, the growth of crystals and spotting is examined.

The changes that occur in the substrate are due to diffusion. The three models of diffusion; vacancy or substitutional diffusion, interstitial diffusion and grain-boundary diffusion are discussed with the relevant mathematical considerations.

Metallic surfaces may experience various forms of corrosion. The surfaces investigated in this study are especially sensitive to galvanic corrosion, pitting and the formation of hydrogen blistering.

## 2.1. Electroplating

There are various ways of producing coated surfaces. Electroplating produces a superior quality product and is therefore used extensively by various industries.

## 2.1.1. Introduction

Electroplating describes the process whereby a coating is deposited onto a substrate via electrolysis. In changing the surface features, the corrosion resistance, appearance and chemical reactivity, amongst others, are also changed. Faraday formulated the laws of electrolysis in 1833, and in doing so, presented the first quantitative account of the electrical nature of matter.

## 2.1.2. Electrolytes and solutions

Water molecules are polar and hydrogen bonds occur between the fractionally negatively charged oxygen atoms and the fractionally positively charged hydrogen atoms (Figure 2-1).



Figure 2-1: Hydrogen bond between water molecules [5]

If a salt is dissolved in water, the presence of the ions alters the arrangement of the water molecules (Figure 2-2). Around the positive ion, the water molecules will turn so that the negative oxygen atoms face the ion. The negative ion will be surrounded by water molecules with the positive hydrogen atoms facing the ion [6]. This hydration of the ions will occur in varying degrees along with the change in charge of the ions.



Figure 2-2: Hydration of ions in solution [7]

The hydration of the ions buffers the ions and therefore impacts on the electrical conductivity and the reactivity of the ions.

The conduction in an electrolyte is due to the flow of ions. The consequence of electron flow in a metal conductor is heat. In an electrolyte there is both heat and a chemical reaction, i.e. the decomposition of the solution, alsoKnown as electrolysis.

## 2.1.3. Electrolysis

Electrolysis requires two electrodes, a cathode and an anode, to be submerged in a solution containing dissolved ions, referred to as the electrolyte, and connected to an external power supply (Figure 2-3).



Figure 2-3: Electrolysis in a salt solution [8].

Since the concentration of the ions in the electrolyte is high, the ions experience interionic attractions, form ion pairs or other structured configurations, and ultimately react differently. This change in behaviour is denoted by the activity of the ions. The

activity of the ions in the solution determines the impact of these on the potential, conductivity and on the diffusion processes [9]. The increase in concentration of solute in a given solute causes a decrease in the conductivity as the attractive forces of the dissociated ions shield the ions from the applied electric field. The water molecules surrounding the ions further prohibit the "free" movement of the ions, resulting in a marked decrease in conductivity at high concentrations [6].

Surplus electrons are made available at the cathode by the external power source. The cathode therefore becomes more negative. The positive ions are attracted towards the negative cathode and will become incorporated into the metallic crystalline lattice. Electrons flow from the external power source to balance out the additional positive charge in the electrode. At the anode, the ions are released and the electrons responsible for the binding of the ions are transferred to the external circuit. The released ions generally become hydrated and move into the solution. The flow of current, which occurs as a result of the addition or removal of electrons, is a process involving the entire lattice rather than a single ion [9].

The reactions that occur at the anode and cathode may differ and therefore the rates of the reactions may also differ. Since the reactions are linked due to the availability of electrons, the net reaction rate is determined by the slowest of the electrode reactions. In a simple plating cell, the electrolyte composition is unchanged as the net effect is simply the transfer of metal from the anode to the cathode. In practice, however, the electrolyte changes as a result of side reactions or because the ions in the solution are plated onto the electrodes [9].

#### **2.1.4.** Anodic dissolution of metals

Whenever a metal is submerged in a solution which contains the metal's ions, the surface ions will become hydrated and dissolve into the solution. Simultaneously metal ions in the solution will be deposited onto the surface. The reaction rates will be governed primarily by the potential differences which exist at the metal-solution interface. Specific potential values, where the two opposing reaction rates are equal, exist for each combination of metal and solution at a given temperature. This

potential, also referred to as the equilibrium potential, will be created over the interface in the absence of an external potential. Standard potentials have been noted at 25°C and unit activity for various metals versus a standard electrode which is used as an arbitrary zero point [9].

Corrosion of reactive metals occurs when the metal is exposed to condensed moisture or electrolytes. The metal cations move into the solution and may be hydrated or hydrolyzed, as described above [10].

Assume that metallic iron is immersed in a solution containing iron ions. The iron atoms will go into the solution:

$$Fe \to Fe^{2+} + 2e^{-} \tag{1}$$

The iron ions in the solution will redepose onto the metal surface:

$$\mathrm{Fe}^{2+} + 2e^{-} \to \mathrm{Fe} \tag{2}$$

In equilibrium these two reactions have the same rate. Corresponding with these reactions is an exchange current density which is also associated with a potentialKnown as the equilibrium potential. This is given by:

$$E_{eq} = E_{eq}^{o} + \left(\frac{RT}{nF}\right) \log\left[Fe^{2+}\right]$$
  
= -0.44 + 0.029 log [Fe<sup>2+</sup>] (3)

 $E_{eq}^{o}$  is the standard equilibrium potential, *R* is the gas constant, *n* is the number of electronic charges per ion and *F* is Faraday's constant.  $[Fe^{2+}]$  is the concentration (or activity) of the iron ion in the solution. If the potential is displaced from the equilibrium value  $E_{eq}$ , a net current results. The difference in the potential between the metal and the solution and the pH of the solution determines the intensity of the reaction [10].

In general then, the deposition of the metal from the solution is given by the following expression:

$$\mathbf{M}^{\mathbf{n}^+} + n e^- \to \mathbf{M}^0 \tag{4}$$

When an electrode is placed in a solution containing its ions, a potential difference can be measured between the metal and the solution. This difference is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{a_M}{a_{M^{n+}}}\right)$$
(5)

In this expression *E* represents the potential difference,  $E^0$  is the standard electrode potential measured against hydrogen, *R* is the gas constant, *T* is the absolute temperature, *n* is the number of electrons involved in the reaction, *F* is Faraday's constant and  $a_M$  and  $a_M^{n+}$  are the activities of the ions.

When anodic polarisation displaces the equilibrium of the metal/solution system, corrosion of the metal occurs. This can also occur in the presence of reduction-oxidation systems, with a more highly anodic equilibrium potential [10]. This is similar to applying an external anodic potential. Without the externally applied potential, the metal adopts a potential, higher than the equilibrium, referred to as the corrosion or free potential. The rate at which the metal corrosion or dissolution will take place is dependent on the species responsible for the corrosion and is equal to the rate at which this species reduces.

In considering the corrosion of steel the following reactions are important [10]:

- 1. At the anodic zones:  $Fe^0 \rightarrow Fe^{2+} + 2e^{-}$
- 2. At the cathodic zones:
  - a. In an acidic media:  $2H^+ + 2e^- \rightarrow H_2$
  - b. In neutral or alkaline media:  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

In a comparison of the standard electrode potentials of the various redox systems present in a solution, it is possible to predict whether or not corrosion will occur. If the potential for any redox system is higher than  $E_{eq}$  corrosion may take place.



Figure 2-4: Pourbaix diagram for iron [11]

The rate of anodic dissolution of the steel may be very low in some systems and therefore inconsequential. The corrosion rate must, therefore, be determined. One technique that is used for the determination entails the Pourbaix diagrams (Figure 2-4).

The metal solution, as well as the pH of the solution, is used to create the diagrams. The diagrams indicate regions of immunity or passivation where corrosion will not take place. There are various ways of forcing the metal into these regions, thereby eliminating or retarding corrosion. These include [10]:

- 1. Applying cathodic protection, thereby creating conditions of immunity
- 2. Creating, or growing layers of, for example, oxides, on the surface by anodic protection or by increasing the pH.

If the potential of an electrode is lowered, by the application of an external power supply, below the equilibrium potential, anodic dissolution will occur. Alternatively, if the potential is raised above the equilibrium potential, the metal will be plated out of the solution. In a bath where the standard metal potential is positive, hydrogen is not evolved since the potential will remain positive. In baths where the potential is negative, as for nickel, hydrogen evolution will occur alongside the plating.

The reaction that needs the least negative potential will occur solely at the cathode unless the potential is sufficiently negative to allow further reactions [9]. The same can be said for the anode where the reaction related to the least positive potential will occur, assuming that the potential is not sufficiently positive to allow further reactions to occur.

It is also interesting to note that the corrosion does not occur uniformly over the surface. The presence of impurities results in localised cathodic areas that may be more noble. The various crystallographic planes also have slightly varying electrode potentials, and therefore react differently. A material under strain will also react in another way to that of its unstrained counterpart [6].

#### 2.1.5. Reaction activation energy

In order for any chemical reaction or process to occur, a minimum energy, above the average energy possessed, must be added to the system. This energy is the activation energy. The activation energy (Figure 2-5) is essentially a potential barrier that the reactants must overcome. The closer the energy of the reactants is to this potential barrier, the higher the likelihood that individual reactants will cross the barrier and undergo reaction. The energy levels of the ions in the double layer [12] are shifted towards that of the potential barrier during cathodic polarisation, increasing the number of ions that can cross the barrier per unit time to react with the surface. At the anode, however, the energy of the ions is shifted away from the barrier, decreasing the rate of dissolution. The activation polarisation therefore consists of two components, one which accelerates the deposition reaction and the other which acts on the dissolution reaction. The deposition reaction is, in part, dependent on the ion's ability to detach itself from the water molecules attached to it, therefore activation includes the distortion of the molecules of the hydrated ion to release the water molecules and thereby create free bonds that can take part in the adsorption and reaction with the cathode [9].



Figure 2-5: Activation energy required for the formation of products from reactants. [13]

The activation polarisation is a logarithmic function of the current density and along with the transfer coefficients is also a function of the mechanism involved, the concentration and nature of the substances used, as well as the temperature.

Once deposition has occurred for some time, the concentration of the metal ions in the double layer would be depleted to such an extent that the concentration cannot be replenished by mass transport. As a result of this change in concentration, the concentration polarisation is defined [9].

Ohmic resistance of the bath itself results in further overvoltage referred to as resistance polarisation. Pseudo-ohmic resistance occurs when the electrodes are covered by a thin film with a different resistance than that of the bath. The total polarisation is then the sum of all the aforementioned overvoltages [9] [14].

### 2.1.6. Mechanism

Metal crystalline lattices consist of metal ions located at regular lattice positions surrounded by moving electrons. The ionic charge of the ions is neutralised by the presence of the electrons. The arrangement of ions in the lattice causes resonating forces and these are responsible for the cohesion of the lattice and the physical properties of the metal crystal [9].

In the solution, the electrode carries an electrical charge which attracts dipole water molecules or ions of the opposite charge. The adsorption forces that hold the water molecules to the surface are quite strong. Ions are held on the surface by electrostatic forces. The electrical double layer which forms at the surface has a measurable capacitance. The metal ions proceed to migrate over the electrode surface until they reach stable positions where they are incorporated into the lattice. Once the metal ions become incorporated into the lattice, they release their ligands, resulting in overall charge neutralisation and spontaneous cathodic current flow. Concurrently, lattice ions may coordinate with the adsorbed water molecules and migrate into the ionic side of the double layer as hydrated ions and eventually into the solution resulting in an anodic or dissolution current. When the cathodic and anodic currents are equal, the electrode potential is at an equilibrium value, with no net charge. The current that flows is referred to as the exchange current. The presence of other stronger ligands or impurities results in lower exchange rates, as the metal ions will react preferentially with the stronger ligands versus the water molecules [9].

If similar electrodes are placed in a solution containing the metal ion, no net current flows, as the anodic and cathodic reactions occur at the same rate. If an external potential, or polarisation, is applied, the potential at the cathode is lowered and the deposition reaction is accelerated, simultaneously retarding the dissolution reaction at the anode. The deposition of the metal corresponds to the net cathodic current that flows. The potential at the anode is raised, retarding the dissolution of the metal resulting in the flow of a net anodic current. The shift in the potential of the electrode is referred to as its polarisation, overpotential or overvoltage.

## 2.1.7. Electrodeposition

Deposition does not occur uniformly or continuously from one end to another. Deposition occurs at favoured sites on the surface (Figure 2-6). The metal ions sacrifice their ligand bonds to attach to the cathode surface, becoming partially neutralised. The metal ions (adions) diffuse over the surface to point defects where they are incorporated into the metal lattice. Multilayer growth often occurs at sites where there are adsorbed impurities. Microsteps also occur at screw dislocations or similar defects or may form by two-dimensional nucleation in the presence of impurities [9].

Growth of the layers proceeds outward from the nucleation sites until the lattices meet to form grain boundaries. Growth generally occurs epitaxially, continuing the crystal lattice of the substrate metal since the force field extended from the substrate. Absorbed substances may alter the growth pattern of the deposited layer. The impurities become incorporated into the deposited layer, preventing the normal lattice formation. If the deposited material's lattice differs markedly from the substrate, the deposited layer may tend to normal lattice and not epitaxial growth. Certain crystal faces may grow preferentially resulting in orientated grains. If the deposition occurs at high rates, the ions may not be allowed time to find the location of highest stability. These depositions break down epitaxy [9]. Growth that occurs at preferential sites results in arborescent outgrowths or coarse, dendritic deposits. In the absence of sufficient agitation and if high current densities are used, the occurrence of these unwanted growths becomes prominent [10]. High current densities result in rapid deposition and possible depletion of ions from the electrolyte. A diffusion-controlled steady-state is attained as the reaction becomes dependent on the availability of ions at the electrode.



Figure 2-6: Electrodeposition of copper on the cathode in a sulphate solution [8]

In order to prevent the depletion of ions at the electrode-electrolyte interface, the agitation in the bath is increased. Hydrogen bubbles that may form on the electrode surface are also removed through agitation, resulting in more regular deposits [10]. A negative result of agitation is the stirring up of sludge resulting in the incorporation and subsequent contamination of the electrodeposit. A filtration system is incorporated into industrial plants to remove these contaminants. The temperature of the electrolyte alters the ionic solubility and viscosity in the electrolyte, thereby decreasing the diffusion time and increasing the availability of ions at the electrode surface.

Solutions of preferably highly ionised salts are used which have high conductivity. This lowers the applied voltage and therefore the consumption of energy is also limited [10]. Since the hydrogen evolution lowers the electrochemical yield, it is imperative to have a sufficient concentration of hydrogen ions in the solution to prevent the formation of basic salts and decrease the hydrogen evolution at the electrode.

If the deposited layer and the substrate's lattice parameters differ, stresses may occur in the layer. The presence of impurities may also result in stresses. Normal lattice formation may be affected or brittle intergranular deposits may appear as a result of these stresses. In the absence of these stresses the mechanical properties of the deposited layer will resemble that of the substrate.

The adhesion strength of the deposited layer is determined by the tensile strength of the substrate, since the first deposited layer slots into the lattice force of the substrate.

#### 2.1.8. Faraday's laws

The plating process is based on two Faraday laws. The first states that the weight of the metal deposited will be in proportion to the current used. The second law states that the rate of deposition will be controlled by the chemical equivalent of the metal being plated, in other words each metal will deposit differently [15]. Since hydrogen is also seen as a metal, certain plating conditions will result in electrolysis of the water in the solution. In some cases the hydrogen evolution will occur alongside the plating of the metal, but it may also occur instead of the metal plating.

Faraday's laws describe quantitatively the electrode reactions that occur during electrolysis. Firstly the weight, W, of an element that is liberated is proportional to both the current, I, and the time, t:

$$W = ZIt \tag{6}$$

where Z is the electrochemical equivalent. Furthermore, the weight of an element that is discharged is proportional to the chemical equivalent, with:

$$W = \frac{ItA}{nF} \tag{7}$$

Here A is the elemental atomic weight.

During electrolysis, all the ions in the solution contribute towards carrying current depending on the concentration and mobility of the species. An excess of positive charges builds up on the cathode and only those species with the most positive charges will be reduced. At the anode there is a build up of negative charges and only the most negative species will be oxidised. More than one discharge or redox reaction

may occur at the electrodes. The cathode current efficiency, *CCE*, is the ratio of the current used in the discharge process versus the total current passing at the electrode. This gives [16]:

$$CCE = \frac{\text{No. of coulombs depositing metal}}{\text{Total no. of coulombs passing}} x100$$
 (8)

Although the theory described above is true, it cannot readily be applied or tested due to the formation of secondary products during the plating process [6]. Faraday's laws refer to the total amount or quantity of all products formed.

## 2.1.9. Bath additions

Various chemicals may be added to the bath to alter the deposition process or the result. The texture of the deposited layer is greatly affected by the presence of ligands on the cathode surface prior to the deposition. The presence of various anions in the solution also profoundly impacts on the deposition even though the anions do not participate directly in the plating process. The presence of nickel chloride, fluoborate and sulfamates give higher current densities compared to sulphate for instance, due to the higher activity of the nickel ion. The addition of chloride ions to a nickel sulphate bath prevents passivation of the anode as it forms a complex ion with the nickel which forms the passive film on the anode [9]. The anion has two influences on the plating process. Primarily, the concentration of the salt and the activity and transport number of the metal ion are influenced. Secondarily, since the anion coordinates the metal ion and the cathode surface, it influences the deposition process by adsorption or bridging effects.

Levelling agents affect the structure of the deposits and tend to reduce the roughness of the deposit. Brighteners, on the other hand, increase the reflectivity of the deposit [10]. Generally, these additions are organic compounds that adsorb to the surface creating nucleation sites with stronger attraction to the deposit than the uncovered substrate.

Hydrogen evolution is a negative side-effect of some plating processes. The hydrogen bubbles adhere to the cathode and create areas where plating cannot proceed, creating a pit in the coating. In order to combat this, wetting agents are added to the solution to prevent the adhesion of the bubbles to the cathode surface [9]. Wetting agents, such as sodium lauryl ether sulphate, are based on surfactant technology. The film adsorbed on the surface of a material, even in the presence of a hydrophobic species, will enable the flow of water over the entire surface.

The addition of sulphuric acid to a sulphate bath increases conductivity and inhibits hydrolysis. Various buffers are also included in the electrolyte to control the pH.

### **2.1.10.** Deposition of various elements

The electrochemical series lists elements in terms of their standard electrode potentials and indicates the degree of ease with which the elements may be ionised [17]. Consider the following elements immersed in a solution containing the element's ions at unit activity. The standard electrode potential, shown here in Table 2-1, is measured versus a hydrogen electrode.

Element	Potential (V)
Manganese	-1.18
Zinc	-0.76
Chromium	-0.56
Ferrous Iron	-0.44
Cobalt	-0.28
Nickel	-0.25
Stannous Tin	-0.14

Table 2-1: Standard electrode potentials.

In general, metals that have more negative potentials are chemically more active. Metals with more negative potentials readily displace metals with less negative potentials. Electropositive metals are deposited preferentially over more electronegative metals. Metals with potential values less positve than hydrogen deposit with some difficulty as the hydrogen will deposit preferentially.

#### 2.1.10.1. Zinc

Zinc plating is done primarily for corrosion protection. Zinc acts as galvanic or anodic protection as it will galvanically or sacrificially react if the coating is damaged in order to protect the steel substrate, hence the reference to electrogalvanising. Normally, zinc plating or electrogalvanising is done on cold rolled sheet steel [10]. The corrosion resistance of the plating is enhanced when the surface is chromated or passivated after deposition. The chemical composition, current density and thickness of the coating must be monitored closely to prevent the formation of an inferior deposit [15]. Zinc sulphate or chloride electrolytes are, industrially, the most popular solutions. In order to achieve high current densities, without extensive corrosion, the acidity of the electrolyte is adjusted. The essential reaction is, therefore, given by [10]:

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$$
(9)

Soluble or insoluble anodes may be used. In the soluble anodes, there is dissolution of the zinc anode, followed by the deposition of the zinc at the cathode. The anodes must eventually be replaced and the shape and arrangement in the tank be designed and monitored carefully. Oxide coated titanium insoluble anodes are also used with electrogalvanising. Since the zinc is deposited from the electrolyte, the solution may become depleted of zinc. It is, therefore, essential that the concentration of the zinc be monitored [10]. As the purity of the electrolyte may be compromised with the use of insoluble anodes, it is essential that the bath conditions be controlled rigorously. The bath temperature, pH, agitation, concentration and addition of reagents, as well as the removal of dirt and secondary products from the electrolyte, are all critical. Since highly corrosive chlorine is generated with chloride baths when used alongside insoluble anodes, this type of solution is not used industrially. Highly advanced equipment is utilised to ensure uniformity in operations.

Although the uncoated surface remains free from contamination after plating, the carbon contamination on the zinc coated side of the sheet steel can amount to several

mg.m<sup>-2</sup> [10]. On line thickness measurements are made with the aid of an X-ray fluorescence gauge. It has been found that there is a 10% variation in the thickness both transversely and longitudinally. The edges (approximately 5 mm into the sheet), however, consist of a thicker coating of poor quality. The compactness of the zinc coating determines the adhesive strength of the coating. Pre-treatment of the coating determines the adhesion of the coating [10]. Although zinc hinders the drawing of the coated sheets, post-treatments or the addition of organic lubricants enable the drawing of zinc coated products.

#### 2.1.10.2. Cobalt

Cobalt is a very stable metal with high corrosion resistance. Although many of the properties are comparable to those of nickel, it is more superior but also more expensive. Cobalt may be polished to a highly reflective surface that will not discolour over time as nickel does.

#### 2.1.10.3. Nickel

Nickel plating produces a dull, but stress-free deposit. Under the general plating conditions the deposit also acts as a levelling agent, thereby reducing or removing surface imperfections. Nickel can be plated in thin, non-porous layers, but must be sufficiently thick if it is to be used as a corrosion resistant layer [15]. At pH of 5 and higher the nickel deposits are rough due to the formation of nickel(II)hydroxide, Ni(OH)<sub>2</sub>. Below pH of 2.3, hydrogen evolution becomes significant and may reduce the current efficiency [6].

#### 2.1.10.4. Alloy plating

Alloy plating or codeposition occurs when two or more metals are deposited from a solution. The sheets undergo bulk "doping" during the electroplating process and are

usually passivated via chromating or phosphating after plating [10]. Industrially, zinc alloy electrodeposits contain cobalt, nickel or iron and may be single or multilayered. These alloy coatings show increased corrosion resistance compared to plain zinc coatings of similar thicknesses. Two techniques are employed to produce the co-deposition of binary alloys:

- 1. The preferential deposition of the more noble metal via regular, irregular or balanced systems is referred to as normal codeposition. Regular systems are diffusion controlled and here the deposition of the more noble metal is determined solely by its availability at the electrode. In irregular systems the cathodic potential determines the deposition, although it has been suggested that diffusion parameters may also play a role in this form of deposition. In balanced systems, the equilibrium potentials of the metals in the solution are equal and the proportions of these metals in the bath and deposit are identical [10].
- 2. In abnormal codeposition the least noble metal deposits preferentially in contrast to predictions.

Since the industrial deposition of zinc-nickel alloys is governed by the diffusion parameters, it is accepted that a regular or balanced system is used. Codeposition only occurs when the redox potentials of the two metals are similar. The applied voltage must be larger than the higher of the two potentials for both metals to be deposited [10]. The potential difference between the two metals may be altered by changing the bath composition and deposition parameters. The addition of complexing agents and the adjustment of the temperature and current density can alter the deposition behaviour of a system.

#### **2.1.11. Industrial electrochemistry**

Electrochemistry is utilised for various industrial applications. Electrodeposition or electrowinning concerns itself with the breakdown of substances into simpler materials, whereas electrochemical synthesis results in the formation of complex substances. Although electrodeposition is simple, the application of Faraday's laws in practice, is much more intricate, an art if you wish [6].
Industrially or commercially, the mere fact that the metal deposits on the electrode (or surface) is not sufficient. The product must be of value with a measurable quality. Coherence, hardness and appearance are all crucial properties of the plating. Various additives are used to manipulate the plating product to the client's specifications. The pH, temperature and agitation as well as the composition of the bath are also monitored closely. The plating substrate is also prepared thoroughly before plating, via various steps such as pickling, scrubbing, rinsing etc. [6]. Various additives in nickel plating baths include levellers or brighteners or even additives that can alter the physical properties of the coating such as the hardness, strength, wear-resistance, temperature-resistance and so forth [6]. The mechanism by which the various additives ingluence the deposition or its properties is only partially understood. Additives may also act as complexing agents that will aid in the co-deposition of various metals. Metals that would not normally co-deposit may, with the addition of, for example, cyanide-ions be deposited simultaneously.

The electrogalvanizing line (Figure 2-7) consists of the following:

- Degreasing
- Pickling
- Electrogalvanizing
- Rinsing
- Passivation
- Oiling



Figure 2-7: Schematic representation of the electrogalvanizing production line

# 2.2. Phosphating of metals

## 2.2.1. Introduction

Conversion treatments such as chromating or phosphating are performed after electroplating and rinsing. The conversion treatments are preparatory for further treatments, such as painting, or simply to protect the surface of the steel from corrosion, fingerprinting etc. The steel is exposed to the chemical solution, by immersion or roll-coat, where a tightly bound, thin layer of the reaction compound is deposited [10].



Figure 2-8: Phosphated surface, clearly indicating the individual phosphate grains. [18]

Phosphating entails the formation of an insoluble phosphate coating on the surface of a metal (Figure 2-8) [19]. Phosphating processes encompass all reactions that result in a useful surface coating. Phosphating reactions include the corrosion of the metal surface and the most important processes are based on aqueous solutions. The coatings may be produced by spraying, immersion or pouring of the solution onto the surface. In recent years, the process has been adapted for the painting industry, whereby the self-etching phosphating solution may be painted onto the galvanized surface. This serves as a primer for painting.

## 2.2.2. Pre-treatment

The conversion treatment process (Figure 2-9) is usually accompanied by a degreasing step to eliminate the presence of any organic residues, lubricants or protective oils. This step aids in the removal of metallic particles that may etch the surface as well as the removal of oxides from the surface. The low cost and high efficiency of alkaline degreasing agents make them suitable for use in the degreasing steps [10]. The degreasing solution contains the following:

- 1. A base, which could be caustic soda or sodium carbonate, that saponifies fats and makes the other oils soluble,
- 2. Surfactants that are either anionic or non-ionic, e.g. dodocylbenzene (anionic) or oxyethoxynonylphenol (non-ionic), detach the oils from the surface, and
- 3. A detergent such as silicates, phosphates, polyphosphates or polyacrylates.



Figure 2-9: The phosphating process follows various steps. [18]

The heated degreasing solution  $(55 - 75^{\circ}C)$  is sprayed (2 bars pressure) onto the surface. The efficiency of the degreasing treatment is greatly dependent on the temperature of the solution. It is essential to rinse the surface thoroughly to remove the degreasing solution and any residual contaminants. The presence of any

contaminants could adversely affect any other surface treatments. In order to prevent the reoxidising of the surface post treatments commence immediately after rinsing [10].

## 2.2.3. Conditioning

After the substrate has been cleaned and rinsed, it is submerged in a solution containing insoluble titanium phosphate crystals. These crystals adsorb to the substrate. Upon further treatment, these sites will act as nucleation sites. The higher the concentration of nucleation sites, the smaller or finer the resultant crystal growth.



Figure 2-10: The impact of conditioning on the structure of the phosphate coating, a) without conditioning and b) with conditioning. [20]

As the quality of the coating is determined by the size of the grains as well as the coverage, it is quite evident that conditioning is essential (Figure 2-10).

# 2.2.4. Phosphating processes

Dilute aqueous solutions are utilised in the phosphating process. The solution contains the phosphate anions as well as some of the metal cations, thus all the main constituents are present in the solution. Ready exchange of the molecules on the surface and those in the solution is allowed by the exposure of the surface to a large quantity of the solution. The exchange takes place between the surface and the nearsurface liquid layer. [19]

#### **2.2.5.** Deposition mechanism

#### 2.2.5.1. Iron phosphate coatings

Iron phosphating results in the deposition of iron phosphate crystals on the surface. In an attempt to move away from the use of coated steels, manufacturers are investigating the possible use of phosphated steel. The uncoated steel can therefore be phosphated and painted directly without the need for electrogalvanising. The bath contains phosphoric acid, alkali phosphates and an accelerating agent such as chlorate, molybdate, bromate or metanitrobenzene sulfonate [10].

When the uncoated steel is phosphated in a chlorate accelerated bath, the following reactions occur:

$$3Fe+6H_{3}O^{+}ClO_{3}^{-} \rightarrow 3Fe^{2+}+Cl^{-}+9H_{2}O$$
 (10)

$$2Fe^{2+} + 3HPO_4 + \frac{1}{2}O_2 + 2H_2O \rightarrow FePO_4 + Fe(OH)_3 + 2H_2PO_4^-$$
 (11)

The accelerators are generally added to, not only accelerate the reaction, but also to act as depolarizers. This is important to prevent the surface from being blocked by hydrogen bubbles that form during the etching process.

#### 2.2.5.2. Zinc phosphate coatings

A bath containing ortophosphorusic acid, zinc metaphosphate and accelerating agents is used to produce a crystalline deposit on the surface of the electrogalvanised steel [10]. The deposition reaction can be accelerated using one or a combination of the following: nitrates, nitrites, chlorates, peroxides or organic acids. Prior to phosphating, the surface is treated in an activation bath to ensure a good quality coating. The liquid in contact with the surface should be more or less in equilibrium with the coating-forming species. The coating forms when the following reaction is forced out of equilibrium:

$$3Zn^{2+} + 2H_2PO_4^{-} + 4H_2O \rightarrow Zn_3(PO_4)_2.4H_2O + 4H^+$$
 (12)

An increase in the pH at the surface results in the deposition of the hopeite (Figure 2-11). Hopeite refers the phosphate mineral  $Zn_3(PO_4)_2$ . It has a distinct orthorhombic structure and deposits in well formed crystals. The determining step to this reaction taking place is, therefore, the dissolution of the metal surface accompanied by a consumption of acid at the surface.



Figure 2-11: An XRD spectrum of the phosphate prepared by Henkel [18].

The phosphating process can be described in three steps.

#### 2.2.5.2.1. Acidic dissolution of the substrate

The acid dissolution or pickling of the metal surface determines, to some extent, the properties of the coating. The pickling reaction aids in the removal of any residual oil, oxides and dirt. The metal surface is also etched by the acid increasing the surface roughness and ultimately increasing the adhesion of the phosphate coating to the surface [19].

The degree to which the metal is etched or removed from the surface is proportional to the amount of free acid or  $P_2O_5$  in the solution. An increase in the  $P_2O_5$ 

concentration beyond the equilibrium value for the bath leads to a decrease in the precipitation of the hopeite and is accompanied by the spontaneous precipitation of other phosphates resulting in a large concentration of sludge in the bath. It is, therefore, imperative that this concentration be monitored closely.

The removal of metal from the surface is further increased by agitation of the solution. The additions of oxidising agents prevent hydrogen evolution and since the hydrogen bubbles are not present, blocking areas on the surface, the etching process is accelerated [19].

$$Zn+2H_{3}PO_{4} \rightarrow Zn(H_{2}PO_{4})_{4} + H_{2}$$
(13)

Due to the consumption of the acid in contact with the substrate, there is an increase of the pH at the surface and a supersaturation of the solution in this region. The rate of growth during this etching or incubation period is low.

The pickling reaction is altered by the deposition of insoluble phosphates or as a result of accelerators or oxidising compounds [21]. The surface of the metal is rarely etched uniformly as a result of the localised cathodic and anodic zones.

#### 2.2.5.2.2. Phosphate nucleation

The formation of a solid crystalline phase from an aqueous solution will only occur if one or more components are present in the solution at concentrations higher than saturation. Nuclei may form spontaneously in the supersaturated solution or may be introduced by either seeding crystals or other solid species with similar crystalline structures [19].

Nucleation occurs at energetically favoured sites on the surface. The presence of dislocations, such as screw dislocations also act as favourable sites for nucleation. The change in the pH at the surface displaces the zinc metaphosphate equilibrium resulting in the precipitation of the zinc orthophosphate (hopeite).

$$3Zn^{2+} + 2H_2PO_4^{-} + 4H_2O \rightarrow Zn_3(PO_4)_2, 4H_2O + 4H^+$$
 (14)

The precipitates arrive and are adsorbed onto the surface, diffuse over the surface to the favoured sites and are incorporated into the structure at the nucleation or favoured sites [19]. The presence of impurities on the surface also impacts on the rate of nucleation. During the nucleation period, the rate of growth is low.

## 2.2.5.2.3. Crystal growth

The crystal precipitation will continue until the entire surface is covered. The rate of growth is exponential, initially, but becomes linear once the surface has been coated. Since the phosphate coating is porous, the etching of the metal may continue and therefore the supersaturated solution is maintained. Once the etching of the metal slows down, the supersaturation cannot be maintained and the precipitation will halt [19].

When nickel and zinc are both present in the bath, the nickel may replace the zinc in the hopeite (Figure 2-12) and produce nickel metaphosphate,  $Ni_3(PO_4)_2$ . The nickel aids in accelerating the phosphating reaction and enhances the adhesion and corrosion resistance of the coating.



Figure 2-12: Fine phosphate crystals on an electrogalvanised substrate [20]



Figure 2-13: Coarse phosphate crystals on an electrogalvanised substrate [20]

As the deposition of coarse grains (Figure 2-13) results in a non-uniform coating and therefore a diminished ability to protect the surface, it is essential that the deposition be fine. In order to ensure a fine deposition, the nucleation rate should be increased. The substrate is treated in a refining bath where titanium colloids are allowed to adsorb on the surface. These colloids act as nucleation sites. Increasing the nucleation sites and rate will result in more and therefore finer crystals. The reactivity of the surface is dependent on the condition of the strip prior to entering the bath. The presence of organic contamination, for example, lowers the reactivity of the surface resulting in the growth of coarse crystals [10].

The addition of additives alters the various properties of the phosphate, including the crystalline structure and size, colour, porosity, roughness and thickness. The final application of the phosphated surface determines the phosphating bath parameters and the properties of the specific phosphate. Therefore, it is not relevant to expand on any one specific bath.

Phosphating is usually followed by rinsing and passivation.

#### 2.2.5.2.4. Trication phosphating

Although the phosphating process had been defined in the early 1920's, the addition of various cations to the phosphate bath only became common practice in the 70's. Along with the zinc, which is the primary cation, nickel and manganese are also added. The resultant product is therefore a combination of zinc phosphate, nickel phosphate and manganese phosphate.

The primary reason for adding the various cations is the beneficial contribution toward corrosion resistance and surface quality attained. Recently, attempts have been made to replace the nickel with another metal, such as iron.

## 2.2.6. Spotting

The presence of impurities such as residual oxides, arsenic, copper, graphite, cementite etc., greatly influences the degree and location of pickling of the metal surface during treatment. If the surface is not prepared properly, there may be some residual oxides or impurities on the surface that create localised polarities. These points undergo intense anodic attack resulting in pitting [21].

Small white rosettes become visible on the surface of the hot-dipped or electrogalvanised steel after phosphating. These etch pits are surrounded by zinc phosphate crystals. The spotting may occur prior to the phosphating, during the rinsing or cleaning stages. The white spots form due to a locally enhanced zinc corrosion with the subsequent deposition of the corrosion products. The problem is addressed by changing the bath parameters via the additives used or process applied or by the conditioning of the rinsing water [19].

## 2.3. Diffusion

Many reactions and surfaces are affected by diffusion. Whether it controls the reaction rate in chemical reactions or the composition of the sample during heat treatment, diffusion is an important aspect that should always be reviewed.

## 2.3.1. Introduction

Diffusion is generally referred to as the mechanism by which fluids or solids mix intimately [22] [23]. This mixing occurs as a result of theKinetic motions of the particles over a time interval in the presence of a concentration gradient [24]. The diffusion of atoms or ions in a metal or alloy in the solid state is restricted by the bonding of the particles in the equilibrium positions. There are distinct models that describe the movement, or diffusion of particles in the solid state. These are:

- 1. Vacancy or substitutional diffusion
- 2. Interstitial diffusion

#### 3. Grain-boundary diffusion

#### 2.3.2. Diffusion mechanisms

Diffusion may occur via different ways, depending on the matrix, diffusing element or the path by which diffusion takes place.

#### 2.3.2.1. Vacancy or substitutional diffusion

During deposition or crystallization, imperfections in the crystalline structure may occur. In the case of Schottky imperfections, vacancies are formed in the structure. Atoms or ions vibrate in the structure due to thermal energy [25]. An increase in this thermal energy will provide enough energy to the adjacent particles to overcome the required activation energy and move into the vacancy (Figure 2-14). An increase in the temperature results in more intense vibrations and thus a higher rate of diffusion. Generally, metals with high melting points have high activation energies. The bonds between the ions (located at regular lattice postions) are stronger and more energy is required to move in the structure. The number of vacancies,  $N_{\nu}$ , in the crystal structure at a specific temperature, T, can be calculated using the following expression:

$$N_{\nu} = N_0 \exp\left(\frac{-E_{\nu}}{RT}\right)$$
(15)

where  $N_0$  is the number of sites in the crystalline structure,  $E_v$ , the energy required to create a vacancy and R, the universal gas constant [26] [27].

#### 2.3.2.2. Interstitial diffusion

During interstitial diffusion (Figure 2-14), small atoms such as nitrogen or oxygen move from one interstitial site to another, without affecting the primary atoms in the crystal matrix. The interstitial atoms literally squeeze between the primary atoms.



Figure 2-14: Schematic representation of vacancy and interstitial diffusion

## 2.3.2.3. Grain-boundary diffusion

During solidification or deposition, numerous grains are formed from the nucleation sites outwards. Where the individual grains meet, boundaries are formed. The structure in this boundary may be irregular, with vacancies and other dislocations. As stated for substitutional diffusion, the atoms or ions may propagate by moving from one vacancy to another. Since the concentration of vacancies in the boundaries is higher, the diffusion along these paths occurs at lower temperatures and with greater ease. Therefore, the rate of diffusion along the grain boundaries may exceed the value for the bulk diffusion significantly [28].

## 2.3.3. Mathematical consideration

Relating the process mathematically provides a way in which to compare various processes with each other and to assess the impact of diffusion on a material.

#### 2.3.3.1. Steady-state diffusion

Consider two atomic planes separated by a distance x. If the concentration at the first plane is higher than the concentration at the second plane, the species will move, or diffuse, towards the second plane to counteract the concentration gradient,  $\frac{dC}{dx}$ . The flux, J, of the particles can be described by the following expression:

$$J = -D\frac{dC}{dx}$$
(16)

*D*, refers to the diffusivity, or the diffusion coefficient. This equation is also referred to as Fick's first law. If the concentrations of the solute atoms at the various planes are constant with time, the diffusion conditions are said to be steady-state.

The diffusivity values depend on the following variables:

- 1. The type of diffusion mechanism, i.e. substitutional, interstitial etc.
- 2. The temperature at which the diffusion takes place
- 3. The type of crystal structure of the solvent lattice
- 4. The type and extent of crystal imperfections present
- 5. The concentration of the diffusing species.

#### 2.3.3.2. Non-steady state diffusion

Contrary to the steady state diffusion, in the non-steady state condition there is a change with time in the concentration of the solute atoms. This condition is best described by Fick's second law:

$$\frac{dC_x}{dt} = \frac{d}{dx} \left( D \frac{dC_x}{dx} \right)$$
(17)

In this expression, the concentration changes with time,  $\frac{dC_x}{dt}$  and over distance,  $\frac{dC_x}{dx}$  [29]. Solutions to Fick's second law are dependent on the initial and boundary conditions and, therefore, there are numerous plausible solutions. The solutions for thin films, semi-infinite solids and infinite systems with constant surface compositions are but a few of theKnown solutions.

#### 2.3.3.3. Diffusivity

The diffusivity can be calculated using the following expression:

$$D_0 = \frac{1}{6} z f \Gamma_0 r^2 \exp\left(\frac{\Delta S_v + \Delta S_m}{R}\right)$$
(18)

In this expression z is the number of nearest neighbour sites; f is the correlation factor;  $\Gamma_0$  is the average jump frequency; r is the step distance;  $\Delta S_v$  is the the excess entropy of one mole of vacancies;  $\Delta S_m$  the entropy of migration and R is the universal gas constant [30].

The diffusion constant, or diffusivity, is determined experimentally using radioactive tracer elements [31].

The diffusivity is, however, also a function of temperature and the relationship between D and  $D_0$  is given by the Arrhenius plot.

$$D = D_0 \exp\left(\frac{-E_d}{k_B T}\right)$$
(19)

This straight line plot has a slope of  $\frac{-E_d}{k_B T}$  and an intercept at  $D_0$ . In this expression  $E_d$  is the activation energy and  $k_B$  is the Boltzmann's constant [32].

## 2.4. Corrosion

The way in which a material responds to its environment is determined by the constituents and structure of the material as well as the nature of the environment it is exposed to. Since the dissolution of the metal surface relates to corrosion principles it is interesting to establish the connection between the various processes [33]. Brief references are made to relevant corrosion processes, including:

- 1. Galvanic corrosion
- 2. Pitting
- 3. Dezincification, and
- 4. Hydrogen blistering

Although these appear to be independent phenomena, surfaces may experience a combination of these processes.

## 2.4.1. Galvanic corrosion

When dissimilar metals are in contact, electrically, in the presence of an electrolyte galvanic corrosion will occur. Generally, the more resistant metal acts as the cathode and the less resistant metal as the anode (Figure 2-15). Therefore the corrosion of the less resistant metal is increased and that of the more resistant metal decreased. Galvanic corrosion is affected by the environment, distance from the junction and the contact area between the metals.



Figure 2-15: Galvanic corrosion of dissimilar metals used in construction [34]

Although corrosion is an undesirable phenomenon, galvanic corrosion can be utilised. Cathodic protection entails the coating of a metal surface with a dissimilar metal, thereby making the substrate the cathode and the coating the anode. In galvanised steel, the substrate iron acts as the cathode and the zinc coating as the anode. The zinc will therefore corrode quickly and preferentially protect the iron substrate in the process.

## 2.4.2. Pitting



Figure 2-16: Corrosion Pit on Type 316 stainless steel due to acidic chlorides [35]

Pitting is an autocatalytic anodic reaction (Figure 2-16). In an aerated acidic solution the metal dissolves quickly as oxygen reduction takes place on the surrounding surface (Figure 2-17). The rapid dissolution of the metal causes an increase in positive charges in the vicinity of the dissolution, attracting more negative ions to the region. Hydrolysis provides high concentrations of hydrogen ions. This combination causes even more dissolution of the metal. The released electrons migrate to the adjacent surface, where oxygen reduction takes place.



Figure 2-17: Pitting of a metallic surface [33]

# 2.4.3. Dezincification

Dezincification is a form of selective leaching of one of the constituents of an alloy, in this case zinc.



Figure 2-18: Plug type dezincification [36]

Dezincification (Figure 2-18) occurs along three steps. Firstly the entire surface dissolves in the medium. If brass, the copper plates back onto the surface in the second step, but the zinc stays in solution in the third step.

## 2.4.4. Hydrogen blistering

A tank containing electrolyte on the one side and exposed to air on the outer side will experience hydrogen blistering (Figure 2-19). As a result of a corrosion reaction on the inner surface, hydrogen is evolved. Some of the hydrogen diffuses through the metal, instead of combining into molecules. Hydrogen bubbles will form on the opposite side of the container.



Figure 2-19: Mechanism of hydrogen blistering [33]

If, however, the hydrogen diffuses into voids in the structure, the combination will occur within the void. The molecular hydrogen cannot diffuse and is therefore trapped in the void. The accumulation of hydrogen atoms and molecules in the void will continue and the pressure in the void can be appreciable. The pressure is sufficient to rupture the material.

# Chapter 3 Background overview

Research and findings regarding zinc and zinc alloy electrogalvinated steel and the corrosion-resistance of steel alloys are discussed in this chapter.

A comparison of conventionally galvanized steel and electrogalvanised steel indicates that electrogalvanised steel has a similar surface lustre and roughness, and improved corrosion resistance, paint adhesion and weldability. (Adaniya)[37]. Additions from the iron group to the zinc coating improve corrosion resistance, with nickel giving better corrosion resistance, formability and weldability. The corrosion rate of coatings is dependent on the texture, morphology, chemical composition of the deposits and the porosity of the surface. The morphology of the zinc and zinc – nickel coatings with 13% nickel on the coating show the highest corrosion resistance. A chromatic conversion on the electrogalvanized surface adds to corrosion resistance.

After electrogalvanising, the surface undergoes activation by immersion in a sodium titanium phosphate solution which accelerates boundary reactions before phosphating. In zinc phosphating, the phosphating reaction is corrosive. The protons are consumed, zinc dissolved and concentration gradients build up in the boundary layer. The growth of the phosphate layer stops when the surface is covered. The structure of the phosphate film is dependent on the weight of the film.

White spotting occurs when the reaction with the phosphating agent occurs with the steel substrate or with a contaminant on the surface. Small quantities of chrome added to the substrate reduce white spotting. White spotting may not only be produced at the phosphate stage but also in any of the pre-treatment stages. Spotting appears to be more prevalent when chlorates are added to the phosphate baths. High agitation and spray phosphating also inhibit spotting. Wyville, R et. al. [48] suggested that the white spot consists of a zinc phosphate compound surrounding an iron centre. A suggested solution is the removal of particulate iron and iron contaminates in the phosphate baths.

The addition of cobalt and nickel to the electrogalvanised layer and the phenomenon of blistering are also discussed in this chapter.

# **3.1. Introduction**

As this study focuses on the galvanised steel produced locally, it is imperative to investigate and understand the zinc and zinc alloy electrogalvanised steel, the galvanising process including all pre and post treatments and, of course, the phosphating process.

# 3.2. Zinc electrogalvanising

The ease with which zinc can be electroplated and its high corrosion resistance in combination with iron has led to an increase in the demand for the metal year by year [37]. Steel is coated with zinc primarily to provide corrosion protection. The zinc coatings are obtained in various ways, including hot-dipping, galvannealing and electrogalvanising. Although the various countries, steel producers and automobile manufactures utilise various ways to produce the coating, the requirements from the automotive industry remain the same. The outer panels should have the following properties:

- Excellent corrosion resistance.
- Wide selection of steel qualities must be available
- Excellent paint adhesion and corrosion resistance after painting
- No flaking or peeling must occur during any of the subsequent treatments
- Weldability without any trouble

A study conducted by Adaniya et. al. [37] in 1978 found that the corrosion resistance of the electrogalvanised steel is approximately twice as high as that of conventionally galvanised steel. The zinc coating can therefore be reduced, making the manufacturing costs more economical.

Any type and size base metal can be used for the electrogalvanising process. The pretreatment stages of the base metal include degreasing, rinsing, scrubbing and pickling. The plating is done electrolitically. The bath, used in the study by Adaniya, contained zinc sulphate or chloride, sodium or ammonium sulphate as electro-conducting agents, sodium acetate as a pH-buffering agent and cobalt and chromium salts. The coating weight could be manipulated by changing the number of galvanising cells, current density and line speed. After plating and rinsing, the steel was post-treated in a chromate bath, rinsed and oil coated, and depending on the final application, possibly put through a phosphate treatment. The co-deposition of the cobalt and chrome was very small. The cobalt was distributed uniformly, whereas the chrome was enriched locally. The chrome enrichment occurred primarily at the substrate layer interface. The concentration of chrome in the electrolyte was very small, thus the chrome only deposited on nucleation sites.

The corrosion resistance of the coated metal was proportional to the thickness of the coating, however, the coated sheets had a given service life which must also be considered. The corrosion progress of the electrogalvanised steel was very low compared to other galvanised products.

Although there was no significant difference in paint adhesion between the various galvanised products, the paint adhesion was greatly dependent on the properties of the phosphate film on the metal surface.

The weldability of the galvanised metal lowered as the coating weight increased. Since the implementation of the electroplating process, the thickness of the coating could be reduced and, therefore, the weldability improved. Industrially, the most beneficial aspect of this process is that conventional electrogalvanising lines can be used for production.

There are various factors that impact on the properties of the electrocoating. The concentration of additives, current density, deposit thickness and agitation in the bath determine the properties of the coating [38]. The morphology, structure, microhardness and residual stress in the coating determines the corrosion resistance [39]. High tensile stress results in the cracking of the coating where compressive stress compromises coating adhesion.

## 3.3. Zinc alloy electrogalvanising

The addition of elements from the iron group (i.e. nickel, cobalt, iron) to the zinc coating improves the corrosion resistance of the coating.

In a study by Zhou et. al. [40], electrogalvanised zinc-nickel alloy coatings ranging in nickel composition between 10-15% nickel were prepared and studied.[40] The study confirmed that the additions of cations such as arsenic and antimony effectively counter the occurrence of anomalous deposition whilst increasing the nickel content of the deposits. The addition of tin also increases the nickel content in the alloy deposit and also gives a smooth, dense deposit.

The research done by Zhou [40] proposed that electrogalvanised coatings are made more functional by alloying metals such as nickel, iron and cobalt. Furthermore, zinc-nickel coatings that contain 10-15% nickel had better corrosion resistance, superior formability and improved weldability.

Generally, the more noble metals deposit preferentially. Anomalous co-deposition does, however, occur where the less noble metal deposits preferentially. The standard electrode potential for zinc is  $E^\circ$ =-0.76V and for nickel  $E^\circ$ =-0.25V. This means that the nickel should deposit more easily than zinc. When the current density is above the transition current density, there will be co-deposition. The transition current density occurs when the bath and the deposit contain equal metal ratios.

Factors such as temperature, agitation intensity, pH value and similar factors are ineffective in altering the anomalous deposition. It has been suggested that the anomalous deposition is the result of simultaneous hydrogen evolution and adsorption of foreign material by the active metal surface and this is referred to as the "addition agent theory". During this process an active agent is produced and the pH of the cathode diffusion layer is increased.

At the transition current density, the pH at the cathode surface rises sufficiently to form metal hydroxides which adsorb preferentially on the cathode. Nickel deposition is retarded by this adsorbed layer but zinc deposits readily through it.

In 1997 Zhou et. al. found that the presence of antimony  $(0.1 - 100 \text{ mg.l}^{-1})$  depolarizes the electrogalvanising reaction by 20 - 40 mV and changes the morphology of the zinc

deposit from hexagonal platelets to round grains. It also effectively minimised the anomalous deposition as the nickel content in the alloy was significantly increased with the addition of low concentrations of antimony.

In order to improve the corrosion resistance of the coating, the chemical composition can be altered, or the physical morphology or topography of the surface can be manipulated.

The corrosion behaviour of metallic coatings is dependent on the texture, morphology and chemical composition of the deposits [41]. The corrosion rate of each grain varies since the binding energy of the atoms between the crystallographic planes differs. The close packed planes or low index planes are more resilient to dissolution as a result of the higher binding energy of the surface atoms. Additionally, the difference in grain boundary character distribution and the texture also impacts on the corrosion resistance. Park et. al. [41] showed that there was a correlation between the chemical composition, crystallographic orientation and the corrosion rate. The porosity of the surface also affected the corrosion rate; the higher the porosity of the coating, the lower the corrosion resistance.

The morphology of the zinc coatings used varied with the applied current. Hexagonal platelets and ridges formed when the applied current density ranged from  $30 - 300 \text{ mA/cm}^2$ . If the current density was increased to a range of  $400 - 500 \text{ mA/cm}^2$ , the morphology changed to a more triangular-based pyramidal grain.

In zinc-nickel coatings a phase transformation was observed with an increase in nickel content. The current density also affected the nickel content of the coating. A nickel coating, with  $\sim$ 13% nickel on the coating, showed the highest corrosion resistance. Coatings with more than 15% nickel had a low corrosion resistance.

As the corrosion behaviour is influenced by the texture, stress in the coating, phase composition, and chemical composition, it is difficult to determine the impact of each of the separate parameters on the corrosion resistance.

## **3.4.** Chromate Conversion

Once coated, the metal can be treated chemically to further enhance the corrosion protection.

A chromate conversion of the electrogalvanised surface adds to corrosion resistance. Sohi et. al. [42] studied the corrosion of the coating by monitoring the formation of white rust, whereas the corrosion of the steel resulted in red rust. Zinc-nickel electroplating was performed using a zinc anode and a current density ranging from  $50 - 150 \text{ mA/cm}^2$ .

The zinc-nickel alloy coatings showed a superior corrosion resistance compared to the zinc coatings. This was due to the barrier protection mechanism theory. The theory predicts that, during corrosion, the zinc dissolves or reacts preferentially, leaving a nickel enriched top layer that prevents further attack. The difference in porosity between the two coatings also impacts on the corrosion resistance exhibited by the coatings.

The study elaborated on how chromate conversion coatings further enhanced the corrosion resistance of the coatings. The chromate solution contained primarily chromate and an active anion such as sulphate, fluoride or chloride. The reaction entailed the dissolution of zinc with hydrogen evolution and the reduction of chromium as the pH increased at the surface.  $Cr^{3+}$  hydroxides precipitated on the surface. The presence of metallic or oxidised nickel, cobalt or iron under the zinc oxide surface may, by a substitution reaction with the zinc, act as local cathodes promoting the dissolution of zinc in the acidic medium, thereby promoting post treatment.

# 3.5. Phosphating

After electrogalvanising, the metal is phosphated prior to painting. Before the phosphating can be done, the passivated surface must first be activated.

## 3.5.1. Activation

Activation of the surface plays an important role in the phosphating reaction [43]. Phase boundary reactions are accelerated or affectedKinetically by activation substances. The activation of metallic substrates is done by physically absorbed nuclei. Aqueous dispersions of sodium titanium phosphates are used to precondition the metallic substrates. The number of crystals per unit area is increased and the crystal size, coating weight and minimum reaction time is reduced. The electrogalvanised sheets or pressed panels are activated after degreasing and rinsing. The activation is done by immersing the steel in the sodium titanium phosphate solution prior to phosphating.

## **3.5.2.** Phosphating

Phosphating is a very important pre-treatment process applied to metal surfaces [44]. It is used to produce a protective layer or a primer for painting purposes. It makes cold formation easier and provides electrical insulation. It also aids in oxidation resistance. The study by Rebeyrat et. al. [45] on the phosphating of iron, used a passivation treatment performed in a volatile organic solvent (Acetone) instead of the aqueous solvent used in other studies. The solvent is not consumed and simplifies the degreasing-rinsing-treatment-rinsing processes.

The Phosphating solution contains:

- Acetone as solvent
- Ortophosphoric acid as agent

At room temperature with agitation the phosphating of an iron surface took 2 hours. At the liquid solid interface, the following reactions occurred:

- Anodic dissolution of the iron and formation of  $Fe^{2+}$  cations
- Reduction of the hydrogen in cathodic reactions

The presence of  $Fe^{2+}$  cations and  $PO_4^{3-}$  anions near the metal surface in sufficient concentrations resulted in the phosphate formation. After phosphating, the sample was rinsed in acetone and dried at 50°C.

Both  $Fe^{2+}$  and  $Fe^{3+}$  phosphates were present in the phosphate layer. Bridging and nonbridging oxygen were also present. No metallic iron oxides had been detected at the surface layer.

In the case of zinc phosphating, the phosphating reaction occurred by the acidic corrosion of zinc, and the subsequent precipitation of the zinc phosphate.[46] The solution contained zinc and phosphoric acid:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 zinc dissolution and (20)

$$2H^+ + 2e^- \rightarrow H_2$$
 hydrogen evolution (21)

The phosphating reaction was a corrosion reaction where protons were consumed, zinc dissolved and concentration gradients were built up in the boundary layer. The phosphating solution was saturated with primary acidic zinc phosphate  $Zn(H_2PO_4)_2$ , the pH increased at the metal surface and the protolytic equilibria of the phosphoric acid changed and therefore the concentration of the  $(PO_4^{3-})$  rose. When the solubility product of the tertiary zinc phosphate was reached, the hopeite precipitated.

$$3Zn^{2+} + 2H_2PO_4^{-} \rightarrow Zn_3(PO_4)_2 + 4H^+$$
(22)

By self inhibition, the growth of the phosphate layer stopped once the surface was covered. The corrosion and the consumption of protons decreased.

The most popular phosphate coatings include zinc, iron and manganese and the purpose of the coatings are for corrosion protection, primer for painting, metal-forming lubrication, wear reduction, electrical insulation or for decoration [47]. It is a

low cost and simple technique. The structure of the phosphate films is dependent on the film weight. Light-weight phosphate coatings  $(0.2-1.4 \text{ g.m}^{-2})$  are an amorphous coating. Middle-weight  $(1.4-7.5 \text{ g.m}^{-2})$  and heavy-weight coatings  $(7.5-30 \text{ g.m}^{-2})$  are crystalline.

Manganese phosphate has a higher corrosion resistance than zinc phosphate. The crystalline phosphate coatings are porous. Under certain conditions, it is possible to determine and express the porosity mathematically. The manganese phosphate has a lower porosity than the zinc phosphate. Lower porosity results in a smaller corrosion rate. The higher porosity does, however, lead to better adhesion to further surface treatments.

Recent phosphating techniques include various cations to the phosphate bath such as zinc, manganese, iron or nickel. The resulting phosphate will have these cations included either chemically or simply trapped in the crystalline structure. The phosphate film, therefore, changes from hopeite to  $Zn_{3x}Mn_x(PO_4).4H_2O$  including some nickel ions [48].

## **3.5.3.** White spots and phosphate defects

Maeda et. al. [46] reported that the presence of carbon or aluminium on the surface prior to phosphating adversely affected the phosphatability of the surface [48]. These elements inhibit the dissolution of zinc accompanied by a hydrogen evolution reaction. This evolution results in an increase in the pH at the local cathodes and the consequence of this is the deposition of the phosphate crystals. In order to combat this problem, an alkaline degreasing agent or mechanical polishing was performed before phosphating.

White spots are small areas on the electrogalvanised surface that have varying chemical, morphological and topographic properties compared to the rest of the surface. The spots occur when the reaction with the phosphating solution occurs either directly with the steel substrate, as a result of poor adhesion to the electrogalvanised layer, or with a contaminant on the surface. Although the white spotting is essentially

a problem in the post treatment stages, it remains a troublesome problem to the steel manufacturers. The inclusions of oxides, micro-laminations, or carbides on the surface (most likely as a result of annealing) have all been associated with white spot formation [49].

The addition of small quantities of chrome to the substrate results in a reduction of the surface carbides on annealing and thus reduces the white spotting sites.

The white spotting of the electrogalvanised steel is not always produced at the phosphate stages [50]. The pre-treatment stages, which include degreasing, rinsing, pickling and activation, may also be responsible for the spot formation. Surface contaminants such as iron accelerate the spot formation. The addition of chlorates to the phosphate bath is done to accelerate the phosphating reaction, but white spot formation seems to be more prevalent with these baths. The agitation in the bath is also a factor in white spot formation, with high agitation and spray phosphating resulting in less to no spot formation.

Wyville et. al. [48] suggested that the white spot consists of an amorphous zinc phosphate compound surrounding an iron centre [50]. Alkaline cleaners containing phosphates were detrimental to the phosphating. When substituted with silicates or carbonates, the spots that formed consisted of either zinc silicate or zinc carbonate surrounding the iron centre. The chemical composition of the spot was therefore dependent on the composition of the cleaner. The presence of iron on the electrogalvanised surface originated either from the iron inclusion during electrogalvanising or was exposed steel as a result of a non-uniform electrogalvanised coating. There was no zinc underneath the iron on the surface and therefore the phosphating reaction could not progress at these points. Since the zinc was sacrificial at this point, it would react rapidly with any electrolyte and form the zinc compound that precipitated around the spot.

Although the addition of sodium nitrite to the cleaning solution inhibited the formation of the white spots, it was consumed quickly, producing ammonia. If this solution was to be applied, the sodium nitrite would have to be replenished regularly which could be a costly process.

Another solution proposed was the removal of particulate iron and iron contamination in aged phosphating baths. This would reduce the redeposition of iron on the surface or surface contamination. Scratches and metal deformations act as nucleation sites for white spots. It is therefore imperative that the surface is not damaged during production [47].

## **3.6.** Cobalt, nickel and electrogalvanised steel

It has already been stated that the addition of nickel or cobalt to the electrogalvanised layer may reduce the rate of corrosion. Before interpreting corrosion data or formulating a hypothesis, it should be noted that the composition and structure of the zinc coating plays an important role in the corrosion behaviour [48].

In the study conducted by Leiheiser and Suzuki [50], the zinc electrogalvanised samples were immersed in solutions of cobalt chloride and nickel acetate before being immersed in a salt corrosion bath. When the zinc electrogalvanised samples were exposed to the salt bath, the rate controlling step in the corrosion of the zinc layer was the cathodic reaction:

$$H_2O + \frac{1}{2}O_2 + 2e^- \to 2OH^-$$
 (23)

When the zinc electrogalvanised samples were immersed in a solution containing high concentrations of cobalt, the surface blackened, suggesting the formation of metallic cobalt on the surface. No blackening occurred at lower cobalt concentrations. Closer inspection of the samples indicated a surface predominated by cobalt oxide. This was as a result of the metallic cobalt reacting with the environment to form the oxide. The oxide was only superficial with metallic cobalt underneath. When the cobalt concentration in the solution was increased, the concentration of cobalt on the surface also increased.

The cobalt on the surface lowered the corrosion rate of the zinc layer. This corrosion inhibiting occurred even at low cobalt concentrations.

The dominant cathodic reaction in the sodium chloride bath was:

$$H_2O + \frac{1}{2}O_2 + 2e^- \to 2OH^-$$
 (24)

The competing cathodic reaction was:

$$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H}_{2} \tag{25}$$

The ratio of these reactions was determined by the number of impurities on the surface as well as the crystallographic nature of the zinc. The reactions were further governed by the rate at which oxygen reached the surface or the rate with which the OH<sup>-</sup> could diffuse away from the surface. This became clear as the agitation in the bath was changed. The corrosion of the zinc was, therefore, determined by a diffusion process and not the availability of electrons at the cathodic surface. At the zinc/oxide surface the following anodic reaction took place:

$$Zn - 2e^{-} \rightarrow Zn^{2+}$$
 (26)

The counter cathodic reaction was:

$$H_2O + \frac{1}{2}O_2 + 2e^- \to 2OH^-$$
 (27)

This reaction took place at the oxide/solution interface. A steady state was reached when there was a balance between the rate of oxide formation and the rate of oxide dissolution in the medium. This continued as long as the solubility limit was not exceeded. The corrosion of the oxide occurred through the oxide layer. The corrosion product precipitated on one point on the surface whilst it dissolved on another point. The precipitates acted as a diffusion barrier on the surface for species in the solution. With cobalt on the surface, the cathodic reaction was governed by the following reaction:

$$\operatorname{Co}^{2^+} + 2e^- \to \operatorname{Co} \tag{28}$$

The unchanged cobalt atoms were incorporated into the oxide layer. Ionic exchange could also be responsible for the cobalt atom incorporation into the oxide layer. This ionic exchange that occurred between the metallic zinc and the ionic cobalt was also referred to as an electron trap. The presence of the cobalt reduced the dissolution of the zinc by reducing the number of electron accepting sites near the zinc/zinc oxide interface. At high cobalt concentrations, the metallic cobalt acted as a catalyst for the competing cathodic reaction and the evolution of hydrogen. The cobalt atoms

remained in the oxide layer and would, therefore, have a long-term corrosion resistance.

The same experiments were performed by dipping the samples in the nickel acetate solution. The immersion of the samples into the nickel solution provided high corrosion resistance even at low nickel concentrations. The nickel atoms became leached out into the solution during the corrosion reaction and did, therefore, not remain on the surface. Since the nickel atoms are systematically removed from the surface, they can no longer contribute to the corrosion resistance. The corrosion resistance, therefore, becomes a function of time, as the nickel concentration changes over time.

# 3.7. Testing electrogalvanised surfaces

Corrosion resistance of the metallic surfaces is determined by a salt-spray or immersion test or via electrochemical tests. The samples are exposed to a sodium chloride solution for a given time. This test is said to simulate the atmosphere [49]. In a salt-spray test, the propagation of white and red rust is monitored. The rate and extent of corrosion is measured and translated to give the corrosion resistance of the samples.

# 3.8. Blistering

Upon heat treatment, certain electrogalvanised samples become blistered. The Mercedes Benz heat treatment entails the heating of the samples to 300°C for a period of 30 minutes. Prior to the heat treatment, no clear difference in the chemical composition of the blistering sample can be identified in comparison with nonblistering samples. After the heat treatment however, there are distinct differences. In the non-blistering sample, the nickel in the electrogalvanised layer diffused to the surface. The iron from the substrate diffuses through the zinc layer, but the iron is not present on the surface. There is a slight presence of manganese on the surface there is a slight enrichment of manganese. The presence of the manganese is presumed to be the cause of the peeling of the zinc layer when a tape test is performed.

In samples that showed blisters, the profile of the nickel in the electrogalvanised part of the surface was markedly different. Instead of the surface enrichment, the nickel accumulates within the sub layers. It would appear that the nickel prevents the movement of the iron and the manganese in the electrogalvanised layers.

The imported sample remained in tact after the heat treatment with no diffusion of either the iron or the manganese into the electrogalvanised layer. The primary difference between the imported and locally produced samples is the use of nickel in the locally produced electrogalvanised samples.

Von Moltke [51] concluded that the reason for the alloy formation is the morphology of the zinc plating. Laboratory prepared samples did not show the same alloy formation as the industrially prepared samples, indicating that the cause of the problem lies in the plating process used by industry [49].

This conclusion was supported by Shindo [52] during a parallel study. Electrogalvanised samples prepared by MSSA with nickel added to the plating solutions were subjected to the blister tests. Voids formed between the substrate and the electrogalvanised layer. The coating itself consisted of small, randomly scattered zinc crystals. It was also stated that the iron in the plating solution co-precipitated with the zinc. The substrate was analysed and no contamination or significant dislocations could be identified.

A sample referred to as the "good specimen" showed no layer by layer structure in the electrogalvanised layer, but did show some iron. The nickel content was too low to be detected with EDS. The iron in the layer influenced the grain size and shape.

A further sample, the "bad specimen", had an oxide or hydroxide layer over the zinc layer. Upon closer inspection, it was found that the blisters form in the centre of the sample, pointing to a problem in the operational parameters. There was an accumulation of nickel underneath the blister and high concentrations of carbon and oxygen in the vicinity of the blister.

The occurrence of voids in the electrogalvanised layer did not necessarily result in blistering as the voids were also present in the "good specimen". There were no irregular elements present in the voids in this specimen, although both carbon and oxygen were detected. Furthermore, the source of the contaminant could not be determined.

Analysis of the substrate did not offer any plausible explanations as no inclusions, roll fragments or micro flaps were present. The aluminium levels were to standard and no reactive sulphides were present near the surface. The sulphur content was stabilised by the titanium and manganese in the substrate.

The morphology of the zinc coating was not discussed fully, although it was determined that the zinc crystals that formed on the surface did not develop from the first zinc layer. [52]

The presence of various contaminants in the plating solution inadvertently alters the morphology and structure of the zinc coating in the electrogalvanised layer. Often various counter measures are enforced to combat the problem. The presence of copper in the electrogalvanised layer results in a powdery phosphate coating during post-treatment of the surface. This is an undesirable outcome, and thus industry has replaced all copper rolls and connectors with stainless steel parts.

Lead anodes were commonly used until it was found that the presence of lead in the electrogalvanised layer results in delamination if the surface is painted. The lead precipitates between the substrate and the zinc coating. Subsequently, the use of lead anodes was reconsidered.

During the preparation of the  $ZnSO_4.7H_2O$  antimony is added to accelerate the precipitation of the salt. When used to produce the electrogalvanised zinc coating, the presence of the antimony results in a coating with a dull appearance. The change from

a bright to a dull coating is attributed to the shape of the crystals, where the latter is deformed.

The presence of cadmium, cobalt and tin in the plating solution results in the formation of pinhole defects in the coating. Although there is no compromise in the corrosion resistance, the defect was still undesirable. The pinhole forms as a result of localised accelerated hydrogen evolution.

The presence of iron in the plating solution alters the crystal structure of the zinc coating. This, in turn, affects the stamping or pressing properties of the coated steel.

Nickel present in the plating solution does not alter the structure of the coating, but does affect the corrosion resistance and also the chromate post-treatments. At first glance it appears that the corrosion resistance is not affected, but the reaction is actually accelerated.

The presence of small quantities of organic compounds may alter the zinc morphology. The organic compounds have numerous sources from the production of the reagents to the transport and packaging of the reagents. These compounds decompose during the plating process and therefore the solutions are deliberately heated to 93°C prior to use.

Pure zinc solutions result in hexagonal crystals. The growth of the crystals results in a pyramidal structure. The presence of the impurities affects the structure of the zinc crystals. Spherical, columnar or twin crystal structures are observed whenever impurities are added to the plating solution [53].

## **3.9.** Dezincification

Dezincification is a process whereby zinc is removed preferentially from an alloy. Zinc is a highly reactive element and therefore reacts preferentially in most alloys. The zinc can therefore be removed when the alloy comes into contact with either an acid or alkaline solution. Zinc also has a low melting point, 412°C at atmosphere and, therefore, sublimes at low pressures. At 300°C zinc will sublime at approximately  $5x10^{-3}$  torr. This is as a result of the weak interatomic bonds in the zinc HCP structure. Metals such as iron have a much higher melting point due to the stronger interatomic forces in the FCC structure [54].

As the zinc in the alloy is removed, whether chemically, or via temperature or vacuum, the resultant structure will be porous and structurally weaker. Any further treatment or use of this resultant material may lead to catastrophic failure [55].



Figure 3-1: Schematic summary of the information supplied by previous studies
# Chapter 4 Experimental work

In this chapter, the experimental work is discussed.

Samples were electroplated in a variety of electrolytes; zinc, nickel, zinc-nickel, zinc-cobalt and zinc-nickel-cobalt. A discussion of the preparation of each electrolyte is given. The samples were electroplated by immersion plating and the phosphating process used is also discussed.

Samples, prepared on site by MSSA using existing plating lines and solutions were supplied with a pure zinc coating, a zinc layer with 380 ppm nickel addition to the electrolyte and a zinc layer with 930 ppm nickel addition. A sample from a different steel manufacturer in America was also studied.

The analytical techniques and instrumentation used in this study are the Glow Discharge Optical Emission Spectroscopy, the Scanning Electron Microscopy and the Energy Dispersive Spectroscopy, as well as X-ray diffraction.

# 4.1. Sample preparation

Various samples were used in this study, and the specific preparation of each directly impacts the results obtained.

#### 4.1.1. Electroplating

The composition of the electroplated samples depends on the composition of the electrolytes used. The morphology or structure depends on the type of electroplating employed. The thickness or coating weight depends, primarily, on the current and duration of the plating. The laboratory samples were prepared utilising immersion

plating. Various samples were prepared using electrolytes with different compositions.

#### 4.1.1.1. Immersion plating

Immersion plating was performed at 60°C with slight agitation (Figure 4-1). The electrodes were placed 6 cm apart. The sample was submerged in such a way as to expose the largest possible surface area (front and rear) to the electrolyte (A = 28 cm<sup>2</sup>). In order to ensure a current density of 250A.m<sup>-2</sup> a stable current of 0.7A was passed through the circuit. The reaction was allowed to proceed for 5 minutes, whilst agitating the solution. The sample was removed from the electrolyte, rinsed with distilled water and air dried.



Figure 4-1: Apparatus used for immersion plating

#### 4.1.1.2. Electrolyte preparation

Numerous samples, with varying compositions, were required and therefore various electrolytes were necessary. The following solutions were prepared:

- Zinc electrolyte with 100 g/l zinc
- Zinc-nickel electrolyte with 100 g/l zinc and 380 ppm nickel
- Zinc-nickel-cobalt electrolyte
- Zinc-nickel-copper electrolyte

The specific compositions' calculations are detailed in the following sections.

#### 4.1.1.2.1. Zinc electrolyte with 100 g/l zinc

The followingKnown values were used:

Description	Value
$M_{Zn}$	65.39g/mole
Salt used	ZnSO <sub>4</sub> .7H <sub>2</sub> O
$M_{ZnSO_4.7H_2O}$	287.54g/mole

Table 4-1: Preparation of the zinc electrolyte

In 1.5l 150g zinc is needed. The number of mole is:

$$n_{\rm Zn} = \frac{m_{\rm Zn}}{M_{\rm Zn}} \tag{29}$$

Thus  $n_{Zn} = 2.294$  mole. The mass of ZnSO<sub>4</sub>.7H<sub>2</sub>O required is given by:

$$m_{\mathrm{ZnSO}_4.7\mathrm{H}_2\mathrm{O}} = n_{\mathrm{Zn}}.M_{\mathrm{ZnSO}_4.7\mathrm{H}_2\mathrm{O}}$$

Thus  $m_{\text{ZnSO}_4.7\text{H}_2\text{O}} = 659.596g$ 

#### 4.1.1.2.2. Zinc-nickel electrolyte with 100 g/l zinc and 380 ppm nickel

This electrolyte was prepared by dissolving the following quantities of salt in 1*l* of the acidic solution. The density of the zinc-electrolyte is 1236 g/l. The mass of the nickel therefore changes accordingly.

380 ppm nickel is given by 0.4697g nickel, which in turn is given by 2.104g NiSO<sub>4.6H<sub>2</sub>O.</sub>

Salt	Mass
ZnSO <sub>4</sub> .7H <sub>2</sub> O	439.73g
NiSO <sub>4</sub> .6H <sub>2</sub> O	2.104g

Table 4-2: Preparation of the zinc-nickel electrolyte

#### 4.1.1.2.3. Zinc-nickel-cobalt electrolyte

This electrolyte was prepared by adding the following quantities of the aforementioned electrolytes.

Electrolyte	Volume	Concentration in solution
100 g/l zinc	250 ml	50 g/l
380 ppm nickel	100 ml	76 ppm
50 ppm cobalt	150 ml	15 ppm

 Table 4-3: Preparation of the zinc-nickel-cobalt electrolyte

#### 4.1.1.2.4. Zinc-nickel-copper electrolyte

This electrolyte was prepared by adding  $0.05g \text{ CuSO}_4.5H_2O$  to the prepared zincnickel electrolyte, resulting in a composition as detailed in the table below:

Cation	Concentration
Zinc	100 g/l
Nickel	380 ppm
Copper	50 ppm

 Table 4-4: Preparation of the zinc-nickel-copper electrolyte

# 4.1.2. Phosphating

The phosphating is done using four baths (Figure 4-2). The first was a cleaning bath consisting of an alkaline solution. This removes the oxide and residual oil on the sample surface. The second bath was a distilled water rinsing bath. The third bath was a conditioning bath containing Ti-colloids that influence the grain size of the

phosphates. The fourth bath was the phosphating bath where the phosphating reaction takes place. After phosphating the samples were rinsed in distilled water and air dried.

The various baths were prepared according to the prescriptions of Henkel, a chemical company that is contracted to prepare and maintain the phosphating baths of various automotive manufacturers.



Figure 4-2: Four baths used to phosphate the electrogalvanised samples

# 4.1.3. Blistering

In order to study the blistering the following samples were used:

- 1. An electrogalvanised sample, supplied by MSSA, that showed blistering after heat treatment at 300°C for 30 minutes and consequently failed the quality test.
- 2. The electrogalvanised sample prior to heat treatment, as produced by MSSA.
- 3. An uncoated steel substrate sample of similar composition and quality as the blister sample prior to coating.
- 4. The corrected recently produced electrogalvanised sample that does not exhibit blistering
- 5. A comparative sample produced in America.

All samples were prepared or supplied MSSA.

# 4.1.4. Industrial samples

Various samples were supplied by MSSA and were prepared on site using the existing plating lines and solutions. These include:

- 1. Electrogalvanised zinc layer with a 380 ppm nickel addition to the electrolyte
- 2. Electrogalvanised zinc layer with a 930 ppm nickel addition to the electrolyte
- 3. Imported electrogalvanised samples with a pure zinc coating



# 4.1.5. Annealing Systems

Figure 4-3: Annealing system

Samples were annealed in a Lindberg annealing system (Figure 4-3). Samples were placed in ceramic boats and carefully positioned in the centre of the oven. A quartz tube runs through the centre of the oven and this houses the ceramic boat. The temperature was regulated and controlled by an external control unit. The annealing chamber can also be connected to a turbo molecular and rotary vane pump to allow for annealing under vacuum.

#### 4.2. Sample analysis

The analytical techniques used in this study are used in combination to paint a complete picture of the mechanisms investigated. Although each technique, on its own, has limitations, the contribution made by each aids in formulating an in depth understanding.

#### 4.2.1. Glow-discharge spectroscopy



Figure 4-4: The LECO GDS 850A apparatus

This relatively new spectroscopic technique can be used to perform depth profiling analysis of solids. The direct bulk analysis can be performed quite rapidly. The Glow Discharge Optical Emission Spectroscope (Figure 4-4) consists of a discharge source and various optical spectrometers enabling the simultaneous analysis of numerous elements (Figure 4-5). Cathodic sputtering removes material from the sample surface (Figure 4-6). The surface atoms are removed uniformly (Figure 4-7). These particles move through a plasma where, via collisions with electrons, the particles are excited. Upon relaxation a characteristic spectrum is emitted which is measured by the spectrometers. The calibrated GDS can be used for quantitative depth profiling as well as compositional depth profiling [56] [57].

The use of GDS versus more conventional techniques such as Auger electron spectroscopy (AES), in this study, is preferred due to the thickness of the coatings. Sputtering times for the two techniques differ greatly. GDS analysis can be completed in less than two minutes, whereas with AES it will take several hours to sputter

through the coatings. Another consideration is the detection of elements in low concentrations, where in this case GDS is more reliable. The peaks of the iron, nickel and zinc overlap in AES making it more difficult to identify specific elements.

The use of the GDS is not always beneficial in comparison with AES. The fingerprinting on spectra cannot be done and therefore the chemical environment of the elements cannot be confirmed.

Glow Discharge Optical Emission Spectroscopy, equipped with an RF unit, is particularly suited to the analysis of non-conductive materials, such as the organic coatings used to coat sheet steel [58].

Prior to analysis samples were submerged in acetone and placed in an unltrasonic bath for 2 minutes to remove any residual oils from the surface after which the samples were air dried.



Figure 4-5: The working of the GDS technique.



Figure 4-6: Cathodic sputtering of the sample surface [57]



Figure 4-7: Cathodic sputter area for GDS analysis (SEM image obtained experimentally)

### 4.2.2. Scanning electron microscopy

Scanning electron microscopes (SEM) produce high resolution images with a unique three dimensional appearance, making it possible to assess the surface structure. Electrons are generated thermionically from a cathode tungsten filament and accelerated towards the anodic sample. The generated electron beam passes through various lenses and can be rastered over the sample surface. The primary electrons enter the surface and interact with the atoms to generate secondary electrons and x-rays. The electrons emitted are detected to produce an image. The brightness of the image depends on the number of secondary electrons that reach the detector. Therefore, the steep and edge sections of the sample appear brighter than the flat surfaces.

Backscattered electrons (SBSE) can be used to discern between areas of differing elemental composition. The number of backscattered electrons is low and the small acceptance angles impacts on the positioning of the detector [59].

The industrial samples were rinsed with acetone and air dried prior to analysis. Although rinsed, the presence of dust on the samples cannot be eliminated. Laboratory prepared samples were analysed without prior treatment as no oils were used to seal the surfaces. As the structure and adhesion of the coatings had not been established, these may have been affected by physical cleaning or handling. These wereKept at a minimum.

Before correctly interpreting results obtained with the scanning electron microscope one must understand the functioning and drawbacks of the components in the apparatus. The following paragraphs outline the primary considerations in the generation of the electron beam, the interaction of the beam with the sample and the image formation.

#### 4.2.2.1. Electron gun

The electron optical columns in scanning electron microscopes consist of various electron lenses and an electron gun. The size of the probe spot and the beam current determine the resolution of the microscope. There are three different types of electron guns, namely: the tungsten filament cathode,  $LaB_6$  rod cathode and the field emission gun.



Figure 4-8: Configuration of self-biased electron gun [60].

The electron beam comprises of a stable flow of electrons, generated by thermionic emission. At sufficiently high temperatures, the electrons in a metal can overcome the work function of the cathode material and escape. The filament, or cathode, is usually tungsten with an approximate diameter of 100µm. The wire is bent to a v-shape tip which has a 100µm radius. Current is passed directly through the filament, which heats the filament to the required value. A negative voltage ranging between 1 - 50kV is used, producing an operating temperature of 2700K. A negative voltage is placed over the cathode and anode plate of between 1000V and 50 000V, which accelerates the electrons towards the sample. The Wehnelt cylinder (Figure 4-8) which surrounds the electron filament has a circular aperture and is also biased. This results in the formation of a cross-over point, with dimensions  $d_0$ , where the emitted electrons converge. The divergence of the beam is given by  $\alpha_0$ . The current density at the crossover represents the current that could be concentrated onto a focussed point on the sample [60].

The resistance, supplied by the bias-resistor, is directly related to the bias voltage, enabling the user to optimise the emission current, brightness and bias voltage. Typical operating values [60] are tabulated in Table 4-5.

Property	Value
Filament	Tungsten
$d_0$	25-100µm
$\alpha_0$	$(3-8)x10^{-3}$ rad
Temperature	2 700K
Cathode current density, $J_c$	1.75A.cm <sup>-2</sup>
Brightness	$60\ 000$ A.cm <sup>-2</sup> ster <sup>1</sup>
Beam current, $i_B$	15-25mA

Table 4-5: Operating properties of a tungsten filament cathode

A stable beam current is another important factor. Increasing the current through the filament increases the temperature and thereby increases the electron emission. The beam current is however not proportional to the filament current. Increasing the filament current beyond the value necessary for emission results in an increase in the bias voltage and a negative field gradient is established around the filament hindering further emission.

The use of a LaB<sub>6</sub> crystal rod instead of the tungsten filament results in a higher electron emission density and therefore increased brightness. The higher emission density is due to the increased evaporation rate of the rod. Since the LaB<sub>6</sub> cannot be heated directly, the configuration changes somewhat. The rod is milled to a fine point with a radius of 10µm. The opposing end is braced in a heat sink. The temperature of the tip ranges from 1700 to 2100K. The bias voltage is typically 1000V or greater [60]. The LaB<sub>6</sub> rod produces a current density of 100A.cm<sup>-2</sup> at 1680°C. The lifetime of the LaB<sub>6</sub> rod may exceed 10 000 hours, depending on the current density. A maximum brightness of 3 x  $10^{6}$ A.cm<sup>-2</sup> ster at a temperature of 25kV can be obtained.

Increased brightness has been generated with the use of field emission as opposed to thermionic emission. A negative voltage is applied over the sharpened point of a

<sup>&</sup>lt;sup>1</sup> The use of the unit ster to indicate brightness stems from the definition of candela. 1 cd = 1 lm/ster, and 1 lm = flux from 1 cd into 1 ster. One watt of monochromatic radiation at 5550 Å is defined as 680 lumens.

metal. The high negative field (around 3000V) drives electrons out of the point. Two anodes are required, the first controls the emission current, and the voltage over the second anode determines the final energy of the electrons. Electrolytic etching is used to create a tungsten tip with a diameter of 200 - 2000Å. The angular spread of the beam is governed by an aperture at the second anode. The field is focussed by electrostatic forces between the anodes. A real image of the field emission tip is formed 3 - 5cm beyond the second anode. Aberrations are minimised by the shape of the anodes. The field emitting tip can produce current densities as high as  $10^{6}$ A.cm<sup>-2</sup>. A focussed spot of electrons smaller than 100Å can be generated without the use of any auxiliary lenses. The brightness of the gun at 23kV is approximately 2 x  $10^{9}$ A.cm<sup>-2</sup> ster.

#### 4.2.2.2. Sample interactions



Figure 4-9: A schematic representation of the interaction of an electron beam with the sample surface.

Numerous interactions occur when an electron beam is incident on a material (refer to Figure 4-9). These interactions can be categorised as elastic and inelastic scattering. Elastic scattering entails the scattering of the electrons by either the nucleus

(Rutherford scattering) or the electron cloud of the atom. Elastic scattering is marked by a significant change in direction with minimal energy loss.

Backscattering of the electrons involves a series of events in the material after which the direction of the electrons changes so that they can travel back to, and escape from, the surface. These backscattered electrons leave the surface with reduced energy due to the inelastic collisions that it may have experienced. Low atomic number elements have large mean free path lengths and a low probability of scattering. Therefore only a few electrons can be scattered through large angles, these are the backscattered electrons. Elements with high atomic numbers will therefore exhibit a higher probability of scattering and a larger number of backscattered electrons will be detected.

Inelastic scatterings are accompanied by energy loss due to interactions with the nucleus or bound electrons. The incident electron beam, or moving electrons, will experience energy loss as a result of the Coulomb field of the nucleus. The emission of a continuum x-ray radiation marks this loss. Collisions with loosely bound electrons may result in the ejection of these secondary electrons. These electrons have energies less or equal to 50eV. If the secondary electrons may escape the surface. The energy of the secondary electrons will have to be high enough to overcome the surface barrier energy which is approximately 2 - 6eV. The secondary electrons are readily absorbed by the material and the probability of escape for electrons released below 100Å is extremely small.

Another consequence of inelastic scattering is the emission of characteristic x-ray lines. The incident electron loses energy equivalent to the binding energies of the electron shells. Along with an electron characteristic x-rays (refer to Figure 4-10) are also emitted.



Figure 4-10: Inelastic interaction of electrons on atoms [61]

#### 4.2.2.3. Image formation

Interpretation of SEM images is complicated since the contrast on the image is determined not only by the topography of the surface, but also the elemental composition. Atomic number contrast refers to the way in which different elements respond to the incident electron beam. The higher atomic number elements produce high backscattered electron signals, whereas the lower atomic number elements produce low signals. Considering a polished sample surface with varying composition, the image produced will also have varying contrast due to the number effect. In this case topography will not play a role.

Topography does play a role in SEM image formation. A sample with a faceted surface will produce an image indicative of these facets. The areas of the sample tilted towards the detector will produce a higher signal compared to surface tilted away from the surface. The path length of the electrons along the tilted surface increases and therefore the signal also increases. The contrast, although formed in a different way, is similar to the contrast seen with diffused reflection of visible light.

### 4.2.3. Energy dispersive spectroscopy

Energy dispersive spectroscopy (EDS) or energy dispersive x-ray spectroscopy is a non-destructive technique for chemical analysis. The semiconductor detector is used to collect the energy spectrum of the x-ray radiation. The peak size and location is indicative of the elements present as well as the concentrations of the elements. This enables one to perform both qualitative and quantitative analysis [62]. Diffraction of the electron beam may affect the peak heights on the EDS spectrum, causing maxima and minima. This may affect the quantitative analysis performed on the peak heights.

#### 4.2.3.1. Shimadzu Superscan SSX-550

The Shimadzu SUPERSCAN SSX-550 (Figure 4-11) is equipped with both SEM and EDS, enabling the user to obtain images and compositional information of samples. Furthermore the quantitative and qualitative analysis can also be done.

The SEM unit has a 3.5nm resolution with magnification abilities ranging from x 20 to x 300 000. The accelerating voltage varies from 0.5 to 30kV. A tungsten hairpin filament is used. The EDS unit has a resolution of 144 eV.



Figure 4-11: The Shimadzu SUPERSCAN SSX-550

#### 4.2.4. X-Ray Diffraction

X-ray diffraction is a well-known technique that utilises the way in which x-rays are diffracted by a crystal lattice to determine the crystalline structure and lattice constant of an unknown sample (Figure 4-12).



Figure 4-12: Bragg's law for X-rays incident on a crystalline lattice [63]

During this study the Phillips x-ray diffractometer (Figure 4-13) was used to assess the changes in surface structure after electrogalvanising.



Figure 4-13: Phillips X-ray Diffractometer

A copper target was used and a nickel filter to ensure that only x-rays with a wavelength of 1.315Å would be incident on the sample. A current of 30mA was passed through the filament and the electrons were accelerated towards the target with a voltage of 40kV. The stepping rate was approximately 1 degree/minute.

# Chapter 5

# **Results and discussion:** White spot and phosphate analysis

The results as well as a detailed discussion of all the images, graphs and maps are given in the following chapters. The results are grouped in three categories. In this, the first instalment, the white spot formation is investigated. This requires an understanding of all precursors to the final surface, namely the substrate, electrogalvanised layer, normal phosphating and finally the formation of the white spots. Various techniques are used to collect data, such as SEM, EDS, GDS and XRD.

## 5.1. Introduction

This section focuses on the white spot formation on the industrial samples (Figure 5-1). Firstly, the substrates are considered to establish the morphology and chemical composition of the samples. Secondly, the electrogalvanised coatings are considered. Thirdly, the phosphated surfaces are investigated and finally the white spots on the surfaces are analysed. The SEM in combination with the EDS can be used to obtain information regarding the surface morphology, chemical composition, as well as the distribution of the elements on the sample surface. The presence of surface anomalies, defects and dislocations can be confirmed and investigated using these analyses. Special attention is given to areas on the sample surfaces where the aforementioned anomalies are found, as opposed to the entire sample surface.

The GDS analysis of the various samples gives information regarding the distribution and concentration of elements through the bulk of the samples. As both the electrogalvanising and phosphating processes change the surface of the samples, these areas enjoy the most attention in this analysis.



Figure 5-1: Methodology followed for the analysis of phosphates and white spot formation

# **5.2. Imported sample**

Since South African steel users make use of both imported and locally produced steels, it is important to identify differences in the two products. The chemical composition of the substrate and the electrogalvanising line used in the production of the imported sample differs from the locally produced product. Therefore the final product will also be different. The consumers of the steel products require consistency between the locally produced and imported products. Comparing the imported steel with the locally produced steel is done to identify the primary reasons for the discrepancies that exist between the two.

## 5.2.1. Substrate

The substrate forms the foundation for the coating and any dislocations on the substrate may cause adherence problems with the coatings. The substrate also dictates the orientation of the coating. The electroplated sample is submerged in Hibatex, an acidic solution that preferentially dissolves the electroplated surface, without affecting the iron substrate. The sample is rinsed in distilled water to remove any residues.



Figure 5-2: SEM image of the imported sample substrate

The imported substrate is reasonably smooth (refer to Figure 5-2), although the effects of rolling can clearly be seen. Some anomalous deposits are seen on the surface, but the surface appears to be free of cracking.



Figure 5-3: SBSE image of the imported sample substrate

The backscattered electron image (Figure 5-3) of the area emphasizes the difference in composition of the substrate and the anomalous deposit. The deposit is merely a dust particle.



Figure 5-4: EDS spectrum of the sample area

The dominant element is iron, with traces of chlorine and manganese present (Figure 5-4). The presence of oxygen on the surface is questionable, but the shape of the low energy iron peak suggests the presence of another element.

As expected, the dust particle appears sharper on the maps (Figure 5-5) of the carbon and chlorine, but consists of distinctly less iron. As the remainder of the elements were only present as traces, these appear to be evenly distributed over the surface, with low peak heights. The accumulation of chlorine on a localised area on the sample surface may be a preface to pitting, where the negatively charged chlorine ions accumulate and corrode isolated areas on a metallic surface [32]. The site therefore reacts markedly differently to its environment than the rest of the surface. It is concluded that the anomaly is simply a dust particle.



Figure 5-5: EDS map of the imported substrate

# 5.2.2. Electrogalvanised sample

The structure of the electrogalvanised layer may impact on the subsequent treatments. Therefore the structures of the electrogalvanised samples are carefully considered.

As mentioned before, the imported sample is electrogalvanised with a pure zinc electrolyte. The coating is therefore assumed to consist predominantly of zinc.



Figure 5-6: SEM image of the electrogalvanised imported sample

The surface of the imported electrogalvanised sample, as in Figure 5-6, exhibits a sharp well-defined hexagonal plate-like structure (a). The section of the sample presented here is representative of the entire sample surface. The individual grains have distinct edges and the plated surface appears to cover the substrate completely. There are some anomalies on the surface. In this section there seems to be a scratch (b).



Figure 5-7: SBSE image of the electrogalvanised imported sample

The backscattered electron image (refer to Figure 5-7) shows a few darker regions indicating compositional differences.



Figure 5-8: EDS spectrum of the imported electrogalvanised sample

An EDS spectrum (Figure 5-8) of the area shows the presence of zinc and iron. Traces of silicon, oxygen and carbon can also be detected. These areKnown contaminants on sheet metals.



Figure 5-9: EDS spectrum of the grains on the imported electrogalvanised sample

The surrounding grains (a) consist predominantly of zinc, as seen in Figure 5-9. A small quantity of iron may have been incorporated into the deposit and is also detected. Oxygen and carbon areKnown contaminants and are also present.



Figure 5-10: The EDS elemental map of the imported electrogalvanised sample

The zinc is distributed uniformly, as seen in Figure 5-10, apart from isolated areas where the concentration appears slightly lower. These areas appear to have a higher occurrence of oxygen and carbon. There is one isolated spot of iron enrichment with a small quantity distributed over the sample surface. Similarly, the silicon also appears to have one enrichment zone, with a low concentration over the remainder of the sample surface.

#### 5.2.2.1. XRD analysis of the imported electrogalvanised sample

X-ray diffraction analysis of the electrogalvanised sample reveals the crystalline structure of the electrodeposited layer.



Figure 5-11: XRD spectrum of the imported electrogalvanised sample

The distinct peaks on the XRD spectrum (Figure 5-11) confirm the presence of crystalline deposits on the sample surface. The presence of the iron, zinc and aluminium in various chemical compounds can be distinguished by the various peaks.

The predominant species identified are  $Al_2O_3$ , ZnS, ZnO, iron and zinc. This is substantiated by the EDS spectrum of the sample area. Since the zinc deposits in its natural form (HCP) it is concluded that the epitaxial growth of the deposit is compromised.<sup>2</sup>

 $<sup>^{2}</sup>$  Epitaxial growth from the iron substrate would result in the zinc deposition simulating the crystalline structure of the iron. The peaks belonging to the zinc standard are present and therefore it has been concluded that the zinc deposits in its natural form and not epitaxially.

#### 5.2.3. Phosphated sample

The unknown imported sample consists of a steel substrate with a pure zinc electrogalvanised coating. In comparison with the zinc-nickel electrogalvanised coatings, the imported sample has a thicker coating and is not as resistant to the formation of white spots.

The imported electrogalvanised sample is prepared as described in section 4.1.2. in accordance with prescriptions from Henkel using chemicals supplied by them that are currently used in industry.



Figure 5-12: SEM image of the phosphated imported electrogalvanised sample

The SEM image of the sample area (Figure 5-12) clearly shows the presence of the phosphate crystals on the surface. The uniformly shaped crystals have varying orientations and coat the entire surface. In the centre of the sample area there seems to be an accumulation of a slightly different crystal. The use of a trication phosphate bath accounts for small variations in structure and composition on the surface. Not only does zinc phosphate deposit onto the surface, but also manganese and nickel phosphates. Each, of course, has a different structure and therefore the sample area may show some deviations.



Figure 5-13: SBSE image of the phosphated imported electrogalvanised sample

The backscattered electron image (Figure 5-13) confirms the slight compositional differences on the sample surface.



Figure 5-14: EDS spectrum of the phosphated imported electrogalvanised sample

The EDS spectrum (Figure 5-14) shows the presence of the trications, manganese, nickel and zinc, as well as some iron that may have dissolved into the phosphate bath. The phosphate, seen in the spectrum as large quantities of phosphorus and oxygen, is also present. No other significant contaminants are present on the surface.



Figure 5-15: EDS elemental map of the phosphated imported electrogalvanised sample

The elemental map of the sample area (Figure 5-15) shows the fairly even distribution of the elements on the sample surface. Due to charging of the sample area, the carbon map cannot be interpreted correctly.

# 5.2.4. Spotted phosphate sample

The electrogalvanised sample is placed in an aggressive phosphate bath following normal preparation. The bath is accelerated by adding 1.67% NaCl to the bath. This accelerates the pickling reaction on the sample surface aiding in the dissolution of the zinc.



Figure 5-16: SEM image of the accelerated phosphated imported electrogalvanised sample

The subsequent phosphate layer shows numerous defects and white spots (refer to Figure 5-16). The multi spot that forms in the centre of the sample is of particular interest due to its unique structure and shape. Below the white spot there is a darker region surrounding a small white protrusion. This region will also be investigated. The sample has numerous anomalous surface defects including white spots, flakes and darker spots.



Figure 5-17: SBSE image of the white spot on the phosphated imported electrogalvanised sample

The backscattered electron image (refer to Figure 5-17) emphasizes the elemental difference spread throughout the surface. The distinct multiple white spot in the centre of the sample as well as the smaller surface anomalies surrounding the spot are clearly and easily identified.



Figure 5-18: SEM image of the white spot on the phosphated imported electrogalvanised sample

The fine phosphate crystal structure on the perimeter of the spot is clearly visible (refer to Figure 5-18). These fine grains indicate numerous nucleation sites and rapid growth. The fine structure is desirable, but the spots are obviously problematic. If one takes a close look at the structure of the spot, the anomalous crystals that deposit on the perimeter of the spot are identifiable. Contrary to previous results, there is some crystalline deposition in the centre of the spot. At the onset of the analysis it is clear that the centre deposit, perimeter deposit and coating deposit differ greatly. The coating deposit consists of small rounded cubic crystals. The orientation of the individual crystals is random and the direction of growth can therefore not be determined. Furthermore, the phosphate coating has a grey appearance<sup>3</sup>. The perimeter deposit is more difficult to classify. The structure can most accurately be described as flaky. The deposit grows upward and literally towers above the substrate. These deposits are white in colour. The centre deposits are needle shaped deposits and appear to grow towards the centre of the spot.

<sup>&</sup>lt;sup>3</sup> The colours on the SEM images are determined primarily by depth. The references made to the grey appearance of the sample and the white of the white spot here refers not to the SEM image, but to the true appearance of the sample.



Figure 5-19: EDS spectrum of the white spot on the phosphated imported electrogalvanised sample

An EDS spectrum of the entire white spot area (Figure 5-19) shows the zinc and nickel from the electrogalvanised layer. The phosphate layer contains oxygen and phosphorusous. Iron and manganese are also present on the surface. The addition of the NaCl to the phosphate solution is vaguely seen in the EDS spectrum, with small sodium and chlorine peaks present.

An elemental map (refer to Figure 5-20) of the area shows a relatively uniform distribution of the elements except for the iron. The iron map clearly shows that the iron is only present in between the needle-shaped crystals inside the spots. This area also has less zinc, nickel and manganese compared to the surrounding areas. The topography of the area is emphasized in the maps of the oxygen and phosphorusous.



Figure 5-20: EDS elemental map of the white spot on the phosphated imported electrogalvanised sample

## 5.2.5. GDS analysis of the imported sample

Prior to analysis the samples are submerged in acetone and placed in an ultrasonic bath for two minutes. The samples are removed from the acetone and air dried. As some of the elements are present in low concentrations, for example nickel, manganese and chromium, the profiles have been magnified. The magnification is noted in the legend.

#### 5.2.5.1. Electrogalvanised layer

The quantitative depth profile (QDP) of the samples prior to treatment is important as it forms the basis of all other interpretations.



Figure 5-21: QDP of the imported electrogalvanised

As the imported sample is electrogalvanised from a pure zinc electrolyte, the coating is predominantly zinc (refer to Figure 5-21). The electrogalvanised layer is approximately  $4\mu$ m thick. The surface is slightly contaminated with carbon, nitrogen and hydrogen, most likely as a result of atmospheric exposure. The substrate consists predominantly of iron, but also has manganese, chrome and nitrogen present in small quantities. The interface between the electrogalvanised layer and the substrate appears clear of contamination. The presence of hydrogen on the surface affects the zinc profile in this region.

#### 5.2.5.2. Phosphating for 30s

The imported electrogalvanised sample is prepared for phosphating and exposed to the phosphating solution for 30 seconds



Figure 5-22: QDP of the imported electrogalvanised after 30s of phosphating

Within the short period, 0.6µm of the surface is dissolved (refer to Figure 5-22). The surface composition changes after phosphating. The surface consists of phosphorus, oxygen, manganese and zinc. Along with the phosphating elements the surface concentration of the chrome and nickel is also affected.

#### 5.2.5.3. Phosphating for 1 minute

The imported electrogalvanised sample is prepared and phosphated for 1 minute.



Figure 5-23: QDP of the imported electrogalvanised after 1min of phosphating

After 1 minute, the deposited layer thickens with  $0.4\mu m$  (refer to Figure 5-23). The surface concentrations of all the deposited elements are also higher. The impact of the surface deposition on the zinc profile also becomes more distinct with the extended exposure to the phosphating solution.

#### 5.2.5.4. Phosphating for 2min

The imported electrogalvanised sample is prepared and phosphated for 2 minutes.



Figure 5-24: QDP of the imported electrogalvanised after 2min of phosphating

Exposing the surface for another minute does not lead to an increase in the phosphate layer thickness, indicating that the reaction has stopped after the surface had been coated (refer to Figure 5-24). The only significant difference is in the increase in the hydrogen concentration in the top  $0.4\mu m$ . The evolution of hydrogen ions during the phosphating reaction acts as a source for the small reactive ions.
## 5.2.5.5. Phosphating for 3min



The imported electrogalvanised sample is prepared and phosphated for 3 minutes.

Figure 5-25: QDP of the imported electrogalvanised after 3min of phosphating

If the same sample is exposed to the phosphating solution for three minutes (refer to Figure 5-25), nitrogen diffuses throughout the electrogalvanised layer and the substrate. The surface coating reduces to  $3.4\mu m$ . There is also a notable change in the surface composition. The distinct phosphate layer is less pronounced. Even though the profile of the chrome has not been altered significantly, the nickel profile differs appreciably.

#### 5.2.5.6. Phosphating for 5min

The imported electrogalvanised sample is prepared and phosphated for 5 minutes in a more aggressive solution.



Figure 5-26: QDP of the imported electrogalvanised after 5min phosphating

In a more aggressive solution the profile changes dramatically after 5 minutes exposure. The phosphate coating is  $0.6\mu m$  thick (Figure 5-26). The hydrogen, manganese and nickel are enriched in the surface layers.

#### **5.2.5.7.** White spot formation

The imported electrogalvanised sample is exposed to an aggressive phosphating bath in order to form white spots.

A similar trend, as for the 5min phosphate, is seen when the sample is phosphated to form white spots (refer to Figure 5-27). Although the total surface layer, including the electrogalvanised and the phosphated layer, is still approximately 3.8µm thick, the phosphated layer accounts for 0.6µm of the surface structure. Surface enrichments of nickel, manganese and hydrogen are clearly present.



Figure 5-27: QDP of the white spotted imported electrogalvanised

# 5.3. MSSA 380 ppm nickel

The MSSA 380 ppm nickel sample is prepared on site by MSSA. The steel substrate is electrogalvanised using a zinc electrolyte which includes 380 ppm nickel.

## 5.3.1. Substrate

Though the end use is the same, the structure and composition of the locally produced steel differs somewhat from the imported version.



Figure 5-28: SEM image of the MSSA 380 ppm substrate

Once again the rolling direction is distinguishable (refer to Figure 5-28). The surface appears to be smoother than its imported counterpart. Again a deposit is seen on the sample surface.



Figure 5-29: SBSE image of the MSSA 380 ppm substrate

The deposit and the small dislocation to the right of the deposit appears darker on the backscattered electron image indicating compositional differences (refer to Figure 5-29).



Figure 5-30: EDS spectrum of the deposit on the MSSA 380 ppm substrate

Similar to the imported sample, the deposit consists primarily of iron and carbon (Figure 5-30). Traces of potassium, chlorine, are also present. This is most likely

because the same cleaning solution was used. The sulphur, silicon and aluminium may simply be dust.



Figure 5-31: EDS spectrum of the area considered on the MSSA 380 ppm substrate

When the area is considered the primary elements present are iron and chlorine (Figure 5-31).

The region where the deposit is seen is markedly void of iron (Figure 5-32), but consists of higher carbon content, so does the spot to the left of the deposit that appeared dark on the backscattered electron image. Aluminium seems to have a localised enrichment, in the vicinity of the dust particle. Carbon enrichment on the surface occurs during annealing in the region where chrome is present on the surface.



Figure 5-32: EDS map of the MSSA 380 ppm substrate

# 5.3.2. Electrogalvanised sample

The MSSA 380 ppm sample is prepared via electroplating using an electrolyte containing zinc and 380 ppm nickel.



Figure 5-33: SEM image of the MSSA 380 ppm electrogalvanised sample

Compared to the imported sample, the structure of this sample, is notably different (refer to Figure 5-33). The surface comprises of individual grains with sharp edges. Protruding from the surface is a defect (a), in the shape of a large bead. The size of the grains changes dramatically as the surface defect is approached, becoming smaller (b) in the vicinity of the defect. The hexagonal plate-like structure of the imported sample changes to a more granular structure (c). A distinct ridge is formed between the two regions of granules. The use of conditioners could be responsible for the changes in surface morphology. The conditioners are added to regulate the size of the deposit. Smaller grains are required and this is achieved by establishing numerous nucleation sites. The grains will grow until they reach their neighbours and here grain boundaries will be formed. Since the sizes of the deposits or grains change, it can be assumed that the concentration of the conditioner in these regions, prior to electroplating, also differed. The presence of the deposit may also be responsible for the change in morphology. Since the surface activity of the surface is affected by surface anomalies the change in the morphology might indicate an increase in surface reactivity in the region of the deposit.



Figure 5-34: SBSE image of the MSSA 380 ppm electrogalvanised sample

The backscattered electron image (Figure 5-34) supports the difference in size, but not the composition of the granules. The dust particle has an obviously different contrast, indicating a change in composition.



Figure 5-35: EDS spectrum of the small grains on the MSSA 380 ppm electrogalvanised (b)

The smaller grains (refer to Figure 5-35) consist of, predominantly, zinc. Carbon is present in significant quantities, with less oxygen and iron detectable.



Figure 5-36: EDS spectrum of the coarse grains on the MSSA 390 ppm electrogalvanised (c)

The coarse grains do not, compositionally, differ much from the finer granules (refer to Figure 5-36). The carbon peak is, however, higher than for the finer granules.



Figure 5-37: EDS spectrum of the dust deposit on the MSSA 380 ppm electrogalvanised (a)

The composition of the dust particle can clearly be identified in the EDS spectrum (Figure 5-37). Some iron and zinc from the underlying structure can also be detected due to the penetration depth of the incident beam.



Figure 5-38: Elemental map of the bead-like deposit and surrounding area on the MSSA 380 ppm electrogalvanised

The elemental map (Figure 5-38) of the region shows the distribution of the elements. Apart from the oxygen the elements are distributed evenly over the surface. The dust has a higher oxygen presence. The iron distribution, however, does not seem to be affected significantly.

### **5.3.3.** Phosphated sample

The electrogalvanised samples are prepared and phosphated in accordance with prescriptions from Henkel using chemicals supplied by them that are currently used in industry. As for the other phosphated samples, the MSSA 380 ppm nickel sample is prepared and phosphated as described in section 4.1.2.



Figure 5-39: SEM image of the phosphated MSSA 380 ppm nickel electrogalvanised

The structure of the phosphate crystals can clearly be distinguished in the SEM image of the phosphates surface (Figure 5-39). Compared to the phosphate that forms on the imported surface (Figure 5-12), it is clear that both the size and structure differ. The MSSA phosphate has a rounder shape and appears thicker in comparison with the phosphate on the imported sample. Still, the phosphate coats the entire surface and the individual crystals appear to have uniform shapes and sizes.



Figure 5-40: SBSE image of the phosphated MSSA 380 ppm nickel electrogalvanised

The backscattered electron image (Figure 5-40) points to compositional uniformity between the individual phosphate crystals but indicates that there are different deposits in and amongst the phosphate crystals. These appear white and black on the image.



Graph 5-1: EDS spectra of the phosphated MSSA 380 ppm nickel electrogalvanised surface

The EDS spectrum of the MSSA 380 ppm nickel electrogalvanised sample (Graph 5-1) shows the presence of the zinc, nickel and manganese – the constituents of the trication bath, as well as the phosphorus and oxygen that form the phosphate ion. The surface also contains iron, most likely dissolved from the substrate and some carbon contamination.



Figure 5-41: EDS elemental map of the phosphated MSSA 380 ppm nickel electrogalvanised

The elemental map of the sample surface (Figure 5-41) shows the uniform distribution of all the elements except the carbon that appears to be enriched on isolated sites on the sample surface.

## 5.3.4. White Spotted Phosphate Sample

The MSSA 380 ppm nickel sample is placed in an aggressive phosphate bath following normal preparation. The bath is accelerated by adding 1.67% NaCl to the bath.



Figure 5-42: SEM image of the phosphate crystals on the spotted MSSA 380 ppm nickel sample

The phosphate structure (refer to Figure 5-42) consists of numerous round disk shaped crystals with random orientations. The majority of the crystals have the same shape and approximate size.



Figure 5-43: SEM image of the white spot on the phosphated MSSA 380 ppm nickel sample

Closer inspection of the white spot reveals four distinct areas (refer to Figure 5-43). The outer area consists of fine phosphate crystals. These have a dark grey colour. The crystals have no distinct growth direction. The perimeter of the white spot appears to have an anomalous structure and seems to be flaky as in the previous sample. Delamination of the coating is severe in this area. There is a smooth uncoated interior section separating the fine granular and needle shaped crystals. The inner circle consists of numerous needle shaped crystals that seem to grow towards to the centre of the spot.



Figure 5-44: SBSE image of the white spot on the phosphated MSSA 380 ppm nickel sample

A backscattered electron image (refer to Figure 5-44) accentuates the structure inside the white spot. A dark spot becomes clear in the top left hand corner of the image.



Figure 5-45: Inverse topography

The inverse topography (refer to Figure 5-45) shows that the white spot is deeper than the phosphate structure and that the black spot is on top of the phosphate layer.



Figure 5-46: EDS spectrum of the phosphated MSSA 380 ppm nickel electrogalvanised

The EDS spectrum (Figure 5-46) indicates the presence of zinc, nickel, manganese, phosphorus and oxygen. Iron, silicon and carbon are also present. The high quantity of the iron on the surface is as a result of the dissolution on the electrogalvanised layer during the phosphating process, thereby exposing the iron substrate. This is evident from the elemental map.

Carbon deposits occur randomly on the surface. Iron is only present in the spotted area (Figure 5-47). The smooth areas consist predominantly of iron. The silicon is enriched in this area, but there is no zinc, phosphorus or nickel present. Oxygen and manganese are present in lower concentrations. The centre spot consisting of the needle shaped deposits contains zinc, nickel and manganese phosphates. The iron present is visible only through the crystals and it can be said that the substrate is visible through the deposit. Therefore, the electrogalvanised layer is dissolved completely exposing the substrate. Some phosphate growth occurs over the exposed regions, but it does not cover the surface completely.



Figure 5-47: Elemental map of the phosphated MSSA 380 ppm nickel electrogalvanised surface

# 5.3.5. GDS Analysis

The samples are prepared in the same fashion as the imported samples (refer to section 5.2.5.).

## 5.3.5.1. Substrate

A depth profile of the untreated sample will reveal important information regarding the electrogalvanised layer's thickness as well as the composition of the substrate. Interface contamination may impact on the cohesion between the layers and the presence of any contaminants will be made clear on the depth profile.



Figure 5-48: QDP of the MSSA 380 ppm nickel electrogalvanised

The electrogalvanised layer is approximately  $3.9\mu$ m thick<sup>4</sup> (refer to Figure 5-48). The layer consists of zinc, nickel and some oxygen contamination. The surface is contaminated with carbon. The chrome on the surface may be as a result of the passivation treatment. Hydrogen is present in the top surface layers. The concentration of the oxygen increases towards the surface. The distribution of the nickel is erratic in the top layers of the electrogalvanised sample. Slight manganese enrichment is present at the substrate-electrogalvanised interface.

#### 5.3.5.2. Phosphating for 30s

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated for 30 seconds.

<sup>&</sup>lt;sup>4</sup> The thicknesses of the layers are measured from 50% of the initial concentration to 50% of the concentration of the subsequent element.



Figure 5-49: QDP of the MSSA 380 ppm nickel electrogalvanised after 30s phosphating

The cleaned and prepared surface is exposed to the phosphating bath for 30 seconds resulting in some phosphate deposition on the surface (Figure 5-49). This is evident from the reduction in the thickness of the electrogalvanised layer by 0.5µm. There is also an associated increase in the oxygen and phosphorus concentrations on the surface. There is a radical impact on the profile of the nickel in the surface layers. At the surface the concentration appears to be higher. This is followed by a slight depletion in the nickel concentration, before it stabilizes to its original value deeper into the layer. Other elements also appear on the surface, including: nitrogen, chrome and manganese. Note that the concentration of the manganese in the substrate is not affected by the surface treatment.

#### 5.3.5.3. Phosphating for 1min

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated for 1 minute.



Figure 5-50: QDP of the MSSA 380 ppm nickel electrogalvanised after 1min phosphating

After a minute's exposure to the solution there is a notable increase in the nitrogen surface concentration, but no further growth of the phosphate layer (Figure 5-50). Once again there is no change in the manganese in the substrate. The chrome at the interface does, however, appear to have a slight enrichment.

## 5.3.5.4. Phosphating for 2min

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated for 2 minutes.



Figure 5-51: QDP of the MSSA 380 ppm nickel electrogalvanised after 2min phosphating

The high nickel concentration on the surface decreases steadily into the layer before the normal concentration is reached and maintained (Figure 5-51). The surface consists of oxygen, phosphorus, nitrogen, chrome and manganese. Carbon is present as contamination on the surface. At this stage it is clear that the profile of the manganese in the substrate changed.

## 5.3.5.5. Phosphating for 3min

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated for 3 minutes.



Figure 5-52: QDP of the MSSA 380 ppm nickel electrogalvanised after 3min phosphating

After three minutes exposure the profiles of the oxygen, chrome and manganese seem to be affected the most (Figure 5-52). The oxygen is present at higher concentrations well into the sublayers of the sample. Where the chrome and manganese followed the same path on the previous samples, the paths differ greatly in this sample. The chrome does not extend as deeply into the structure as the manganese. The phosphorus concentration is also higher into the sublayers of the sample. The sample. The sample interface is affected by the surface treatment.

#### **5.3.5.6.** Phosphating for 5min

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated for 5 minutes in a more aggressive phosphating solution.



Figure 5-53: QDP of the MSSA 380 ppm nickel electrogalvanised after 5min phosphating

The sample is exposed to a slightly more aggressive solution for five minutes resulting in a remarkably different profile (Figure 5-53). The phosphorus extends well into the electrogalvanised layer, along with the oxygen, nitrogen and hydrogen. The manganese and nickel are enriched in the surface layers resulting in a decrease in the zinc concentration in this region.

#### 5.3.5.7. White spot formation

The MSSA 380 ppm nickel electrogalvanised sample is prepared and phosphated in an aggressive phosphating solution to allow white spot formation. The sample is exposed to the solution for up to four minutes.



Figure 5-54: QDP of the MSSA 380 ppm nickel electrogalvanised after white spot formation

In a more aggressive solution, the surface will exhibit the formation of white spots. Closer inspection of the depth profile (Figure 5-54) shows the remarkable changes that occur within the electrogalvanised layer. The phosphorus, oxygen and hydrogen extend well into the surface. The manganese is enriched on the surface. Just beyond the manganese peak the nickel concentration peaks. This peak subsides into a region of nickel depletion. The substrate interface is marked by chrome enrichment.

# 5.4. MSSA 930 ppm nickel

The MSSA 930 ppm nickel samples are prepared by MSSA, utilising an electrolyte consisting of zinc and 930 ppm nickel. The 380 ppm nickel electroplated and the 930 ppm nickel electroplated samples do not have the same substrates.

## 5.4.1. Substrate

Since the various consumers of steel products have different requirements, it is imperative to consider another locally produced substrate.



Figure 5-55: SEM image of the MSSA 930 ppm substrate

Although not as distinct, as for the previous samples, the rolling direction is still distinguishable on this sample (refer to Figure 5-55). The surface of the MSSA 930 ppm substrate consists of numerous pits and crevices. A large deposit is visible in the centre of the sample. Small tracks are also visible on the surface. These are most likely the grain boundaries. The darker spots on the tracks indicate intergranular contamination.



Figure 5-56: SBSE image of the MSSA 930 ppm substrate

The backscattered electron image, in Figure 5-28, emphasizes the compositional differences between the deposit and the substrate. The tracks and contaminants are more distinct in this image.



Figure 5-57: EDS spectrum of the MSSA 930 ppm substrate area

As a whole the sample area consists predominantly of iron, but there is chlorine contamination (refer to Figure 5-57).

The deposit in the centre of the sample shows a lesser presence of iron, as denoted by Figure 5-58, but the elemental distribution indicates an increased presence of oxygen, silicon, carbon, chlorine, calcium and aluminium (indicative of dust). The remainder of the elements are distributed evenly.



Figure 5-58: EDS map of the MSSA 930 ppm substrate

# 5.4.2. Electrogalvanised sample

The MSSA 930 ppm sample is prepared via electroplating using an electrolyte containing zinc and 930 ppm nickel.



Figure 5-59: SEM image of the MSSA 930 ppm nickel electrogalvanised surface

The surface of the 930 ppm nickel electrogalvanised sample does not appear to have a distinct structure (a) (refer to Figure 5-59). The surface appears porous and amorphous. The pores or holes in the structure appear darker and are therefore subsided beneath the surface. A small pit (b) appears in the centre of the sample and a scratch (c) appears to the left of the pit.



Figure 5-60: SBSE image of the MSSA 930 ppm nickel electrogalvanised surface

The backscattered electron image (Figure 5-60) clearly indicates the compositional differences between the surface (a) and the pores. The pit at (b) appears slightly darker than the surrounding structure.



Figure 5-61: EDS spectrum of the MSSA 930 ppm nickel electrogalvanised surface (a)

The surface (a) consists of zinc, iron, carbon oxygen and phosphorus as denoted by the EDS spectrum in Figure 5-61.



Figure 5-62: EDS spectrum of the pit on the MSSA 930 ppm nickel electrogalvanised surface (b)

The pit (b) contains numerous contaminants including calcium, sulphur, phosphorus, carbon and oxygen. Zinc and iron are present as well as a small quantity of nickel (refer to Figure 5-62).



Figure 5-63: EDS map of the MSSA 930 ppm nickel electrogalvanised surface

A slight change in the distribution of the oxygen on the sample surface is visible in the Figure 5-63. The carbon appears more prominent in the pores on the surface. The remainder of the elements appear to be distributed evenly. It is unclear whether the carbon deposits in the pores during or after electrodeposition. Regardless the mechanism, the effect of the carbon presence on the surface will affect any treatment that the surface may be subjected to.

#### 5.4.2.1. Annealed sample

A typical weldability test entails the annealing of a sample at 300°C for 30 minutes. If the sample's surface changes during the annealing the sample will fail the test. The sample is either bent or a scotch tape is applied to the surface. If, when the tape is removed, the surface layer becomes detached from the sample, the sample will also fail. During the bend test the surface should not crack or peel to prove its durability.



Figure 5-64: SEM image of the annealed MSSA 930 ppm nickel electrogalvanised surface

The MSSA *930* ppm nickel sample is heated under vacuum to 300°C for 30 minutes. The quartz tube in which the sample was heated became coated with a metallic deposit - an evaporant from the sample surface. The coating on the sample surface became powdery. There are a few surface anomalies and at least one at (a) protrudes from the surface. A SEM image (refer to Figure 5-64) of the surface shows the porous nature (b) of the surface.



Figure 5-65: SBSE image of the annealed MSSA 930 ppm nickel electrogalvanised surface

The backscattered electron image (Figure 5-65) shows reasonable uniformity. The protruding defect (a) appears dark indicating a change in composition. The pore at (b) is dissimilar to (a), but also to the surrounding structure such as at (c).



Figure 5-66: EDS spectrum of the annealed MSSA 930 ppm nickel electrogalvanised surface



Figure 5-67: EDS map of the annealed MSSA 930 ppm nickel electrogalvanised surface

The elements appear to be distributed evenly, except for the carbon and oxygen distribution (refer to Figure 5-67). The dark spot on the backscattered electron image is void of zinc, but shows a higher presence of oxygen, as indicated by the elemental map of the region.

A strip of scotch tape is used to remove the powdery residue on the surface in order to determine the changes in the underlying structure.



Figure 5-68: SEM image of the annealed MSSA 930 ppm nickel electrogalvanised surface after clearing with scotch tape

The SEM image (refer to Figure 5-68) of the surface clearly shows the formation of large recessions. Similar to dezincification where the zinc is preferentially removed

leaving pores in the original material. The evaporation of a metallic substance reminds one of the dezincification phenomenon.



Figure 5-69: SBSE image of the annealed MSSA 930 ppm nickel electrogalvanised surface after clearing with scotch tape

The backscattered electron image (seen here in Figure 5-69) has numerous isolated regions with varying composition denoted by the darker regions on the surface. The initial delamination of the electrogalvanised layer is visible in the bottom right-hand corner of the image.



Figure 5-70: EDS spectrum of the annealed MSSA 930 ppm nickel electrogalvanised surface after clearing with scotch tape

The EDS spectrum of the region (Figure 5-70) shows that the composition of the sample has not changed appreciably.



Figure 5-71: EDS map of the annealed MSSA 930 ppm nickel electrogalvanised surface after clearing with scotch tape

The darker regions on the backscattered electron image are carbon as is depicted by the elemental map of the region (refer to Figure 5-71). The iron is not distributed evenly, showing regions of slight enrichment. This supports the interpretation of dezincification, as the iron from the substrate becomes more definite, indicating a thinner electrogalvanised layer. The remainder of the elements are distributed evenly over the surface.

Carbon tape is used to remove some of the evaporant from the quartz tube onto which it deposited during annealing of the sample.



Figure 5-72: SEM image of the captured evaporant



Figure 5-73: EDS analysis of the evaporant

The EDS analysis (in Figure 5-73) of the evaporant (shown here in the SEM image, Figure 5-72) clearly shows that it is the zinc in the coating that evaporates. Therefore, dezincification occurs.

# 5.4.2.2. XRD analysis of the MSSA 930 ppm nickel electrogalvanised sample

X-ray diffraction is performed to determine the crystalline structure of a material. Theoretically the electroplated coating should grow epitaxially onto the substrate, as long as there aren't vast differences in the crystal properties between the substrate and the coating.





Figure 5-74: XRD spectra of the substrate and MSSA 930 ppm nickel electrogalvanised

It is clear from the XRD spectra (Figure 5-74) that there is no distinguishable signal from the substrate. This is undoubtedly as a result of the rolling of the steel, which alters the crystal structure and therefore impacts on the conditions for x-ray diffraction. The electrogalvanised layer, however, has a definite diffraction pattern.

The multitude of peaks that form is indicative of, not only the crystalline nature of the electrogalvanised surface, but also of the possibility of different phases and combinations of zinc and nickel present on the surface. A distinction can be made between the various crystalline planes of the zinc, nickel and possibly iron that contribute to the x-ray diffraction pattern.

Since the substrate has no definite crystalline nature, it is improbable that the electrogalvanised layer will grow epitaxially. Therefore the coating will not conform or inherit the properties of the substrate, but will deposit in its natural state. In the case of zinc this will be the HCP structure with weak interatomic forces, as indicated by the low melting point at 419°C. The coating will therefore be subject to all the weaknesses of the zinc structure. The interface between the two structures may also be stressed as a result of the lattice differences. This, in turn, may attribute to the evaporation of the zinc when annealed.

At this stage it is also important to note the differences in crystallographic growth and orientation between the imported sample (Figure 5-11) and the MSSA sample (Figure 5-74). It becomes clear that the differences in both the substrates and the electrolytes affect the properties of the electrogalvanised layer. One would expect the zinc to deposit similarly on all surfaces, but the physical properties of the substrates play a role (refer to section 2.1.4.). The production of the steel substrates entails both the hot and cold rolling of the steel and subsequently the surface is placed under strain. This will cause the surface to react differently and may result in differences in the zinc deposition.

## 5.4.3. Phosphated sample

The electrogalvanised samples are prepared and phosphated in accordance with prescriptions from Henkel using chemicals supplied by them that are currently used in industry.

The MSSA 930 ppm nickel electrogalvanised sample is prepared as stipulated in section 4.1.2.



Figure 5-75: SEM image of the phosphated MSSA 930 ppm nickel electrogalvanised sample

The shape of the phosphate crystals that form on the MSSA 930 ppm nickel samples (Figure 5-75) differ predominantly in size from the phosphate crystals on the MSSA 380 ppm nickel (Figure 5-39). The crystals appear uniform and completely cover the electrogalvanised surface.
#### 5.4.4. Spotted phosphate sample with agitation

The MSSA 930 ppm nickel sample is placed in an aggressive phosphate bath following normal preparation. The bath is accelerated by adding 1.67 vol % NaCl to the bath.



Figure 5-76: SEM image of a white spot on the phosphated MSSA 930 ppm nickel electrogalvanised sample

The white spot (Figure 5-76) consists of the same components as the white spots on the previous samples. The phosphate crystals around the white spot do not appear to be affected by the presence of the spot. The perimeter of the spot consists of an anomalous white deposit that extends upward. The inner part of the white spot consists of a multitude of elongated crystals that appear to have grown inward. These too extend upward and stand up above the surface.



Figure 5-77: SBSE image of a white spot on the phosphated MSSA 930 ppm nickel electrogalvanised sample

The elongated crystals inside the white spot differ somewhat compositionally from the phosphate crystals that form on the surface. The structure of these elongated crystals is also accentuated in the backscattered electron image.

Scattered over the surface, in between the phosphate crystals, there is another substance, depicted by small white spots on the image.



Figure 5-78: EDS analysis of a white spot on the phosphated MSSA 930 ppm nickel electrogalvanised

The EDS analysis of the sample area (Figure 5-78) confirms the presence of zinc, manganese and nickel (the trications), iron (dissolved from the substrate), oxygen and phosphorus (the constituents of the phosphate ion), chlorine (the accelerant), as well as carbon and silicon as contaminants.

The elemental map (Figure 5-79) depicts the distribution of the elements over the sample surface. The carbon contamination is spread over the whole sample surface, though some charging is visible on the lower part of the sample area. The charging can be seen on the monitor as lines or when parts of the sample start to glow. The oxygen, though present over the entire sample surface, is more pronounced where the white spots are found. Similarly, the phosphorus, which is also present over the whole surface, is also accentuated at the white spots. The white spots also contain less

manganese, zinc and nickel. The iron is visible through the elongated crystals that form in the right-hand white spot, indicating that the substrate is exposed.



Figure 5-79: EDS elemental map of a white spot on the phosphated MSSA 930 ppm nickel electrogalvanised

## 5.4.5. Spotted phosphate sample without agitation

The MSSA 930 ppm nickel sample is placed in an aggressive phosphate bath following normal preparation. The bath is accelerated by adding 1.67% NaCl to the bath. The effect of agitation is questioned and therefore the agitation is switched off during the preparation of this sample.



Figure 5-80: SEM image of the white spot on the phosphated MSSA 930 ppm nickel electrogalvanised

The characteristic white spot is visible in the centre of the sample area in Figure 5-80. The structure of the surrounding phosphate varies somewhat between round disks and fine needles. The perimeter of the spot is once again flaky with large towering flakes protruding from the surface. During the SEM analysis the flakes experience charging which, upon discharging adversely affects the imaging. The interior of the white spot consists of the needle-shaped deposits observed in the previous samples.



Figure 5-81: SBSE image of the white spot on the phosphated MSSA 930 ppm nickel electrogalvanised

The backscattered electron image (refer to Figure 5-81) shows that there are various other flaky deposits in the area surrounding the white spot.



Figure 5-82: EDS spectrum of white spot on the phosphated MSSA 930 ppm nickel electrogalvanised

Although predominantly zinc is present, there is also nickel, iron, manganese, silicon, phosphorus, oxygen and carbon present as denoted by the EDS spectrum of the white spot area given here in Figure 5-82.

Carbon is regularly distributed all over the surface with no distinct areas of enrichment (refer to Figure 5-83). The iron is only detectable in the white spot with a ridge of enrichment within the white spot. This ridge is markedly void of zinc as is the case in the centre of the white spot. The manganese concentration in this region is also lower with one spot of enrichment in the vicinity of an anomalous deposit.



Figure 5-83: EDS spectrum of the white spot on the phosphated MSSA 930 ppm nickel electrogalvanised sample

# 5.4.6. GDS analysis

The samples are prepared in the same fashion as the imported samples (refer to section 5.2.5.).

## 5.4.6.1. Substrate

The preparation of the electrogalvanised layer determines the properties of the surface as well as the way in which the surface will respond to heat and chemical treatment.



Figure 5-84: QDP of the MSSA 930 ppm nickel electrogalvanised

The electrogalvanised layer consists of, predominantly, zinc as well as a small concentration of nickel (Figure 5-84). The oxygen level in the electrogalvanised layer is lower than in the substrate. Carbon is also present at the surface as a contaminant. The nickel is not distributed evenly. At the surface it has a slightly higher concentration followed by a recession in the concentration. At a depth of 1µm the concentration of the nickel increases again. The value remains constant up to the substrate interface. The surface coating is approximately 3.8µm thick. No significant contamination is visible.

#### 5.4.6.2. Phosphating for 30s

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated for 30 seconds.



Figure 5-85: QDP of the MSSA 930 ppm nickel electrogalvanised after 30s phosphating

The sample surface is prepared according to the manufacturer's prescriptions. After 30 seconds exposure to the phosphating solution, the surface is coated with phosphorus and oxygen (Figure 5-85). The phosphorus stretches well into the sample surface. There is also an increase in the manganese concentration at the sample surface. There is no notable difference in the profile of the nickel. The zinc profile changes, as it is affected by the presence of all the other elements on the surface. Along with the phosphated layer, the sample is slightly thicker than the untreated sample.

#### 5.4.6.3. Phosphating for 1min

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated for 1 minute.



Figure 5-86: QDP of the MSSA 930 ppm nickel electrogalvanised after 1min phosphating

Exposing the sample to the phosphating solution for 1 minute results in a surprisingly different profile (Figure 5-86). The thickness of the electrogalvanised layer is reduced to 3.3µm. The surface appears to be covered with a thicker coating consisting of nitrogen, oxygen, phosphorus and carbon. The oxygen concentration decreases rapidly to 0.3µm, deeper into the surface. The oxygen concentration increases sharply, after which it decreases slowly. The phosphorus follows the same trend. The phosphorus profile does not experience the same decrease and the increase is more distinct and to a higher concentration. The nitrogen surface concentration is high and decreases slowly into the bulk of the electrogalvanised layer.

#### 5.4.6.4. Phosphating for 2min

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated for 2 minutes.



Figure 5-87: QDP of the MSSA 930 ppm nickel electrogalvanised after 2min phosphating

The prepared sample is exposed to the phosphating solution for 2 minutes (Figure 5-87). The remaining zinc layer is thicker than for the 1 minute counterpart. This could point to a possible inconsistency in the overall thickness and distribution of the electrogalvanised layer. The surface of the sample consists of various elements including: oxygen, phosphorus, hydrogen, nitrogen, manganese, nickel and zinc. The oxygen concentration drops sharply in the first few micrometers. Most probably this is merely adsorbed oxygen. The initial decline in concentration is followed by a sudden increase in concentration. The concentration reaches a peak and then declines slowly to bulk value. The hydrogen value declines slowly from a high surface value to a minimum value, but the contamination reaches well into the surface layers. The phosphorus also experiences a sudden decrease in concentration followed by a steep

rise in concentration. The concentration peaks at 78% and then decreases slowly. This element also extends well into the electrogalvanised layer. The elements oxygen, phosphorus, manganese and nitrogen all peak at the same point. The initial values are low. With depth these values increase to the peak, after which there is steady decline in the values. The nickel value increases from the surface until it peaks at  $0.4\mu m$ . The value declines slowly to the bulk value.

#### 5.4.6.5. Phosphating for 3min

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated for 3 minutes.



Figure 5-88: QDP of the MSSA 930 ppm nickel electrogalvanised after 3min phosphating

The predominant changes in the profiles of the 2 minute exposed sample and the 3 minute exposed sample is the location where the concentration profiles peak as well as the high concentration of nitrogen (Figure 5-88). Furthermore, there is no initial decline and peak of the oxygen and phosphorus profiles. The values merely decline,

but undergo a step in the profile before the values decline steadily to the bulk value. A similar step in the profile is visible in the zinc profile. The manganese enriches the initial surface layers and declines rapidly to bulk value. The degree of enrichment is higher in comparison with the previous samples. The hydrogen also follows this trend, peaking alongside the manganese and then declining rapidly into the bulk.

#### 5.4.6.6. Phosphating for 5min

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated for 5 minutes.



Figure 5-89: QDP of the MSSA 930 ppm nickel electrogalvanised after 5min phosphating

The profile changes even more if the sample is exposed for 5 minutes. Again, the manganese enrichment occurs close to the surface (Figure 5-89). The degree of enrichment, denoted by the value of the peak concentration, is similar to the 3 minute exposure sample. The phosphorus concentration increases sharply at the surface and then declines, through a step, to the bulk value. The phosphorus reaches well into the

bulk of the electrogalvanised layer. The oxygen follows the same trend, experiencing a step where the manganese reaches a peak. The initial nitrogen concentration is high. In the initial layers the concentration decreases slowly, but beyond the manganese peak the rate of decline increases. The zinc concentration increases, also through a step, to the initial layer value. The hydrogen duplicates the profile of the manganese, with a peak, though at a lower value, at the same depth beneath the surface. The nickel enriches the sub-surface layers, reaches a peak at  $0.5\mu m$ , after which it declines to its bulk value. There is some carbon contamination of the surface, but this does not extend into the surface.

#### **5.4.6.7.** White spot formation

The MSSA 930 ppm nickel electrogalvanised sample is prepared and phosphated in a more aggressive phosphating solution to allow white spot formation.



Figure 5-90: QDP of the MSSA 930 ppm nickel electrogalvanised after white spot formation

The prepared sample is exposed to a more aggressive solution resulting in the formation of white spots. The depth profile (refer to Figure 5-90) differs significantly from the previous samples. The manganese enrichment is a lot less pronounced even though it still peaks in the sub-surface layers. The nickel does not show any significant enrichment. There is some hydrogen on the surface, but does not extend into the sample. Nitrogen appears on the surface and declines steadily into the sample. The oxygen and phosphorus decline steadily from initial high concentrations to bulk values. The phosphorus reaches deeper into the structure than the oxygen.

#### 5.5. Summary

The white spot formation on the electrogalvanised surfaces is closely related to the presence of contaminants on the electrogalvanised surface and at the interface between the substrate and the electrogalvanised surfaces. The accelerated phosphate reaction results in complete dissolution of the electrogalvanised surface, thereby exposing the iron substrate. The white spot consists of an anomalous protruding perimeter with elongated crystals that grow towards the centre of the spot present inside the spot. The general shape and composition of the white spots remained consistent for all electrogalvanised samples considered, even though the structure and colour of the phosphated layers differed. The surface treatment does not affect the substrate or interface.

Partial dissolution is required in order for the phosphate process to occur. Complex phosphates deposit on the surface comprised of various cations, such as zinc, manganese and nickel. The zinc dissolution is the preferred reaction and therefore there is a slight enrichment of nickel in the sublayers of the phosphate. The manganese deposited on the surface must not be confused with the manganese present in the substrate. The structure and colour of the phosphated layer is affected by the composition of the electrogalvanised layer. There is a marked change in the structure with the addition of the nickel to the zinc electrolyte. A further increase in the nickel concentration results in further differences in the electrogalvanised, and phosphated surfaces.

The addition of nickel to the electrolyte results in a notably different structure in the electrogalvanised layer, varying from a well-defined rigid structure to a more granular structure as the nickel concentration is increased. The phosphating process also results in the deposition of anomalies and contaminants that may impact on further treatments. Contaminants and dislocations on the substrate influence both the adhesion and chemical nature of the electrogalvanised surface in the vicinity of the dislocation.

The surface of the steel substrate clearly shows the rolling direction suggesting the presence of residual stress and strain in the surface. This compromises the epitaxial growth of the electrogalvanised layer.

The application of the coated steel dictates the composition and physical properties of the steel. It is therefore impossible to compare the samples and select one as the most suited for all applications. The following is however apparent:

- Contamination, physical or chemical, at any of the interfaces may result in adherence problems
- The structure of the electrogalvanised layer is affected dramatically by the addition of cations to the electrolyte
- The colour and structure of the phosphated layer is also affected by the presence of the added cations in the electrogalvanised layer
- Phosphating in accordance to prescription does not result in white spot formation
- The formation of white spots can be induced by the addition of chlorine to the phosphate bath
- All electrogalvanised surfaces considered resulted in white spots of similar shape and substructure

# Chapter 6 Results and discussion: Blister formation

The second category looks at blistering on the electrogalvanised coating that occurs after annealing at 300°C for 30 minutes. This standard weldability test is performed to determine the viability of the steel. The surface must remain sound and no structural changes must occur during annealing. The substrate and electrogalvanised surfaces of the various samples are analysed using SEM, EDS and GDS.

# 6.1. Introduction

The fact that the sample composition and structure of the electrogalvanised surfaces change during annealing, leads to yet another problem experienced by MSSA. During the weldability test blister formation occurs on the electrogalvanised samples.

The weldability test entails annealing of the sample at 300°C for a period of 30 minutes. During this annealing process there should not be any structural or chemical changes in the sample, as this could compromise the integrity of the final product upon welding.

A number of samples are considered for this analysis (Figure 6-1). Firstly, as stated previously, the composition of the substrate and any contamination that may be present at the interface will determine the nature of the electrogalvanised layer. Therefore, the substrate as well as the electrogalvanised sample is considered. Note that the samples used in this section are not the same as those used in the previous section.

The electrogalvanised sample is annealed, according to the weldability test, and analysed. During the annealing process, blisters form on the sample surface. A second electrogalvanised sample, one that has recently been produced, is also analysed. The recently produced sample does not exhibit blister formation. As a means of comparison an imported sample is also included in the analysis. The imported sample does not exhibit blister formation.



Figure 6-1: Methodology for blister sample analysis

# **6.2.** Imported sample

As a measure of comparison the locally produced sample is compared with an imported counterpart. This sample is not the same as the imported sample from the previous chapter.



Figure 6-2: SEM image of the imported electrogalvanised sample

The structure of the sample, shown in Figure 6-2, is rigid with a distinct contour or concentric structure. In the centre of the sample a white grain protrudes from the surface. There are also darker deposits on the surface.



Figure 6-3: SBSE image of the imported electrogalvanised sample

The white grain protruding (as seen in Figure 6-2) from the surface appears as a dark spot in the backscattered electron image (refer to Figure 6-3). Several other darker spots are also present on the sample surface.



Figure 6-4: EDS spectrum of the white deposit on the imported electrogalvanised

The white deposit consists of numerous elements, including: zinc, iron, carbon, oxygen, titanium, calcium, potassium, chlorine, phosphorous, sulphur, silicon, aluminium and magnesium (refer to Figure 6-4). The titanium is used as a grain refiner prior to plating, and the presence of the titanium on the surface appears to be a residual of the pre-treatment. Though most of the elements areKnown to be present on the sample surface, or in the substrate the presence of the magnesium, chlorine, calcium and potassium is cumbersome. These are localised and may therefore cause further problems at these sites as the chemical properties in this region can be adversely affected.



Figure 6-5: EDS spectrum of the dark spot on the imported electrogalvanised

Contrary to the white deposit, the darker deposit (Figure 6-5) contains less carbon. This deposit does not contain aluminium, titanium or silicon. Zinc is the dominant element and a high quantity of carbon and oxygen is present in the deposit. The remainder of the elements are assumed to be present as additions to the electroplating solution, or in the pre-treatment solutions. These deposit on favourable sites on the surface and thereby contaminate the surface.



Figure 6-6: EDS spectrum of the sample area on the imported electrogalvanised

The impact of the aforementioned contaminants on the surface area is brought into context when the EDS spectrum of the sample area is considered (refer to Figure 6-6). The zinc that is electroplated onto the substrate appears as the dominant element. The iron detected may have dissolved into the electrolyte as a result of the exposure to the acid and incorporated electrolitically in the deposit. The iron detected may also be from the substrate, and is detected due to the penetration depth of the incident beam.

The metallic surface, when exposed to the environment, will be oxidised and subsequently oxygen is present on the surface. As for the oxygen contamination, the presence of carbon contamination on the surface is a common occurrence. The downside to this form of contamination is that, if not removed prior to further treatment, it may affect the quality or adherence of any surface treatment.

The elemental map (refer to Figure 6-7) clearly indicates that the elements present in the white deposit (refer to Figure 6-4), such as silicon, aluminium and calcium appear here in larger quantities.

The oxygen, even though present all over the surface, has a higher presence in the region of the white deposit. This region is notably void of zinc. The carbon appears to be enriched in the vicinity of both the white and darker deposits.

The zinc concentration on the surface where the darker deposits occur is markedly low. The iron appears at an isolated spot on the surface that can be identified on the elemental map, but not on the image of the area. The remainder of the elements appear to be distributed evenly.



Figure 6-7: EDS map of the imported electrogalvanised surface



Figure 6-8: QDP of the imported electrogalvanised sample

The surface is contaminated with a small concentration of carbon and hydrogen (refer to Figure 6-8). Nitrogen is also present at the surface and this contamination extends into the surface to 0.5µm. The imported sample is coated with zinc and not the zinc-nickel alloy that is used by MSSA. Consequently, the imported sample has a thicker electrogalvanised layer. The interface between the substrate and the electrogalvanised layer is clear of contamination. The substrate consists of, predominantly, iron. The substrate also contains manganese and phosphorus, used to enhance the properties of the steel.

# 6.2.1. Annealed imported electrogalvanised sample



The imported electrogalvanised sample is annealed at 300°C for 30 minutes.

Figure 6-9: SEM image of the annealed imported electrogalvanised sample

The surface morphology changes significantly as a result of the annealing (refer to Figure 6-9). The concentric, sharp, rigid structure of the electrogalvanised structure changes to a more granular structure. The topography becomes more erratic, with peaks and valleys visible on the surface. Isolated grains also form on the surface. Even though the surface changes, no blistering is visible.



Figure 6-10: SBSE image of the annealed imported electrogalvanised sample

The backscattered electron image (refer to Figure 6-10), shows that the ridges as well as the isolated grains differ compositionally from the surrounding structure.



Figure 6-11: EDS spectrum of the annealed imported electrogalvanised sample

There are two distinct differences in the EDS spectra taken before and after annealing. After annealing (Figure 6-11), the quantity of iron on the surface increased, but the carbon on the surface decreased. This change in the carbon presence may be attributed to the evaporation of oils from the surface.



Figure 6-12: EDS elemental map of the annealed imported electrogalvanised sample

The distribution of the elements on the surface does not appear to be affected by the annealing (Figure 6-12). There is some sulphur visible on the surface.

# 6.3. MSSA sample substrate

The MSSA substrate, prior to treatment is considered. Any dislocations or contamination of the uncoated surface will affect further treatment and therefore these must be identified.



Figure 6-13: SEM image of the MSSA substrate

The SEM image of the substrate (refer to Figure 6-13) appears reasonably smooth, though the rolling direction is clearly visible. There is a deposit protruding from the surface. There are some darker regions on the surface.



Figure 6-14: SBSE image of the MSSA substrate

The backscattered electron image (refer to Figure 6-14) clearly indicates the compositional differences between the substrate and the protruding deposit. The regions that appeared darker in the SEM image also differ compositionally as depicted in the SBSE image.



Figure 6-15: EDS spectrum of the MSSA substrate region

The EDS spectrum of the region (Figure 6-15) indicates that the substrate consists of iron, with traces of carbon present on the surface.



Figure 6-16: EDS spectrum of the protruding deposit

The white deposit as denoted by the EDS spectrum (refer to Figure 6-16) is a salt deposit.



Figure 6-17: EDS spectrum of the dark deposit on the MSSA substrate

The dark deposit (refer to Figure 6-17) consists of carbon with traces of sodium, chlorine, potassium, sulphur, silicon and aluminium also present. Though the aluminium, silicon, chromium, manganese and sulphur areKnown alloy elements, the presence of the remainder of the contaminants is attributed to the chemicals used to clean the substrate prior to electrogalvanising. The way in which these contaminants accumulate in isolated regions is of particular interest, as it points to the uneven distribution of energetically favourable sites on the sample surface.

The elemental map of the sample area (Figure 6-18) clearly indicates the accumulation of carbon in the vicinity of the surface deposit. Sodium, potassium, chlorine, titanium and oxygen are present in higher quantities in or near the deposit. This region is distinctly void of iron. The remainder of the elements appear to be distributed evenly over the sample surface.

The substrate is merely an iron substrate containing traces of standard alloy elements or contaminants.



Figure 6-18: EDS elemental map of the MSSA substrate



Figure 6-19: Uncoated MSSA substrate

The MSSA substrate consists predominantly of iron, but the presence and distribution of alloy elements and contaminants alter the reactivity of the surface (refer to Figure 6-19). The surface is contaminated with carbon, which stretches into the bulk of the sample. Hydrogen is also present in the first layers of the sample. The manganese is enriched in the sublayers of the sample and reaches a maximum value of 34 at% at a depth of  $0.4\mu m$ . The concentration decreases rapidly to 14 at% at a depth of  $0.8\mu m$ , after which the value stabilises throughout the bulk.

# 6.4. MSSA electrogalvanised sample (As produced)

The MSSA substrate is electrogalvanised by MSSA. The "As produced" sample exhibits blister formation on annealing.



Figure 6-20: SEM image of the as produced MSSA electrogalvanised sample

The coated surface has a distinct granular structure, and completely coats the substrate (refer to Figure 6-20). A white dust particle stands out on the surface.



Figure 6-21: SBSE of the as produced MSSA electrogalvanised sample

The white dust particle in the SEM image appears dark in the backscattered electron image (refer to Figure 6-21). The periphery of the scratch on the surface appears darker on the SBSE image.



Figure 6-22: EDS spectrum of the darker metallic deposit on the as produced MSSA electrogalvanised

The darker deposit is not contaminated as severely as the white deposit and consists of zinc, iron, oxygen and carbon (refer to Figure 6-22). The difference in this area of the sample is therefore merely morphological due to physical and not chemical reasons.



Figure 6-23: EDS spectrum of the as produced MSSA electrogalvanised

The spectrum of the considered sample area (Figure 6-23) shows the presence of the zinc, iron, oxygen and carbon.

The region (refer to Figure 6-24) where the white dust particle is found is notably void of zinc, but clearly shows an increased presence of carbon, aluminium, iron, potassium, chlorine, oxygen and silicon. The distribution of the carbon appears irregular. The silicon appears distinct in two regions, along with the oxygen. The sulphur and calcium appear to be distributed evenly, but these are present in small quantities.



Figure 6-24: EDS elemental map of the sample area



Figure 6-25: QDP of the MSSA electrogalvanised sample

The MSSA electrogalvanised sample differs significantly from the imported sample. The surface contamination is similar; consisting of carbon, nitrogen, phosphorus and hydrogen (refer to Figure 6-25). The hydrogen, however, in this case, extends deeper into the sample, but not as deeply as the nitrogen. The nickel that is used in the electrogalvanised layer is not distributed evenly and exhibits a decrease in concentration at a depth of  $1.5\mu$ m. The interface of the substrate-electrogalvanised layer is clear of contamination. Just beneath the surface of the substrate there is a region of manganese enrichment. The value peaks  $0.4\mu$ m into the substrate and then declines into the bulk of the sample. The bulk of the substrate is contaminated with oxygen and nitrogen.

# 6.5. MSSA electrogalvanised annealed sample (As Produced)

The "As produced" sample is annealed at 300°C for 30 minutes, upon which small blisters form on the surface.



Figure 6-26: SEM image of the annealed sample

The SEM image (refer to Figure 6-26) of the sample surface clearly shows the small blisters that form on the sample surface. It is interesting to note that the entire surface is covered with blisters. Some cracking is also visible on the surface.



Figure 6-27: SBSE image of the annealed sample

The backscattered electron image (refer to Figure 6-27) shows slight differences. This suggests that there are small changes in the composition between the surface and the

blisters. There are a few darker regions on the surface that show some distinct compositional changes.



Figure 6-28: SEM image of the blister on the annealed sample

A closer look at the blisters (refer to Figure 6-28) shows a white deposit on the sample surface as well as distinct changes to the surface. The well defined granular appearance has become a composite of different structures.



Figure 6-29: SBSE image of the blister on the annealed sample

The backscattered electron image (refer to Figure 6-29) shows how the surface composition has changed. The blister appears darker on the background of the substrate. The white deposit on the SEM image (refer to figure 5-31) appears lighter than the surrounding areas. There are also several darker regions on the sample surface. The definite changes and distribution of the constituents of the sample surface indicate that the annealing process has inadvertently changed the surface.


Figure 6-30: EDS spectrum of the darker grains on the SEM image of the annealed MSSA electrogalvanised sample

The darker grains on the SEM image (Figure 6-26) consist of zinc and carbon, as denoted by the EDS spectrum of Figure 6-30. A small quantity of oxygen is present as well as iron, most probably from the substrate. Nickel is also present, contrary to the electrogalvanised sample prior to annealing (refer to Figure 6-23).

The white grains on the SEM image consist of zinc, iron and nickel as depicted by the EDS spectrum in Figure 6-31. No other distinguishable contaminants are present.



Figure 6-31: EDS spectrum of the white deposit on the SEM image of the annealed MSSA electrogalvanised sample



Figure 6-32: EDS spectrum inside the blister on the annealed MSSA electrogalvanised sample

The blister (refer to Figure 6-32) contains a large quantity of zinc, as expected, but iron and nickel are also present. There is a large quantity of silicon inside the blister. Oxygen, carbon, aluminium, chlorine and potassium are also present.



Figure 6-33: EDS spectrum of the annealed sample

The annealed sample (refer to Figure 6-33) differs from the unannealed sample. The nickel in the electrogalvanised layer becomes more defined. Even though the annealing temperature is low, there are undeniable changes in the sample.

Although zinc and carbon dominated the surface, the way in which the carbon is distributed over the surface is of particular interest (refer the Figure 6-34). The periphery of the blister contains less carbon than the inside of the blister or for that matter, the remainder of the surface. The oxygen is more concentrated in the centre of the blister and on the outskirts of the periphery of the blister. The nickel presence on the surface has become more pronounced. Both the aluminium and the iron are only pronounced in isolated regions on the surface, not in or near the blister.



Figure 6-34: EDS elemental map of the annealed MSSA electrogalvanised surface.



Figure 6-35: QDP of the blistering MSSA electrogalvanised sample

The heat treatment causes the depth profile to change dramatically (refer to Figure 6-35). The carbon, phosphorus and hydrogen surface contamination is not affected, but the nitrogen contamination becomes more distinct and stretches well into the sample. The zinc profile changes from a smooth, even distribution. Beyond the surface contaminants the zinc concentration reaches a maximum value, after which it declines slowly. The location of the interface is also affected by the annealing. The original sample has an interface at a depth of 2.9µm. The annealed sample has an interface at 3.6µm. The zinc profile extends well into the substrate instead of ending sharply at the interface. The iron is also present in the deeper regions of the electrogalvanised layer, indicating some interdiffusion of the zinc and iron. The shape of the zinc and iron profiles in the region between 2 and 3µm where there is approximately 10 atomic percent iron in the zinc matrix may very well be a  $\delta$  phase of zinc and iron. The nickel is forced out of this region due to the phase formation. The profile of the manganese is also affected by the annealing. Previously the manganese was not present in the electrogalvanised layer, where after annealing it stretches halfway into the electrogalvanised layer from the substrate. The enriched area at the interface is still present at the interface though at a lower atomic percentage after the annealing.

## 6.6. MSSA electrogalvanised sample (Recently produced)

MSSA has altered the composition of the electrogalvanised layer, in order to prevent the blister formation.



Figure 6-36: SEM image of the recently produced MSSA electrogalvanised steel

The structure of the electrogalvanised surface differs drastically from the previously produced substrate (refer to Figure 6-36). The surface coating is less granular, but more rigid. Pores appear on the surface, although it appears that the coating completely covers the substrate. Extending well above the surface is a flake-like deposit, as well as some smoother, yet darker, deposits.



Figure 6-37: SBSE image of the recently produced MSSA electrogalvanised steel

The backscattered electron image (refer to Figure 6-37) emphasizes the compositional differences that exist between the flaky deposit, the background structure and what appears to be darker deposits on the SEM image (refer to Figure 6-36).



Figure 6-38: EDS spectrum of the white flakes on the recently produced MSSA electrogalvanised steel

The white flakes on the recently produced steel consist of various elements (Figure 6-38), including: zinc, iron, calcium, sulphur, phosphorus, silicon, oxygen and carbon. The presence of the calcium on the surface and the fairly high concentration of sulphur on the surface may be responsible for the differences in morphology and conductivity. Phosphorous is added to steel as an alloy element and this binds the grain boundaries together to strengthen the steel. The addition of silicon is usually accompanied by the addition of other cations, such as aluminium and this aids in the hardening and strengthening of the steel. Similarly the addition of carbon to the steel also hardens the steel.

Contrary to the white flakes, the darker flakes differ compositionally (refer to Figure 6-39). The carbon content has increased along with the silicon. The sulphur, phosphorus and calcium content have decreased significantly. The zinc peak at 8.6keV is more pronounced in this sample indicating a change in the chemical environment of the zinc.



Figure 6-39: EDS spectrum of the dark flakes on the recently produced MSSA electrogalvanised steel



Figure 6-40: EDS spectrum of the recently produced MSSA electrogalvanised steel

The sample area considered (Figure 6-40) consists of predominantly zinc although traces of iron, carbon and oxygen are also present. The remainder of the contaminants from the deposits do not contribute significantly to the spectrum.

The elemental map of the sample surface (refer to Figure 6-41) shows the distribution of the elements. The accumulation of elements such as sulphur, oxygen and carbon in the vicinity of the white flakes is of particular interest. This area is also void of zinc.

The carbon also appears to accumulate in the smaller darker deposits on the surface. The iron and silicon are only truly pronounced in a few isolated spots on the surface. The remainder of the elements appear to be distributed evenly over the sample surface.



Figure 6-41: EDS elemental map of the recently produced MSSA electrogalvanised steel



Figure 6-42: QDP of the recently produced MSSA electrogalvanised sample

The new sample consists of a zinc-nickel alloy electrogalvanised coating, plated onto an iron substrate (refer to Figure 6-42). The surface of the electrogalvanised layer is still contaminated with carbon, nitrogen, phosphorus and hydrogen. The nickel profile differs strikingly from that of the previous sample. The surface consists of a high value that decreases sharply into the first 0.5µm of the sample. Deeper into the coating the value stabilises until the interface is reached. The substrate is predominantly iron, but traces of manganese, oxygen, nitrogen and phosphorus are also present. The profile of the manganese is stable throughout the bulk contradictory with the previous sample. This sample also contains less phosphorus than the imported sample.

#### 6.6.1. Recently produced annealed sample

As the annealing of the electrogalvanised sample causes structural and compositional changes on the surface it is not sufficient to assess the sample simply on its composition and structure. For this reason the sample is annealed at 300°C for 30 minutes.



Figure 6-43: SEM image of the annealed recently produced electrogalvanised sample

After annealing the surface morphology differs distinctly from its unannealed counterpart. The previously porous structure becomes smoother and more uniform (Figure 6-43). The deposits present prior to annealing are still present after annealing. No blistering is visible on the surface.



Figure 6-44: SBSE image of the annealed recently produced electrogalvanised sample

The backscattered electron image (Figure 6-44) depicts the compositional differences between the deposits on the surface and the surrounding structure. Of particular interest in this image are the cracks that appear on the surface, visible as dark lines that run across the sample surface.



Figure 6-45: EDS spectrum of the annealed recently produced electrogalvanised sample

The EDS spectrum (Figure 6-45) of the annealed sample differs from the unannealed sample. The surface of the annealed sample contains zinc, iron, carbon and oxygen, as in the unannealed sample, but also contains nickel and calcium, that do not appear on the EDS spectrum of the unannealed sample area. Furthermore, there is a change in the carbon oxygen ratio, with a smaller quantity of carbon present on the annealed sample.

The change in the surface composition can be attributed to dezincification, as the temperature is not sufficient for diffusion of the iron or nickel through the zinc matrix. The dezincification selectively affects the amount of zinc present on the surface, but does not affect the nickel in the electrogalvanised layer. Thinning of the layer will also result in an increased contribution of the substrate, thus a higher iron signal.



Figure 6-46: EDS elemental map of the annealed recently produced electrogalvanised sample

The carbon contamination is most pronounced at the deposit on the surface (Figure 6-46). The oxygen is enriched in isolated regions, corresponding to the darker regions in Figure 6-44: SBSE image of the annealed recently produced electrogalvanised sample. Though a small quantity of sulphur is distributed over the area, slight enrichment is visible on one section of the sample. Both the iron and nickel appear to be distributed evenly over the surface. The zinc however is void in the vicinity of the deposit.

## 6.7. Summary

Even though annealing of the electrogalvanised samples causes structural changes in the samples, blister formation only occurred in the "as produced" sample. A closer look at the sample indicated a manganese enrichment at the electrogalvanised and substrate interface. Upon annealing the zinc and iron diffuse to form a phase in the zinc matrix with a 10 atomic percent iron content. The nickel is forced out of this region and forms a region of enrichment within the electrogalvanised layer. The manganese enrichment in the substrate is not seen in any of the other samples. As this is the only significant difference in the samples, the blister formation is associated with this enrichment.

# Chapter 7 Results and discussion: Immersion plated samples

The third and final category aims to determine the impact of additions to the electrolyte in the structure, composition and chemical nature of various electrogalvanised samples. The electrogalvanised samples, as well as the annealed, phosphated and white spotted samples are analysed using SEM and EDS. The electrolytes used comprise of combinations of the following cations: zinc, nickel, cobalt and copper.

#### 7.1. Introduction



Figure 7-1: Methodology for analysis of prepared samples

A series of samples was prepared using a combination of different electrolytes to assess the impact of the various elements on the electrogalvanised structure (Figure 7-1). Any changes on the surface will undoubtedly affect the post-treatments.

#### 7.2. Zinc samples

This series of samples was prepared following electrogalvanising with a pure zinc electrolyte.

#### 7.2.1. Zinc electrogalvanised sample

The zinc electrogalvanised sample is electroplated using the prepared electrolyte described in section 4.1.1.2.1. Immersion plating is utilised using the apparatus and parameters set out in section 4.1.1.1.



Figure 7-2: SEM image of the zinc electroplated sample

The electroplating of the sample using the zinc electrolyte results in the formation of numerous, interlocked crystals in the sample surface (Figure 7-2). The crystals have a lamellar appearance with rigid edges. The orientation of the individual crystals is random. Furthermore, the substrate is completely covered. The crystals grow from the nucleation sites, outward until it reaches the neighbouring crystal. At this point a grain boundary is formed. The crystals then grow upward. The numerous grain boundaries can also be seen on the SEM image of the surface.



Figure 7-3: SBSE image of the zinc electroplated sample

The backscattered electron image (Figure 7-3) shows the fair homogeneity of the surface. Slight differences in contrast at the grain boundaries may indicate compositional differences or contamination at these sites.



Figure 7-4: SEM image of the zinc electroplated sample

Considering a larger surface area, some inconsistencies or surface dislocations become visible (Figure 7-4). There are numerous protruding deposits visible and some subsiding regions. These represent regions where the deposition of the zinc is accelerated (protrusions) or retarded (subsidence). The inconsistencies are attributed to the presence of dislocations or contaminants on the substrate that impact the deposition on the various sites on the surface. Below the subsiding deposit there is another protruding deposit that appears to have an anomalous structure. This is possibly some form of surface contamination.



Figure 7-5: SBSE image of the zinc electroplated sample

The backscattered electron image (Figure 7-5) of the sample area accentuates the compositional differences between the surface deposit, the protruding deposits and the subsiding deposits. The perimeter of the subsiding deposit has a darker appearance and therefore it can be concluded that it differs compositionally from the surrounding deposit.



Figure 7-6: EDS spectrum of the subsiding deposit

The subsiding deposit (Figure 7-6) consists of zinc, sulphur and oxygen (all deposited from the electrolyte) as well as a significant quantity of iron (undoubtedly from the substrate). The electrodeposition occurs to a lesser extent at this site and therefore the contribution of the substrate or the iron in this case, is higher.



Figure 7-7: EDS spectrum of the zinc electrogalvanised sample area

When considering the EDS spectrum taken of the entire sample area (Figure 7-7) the impact of the contaminants becomes clear. Since only the sulphur and oxygen are detected it can be concluded that the contamination discussed on the previous sites is localised.

The elemental map of the sample area (Figure 7-8) indicates the localised presence of the iron, present only in the subsiding deposit. The carbon appears to be enriched in the vicinity of the dark deposit, along with an increased presence of the oxygen, calcium, silicon and aluminium. This region as well as the subsiding deposit contains less zinc.



Figure 7-8: EDS elemental map of the zinc electrogalvanised sample

## 7.2.2. Annealed zinc electrogalvanised sample

The zinc electrogalvanised sample is annealed at 300°C for 30 minutes.



Figure 7-9: SEM image of the annealed zinc electrogalvanised sample

The annealing of the sample results in significant changes in the surface morphology (Figure 7-9). The rigid, uniform structure changes to composite structure varying between the original rigid crystals and a smoother unpronounced structure.



Figure 7-10: SBSE image of the annealed zinc electrogalvanised sample

The backscattered electron (Figure 7-10) image emphasizes the compositional differences that occur on the sample surface.



Figure 7-11: EDS spectrum of the annealed zinc electrogalvanised

The EDS spectrum (Figure 7-11) confirms the presence of the electroplated zinc, along with the trapped oxygen and sulphur from the electrolyte, but also a significant quantity of iron on the sample surface.



Figure 7-12: EDS elemental map of the annealed zinc electrogalvanised

The elemental map of the annealed sample surface (Figure 7-12) shows the regular and uniform distribution of the carbon, oxygen, sulphur and zinc. The distribution of

the iron is of particular importance as this element is present in the regions on the surface in which the structural changes were the most significant.

## 7.2.3. Phosphated zinc electrogalvanised sample

The zinc electroplated sample is prepared as prescribed and phosphated accordingly.



Figure 7-13: SEM image of the phosphated zinc electrogalvanised

The structure of the phosphate on the zinc electrogalvanised sample agrees with previous results. The entire surface appears to be coated with the phosphate crystals. The small crystals appear uniform in shape and size, but have random orientations. There is an anomalous deposit protruding from the surface.



Figure 7-14: SBSE image of the phosphated zinc electrogalvanised

The backscattered electron image of the phosphated zinc electrogalvanised (Figure 7-14) accentuates the compositional difference between the surrounding phosphate and the anomalous deposit.



Figure 7-15: EDS spectrum of the phosphated zinc electrogalvanised

The EDS spectrum of the sample area (Figure 7-15) consists of the trications zinc, manganese and nickel. Iron is present due to dissolution of the substrate as well as the phosphorus and oxygen that form the phosphate ion.

The higher oxygen, with respect to the phosphorus, points to the presence of oxides and adsorbed oxygen on the sample surface.

The elemental map of the sample area (Figure 7-16) confirms the regular distribution of the elements over the sample surface, with the exception of zinc that is not as prominent in the anomalous protruding phosphate on the sample surface.



Figure 7-16: EDS elemental map of the phosphated zinc electrogalvanised

## 7.2.4. White spots on the zinc electrogalvanised sample

The zinc electrogalvanised sample is phosphated in an aggressive solution in order to facilitate white spot formation.



Figure 7-17: SEM image of the white spot on the zinc electrogalvanised

The white spot on the zinc electrogalvanised (Figure 7-17) has a slightly different appearance compared to previous spots considered. Even though the same circular shape and anomalous perimeter is present, the inner part of the spot appears to have the same structure as the surrounding phosphate structure.



Figure 7-18: SBSE image of the white spot on the zinc electrogalvanised

The backscattered electron image (Figure 7-18) indicates that there are compositional differences between the phosphate on the sample surface and inside the white spot. Further differences are found between the perimeter and some of the flaky deposits that are present on the sample surface.



Figure 7-19: EDS spectrum of the white spot sample area on the zinc electrogalvanised

The EDS spectrum (Figure 7-19) compares well with the spectrum taken of the phosphated sample. The primary difference that can be seen is in the phosphorus oxygen ratios. The white spot sample contains a higher phosphorus content, with respect to the oxygen.



Figure 7-20: EDS elemental map of the white spot on the zinc electrogalvanised

The most distinct changes in the distribution of the elements (Figure 7-20) are found in the distribution of the zinc, phosphorus and oxygen. Where the oxygen and phosphorus are more pronounced on the perimeter of the white spot, the zinc is less pronounced. The secondary flaky deposit to the left of the white spot also contains less zinc.

## 7.3. Zinc-nickel samples

The zinc-nickel series of samples are prepared using a combination of zinc and nickel in the electrolyte.

#### 7.3.1. Zinc-nickel electrogalvanised sample

The zinc-nickel electrogalvanised is prepared using the electrolyte described in section 4.1.1.2.2.



Figure 7-21: SEM image of the zinc-nickel electrogalvanised sample

The structure of the zinc-nickel electrogalvanised sample (Figure 7-21) is a composite structure with two distinct structures. The first is the smooth surface coating; the second the thin plates that seem to be contained within the smoother coating.



Figure 7-22: SBSE image of the zinc-nickel electrogalvanised sample

The backscattered electron image (Figure 7-22) emphasizes the compositional differences between the smooth surface coating and the oblong deposits. The areas in between the plates also appear to have a different composition.



Figure 7-23: EDS spectrum of the zinc-nickel electrogalvanised

The EDS spectrum of the sample area confirms the presence of the zinc and a miniscule quantity of nickel from the electrolyte. The surface is contaminated with both oxygen and chlorine (possibly a residual of the cleaning process). Iron is also present on the sample surface.



Figure 7-24: EDS elemental map of the zinc-nickel electrogalvanised

The elemental map (Figure 7-24) shows the irregular distribution of the carbon, oxygen and zinc on the sample surface. The plates appear to contain more carbon and oxygen, but less zinc.

## 7.3.2. Annealed zinc-nickel electrogalvanised sample

The zinc-nickel electrogalvanised sample is annealed for 30 minutes at 300°C.



Figure 7-25: SEM image of the annealed zinc-nickel electrogalvanised

The structural changes of the surface upon annealing are unquestionable (Figure 7-44). Large protrusions form on the surface that appears to be cracked. The bulk

structure of the electrogalvanised also changes to a smoother structure, though more anomalies are visible on the surface.



Figure 7-26: SBSE image of the annealed zinc-nickel electrogalvanised

The backscattered electron image (Figure 7-26) of the annealed surface shows that there are not only structural but also composition differences between the sample structure and that of the protrusions.



Figure 7-27: EDS spectrum of the annealed zinc-nickel electrogalvanised

The changes in the surface composition are expressed in the EDS spectrum of the sample area (Figure 7-27). The quantity of chlorine on the surface decreased, and that of the sulphur increased.

The elements appear to be distributed evenly over the surface (Figure 7-28), with changes in the zinc and oxygen maps due to morphological effects.



Figure 7-28: EDS elemental map of the annealed zinc-nickel electrogalvanised sample

## 7.3.3. Phosphated zinc-nickel electrogalvanised sample

The electrogalvanised sample is prepared and phosphated as prescribed. The phosphate structure is similar to the structure found on the previous samples, with isolated flaky deposits on the surface.



Figure 7-29: SEM image of the phosphated zinc-nickel electrogalvanised sample

The phosphate structure (Figure 7-29) corresponds to the structure on previous samples. Some flakes are visible on the surface. The deposits appear less disk-shaped. The phosphate covers the entire surface, and protrusions are limited.



Figure 7-30: SBSE image of the phosphated zinc-nickel electrogalvanised sample

The backscattered electron image (Figure 7-30) indicates the uniformity of the surface, though some compositional differences are present at the grain boundaries.



Figure 7-31: EDS spectrum of the phosphated zinc-nickel electrogalvanised sample

The presence of the phosphate (comprising of the phosphorus and oxygen) as well as the trications; manganese, nickel and zinc, is confirmed in the EDS spectrum of the sample area (Figure 7-31). The iron on the spectrum is partly as a result of iron dissolution (from the substrate) and being trapped in the depositing phosphate structure. Another contribution can be made by the substrate, as the thickness of the surface coating is reduced.

The elemental map of the sample area (Figure 7-32) shows that in the vicinity of the flakes deposited on the surface there is a lesser presence of zinc. These regions have a more pronounced phosphorus and oxygen presence, suggesting the deposition of an anomalous phosphate.



Figure 7-32: EDS elemental map of the phosphated zinc-nickel electrogalvanised sample

#### 7.3.4. White spots on the zinc-nickel electrogalvanised sample

The electrogalvanised sample is prepared as prescribed and then phosphated in a more aggressive phosphate bath to induce white spot formation.



Figure 7-33: SEM image of the white spot on the zinc-nickel electrogalvanised

The white spot (Figure 7-33) is surrounded by the regular phosphate structure, and differs significantly from the regular phosphate structure. The perimeter of the spot consists of numerous flakes that extend well above the sample. These flakes also extend into the white spot, though the base of the spot is not coated with the same structure as the remainder of the surface. There are numerous spots in this area. The sizes of the spots differ, but the general structures remain the same.



Figure 7-34: SBSE image on the white spot on the zinc-nickel electrogalvanised

The backscattered electron image (Figure 7-34) accentuates the compositional differences in the white spot, on the perimeter of the spot and on the remainder of the sample.



Figure 7-35: EDS spectrum of the white spot on the phosphated zinc-nickel electrogalvanised sample

The addition of chlorine to the phosphate bath, to induce white spot formation, results in the presence of the chlorine on the sample surface (Figure 7-35). There is a related decrease in the manganese on the surface. Since the substrate is exposed there is a larger contribution towards the iron peak from this exposed region.



Figure 7-36: EDS elemental map of the white spot on the phosphated zinc-nickel electrogalvanised sample

During the phosphate process the electrogalvanised layer is dissolved before deposition of the phosphates. In the case of the white spot formation, the entire electrogalvanised layer is dissolved at localised sites. Though some deposition of the phosphate may take place on the exposed substrate, the white spots are characterised
by the exposed iron in the centre of the spot (Figure 7-36). The perimeter of the white spot consists of a more pronounced oxygen and phosphorus profile. Both the centre and the perimeter of the white spot contain less zinc. The iron is only detected in the centre of the white spot, where there is also an increase in the silicon concentration.

#### 7.4. Zinc-nickel-cobalt sample

The zinc-nickel-cobalt electrogalvanised sample is prepared using the electrolyte described in section 4.1.1.2.3.

#### 7.4.1. Zinc-nickel-cobalt electrogalvanised sample



Figure 7-37: SEM image of the zinc-nickel-cobalt electrogalvanised

The composite structure (Figure 7-37) consists of a regular, but rigid crystal, with a fine web-like substructure. Once again the electrogalvanised coating coats the entire substrate.



Figure 7-38 SBSE image of the zinc-nickel-cobalt electrogalvanised

The backscattered electron image (Figure 7-38) confirms slight compositional differences that occur at the grain boundaries.



Figure 7-39: SEM image of the zinc-nickel-cobalt electrogalvanised

Elsewhere on the sample there are protrusions that extend above the electrogalvanised layer (Figure 7-39). The hexagonal plate-like structure, similar to the zinc electrogalvanised surface, can clearly be seen on the surface.



Figure 7-40 SBSE image of the zinc-nickel-cobalt electrogalvanised

The backscattered electron image (Figure 7-40) of the surface reveals the layered structure of the protruding deposit, as well as the compositional differences between these structures and the surrounding crystals.



Figure 7-41: EDS spectrum of the zinc-nickel-cobalt electrogalvanised sample

The EDS spectrum of the electrogalvanised sample area (Figure 7-41) confirms the presence of the zinc and nickel but not of the cobalt. Instead some iron is present on the sample surface. As a sulphate-based electrolyte is used, some sulphur and oxygen are included in the electrodeposited structure.

Though the structure of the electrogalvanised changed as a result of the cobalt addition, the concentration of the cobalt on the sample surface is below the detectable value, therefore there is no deflection at 6.9keV (the position of the K $\alpha$  peak for cobalt).

The elemental map of the sample area (Figure 7-42) indicates that the protrusions contain more oxygen. The remainder of the elements are distributed evenly over the sample area.



Figure 7-42: EDS elemental map of the zinc-nickel-cobalt electrogalvanised sample

#### 7.4.2. Annealed zinc-nickel-cobalt electrogalvanised sample

The zinc-nickel-cobalt electrogalvanised sample is annealed at 300°C for 30 minutes.



Figure 7-43: SEM image of the annealed zinc-nickel-cobalt electrogalvanised

Upon annealing, the surface (Figure 7-43) of the electrogalvanised sample changes dramatically. The regular, hexagonal plate-like structure disappears, and is replaced by cracked, porous surface.



Figure 7-44: SEM image of the annealed zinc-nickel-cobalt electrogalvanised

Considering a larger area (Figure 7-44), it is evident that the impact of the annealing includes not only changes to the electrogalvanised structure, but also to the protrusions on the surface. The cracking of the electrogalvanised structure points to structural failure and may result in delamination of the electrogalvanised layer.



Figure 7-45: SBSE image of the annealed zinc-nickel-cobalt electrogalvanised

The backscattered electron image (Figure 7-45) shows slight compositional changes on the surface.



Figure 7-46: EDS spectrum of the annealed zinc-nickel-cobalt electrogalvanised sample

Along with the reduction in the zinc on the surface, due to dezincification, the presence of the iron and the nickel in the layer becomes more apparent (Figure 7-46).

The sulphur appears to be concentrated in one section on the surface (Figure 7-47), whereas there are a few isolated sites where there is a higher concentration of oxygen on a backdrop of an even lower quantity distribution of the oxygen. Though the carbon is present all over the sample, it appears to be enriched on random sites on the surface. The cations; iron, nickel and zinc are present on the entire surface area and do

not appear to have sites of enrichment. Furthermore, the cobalt does not appear on the surface.



Figure 7-47: EDS elemental map of the annealed zinc-nickel-cobalt electrogalvanised sample

#### 7.4.3. Phosphated zinc-nickel-cobalt electrogalvanised sample

The zinc-nickel-cobalt electrogalvanised sample is phosphated according to prescription.

The phosphated electrogalvanised surface (Figure 7-48) contains small disk shaped crystals. The edges of the crystals appear more rigid. There is a large deposit suspended onto the phosphate structure with a notably different structure.



Figure 7-48: SEM image of the phosphated zinc-nickel-cobalt electrogalvanised



Figure 7-49: SBSE image of the phosphated zinc-nickel-cobalt electrogalvanised

The backscattered electron image (Figure 7-49) does not indicate significant changes in composition on the sample surface.



Figure 7-50: EDS spectrum of the phosphated zinc-nickel-cobalt electrogalvanised sample

Upon phosphating the zinc electrogalvanised is partially dissolved, thereby increasing the iron and nickel concentration in the layer (Figure 7-50). The zinc in the solution deposits onto the surface as phosphates along with the manganese and the nickel that comprise the trication addition to the phosphate. Accordingly there is also an increase in the oxygen and phosphorus peaks.

The large deposit on the surface appears to be manganese phosphate, as these elements are enriched in the vicinity of the deposit (Figure 7-51). This area is also notably void of zinc. One isolated spot appears to contain a significant quantity of silicon. The iron and nickel appear to be distributed evenly.



Figure 7-51: EDS elemental map of the phosphated zinc-nickel-cobalt electrogalvanised sample

# 7.4.4. White spots on the zinc-nickel-cobalt electrogalvanised sample

The zinc-nickel-cobalt electrogalvanised sample is phosphated in a more aggressive phosphate bath thereby producing white spots on the sample surface.



Figure 7-52: SEM image of the white spot on the zinc-nickel-cobalt electrogalvanised

The white spot on the surface (Figure 7-52) resembles the pits found on previous samples as opposed to the white spots. The pit appears to be collapsed into the phosphate structure.



Figure 7-53: SBSE image of the white spot on the zinc-nickel-cobalt electrogalvanised

The backscattered electron image (Figure 7-53) shows the distinct compositional differences that are present on the surface and the base of the pit.



Figure 7-54: EDS spectrum of the white spot on the phosphated zinc-nickel-cobalt electrogalvanised sample

Due to the accelerated dissolution of the zinc layer, there are sites where complete dissolution of the zinc layer will occur exposing the iron substrate (Figure 7-54). This results in a high iron peak. The surrounding structure will undergo phosphating as

usual resulting in peaks for the oxygen, phosphorus, manganese and nickel. Some carbon and silicon contamination is also present on the sample surface.



Figure 7-55: EDS elemental map of the white spot on the phosphated zinc-nickel-cobalt electrogalvanised sample

The inside of the white spot consists of carbon, iron and silicon. There is also an increase in the cobalt concentration in the white spot, but the area is void of zinc. The flaky deposits on the surface consist of manganese, oxygen and phosphorus.

#### 7.5. Zinc-nickel-copper sample

The zinc-nickel-copper electrogalvanised sample is prepared using the electrolyte described in section (4.1.1.2.4).

#### 7.5.1. Zinc-nickel-copper electrogalvanised sample



Figure 7-56: SEM image of the zinc-nickel-copper electrogalvanised

The structure of the zinc-nickel-copper electrogalvanised surface consists of grains attached to the substrate (Figure 7-56).



Figure 7-57: SBSE image of the zinc-nickel-copper electrogalvanised

Even though the SEM image does not allow for the interpretation of the presence of anomalies, the backscattered electron image (Figure 7-57) clearly shows the compositional differences of the various regions on the sample surface.



Figure 7-58: SEM image of the zinc-nickel-copper electrogalvanised

Considering a larger sample area it is clear that there are different structural deposits present on the surface (Figure 7-58). In the centre of this image an anomaly is visible.



Figure 7-59: SBSE image of the zinc-nickel-copper electrogalvanised

The backscattered electron image (Figure 7-59) shows the compositional differences on the surface.

The electrogalvanised sample contains zinc, copper and nickel, but is contaminated with carbon, oxygen and sulphur (Figure 7-60).



Figure 7-60: EDS spectrum of the electrogalvanised zinc-nickel-copper sample

The smaller deposits on the surface consist of carbon, sulphur, chlorine and oxygen and do not contain any zinc (Figure 7-61). The large anomaly in the centre of the sample is also void of zinc, but contains more oxygen. The nickel, iron and copper are distributed evenly over the sample surface.



Figure 7-61: EDS elemental map of the zinc-nickel-copper electrogalvanised sample

#### 7.5.2. Annealed zinc-nickel-copper electrogalvanised sample

The zinc-nickel-copper electrogalvanised sample is annealed at 300°C for 30 minutes.



Figure 7-62: SEM image of the annealed zinc-nickel-copper electrogalvanised

There are marked changes to the surface of the sample (Figure 7-62). Some of the grains dissipate to reveal an underlying structure. There are some grains that remain on the surface.



Figure 7-63 SBSE image of the annealed zinc-nickel-copper electrogalvanised

The backscattered electron image (Figure 7-63) points to definite compositional differences between the remaining grains and the substructure.



Figure 7-64: EDS spectrum of the annealed zinc-nickel-copper electrogalvanised sample

Apart from the structural changes that occur, the chemical composition of the surface also changes (Figure 7-64). Due to selective removal of zinc from the coating, the quantities of the remaining cations will increase. Therefore the iron, nickel and copper peaks increase. The iron may have been incorporated into the electrogalvanised structure, but a larger contribution towards the peak may come from the substrate as the coating is thinner after annealing.

The grains in the surface consist of copper, carbon and oxygen (Figure 7-65). These grains contain less zinc than the surrounding structure. The sulphur is more pronounced in the regions between the grains, along with the iron.



Figure 7-65: EDS elemental map of the annealed zinc-nickel-copper electrogalvanised sample

#### 7.5.3. Phosphated zinc-nickel-copper electrogalvanised sample

The zinc-nickel-copper electrogalvanised sample is phosphated as prescribed.



Figure 7-66: SEM image of the phosphated zinc-nickel-copper electrogalvanised

The phosphated sample has a unique structure (Figure 7-66). The phosphates grow upward, away from the surface and it appears that the growth of these crystals may continue even after the surface has been coated, which is contradictory to theory.



Figure 7-67: SBSE image of the phosphated zinc-nickel-copper electrogalvanised

There aren't any significant compositional variances on the surface, as denoted by the backscattered electron image (Figure 7-67).



Figure 7-68: SEM image of the phosphated zinc-nickel-copper electrogalvanised

The surface is irregular and staggered as a result of the almost dendritic growth of the phosphates (Figure 7-68).



Figure 7-69: SBSE image of the phosphated zinc-nickel-copper electrogalvanised

Considering a larger sample area reveals some variations in composition on the surface (Figure 7-69).



Figure 7-70: EDS spectrum of the phosphated zinc-nickel-copper electrogalvanised sample

Similarly with previous samples, the phosphated zinc-nickel-copper sample contains oxygen, phosphorus, manganese, iron, nickel and zinc (Figure 7-70). Since the electrogalvanised sample contained copper, a minuscule quantity is present on the surface. The carbon contamination was also inherited from the electrogalvanised structure. The phosphated layer contains more manganese compared to the other samples.



Figure 7-71: EDS elemental map of the phosphated zinc-nickel copper electrogalvanised sample

## 7.5.4. White spots on the zinc-nickel-copper electrogalvanised sample

In a more aggressive phosphate bath the electrogalvanised sample will exhibit white spot formation.



Figure 7-72: SEM image of the white spot on the zinc-nickel-copper electrogalvanised

The white spot on the zinc-nickel-copper surface consists of a protruding accumulation of an anomalous deposit (Figure 7-72). The surrounding structure is similar in form to the phosphated sample.



Figure 7-73: SBSE image of the white spot on the zinc-nickel-copper electrogalvanised

The backscattered electron image (Figure 7-73) shows distinct compositional differences between the white spot and the surrounding structure. The flaky deposit on the perimeter of the white spot can also be distinguished on this image.



Figure 7-74: EDS spectrum of the white spot on the phosphated zinc-nickel-copper electrogalvanised sample

The EDS spectrum of the white spot region on the phosphated zinc-nickel-copper electrogalvanised sample (Figure 7-74) does not differ significantly from the

phosphated sample. Since the white spot is covered by the anomalous deposit the iron peak is still reasonably low as the iron substrate is not exposed, in comparison with other white spot samples.



Figure 7-75: EDS elemental map of the white spot on the zinc-nickel-copper electrogalvanised sample

The elemental map of the sample (Figure 7-75) shows an accumulation of manganese, phosphorus and oxygen in the vicinity of the anomalous deposit. The perimeter of the spot contains less zinc, nickel and copper compared to the surrounding structure. Furthermore, there appears to be an accumulation of carbon on the vertices of the white spot.

#### 7.6. Summary

The structure of the various deposits changed with the changes in the composition of the electrolyte. The electrogalvanised structures change from a well-defined rigid structure (as for the zinc electrolyte) to a complex structure consisting of both grains and a fine intricate network of small deposits.

The annealed structures differ significantly from the electroplated surfaces. A common factor in all the annealed samples is the deterioration of the zinc in the layer, with an associated increase in the iron peak (from the substrate), indicating a decrease in the layer thickness.

The phosphated samples have varying structures, since the electrogalvanised surfaces differ. The presence of cobalt and copper in the electrolyte resulted in an increase in the deposition of manganese phosphates on the surfaces. The manganese phosphates grow upward, away from the surface as opposed to the zinc phosphates that grow along the sample surface. The growth of the zinc phosphates only continues until the surface is covered.

The formation of the white spots on the laboratory prepared samples compares well to the industrial samples. The complete dissolution of the electrogalvanised layer occurs, thereby exposing the steel substrate. The deposition mechanism of the phosphates on the exposed area differs from the deposition on the zinc layer. Therefore the structure of the phosphate in and around the white spot differs. The perimeter of the white spots contains anomalous phosphate crystals that extend upward.

Coating	Zinc	Zinc-nickel	Zinc-nickel-	Zinc-nickel-
			cobalt	copper
Electrogalvanised	Well-defined	Composite	Rigid structure	Numerous round
surface	structure of rigid	structure, thin	as for Zn, with	grains deposited,
Surface	plates	plates inside	web-like	severe carbon
		smooth exterior	network of fine	contamination
		structure	crystals	
			superimposed	
Annealed surface	Severe structural	Structural	Cracking and	Reduction in
	changes	changes with the	pore formation	carbon deposits,
		formation of	dominate	substructure in
		globules	structural	tact
			changes	
Phosphated surface	Small rounded	Small elongated	Smooth surface	Continuous
	crystals	crystals	with fine crystals	upward growth
			on top	of phosphate
				crystals
White spot on surface	Well-defined	Perimeter	Pit-like spot,	No pit
	perimeter, no	comprising of	without	formation, but
	elongated	protruding	perimeter	accumulation of
	crystals in the	crystals and	deposits	Mn phosphates
	centre	exposed Fe in		protruding from
		centre		the surface

Table 7-1: Summary of the sample properties

Comparing the various samples the following becomes evident. The composite zincnickel-copper sample experiences the least structural changes during annealing, but the high carbon presence may prove to be detrimental in other surface treatments. The zinc-nickel-cobalt coating preserved the rigid structure of the zinc coating and is more resistant to the formation of manganese phosphates on the white spot perimeter. Although the addition of nickel to the electrolyte reduces the likelihood for white spot formation the surface experiences structural changes during annealing. Furthermore, the addition of small quantities of cations to the electrolyte affects all post plating processes.

### Chapter 8 Conclusion

#### 8.1. Final deductions

In an ideal situation, the substrate and electrogalvanised layers will be void of scratches or defects and the interface between the layers free of contaminants. The industrial samples, however, differ markedly from this idealised scenario. During the production process the substrate surface is scratched, roller fragments are included in the surface and oxidation or other forms of contamination may occur. The substrate also contains various alloy elements, without which the steel will not exhibit the required properties. These alloy elements react differently to further treatments than the iron substrate.

Various techniques are utilised to clean and prepare the steel substrate for electrodeposition. These are usually designed for cleaning the iron sheet, but the presence of dislocations or different elements on the surface may result in adverse surface reactions. Deposition of the constituents of the cleaning solutions may occur at chemically reactive sites.

The structure and composition of the electrogalvanised layer is closely related to the bath parameters and the properties of the substrate. It is therefore crucial for these to be monitored continuously. The presence of any cations in the electrolyte, intentional or otherwise, will also result in radical changes in the electrogalvanised layer's structure and composition. Post-analysis of the electrogalvanised layer may not necessarily confirm the presence of these cations.

Upon annealing the weak adherence of the electrogalvanised layer becomes apparent, since the layer undergoes dezincification via evaporation. This results in both structural and compositional changes of the electrogalvanised layer. The interface

between the electrogalvanised layer and iron substrate is also affected by the annealing.

The phosphating of electrogalvanised surfaces entails the partial dissolution of the zinc in the electroplated layer. This causes a change in the localised pH and saturates the liquid in contact with the surface. These all contribute to making the environment favourable for zinc phosphate deposition. Along with the zinc phosphate there is also deposition of manganese and nickel phosphates. The deposition will cover the surface and then stop. Altering the surface composition, however, will also alter the deposition of the phosphates. An increase in the deposition of manganese phosphates results in a surface with numerous anomalous deposits that extend upward away from the surface.

At sites on the electrogalvanised surface where dislocations are present, the dissolution of the zinc may be accelerated and complete dissolution may occur (Section 2.2.6. Spotting). Alternatively, contamination at the substrate-electrogalvanised layer interface, the adhesion of the electrogalvanised layer may be compromised easing the complete dissolution of the zinc in this region. The phosphating around this region will proceed normally, but on the exposed substrate the phosphating reaction is altered. This results in the deposition of crystals with alternative structures. An increase in the deposition of the phosphate occurs at the perimeter of the white spot.

#### **8.2.** Suggestions for further investigations

Though some speculation has been made regarding the surface strain of the substrate, this should be investigated more thoroughly along with the origin of the various contaminants present on the surface. Understanding the origin or nature of the surface will aid in manipulating or correcting the deviations. It might be possible to alter the post-treatments to compensate for the shortcomings of the surface.

The properties of the electrogalvanised surfaces are closely related to the pretreatment of the surface as well as the bath parameters. Closer inspection of the surface prior to electrogalvanising and continuous monitoring of the baths is therefore of utmost importance. This requires the design of specialised apparatus and testing techniques.

Further manipulation of the electrogalvanised layer is necessary to increase the adhesion of the coating and prevent dezincification or blister formation during annealing.

Since the automotive design requires various types of steel, varying in composition and morphology, the phosphating baths should be adjusted to the panels that exhibit the most extensive white spot formation. The likelihood of white spot formation will therefore be reduced considerably. The texture of the final product will inevitably vary as the different surfaces will phosphate differently.

The chemical nature of all the surfaces can also be considered and with the aid of XPS the presence of various phases and compounds on the surfaces can be confirmed.

### Chapter 9 Bibliography

- 1. Electronic source, The Henry Ford, www.hfmgv.org, [Access date: 11 November 2005]
- 2. Electronic source, Ferrari Sportscars, www.rsportscars.com, [Access date: 11 November 2005]
- 3. Davies, G.M. and Holliday, R.J. MBM, August, 1998, pp.22-27
- Electronic source, Volkswagen Production, hem.passagen.se, [Access date: 18 August 2006]
- Electronic source, Department of Biochemistry and Molecular Biophysics, www.biology.arizona.edu, University of Arizona, 2003, [Access date: 25 October 2006]
- 6. Groves, P.D., Electrochemistry, John Murray, London, 1974
- 7. Fichte, P., www.madsci.org, Faculty, Chemistry, Coker College, 2005, [Access date: 11 August 2006]
- 8. Noble Eco Systems Pvt Ltd, www.noblechlor.com, [Access date: 11 August 2006]
- 9. Lowenheim, F.A., Modern electroplating, John Wiley & Sons, New York, 1974
- 10. Béranger, Gérard, Henry, Guy and Sanz, Germain, The Book of Steel, Lavoisier,
- 11. Western Oregon University, www.wou.edu/las/physci/ch412/pourbaix.htm, [Access date: 13 July 2005]
- 12. Gellings, P.J. and Bouwmeester, H.J.M., Handbook of Solid State Electrochemistry, CRC, New York, 1997
- 13. Electronic source, Purdue University, www.chemed.chem.purdue.edu, [Access date: 11 August 2006]
- Crow, R., Principles and applications of electrochemistry, Blackie Academic & Professional, London, 1994
- 15. Ross, R.B., Handbook of metal treatments and testing, E.&F.N. Spon Ltd., London, 1977
- Gabe, D.R., Principles of Metal surface treatment and protection: Second Edition, Pergamon Press, Oxford, 1978

- Canning, W, The Canning Handbook on Electroplating: Twenty Second Edition, W. Canning Limited, Birmingham, 1978
- Stephan, H.O., Electrolytic Phosphating for In-Line Pretreatment of Wire, EuroWire Magazine, www.read-eurowire.com/techpics, 2006, [Access date: 11 August 2006]
- 19. Rausch, W., The Phosphating of Metals, Finishing Publications Ltd., 1990
- 20. Nittel,K.D., Choosing among phosphating processes, Wire & Cables Asia, www.read-wca.com/techartpics, 2006, [Access date: 11 August 2006]
- 21. Lorin, G., Phosphating of Metals, Finishing Publications Ltd., Middlesex, 1974
- 22. Smith, W.F., Principles of materials science and engineering Third edition, McGraw-Hill, New York, 1996
- Cullerne, J.P., The Penguin dictionary of Physics Third Edition, Penguin Books, London, 1977
- 24. Sears, F.W. and Salinger, G.L, Thermodynamics, Kinetic theory, and statistical thermodynamics third edition, Addison-Wesley publishing company, Reading Massachusetts, 1986
- Kittel, C., Introduction to Solid State Physics Sixth Edition, John Wiley & Sons, New York, 1986
- Terblans, J.J., Modellering en eksperimentele ondersoek van Sb-oppervlak segregasie in copper-enkelkristalle, Ph.D. Thesis, University of the Free State, South Africa, 2001
- 27. Jost, W., Diffusion in solids, liquids, gases, Academic Press Inc., New York, 1952
- Swart, H.C., Diffusiestudies van aluminium, Pt en cobalt in enkelkristal Si m.b.v. AES en XPS, M.Sc. Thesis, University of the Free State, 1986
- Shewmon, P.G., Diffusion in Solids, McGraw-Hill Book Company, New York, 1963
- B. Tuck, *Introduction to diffusion in semiconductors*, IEE Monograph Series 16, Peter Peregrinus Ltd., 1974
- Kittel, C., Introduction to Solid State Physics, Sixth Edition, John Wiley & Sons, New York, 1953
- 32. Binh, V.T., Surface Mobilities on Solid Materials: Fundamental Concepts and Applications, Series B: Physics, Vol. 86, Plenum, New York, 1981
- Fontana, M., Corrosion Engineering Third Edition, McGraw-Hill, New York, 1986

- 34. Wright, www.wrights-trainingsite.com, [Access date: 25 October 2006]
- 35. Matco Associates, www.matcoinc.com, [Access date: 11 August 2006]
- McIntyre, S.M., DeWitt-Dick, D.B. and Hofilena, D.J., Metallurgical Examination of Cooling Water Equipment Failures, www.awt.org, 2005, [Access date: 11 August 2006]
- 37. Adaniya, T., Sheet Metal Industries International, pp. 73-82, December 1978
- Alota, S., Azzerri, N., Bruno, R., Memmi, M. and Ramundo, S., 3<sup>rd</sup> International Congress on Surface Technology, Berlin, October 1985, pp. 367-373
- Barcelò, G., Sarret, M., Müller, C. and Pregonas, J., Electrochimica Acta, Volume 43, No. 1-2, pp. 13-20, 1998
- Zhou, Z. and O'Keefe, T.J., Surface and Coatings Technology Volume 96, 1997, p. 191-197
- 41. Park, H. and Szpunar, J.A. Corrosion Science, Vol. 40, Nr. 4/5, pp. 525-545, 1998
- 42. Sohi, M.H. and Jalali, M. Journal of Materials Processing Technology, Volume 138, pp. 63-66, 2003
- 43. Wolpers, M, Applied Surface Science, Volume 179, 2001, p.281-291
- 44. Rebeyrat, J.L., Grosseau-Poussard, J.L., Silvain, J.F., Panicaud, B. and Dinhut, J.F., Applied Surface Science, Volume 199, 2002, p. 11-21.
- 45. Weng, D., Jokiel, P., Uebleis, A. and Boehni, H., Surface and Coatings Technology, Volume 88, 1996, p.147-156
- 46. Maeda, S. Progress in Organic Coatings, Volume 28, 1996, pp.227-238
- 47. Redelinghuys, N, Laboratory electroplating of zinc part 1, MSSA internal memorandum, 1997
- 48. Wyville, R.D. and Cape, T.W., Conference on Corrosion: Coatings and Steels, Detroit, Michigan, 1986.
- 49. Levey, P.R., 40<sup>th</sup> MWSP Conference Proc., ISS, 1998
- Leidheiser, H. Jr, and Suzuki, I. in Atmospheric Corrosion, Ailor, W. H. (Ed.), pp. 615-629, John-Wiley & Sons, New York, 1982
- 51. Von Moltke, T., IMMRI Internal Report, 4 January 2006
- 52. Shindo, Y., Mittal Steel US Internal Report, 6 January 2006
- 53. Shindo, Y., Ispat Inland Inc. Research and development Internal report, 2006
- Corrosion Doctors, Dezincification, www.corrosion-doctors.org, [Access date: 11 October 2006]

- 55. Kuperman, M.N. and Troiani, H.E., Applied Surface Science, Volume 148, 1999, p. 56-63
- Payling, R. and Nelis, T., The spectroscopy net, http://www.glow-discharge.com, 1999 [Access date: 25 October 2006]
- Leco, GDS850A, www.leco.com/products/inorganic/gds/gds\_850a, [Access date: 10 March 2005 ]
- 58. Electronic source, Glow Discharge Optical Emission Spectroscopy (GD-OES) A Depth Profiling Technique, www.azom.com, [Access date: 10 March 2005]
- 59. Electronic source, en.wikipedia.org/wiki/Scanning\_electron\_microscope, [Access date: 14 October 2006]
- 60. Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Fiori, C. and Lifshin, E., Scanning Electron Microscopy and X-ray Microanalysis, Plenum, New York, 1981.
- Electronic Source, www-outreach.phy.cam.ac.uk/camphy/xraydiffraction/xraydiffraction7\_1.htm. [Access date: 17 March 2007]
- 62. Electronic source, en.wikipedia.org/wiki/Energy\_dispersive\_X-ray\_spectroscopy, [Access date: 14 October 2006]
- 63. Electronic source,

www-outreach.phy.cam.ac.uk/camphy/xraydiffraction/xraydiffraction7\_1.htm [Access date: 3 March 2007]

## Appendix A Stereo images

The following images can be viewed through a stereoscope.



Figure 9-1: White spot on the imported electrogalvanised surface



Figure 9-2: White spot on the 380 ppm nickel electrogalvanised MSSA surface



Figure 9-3: White spot on the 930 ppm nickel electrogalvanised MSSA surface