GALVANNEALING OF DUAL PHASE STEELS

GALVANNEALING OF DUAL PHASE STEELS

By

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ABSTRACT

The high strength and ductility of dual phase (DP) steels makes them ideal for use in the automotive industry. However, to be used in automotive exposed parts galvanizing (GI) and galvannealing (GA) processes are essential to provide corrosion protection. Galvannealing of dual phase steels has three major steps: i) heat treatment of the steel strip to obtain a suitable substrate microstructure and reduce iron oxides at the substrate surface ii) dipping of the steel strip in the zinc bath to obtain a soft and ductile metallic zinc coating on the steel and iii) heat treatment of the coated substrate in the galvannealing furnace after removal from the zinc bath to form an Fe-Zn intermetallic coating on the steel.

The major challenges in galvannealing of dual phase steels are selective oxidation of the alloying elements used in DP steels such as Mn which may result in poor galvannealed coatings, and galvannealing time and temperature that can affect the microstructure and formation kinetics of galvannealed coating. Both of these issues have been investigated in this research using three industrial steel substrates: EDDS (Extra Deep Drawing Steel), CMn (Carbon Manganese) and DP590 (Dual Phase).The concentration of carbon, manganese and some other alloying elements was different in these substrates.

The effect of process atmosphere oxygen partial pressure on oxidation was determined for all experimental steels at dew point (dp) -30° C using a N₂-5%H₂ process atmosphere. The steel chemistry and oxygen partial pressure of the process atmosphere

affected oxide thickness and morphology. For all alloys the lowest oxygen partial pressure process atmosphere resulted in the highest concentration and thickest oxide layer of Mn at the surface of dual phase steel (DP590). Also, the lowest segregation of Mn and thinnest oxide layer of Mn at the surface was obtained for the EDDS steel. The predominant oxide morphology observed at the surface of the DP590 steel comprised large oxide nodules or thick oxide films with irregular shaped/faceted nodules whereas the other two steels had an oxide morphology that generally comprised spherical cap shaped nodules at grain boundaries.

Four galvannealing times (10, 20, 30 and 40 s) and three galvannealing temperatures (480, 500 and 520 °C) were used to evaluate the effects of GA time/temperature on the microstructural evolution and formation kinetics of coating as a function of substrate Mn content. By increasing the galvannealing time and temperature, it was observed that for all steels, the Fe-Zn growth rate (alloying rate), thickness of gamma layer (Γ -Fe₃Zn₁₀) and iron content of the galvannealed coating were increased. It was concluded that galvannealing kinetics of DP and CMn steels at 480°C are faster than those of the EDDS steel. However, the galvannealing kinetics of DP and CMn steels at 500 and 520°C were relatively similar to each other and insignificantly different than those of EDDS. Accelerated galvannealing kinetics of higher Mn containing steels in this research, i.e. DP and CMn, could be ascribed to the presence of thicker oxide film/larger oxide particles at the surface that may have been reduced by aluminothermic reduction and accelerated inhibition layer breakdown. Considering the alloying rate and chemistry

of the GA coating, it was found that 500 and 520 °C are not suitable industrial galvannealing temperatures for experimental steels in this research.

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1 INTRODUCTION

Weight-saving design is one of the high priorities for the automotive industry. Some other considerations, such as greater comfort and safety, and at the same time, fuel economy and environmental constraints must be also considered. Among different materials to obtain these goals, dual phase (DP) steels are amongst the most promising candidates (Mintz 2001, Bode et al. 2004). Dual phase steels are characterized by a microstructure that includes a ferritic matrix and hard martensite islands that are distributed in this matrix. The ferritic matrix provides ductility and fracture resistance while the martensitic islands improve the strength of the material (Rashid 1981, Baudin et al. 2001, Tumuluru 2007). Due to their continuous yielding and low ratio of yield stress to ultimate tensile strength, it is possible to design car bodies with lower weights while maintaining passenger safety and lowering fuel consumption (Mintz 2001, Bode et al. 2004). However, because of the low corrosion resistance of DP steels, special importance is attached to protecting DP steels against corrosion. Continuous galvanizing is widely used for this purpose because it has distinct advantages over other galvanizing methods, such as relatively low cost and high-volume processing capacity (Chen et al. 2008, Baril and L'Esperance 1999).

One of the challenges associated with the continuous galvanizing of dual phase steels is the enrichment of the alloying elements necessary to control the microstructure, such as Mn, Cr and Si, at the surface of the substrate during continuous galvanizing (Bellhouse and McDermid 2010, Khondker et al. 2007, De Cooman 2006, Loison et al. 2001, Drillet et al. 2004, Parezanovic et al. 2004, Mahieu et al. 2004), whereby the oxides of these elements are formed at the surface or subsurface regions and cannot be reduced under standard industrial annealing conditions. Due to the presence of these oxides at the surface, the galvanizability and thus, the quality of the coating can be decreased (De Cooman 2006, Ebrill et al. 2001).

Galvannealing is another process that is performed on the galvanized coating to increase the spot weldability, corrosion resistance and paintability of the coating (Marder 2000, Baril and L'Esperance 1999, Kao et al. 2009). To obtain the desired coating properties, the coating microstructure and iron content of the coating must be carefully controlled. Several parameters can affect the microstructure of the galvannealed coatings, such as substrate chemistry, galvanizing bath composition (i.e. dissolved Al content) and temperature, immersion time and galvannealing temperature and time (Marder 2000, Baril and L'Esperance 1999, Hisamatsu 1989, Jordan et al. 1992, Jordan and Marder 1994).

Understanding the effect of process parameters in the galvannealing of DP steels will lead to better management of these processes and higher quality products. Unfortunately, fundamental knowledge concerning the effect of the above process parameters is scarce. For example, segregation of different alloying elements, particularly Mn, at the surface or formation of different oxides and their influences on the galvanneling process are not clearly understood. In the present research, the primary focus is on the effects of substrate Mn concentration, galvannealing time and galvannealing temperature on the microstructure and formation kinetics of galvannealed coatings. Also, the effect of some alloying elements such as Mn and Cr on the selective oxidation of the steels will be studied. Furthermore, the effect of selective oxidation on the galvannealing kinetics and microstructural development will be investigated.

2 LITERATURE REVIEW

2.1 **Dual Phase Steels**

2.1.1 Introduction

Dual phase (DP) steels are characterized by a microstructure which consists of hard martensitic islands (and sometimes small amounts of bainite and/or retained austenite) embedded in a ductile ferritic matrix. These steels usually have 0.05 to 0.2 wt.% C and about 1-2 wt.% Mn but selected DP alloying elements such as Si, Mo, Cr and Nb are added to DP steels to increase their strength and/or hardenability. It should be mentioned that carbon is the most important element which affects the mechanical behaviour of DP steels by controlling the volume fraction and strength of the martensite phase. It is noteworthy that any element that affects the phase diagram significantly (e.g. Mn) will also affect the volume fraction of martensite.

Manganese is a cost effective element in promoting hardenability, Silicon delays cementite formation and also increases the strength of the ferrite phase by solid solution strengthening. Chromium and molybdenum increase the hardenability and also suppress carbide formation. Niobium decreases the grain size and increases the ferrite strength by precipitation hardening (Mintz 2001, Tanaka et al. 1979, Crawley et al. 1981, Liewellyn and Hillis 1996, Kato et al. 1981).

Continuous yielding behaviour, low yield strength to tensile strength ratio, high initial work hardening rate and relatively high ductility are the interesting mechanical properties

of DP steels in comparison to conventional high strength low alloy steels or conventional ferrite-pearlite steels (Mintz 2001, Bode et al. 2004). As can be seen in Figure 1.1, dual phase steels, with tensile strength and total elongation in the range of 500-1000 MPa and 20-35%, respectively, exhibit a superior combination of strength and ductility in comparison to other types of steels. These interesting properties are attractive for the automotive industry because when using these steels, it is possible to design car bodies with lower weights, thereby improving fuel economy, without sacrificing passenger safety and comfort.

2.1.2 Manufacturing methods

In general, there are two different methods to produce dual phase steels: intercritical annealing of cold-rolled steels and accelerated cooling on the runout table following the hot-rolling process. In the intercritical annealing process, cold rolled steel is first heated to the intercritical temperature range (Rigsbee and Vanderarend 1979, Klaar 1990). In this temperature range, the austenite is formed at the pearlite colony boundaries or on grain boundary carbides and then, by quenching below the M_s temperature, at a cooling rate above that required to avoid ferrite, pearlite or bainite formation per the applicable continuous cooling transformation (CCT) diagram, the austenite will transform to martensite (Figure 2.2). In the case of hot-rolled dual phase steels, that cooling is controlled through the ferrite nose and then cooling continues such that further ferrite transformation and bainite formation are prevented such that martensite is formed. During accelerated cooling on the runout table, the austenite is transformed to martensite (Rigsbee and Vanderarend 1979, Waterschoot 2001). The production steps are shown in

Figure 2.3. It should be mentioned that in the present research work, cold worked steels have been used and for this reason, the main concentration will be on cold rolled steels.



Figure 2.1: Ultimate tensile strength and total elongation of dual phase steels

compared to other low alloy steels (Davies and Magee 1979).



Figure 2.2: Schematic diagram showing the production route of a cold-rolled dual

phase steels (Wolfgang et al. 2002).



Figure 2.3: Schematic diagram showing the production route of hot-rolled dual phase steels (Wolfgang et al. 2002).

2.1.3 Microstructure and transformation

The starting microstructure to produce dual phase steels from cold rolled sheet is a ferritic matrix with iron carbides at the grain boundaries and small regions of pearlite. By heating the steel above the lower critical temperature (Ac_1), austenite islands form preferentially at grain boundary cementite particles or pearlite colony boundaries. The intercritical temperature determines the volume fraction and carbon content of the austenite. Then, the steel is cooled rapidly at a rate such that austenite transforms to martensite and this critical cooling rate is determined by the alloy composition. In steels that are heated just above the lower critical temperature, the percentage of austenite is very low but its carbon content is high. Conversely, at higher intercritical temperatures, the volume fraction of austenite is higher, with lower carbon content and consequently, lower hardenability (Rashid 1981, Speich et al. 1981, Messien et al. 1981).

Concerning the partitioning of carbon and manganese in austenite, it has been shown that austenite will be enriched in both manganese and carbon if true equilibrium is achieved during intercritical annealing (Gilmour et al. 1972). However, some researchers have shown that due to the short annealing times employed industrially, only massive carbon redistribution occurs between ferrite and austenite because manganese diffuses much more slowly than interstitial carbon. This situation can be considered as paraequilibrium (Speich 1981). In practice, neither true nor paraequilibrium exists during intercritical annealing and there is an intermediate situation in which some enrichment of the austenite occurs near the ferrite/austenite interface. The thickness of this enriched layer depends on the annealing time (Wycliffe et al. 1981).

The transformation products after cooling to room temperature depend on the cooling rate and composition of the austenite. Silicon delays the formation of pearlite while manganese and carbon stabilize the austenite and lower the M_S temperature. At low cooling rates such that the noses of pearlite or bainite regions are cut, depends on the composition of the austenite, different proportions of austenite will transform to martensite, bainite, and ferrite, with some retained gamma.

Due to the volume change and shear strains that are created during the transformation of austenite to martensite, many new fresh and mobile dislocations are generated in the surrounding ferrite matrix. (Rashid 1981, Liewellyn and Hillis 1996, Gilmour et al. 1972, Rashid 1977, Davis 1979, Abramowitz and Moll 1970, Heheman 1970).

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2.1.4 Mechanical properties

In general, the mechanical properties of dual phase steels are significantly affected by steel carbon content, the intercritical annealing temperature and, consequently, by the amount of martensite in the microstructure. Figure 2.4 shows the effect of steel carbon content at different intercritical annealing temperatures on the amount of martensite for a 1.5wt.% Mn alloy; it can be seen that by increasing the carbon content of the steel (at a fixed intercritical temperature), or by increasing the intercritical temperature (at a fixed carbon content), the percentage of martensite is increased. However, it should be mentioned that the equilibrium carbon concentration of the austenite phase in hypoeutectoid alloys, which is formed at a fixed intercritical temperature, is independent of the steel carbon content.



Figure 2.4: Percent of martensite in 1.5%Mn dual phase steels as a function of steel carbon concentration and intercritical annealing temperature (Speich and Miller 1979).

Figure 2.5 shows the tensile true stress-true strain curves of a series of 1.5 wt.% Mn dual phase steels with different carbon contents and martensite percentages. It can be seen that dual phase steels show higher initial work hardening rates and greater tensile strengths in comparison to the 0C ferritic alloy but, due to the presence of martensite in the microstructure, the uniform elongation is decreased. Another point in this diagram is that by increasing the martensite percentage in the microstructure, the yield/tensile strength and initial work hardening rate are increased.



Figure 2.5: The true stress-strain curve of 1.5%Mn dual phase steels with different carbon concentrations and martensite contents intercritically annealed at 760°C compared to

ferrite (Speich and Miller 1979).



Figure 2.6: The yield strength and ultimate tensile strength of 1.5% Mn dual phase steels annealed at different temperatures as a function of percent martensite (Speich and Miller 1979).

Figure 2.6 to 2.8 shows the effect of martensite content on the strength, uniform and total elongation of the steels shown in Figure 2.4. In Figure 2.6, the yield and tensile strengths increase with the martensite percentage but, both the effect of carbon concentration of the steels and annealing temperatures should also be considered.



Figure 2.7: Variation of the uniform elongation of dual phase steels with percent martensite (1.5% Mn dual phase steels) (Speich and Miller 1979).



Figure 2.8: The total elongation of dual phase steels as a function of percent martensite (1.5%Mn dual phase steels) (Speich and Miller 1979).

In Figure 2.7, the effect of martensite content on uniform elongation is shown. It is clear that by increasing the martensite content in the microstructure, the uniform

elongation decreased for all annealing temperatures. The percentage of martensite shows a similar trend on the total elongation (Figure 2.8).

Another important characteristic of martensite islands is their distribution. For example, when the martensite islands are uniformly distributed and widely spaced in the microstructure, the ductility is higher. However continuous or discontinuous chains of martensite are detrimental for the ductility because these chains are easy crack propagations paths and thus the failure occurs rapidly. As the distribution of martensite islands is determined by the nucleation of austenite at cementite or pearlite in the starting microstructure, it is important in intercritically annealed dual phase steels that this microstructure be as uniform and fine as possible (Speich et al. 1981, Speich 1981, Speich and Miller 1981, Marder and Bramfit 1979).

-An introduction to IF Steel

As was explained before, owing to a great demand for fuel efficiency of automobiles, the steelmakers have focused on manufacturing steel sheets with high strength and good formability for automobile panels. After cold rolling, the steel strip is submitted to a recrystallization annealing in the austenitic region in order to obtain the required mechanical properties. By continuous annealing, the strong (111) texture that is requested for Extra Deep Drawing Steel (EDDS) can only be built with a steel grade free of interstitial atoms. That is the reason why interstitial free (IF) steels have been developped by the steelmakers (Pandey 2011). Also, interstitial free steel has largely replaced Al-killed steel in the manufacture of body panels in the automobile industry because it has good drawability, surface quality, and is relatively easily recycled. From the steel manufacturers viewpoint it is attractive because it can be processed in minutes rather than the tens of hours required for Al-killed steels, and robustness to varying processing conditions.

However, these high quality steel grades suffer several drawbacks such as a rather weak mechanical strength, a high reactivity in the grain boundaries during the galvannealing process leading to outburst structures and higher powdering or flaking during forming (Inagaki et al. 1995). For facing each problem, specific solutions have been proposed. A first group of improvements involves additive elements such as P additions to increase the mechanical strength without impairing too much the drawability (Bleck 1992), and B additions to lower the brittle-ductile transition temperature (Yasuhara 1994). Besides, it has been attempted to obtain soluble carbon after the recrystallization process, by higher annealing temperature and fast cooling rates associated either with Nb additions or with under-stoichiometric stabilizing additions (Satoh 1985). These procedures lead to bake hardening capabilities and better controlled reactivity. Unfortunately, each solution has its own weak points in terms of process control and productivity (annealing temperature, cooling rate, galvannealing temperature) (Arai et al. 1992) and in terms of loss of properties (grain boundary cohesion, drawability) (Yasuhara 1994).

In galvannealing process, steel strip is annealed in annealing furnace before dipping to recrystallize the steel microstructure. However, due to galvannealing times and temperatures which is used during the galvannealing of IF and EDDS steels, the

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microstructure of the recrystallized steel will be affected. Thus, controlling the microstructure of steel substrates during the galvannealing process is so important. In other words, after galvannealing process, both the substrate and coating should have high quality properties and the whole composite (galvannealed strip) should have reasonable properties.

2.2 Continuous Hot- dip Galvanizing

Zinc coatings are widely used to improve the corrosion resistance of steels by a combination of barrier and galvanic protection. There are different methods that can be used to produce zinc coatings including hot-dip galvanizing, thermal spraying and electrodeposition. Amongst these methods, continuous hot-dip galvanizing is used for coiled products such as sheets, wires and tube because this process is economical and high tonnages of steels can be coated by this method (Mintz 2001).

In continuous hot-dip galvanizing, in general, prior to the immersion in the zinc bath, the steel sheet is first cleaned using mechanical and chemical methods to remove organic contaminants, loose oxides and other surface contaminants. After cleaning, the steel sheet is sent to an atmosphere controlled annealing furnace in which iron oxides at the surface are reduced and the desired mechanical properties and microstructure are obtained after passing through the cooling section. The sheet then enters the zinc bath. After hot-dipping, in which the steel sheet reacts with the liquid zinc in the zinc bath, the sheet is withdrawn, cooled and sometimes subsequently heat-treated (galvannealed). Several steps of this process have been shown in Figure 2.9.



Figure 2.9: Schematic of a typical continuous hot-dip galvanizing line (Marder 2000).

2.2.1 The Zn (Al, Fe) bath and Fe-Al interfacial (inhibition) layer formation

It is common to add small amounts of Al to the continuous galvanizing zinc bath to improve the reflectivity of the coating, reduce the oxidation of the zinc bath and suppressing the formation of Fe-Zn intermetallics to produce a ductile, more corrosion resistant and adhesive coating. Generally, 0.1 to 0.3 wt.% Al is added to the zinc bath and it has been shown that for the concentrations as low as 0.10 wt.% Al and more, a thin layer of Fe-Al is formed and inhibits the formation of Fe-Zn intermetallics (Marder 2000, Chen et al. 2008, Baril and L'Esperance 1999, Toussaint 1998, Giorgi and Guillot 2004, Lin et al. 1995). The Fe-Al reaction has a much higher driving force than the Fe-Zn reaction and for this reason, this reaction dominates in Fe-Al-Zn system even for low aluminum contents. Figure 2.10 shows the Zn-rich corner of the Zn-Al-Fe phase diagram at 460 °C. Another factor, that can affect the Fe solubility, is the temperature of the zinc bath; increasing the bath temperature will increase the Fe solubility (McDermid et al. 2007, McDermid et al. 2004).



Figure 2.10: Zn-rich corner of the Zn-Fe-Al system; L is liquid, δ (delta) is FeZn₁₀ and ζ (zeta) is FeZn₁₃ (McDermid et al. 2007).

Due to the limited solubility of Al and Fe in liquid Zn, as shown by the Zn rich corner of the Zn-Al-Fe phase diagram in Figure 2.10, intermetallic phases will precipitate from the bath forming particles commonly referred to "dross". Fe₂Al₅Zn_x floats on top of the surface of the bath and can easily be removed from the bath by skimming the surface. At lower bath Al contents δ -FeZn₁₀ (delta) or ζ -FeZn₁₃ (zeta) will precipitate from the bath. These intermetallics have a higher density than liquid Zn and sink to the bottom of the bath and are more difficult to remove. Oxidation of bath metals (ZnO and Al₂O₃) also contributes to dross formation in the bath (Marder 2000).

Generally, increasing the Al content or decreasing the bath temperature will increases the stability of the Fe-Al interfacial layer (Marder 2000, Chen et al. 2008, Baril and L'Esperance 1999, Toussaint et al. 1998, Giorgi and Guillot 2004, Lin et al. 1995, Tang 1998). When the bath contains more than 0.15wt%Al a continuous Fe-Al interfacial layer forms. It is worthy of note here that there are some disagreement and

inconsistencies in the literature concerning the composition of the interfacial layer. Many authors have found that the interfacial layer is composed of a Zn-bearing Fe₂Al₅ (often referred to as Fe₂Al₅Zn_x) (Baril and L'Esperance 1999, Lin et al. 1995, Guttmann 1994, Harvey and. Mercer 1973), and the other authors have identified that the initial, very short time layer contained some FeAl₃ but that the longer time layer was solely Fe₂Al₅Zn_X (Chen et al. 2008, McDevitt et al. 1977, Morimoto et al. 1977, Perrot 1992). Generally, it has been found that the Al-rich interfacial layer has a thickness of about 250 nm and is composed of two sublayers (Figure 2.11). The layer in contact with the substrate (lower layer) is a compact layer with very small, equiaxed, closed packed crystals, with a diameter of around 60 nm (Figure 2.12). There is an orientation relationship between the substrate and this layer which is reported to be $(311)_{Fe2Al5} \parallel (110)_{\alpha}$ or $(221)_{Fe2Al5} \parallel (110)_{\alpha}$ (Guttmann 1994). Another sublayer (upper layer) has coarser, pancake shaped crystals, approximately 300-600 nm in diameter and approximately 200 nm in thickness (Figure 2.12). This layer has random crystalline orientations and morphologies and the grain boundaries are of high angle boundary type (Chen et al. 2008, Baril and L'Esperance 1999).



Figure 2.11: Two layers of inhibition layer (Baril and L'Esperance 1999).



500 nm



500 nm

Figure 2.12: Two types of morphology of the inhibition layer (a) equiaxed (b) coarse granular (Baril and L'Esperance 1999).

The steps in inhibition layer formation for an IF steel galvanized in a 0.2 wt. % Al bath were explained by Chen et al. (2008) and are shown in Figure 2.13. As was discussed previously when the steel substrate is immersed in the Zn bath, there is iron dissolution from the steel. This is followed by nucleation and growth of the metastable FeAl₃ phase which forms a compact layer of fine crystals on the steel surface. Further dissolution of the steel substrate is prevented after formation of this layer. However, iron continues to migrate towards the Zn bath by diffusion through the inhibition layer. Also,

Zn and Al diffuse towards the steel substrate. Then the metastable FeAl_3 begins to transform to $\text{Fe}_2\text{Al}_5\text{Zn}_x$:

$$FeAl_3 + 2Al_{bath} + Fe_{subs} + x Zn_{bath} \rightarrow Fe_2Al_5Zn_x$$
(2.1)

This reaction is followed by the growth of an upper, coarser layer of iron. The final inhibition layer morphology has a two layer structure with a layer of fine and compact $Fe_2Al_5Zn_x$ crystals which is preferentially oriented adjacent to the steel substrate and a layer of coarser randomly oriented $Fe_2Al_5Zn_x$ crystals on top of the fine layer. It should be mentioned that nucleation of Fe-Al phases has not been captured experimentally because these reactions happen very quickly. A continuous Fe-Al layer is formed at the steel/coating interface within two seconds (dipping + solidification time) (Chen et al. 2008).

Due to the presence of considerable concentration of zinc in the inhibition layer, the chemical formula of the inhibition layer is considered as $Fe_2Al_5Zn_x$ rather than Fe_2Al_5 (Guttmann 1994, Baril and L'Esperance 1999, Marder 2000, Dionne et al. 2002).



Figure 2.13: Steps in inhibition layer formation on a galvanized IF steel in a 0.2 % Al bath (Chen et al. 2008).

2.2.2 Growth kinetics

Power-law growth equation, Y=Ktⁿ, was used to estimate the growth rate of each Fe-Zn intermetallic compound. By applying a logarithmic function in either side of the equation, the following relation is obtained:

$$Y = \log K + n \log(t) \tag{2.2}$$

Using this equation, a plot of the log value of the total alloy layer thickness (Y) as a function the log value of immersion time in the bath (t) can be fitted to the data to determine a line; the slope of this line is defined as 'n', the growth rate time constant
value. The growth rate time constant value is an indication of the type of kinetics controlling the growth. An n value of 0.5 is indicative of parabolic diffusion-controlled growth, while an n value of 1 is representative of linear kinetics in which growth is interface controlled (Jordan and Marder 1997).

For example, in a 0wt% Al bath, the n value was 0.33, indicative of grain boundary diffusion during the coarsening of the gamma layer grains. The gamma phase showed an n value of 0.25 which is indicative of grain boundary growth kinetics of diffusion along grain boundaries of growing grains. Values of n, for delta layer growth, were reported in the range of 0.49 to 0.65. Zeta phase n values were between 0.16 and 0.36. Limited Zn transport along the columnar boundaries of the zeta phase would be responsible for the 0.33 value of n (Jordan and Marder 1997).

2.2.3 Selective oxidation

2.2.3.1 Gas-metal reactions in the annealing furnace

As it was explained previously, prior to the zinc immersion process, the steel sheet will pass through a controlled atmosphere annealing furnace such that iron oxides are reduced under the N₂-H₂ reactive atmosphere. However, it should be mentioned that although this atmosphere is able to reduce iron oxides, but it is oxidizing for some of the alloying elements commonly employed in DP steels such as Mn, Cr, Al and Si. In fact, iron oxides present at the surface of the steel sheet should be fully reduced during the annealing process (Khondker et al. 2007, De Cooman 2006, Loison 2001, Drillet 2004, Parezanovic 2004, Mahieu 2004). Oxygen partial pressure should be controlled in the

furnace and it is a strong function of temperature, therefore the variables of H_2 content and partial pressure of water vapour (i.e. dew point (dp)) are controlled.

The dew point temperature, T_{dp} , is the temperature at which the following equation is in equilibrium:

$$H_2O(l) \Leftrightarrow H_2O(g) \tag{2.3}$$

at equilibrium, $\Delta G=0$ and thus:

$$\Delta G^{\circ} = -RT_{dp} \ln K_{1} = -RT_{dp} \ln \left[\frac{p_{H_{2}O(g)}}{a_{H_{2}O(l)}}\right] \text{ and } \Delta G^{\circ} = \Delta G_{f, H_{2}O(g)} - \Delta G_{f, H_{2}O(l)}$$
(2.4)

Where ΔG° is the standard Gibbs free energy change for the reaction, R is the universal gas constant and K₁ is the equilibrium constant for the reaction. It should be mentioned that $a_{H_2O(l)} = 1$ because H₂O(l) is assumed to be a pure condensed species and H₂O(g) is assumed to be an ideal gas. Thus:

$$\Delta G^{\circ} = -RT_{dp} \ln K_1 = -RT_{dp} \ln p_{H_2O(g)}$$
(2.5)

Since the hydrogen content of the process atmosphere is fixed, the oxygen partial pressure is determined at the annealing temperature (T) from the following reaction:

$$H_2(g) + 1/2O_2(g) \Leftrightarrow H_2O(g)$$
(2.6)

at equilibrium: $\Delta G=0$ then: $\Delta G^{\circ} = -RT \ln K_2 = -RT \ln \ln \left[\frac{p_{H_2O(g)}}{p_{H_2}(p_{O_2})^{0.5}} \right]$ (2.7)

The thermodynamic stability of the oxides of iron and the alloying elements with respect to oxygen partial pressure can be determined using:

$$(x/y)M_xO_y + 1/2O_2 \Leftrightarrow (1/y)M_xO_y$$
(2.8)

at equilibrium: $\Delta G^{\circ} = -RT \ln [\frac{a_{M_x O_y}^{1/y}}{a_M^{x/y}(p_{O_2})^{0.5}}]$ and $M_x O_y$ is assumed to be a

pure condensed species with an activity 1 therefore:

$$\Delta G^{\circ} = -RT \ln K_3 = -RT \ln \left[\frac{1}{a_M^{x/y}(p_{O_2})^{0.5}}\right]$$
(2.9)

Using the above equation, it is possible to determine the stable/unstable regions for the oxides versus the applicable metallic species. The thermodynamic stability of the oxides of Fe, Mn, Si and Al is shown in Figure 2.14. An activity of 1 was assumed for all metal species in this diagram.

The experimental annealing atmosphere pO_2 as a function of temperature is shown in Figure 2.15. For the +5 °C dp and -30 °C dp atmospheres the H₂ content of the atmosphere is 5% and for the -50 °C dp and -53 °C dp the H₂ content is 20%. Increasing the H₂ content of the process atmosphere decreases the oxygen partial pressure (equation 2.7). The lower the dew point the lower the oxygen partial pressure. The important point in here is that in the temperature range of 465 °C to 900 °C all experimental annealing atmospheres are predicted to reduce iron oxides but will be oxidizing for the alloying elements, when using an activity of 1 for all metal species.



Figure 2.14: Thermodynamic stability of oxides with respect to annealing temperature



and oxygen partial pressure (Bellhouse 2010).

Figure 2.15: The oxygen partial pressure of the experimental process atmospheres as a function of annealing temperature. The hydrogen content was 5 volume % for the +5 °C dp and -30 °C dp process atmospheres and 20 volume % for the -50 °C dp and -53 °C dp process atmospheres (Bellhouse 2010).

According to Huin (Huin 2005), the following formulae which were adjusted using experimental data provided by the Thermodata (Thermodata 2005) can be used to calculate the saturated pressure of water vapour in atm as a function of dew point (dp) in Celsius:

$$\log_{10} (H_2O) = [9.8dp/(273.8+dp)] - 2.22 \text{ if } dp \le 0$$
 (2.10)

$$\log_{10} (H_2O) = [7.58 dp/(240 + dp)] - 2.2 \text{ if } dp > 0$$
 (2.11)

At high temperatures:

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$$
 (2.12)

Then the partial pressure of oxygen in atm is (Rist et al. 1974):

$$\log_{10}^{p_{O_2}} = 6.00 - 26176/T + 2\log_{10}[p_{H_2O(g)} / p_{H_2}] \text{ (T in Kelvin)}$$
(2.13)

And the concentration of dissolved oxygen at the surface in ppm is given by (Swisher and Turkdogan 1967):

$$\log_{10}^{C_{surf}} = [-3690/T] + \log_{10}[p_{H_2O(g)}/p_{H_2}]$$
(2.14)

2.2.3.2 Transition from internal to external oxidation

Generally, there are two types of selective oxidation: internal and external. When the inward diffusion of oxygen dominates, oxygen diffuses into the subsurface regions and meets the atoms of the alloying elements in those regions and thus, oxide particles will be formed. This process is referred to as internal oxidation. It should be mentioned that some criteria must be satisfied to have internal oxidation: 1) for an alloy A-X, where X is the solute metal, the Gibbs energy of formation of the oxide must be more negative than that of the most stable oxide formed by the matrix, 2) the solubility and diffusivity of

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oxygen in the matrix must be sufficient for the activity of the dissolved oxygen to be high enough for the Gibbs energy of the oxidation reaction to be negative,3) the concentration of the solute in the matrix must be such that solute does not exceed the critical concentration which results in the transition from internal to external oxidation and 4)there must not be any surface film to prevent the dissolution and diffusion of oxygen into the surface (Birks et al. 2006, Rapp 1965).

In external oxidation, the outward diffusion of any reactive element atoms dominates and therefore, oxygen reacts with them at the surface and oxides are formed at the surface (Figure 2.16) (De Cooman 2006, Marder and Bramfit 1979, Dieter 1976, Gladman 1997). The oxidation mode is a function of temperature, partial pressure of oxygen and the concentration of the oxidizing alloying elements (Khondker et al. 2007, De Cooman 2006, Loison et al. 2001, Drillet et al. 2004, Parezanovic and Spiegel 2004, Mahieu et al. 2004, Ebrill et al 2001, Kao et al. 2009, Rao and Sachdev 1981, Speich and Miller 1979, Bag et al. 1999).



Figure 2.16: Mechanism of selective oxidation in an atmosphere at low dew point (top) and high dew point (below) which causes external and internal oxidation, respectively.
Me_{tot} and Me_{ss} are the total content of the alloying element and the content in the solid solution, respectively (De Cooman 2006).

2.2.3.3 Wagner's model

Wagner (Wagner 1959) has developed a criterion for the transition between internal and external oxidation for a binary alloy single crystals. The following are the assumptions made in Wagner's theory:

1. The oxide scale is dense, non-porous and well adhered to the metal surface.

2. Solubility of oxygen in the metal is limited.

3. There are no space charge effects across the oxide, at the metal/oxide and oxide/gas interface.

4. At each place in the scale as well as at the interfaces local thermodynamic equilibrium is established.

The basic assumption of Wagner's theory is that lattice diffusion of cations and/or anions associated with the transport of electrons through the dense scale are rate determining in the overall oxidation reaction.

For a single crystal binary system, when the bulk molar fraction of the oxidizing element X is more than a critical value ($N_{X,crit}$), the internal to external transition happens:

$$N_{crit}^{X} = \left(\frac{g^{*}V_{m}\pi D_{O}N_{O}}{2V_{XO_{0}}\upsilon D_{X}}\right)^{1/2}$$
(2.15)

where N_0 is the molar fraction of dissolved oxygen at the surface (equation 2.14), V_m is the alloy molar volume, V_{XO_v} is the molar volume of oxide XO_v and g* is the critical volume fraction of oxides which blocks all inward oxygen diffusion (Wagner 1959). According to Rapp (Rapp 1965), g* is equal to 0.3. Also, in this model, the solubility of

is negligible. D_O is the diffusion coefficient for oxygen where $D_O = D'_O \exp(-Q_O/RT)$ and D_B is the diffusion coefficient of the alloying element where $D_B = D'_O \exp(-Q_B/RT)$.

As was mentioned above Wagner's equation assumes a binary single crystal geometry. Furthermore, the effects of grain boundaries, dislocations and interactions between different alloying elements have not been considered. In reality, especially in the case of TRIP, TWIP and DP steels, the effects of grain boundaries, multiple phases during annealing or interactions between alloying elements will affect the value of N_{crit}^{X}

[De Cooman 2006, Rapp 1965, Liu et al. 2009]. Considering the contribution of different alloying elements in real steels, the Wagner model can be written as (Grabke et al. 1995):

$$\sum N_X (V_{XO_v} \nu D_X)^{1/2} = \left(\frac{g^* V_m \pi D_O N_O}{2}\right)^{1/2}$$
(2.16)

The left side of this equation is the sum of the outward diffusion of oxidizing alloying elements and the right side the inward diffusion of oxygen. When the left side is larger, external oxidation occurs and when the right side is larger, the mode of selective oxidation is internal.

Also, it has been shown that N_{crit}^{X} can be calculated for grain boundary oxidation by halving the activation energy resulting in the modified Wagner model for internal/external oxidation transitions at grain boundaries (Mataigne et al. 1992):

$$N_{crit,gb}^{X} = \left(\frac{g^{*}V_{m}\pi N_{O}D_{O}'\exp(-Q/2RT)}{2V_{XO_{O}}\nu D_{X}'\exp(-Q/2RT)}\right)^{1/2}$$
(2.17)

Other factors that can affect the selective oxidation of alloying elements phenomenon are sheet thickness and surface conditions. The thinner the sheet, the more rapidly it warms up for a given energy input and the temperature level corresponding to the beginning of oxide formation will thus be reached earlier for a thin sheet than for a thick one. Also, it has been observed that polished surfaces (low roughness) are oxidized later than pickled samples (high roughness). In fact, roughness will promote the heat transfer from furnace to steel sheet and thus the sheet heating; another point is that roughness will increase the surface area for oxidation (Raymond et al. 2004). Besides, rougher surfaces can have high dislocation densities which enhance diffusion and, therefore, oxidation rate.

2.2.3.4 Effect of selective oxidation on reactive wetting

Selective oxidation of the alloying elements at the steel surface can result in poor reactive wetting during galvanizing. These oxide can prevent Al in the zinc bath from reacting with the metallic iron on the steel substrate to form the desired Fe-Al interfacial layer, causing bare spot defects in the galvanized coating (Figure 2.17) and overall poor coating quality (Khondker et al. 2007, De Cooman 2006, Drillet et al. 2004, Tanaka et al. 1974, Liu et al. 2009, Bellhouse and McDermid 2010, Yasui et al. 2007, Swaminathan and Spiegel 2007, Mahieu et al. 2002, Mahieu et al 2000, Maki et al 2003).

In particular, Si containing oxides are on the steel surface cause wettability problems, due to the full coverage of the surface with Mn₂SiO₄ and SiO₂ (Drillet et al. 2004, Mahieu et al. 2002, Mahieu et al 2000, Maki et al 2003). However, it has been shown that the reactive wetting of Si-containing steels can be improved by increasing the oxygen partial pressure of the annealing atmosphere to -26°C dew point versus -35°C dew point process atmosphere. In this case, the poor wettability at -35°C was attributed to full coverage of the steel surface by amorphous SiO₂ and the improved wetting observed at -26°C was ascribed to the sufficient density of holes in the oxide layer (Mahieu et al. 2000). Also, it is possible to replace, partially or completely, Si with Al or P to improve the wettability of these steels. By replacing Si with Al, the surface was partially covered

with $MnAl_2O_4$ and the presence of this oxide does not result in poor galvanizability (Mahieu et al. 2002, Mahieu et al. 2004, Bellhouse et al. 2007).

It has also been shown that oxide morphology is an important factor which is critical for the promotion of reactive wetting. For example, it has been shown that full coverage of the steel surface with continuous nonporous films results in poor reactive wetting (Drillet et al. 2004, Mahieu et al. 2004, Bellhouse and McDermid 2011). For example, it has been observed that when the presence of $MnAl_2O_4$ and MnO_2 is limited at the surface, in the TRIP steels, sufficient wetting will happen (Mahieu et al. 2004, Bellhouse and McDermid 2011). Other researchers have shown that good reactive wetting can happen when widely spaced, large oxides are present at the surface because Fe₂Al₅ can form between these particles; in the case of having closely spaced oxide nodules, which impede the formation of Fe₂Al₅, the wetting was poor (Bellhouse and McDermid 2011).

Cracking of oxide particles, that allows liquid infiltration of bath metal between the oxide and substrate, was another factor which contributed to the good reactive wetting. Cracking and spalling of the oxide from the surface likely occurred as a result of the difference in coefficients of thermal expansion between oxide (MnO) and substrate, resulting in large stresses being imposed on the oxide upon cooling (Bellhouse and McDermid 2010, Bellhouse and McDermid 2011).

Furthermore, the size and thickness of the oxide particles or layers can also affect the wetting process (De Cooman 2006, Bellhouse and McDermid 2010, Bellhouse and McDermid 2011). When oxide particles are fine, the dissolution of the surrounding steel can cause their removal from the surface or their incorporation into the inhibition layer (De Cooman 2006). For example, in TiNb IF steels, small oxide particles, typically 100 nm in size, containing both Mn and P have been observed to be embedded in the inhibition layer and their presence has not prevented the formation of the homogenous inhibition layer and usually no coating defects have been seen on the galvanized samples

(De Cooman 2006).



Figure 2.17: Effect of external oxidation on the formation of the coating (De Cooman 2006).

2.2.3.5 Aluminothermic reduction

Other routes have been proposed to promote reactive wetting on the surfaces of advanced steel. For example, in the case of manganese oxide (MnO) it has been shown that reduction of MnO in contact with a 0.20wt% Al bath at 460° C – typical of continuous galvanizing – is thermodynamically possible via the following reaction:

$$3MnO + 2[Al] \rightarrow Al_2O_3 + 3[Mn]$$
(2.18)

By reduction of MnO, even steels with 1.5wt% Mn, can be properly galvanized in spite of the selective oxidation of Mn (Khondker et al. 2007). Even in the case of having 5.1wt% of Mn in the steel substrate, it has been shown that the reactive wetting can be

suitable because of the aluminothermic reaction (Meguerian and McDermid 2007, Alibeigi et al. 2011).

More recently, the reduction of manganese silicates ($xMnO\cdot SiO2$) by the dissolved Al in the Zn bath to form $MnAl_2O_4$ has been proposed after dipping a martensitic steel having 0.15 wt. % C, 2.0 wt. % Mn and 0.33 wt. % Si in Zn baths with 0.13 and 0.2 wt. % Al at 460 °C (Gong et al. 2009).

In another research, the validity of aluminothermic reduction mechanism has been proved (Kavitha and McDermid 2011). In this research, thick (410 nm), compact and stoichiometric MnO films were grown on a 5.1 wt.% Mn steel by annealing at 770°C for 600 s using a conventional -30 dew point $95\%N_2$ - $5\%H_2$ process atmosphere. The film were then reacted with a 0.2wt.% dissolved Al bath at 460°C for several immersion times. It was observed that significant reductions of MnO film thickness had taken place for all immersion times and the thickness was decreased by approximately 90 nm for a 4 sec. TEM-EDX point analysis across the MnO-Zn interface showed a partially decomposed Mn metal-MnO layer with decreasing oxygen content towards the MnO-Zn interface. An enriched layer was also identified at the MnO-Zn interface by TEM-EELS and it was found to be Al₂O₃.

To date, there is no reliable and accurate method to predict the reactive wetting behaviour for a given alloy and different processing parameters because of having a large number of variables in the galvanizing process such as steel chemistry, annealing time/temperature and oxygen partial pressure of the process atmosphere. All of these variables can affect the chemistry thickness and morphology of the oxides and this can affect the reactive wetting behaviour.

2.2.4 Fe-Al interfacial layer (inhibition layer) breakdown

It should be mentioned that the inhibiting effect of the Fe₂Al₅Zn_x layer is transient, delaying the formation of Fe-Zn intermetallics rather than suppressing them completely and finally, Fe-Zn outbursts will form. Even thick layers of Fe₂Al₅ will be destroyed after long immersion times in high aluminum baths. There are several parameters that affect inhibition layer breakdown such as the Al concentration in the bath, grain size of the substrate, bath temperature, strip entry temperature, agitation and surface roughness (Dionne 2006, Marder 2000, Baril and L'Esperance 1999, Jordan and Marder 1997, Lin et al. 1995, Proskurkin and Gorbunov 1975).

Several mechanisms have been proposed for the breakdown of the inhibition layer. For example it has shown that the first step of the breakdown of the inhibition layer is the enrichment of the inhibition layer with Zn or Al. As the second step, enriched Fe_2Al_5 transforms to delta crystals (Guttmann 1994).

Some researchers have used thermodynamic equilibrium to explain the breakdown of the $Fe_2Al_5Zn_x$ layer. When some regions of the overlay/substrate interface have small amounts of Al, Zn atoms attack the substrate through the ferrite grain boundaries which can be considered as short circuit paths for Zn diffusion. When the Zn reaches the substrate, after reacting and saturating the Fe, Fe-Zn intermetallic phases at the Fe₂Al₅ inhibition layer/substrate interface nucleate and mechanically remove the $Fe_2Al_5Zn_x$ layer into the surrounding bath (Marder 2000).

Other researchers have claimed that inhibition layer breakdown does not occur via the outburst mechanism and the main cause of inhibition breakdown is the dissolution of the inhibition layer into the substrate and possibly consumption by the gamma phase. This mechanism can be explained by considering the Al concentration gradient between the substrate and the inhibition layer. It was observed that the thickness of the inhibition layer decreased with time and also, the concentration of Al in the substrate, near the coating/substrate interface increased when the inhibition layer disappeared. These conditions and observations support a dissolution mechanism in which the inhibition layer is dissolved by Al diffusing from this layer to the substrate.

In fact, Al diffuses into the substrate as the chemical potential of Al in the substrate (Fe) is lower than the chemical potential of Al in Fe_2Al_5 until the Al concentration of the Fe exceeds 17wt%. But, comparing the thickness and volume of the substrate (Fe) to that of Fe_2Al_5 layer, there is no enough Al available for Fe to establish the equilibrium concentration of Al. Thus, there is always an Al concentration gradient between the substrate and the inhibition layer so that Al diffuses from the inhibition layer towards the substrate and the dissolution of the inhibition layer continues. Besides, it has been observed that Al concentration at Fe substrate grain boundaries was higher than the grain interior and it indicates the grain boundary diffusion which is significantly faster than bulk diffusion, is working for Al diffusion into the Fe (Abe and Knbara 1983).

In general, the mechanisms of inhibition layer breakdown can be summarized as:

1-One of the elements, Al or Zn, will enrich the inhibition layer and when the solid solubility is reached, the saturated inhibition layer transforms to other phases. It should be mentioned that using this mechanism, it is not possible to justify the mechanical breakdown of the inhibition layer (Marder 2000, Guttmann 1994).

2-Due to the depletion of Al at the vicinity of the inhibition layer, this layer is dissolved and other Fe-Zn phases are formed. Also, it has been shown (Figure 2.18) that because of the precipitation of Fe_2Al_5 at the grain boundaries of the substrate, a greater depletion of Al occurs at the grain boundaries than inside the grains (Hisamatsu 1989, Lin et al. 1995, McDevitt et al. 1998, Abe and Knbara 1983, Yamagushi and Hisamatsu 1979, Urednicek et a. 1987). Reduction of the surface oxides by the bath Al could also be considered as another factor for Al depletion in the zinc bath (Khondker et al. 2007).



Figure 2.18: Schematic diagram of the formation of Fe-Zn phase growth at substrate grain boundaries (Hisamatsu 1989).

3- Zn atoms reach the substrate, after which, Fe-Zn intermetallics can form at the interface of the Fe₂Al₅/substrate. It has been proposed that Zn can diffuse through the inhibition layer using short circuit paths and destabilize the inhibition layer. In fact, Fe-Zn intermetallics nucleate at grain boundaries and form outbursts and then, continue to grow laterally. Finally, this process will mechanically destroy the inhibition layer into the surrounding bath (Figure 2.19) (Marder 2000, Baril and L'Esperance 1999, Guttmann 1994, Proskurkin, and Gorbunov 1975, Nishimoto et al. 1986).

It should be mentioned that in this mechanism, some factors such as curvature, width and reactivity of the grain boundaries should be considered. The short circuit paths through the inhibition layer would be the grain boundaries of the compact layer or interfaces between oxides and the compact layer and would coincide with the substrate grain boundaries. Oxide/ Fe₂Al₅ interface short circuits may also be preferentially located

at substrate grain boundaries (Figure 2.20) (Marder 2000, Guttmann 1994, Nishimoto et al. 1986). Another factor that can accelerate the diffusion of Zn is the presence of cracks that are produced by growth stresses between the inhibition layer and the substrate. At high temperatures, these stresses can be relieved by creep or sliding of the grain boundaries but at low temperatures, the relief of these stresses would be performed by fracture (Marder 2000).



Figure 2.19: Schematic diagram showing the Fe-Zn outburst growth behaviour

(Nishimoto et al. 1986).



Figure 2.20: Short circuit Zn diffusion path through Fe₂Al₅ (Toussaint et al. 1998).

2.3 Galvannealing

On a continuous galvanizing line, hot-dip galvanized sheet can be annealed immediately after coating to produce galvannealed (GA) coating with an average of 10 to 12wt.% iron in the coating. In general, this average of iron is indicative of a galvannealed microstructure that consists of a very thin brittle gamma layer, relatively thick delta layer and a very thin zeta layer. In galvannealing, due to the brittle nature of gamma layer and its low corrosion resistance, the thickness of this layer should be carefully controlled and restricted. Also, higher iron content than this optimal value will result in some problems during the forming process of galvannealed coatings such as powdering and flaking. The coating has been shown to have improved weldability, paintability and corrosion resistance in comparison with galvanized coatings. The variables involved in producing the desired galvannealed microstructure and properties include holding temperature and time. Variations in bath and substrate chemistries can also affect the final microstructure (Marder 2000, Jordan and Marder 1994, Hertveldt et al. 2000, Feliu and Perez-Revenga 2005, Lin et al. 1995).

2.3.1 Galvanneal coating microstructure

It has been shown that, in general, it is possible to consider three different industrially relevant microstructural classifications for galvannealed coatings (Figure 2.21) (Jordan and Marder 1994):

Type 0 – underalloyed coatings that contains an overlay containing metallic zinc phase (metallic zinc) with delta and zeta phases interspersed in it.

Type 1- optimum (fully) alloyed coatings with an overlay containing delta phase interspersed with a small amount of zeta phase and also a very thin layer of gamma phase at the coating-substrate interface (less than $1\mu m$).

Type 2- overalloyed coatings with an overlay containing a delta phase with some cracks perpendicular to the coating surface (due to the volume changes during phase transformations) and a top layer of zeta and also a relatively thick gamma layer (more than 1μ m).

The topography of galvannealed coatings is also important. Some researchers have found the existence of craters at the coating surface that result in significant fluctuations in coating thickness (Van der Heiden 1994, Jordan and Marder 1994, Coffin and Thompson 1994). The proposed mechanism for crater formation is that after the

outbursts form at the grain boundaries, the Fe-Zn phases will grow very rapidly towards the liquid such that liquid zinc remains between the crystals, allowing very rapid transport of iron from the substrate. Then, because of capillary effects between the Fe-Zn crystals, regions in which there is no alloy reaction are drained and craters are formed (Hisamatsu 1989).



Figure 2.21: Representative examples of (a) Type 0, (b) Type 1 and (c) Type 2 coating morphologies (Jordan and Marder 1994).

2.3.2 Kinetics of formation

The kinetics of galvannealed coating formation depends on galvannealing time and temperature and the bath and substrate chemistries. However, the time sequence has been proposed to be as follows (Figure 2.22):

t₀- an inhibition layer has been formed at the surface due to the reaction between the Al and Fe and presence of this layer will inhibit the formation of Fe-Zn intermetallic layers. The effectiveness of this layer depends on the Al content of the zinc bath, the temperature of the galvanizing bath and the time of immersion. By increasing the dissolved Al content of the zinc bath, the thickness and stability of the inhibition layer increases and interfacial layer breakdown delayed. In low dissolved Al baths (like GA baths), by increasing the bath temperature the Al uptake decreases and the inhibition layer breakdown accelerates since increasing the bath temperature results in higher diffusion of zinc into the inhibition layer and grain boundaries. In low Al zinc baths, inhibition layer breakdown happens at very short reaction times since the Al uptake decreases by decreasing the reaction time. (Marder 2000, Chen et al. 2008, Baril and L'Esperance 1999, Toussaint et al. 1998, Giorgi et al. 2004, Lin et al. 1995, Claus et al. 1995).

 t_1 - In this stage, the inhibition layer breaks down and due to the occurrence of the outbursts, initial nucleation of zeta phase takes place at the interface of coating/substrate. Substrate chemistry and galvannealing time and temperature will affect the rate of Zn diffusion through the inhibition layer and consequently, the rate of the breakdown is affected (Hertveldt et al. 2000, Feliu and Perez-Revenga 2005, Lin et al. 1995). This stage

will result in the production of Type 0 microstructure (Figure 2.21) (Jordan and Marder 1994).

 t_2 - By continuing the galvannealing process, the delta phase grows with a columnar pattern. Zeta phase nucleates due to oversaturation of iron in the liquid zinc phase (Van der Heiden 1994).

 t_3 - Due to Zn consumption by the formation of the Fe-Zn intermetallics, the liquid zinc phase is completely consumed and because of the growth of delta phase, the iron content of the coating is increased. Zeta phase is pushed to the surface by the delta phase and also gamma phase is formed at coating/substrate interface due to the oversaturation of iron in delta phase (Coffin and Thompson 1994, Claus et al. 1995). The microstructure can be considered as Type 1 in Figure 2.21 (Jordan and Marder 1994).

t₄- The delta phase continues to grow towards the surface and consumes the zeta phase. The gamma layer is present in the microstructure with a constant thickness (Coffin and Thompson 1994).

t₅- The delta phase reaches the coating/air interface and the gamma phase will continue to grow at the expense of delta phase/substrate. The solid state growth of the gamma layer can be ascribed to the increased amounts of iron present at the steel/coating interface (Goggins and Marder 1991). Cracks can appear in the microstructure. It is the Type 2 in Figure 2.21(Jordan and Marder 1994).

The point that should be mentioned about the above mechanism is the formation of delta (δ -FeZn₁₀) phase at 't₂'. Zeta phase (ζ -FeZn₁₃) because of having the lowest nucleation barrier as a result of the epitaxial growth of ζ -FeZn₁₃ on ferrite will form as the first layer in galvannealing (as outburst structure) and after that, delta phase will form at the root of zeta blocks due to the oversaturation of iron in zeta phase. There is, however, some discrepancy in the literature regarding the phases present in outbursts and the order in which they form. For example, Leprêtre et al. (1998) found delta containing outbursts with a thin gamma (Γ -Fe₃Zn₁₀) layer at the delta/steel interface. The lack of zeta phase in these outburst structures was likely due to the short times in which these reactions could take place. The delta phase grows at the expense of zeta phase (Guttmann 1994) and this reaction may have taken place prior to analysis.



Figure 2.22: Schematic of the phenomenological model of galvanneal morphology

development (Jordan and Marder 1994).

2.3.3 Factors affecting the formation kinetics of galvannealed coatings

As was mentioned before, there are some parameters that affect the morphology and kinetics of galvannealed coatings such as holding temperature, holding time, substrate chemistry and composition of the zinc bath (Marder 2000, Chen et al. 2008, Baril and L'Esperance 1999, Hertveldt et al. 2000, Feliu and Perez-Revenga 2005, Lin et al. 1995). In the case of the effects of galvannealing time and temperature , process maps for some grades of steel that show the transition between the different coating morphologies have been developed. For example in Ti-IF and DQSK steels (Figure 2.23) by changing the galvannealing time and temperature, when other parameters are constant, the morphology is changed. The effects of galvannealing time and temperature on the iron content of the galvannealed coating on these two grades are shown in Figure 2.24. As can be seen by increasing the galvannealing temperature, that increases the iron diffusion, the required time to obtain the same iron content is decreased (Jordan and Marder 1994).



Figure 2.23: Transition between different morphologies of the coating for DQSK steel (left) and IF steel (right) (Jordan and Marder 1994).





Figure 2.24: Effect of time and temperature on the galvannealing kinetics for DQSK steel (left) and IF steel (right) (Jordan and Marder 1994).

Another important factor, as was mentioned previously, is the composition of the bath and amongst the alloying elements which are present in the zinc bath, Al has a key role in determining the microstructure and kinetics of the coating. Ideally, for galvannealing, there should be no inhibition layer, partially or continuously, in the galvanized coating so that during the galvannealing process, Fe-Zn alloying is not impeded. At the same time, the Al content of the zinc bath should be sufficient to prevent the formation of bottom dross.

It has been proposed that the optimum Al content in the GA zinc bath for IF steels could be 0.135wt.% (De Cooman 2006, Tang 1998). In general, by increasing the Al content of the bath, the galvannealing kinetics slow down. This effect is obvious for DQSK steels (Figure 2.25). It has been shown that by increasing the Al content of the zinc bath, due to the increase in the thickness and stability of the inhibition layer, longer times are required to obtain the optimum galvannealing microstructure (Jordan and Marder 1994, Mercer 1992). Thus, the Al content of GA baths is adjusted to obtain an

inhibition layer that is sufficient to prevent the formation of Fe-Zn intermetallics during hot dipping but thin enough to permit the alloying reaction during galvannealing (Dionne 2006).

In the field of the effects of the substrate chemistry, there are some results in the literature. For example, it has been shown that when Ti is added to IF steels, alloying (formation of Fe-Zn intermetallics) will occur at about 70°C lower than a low carbon steel (both galvanized at 470°C, 0.13 wt.% Al) (Hisamatsu 1989). Also, it has been observed that Ti-stabilized steels are more reactive than Al killed steels at different galvannealing temperatures (Mercer 1992). To justify the results, the composition of the substrate should be considered. For example, in high strength interstitial free steels (HSLA), some elements such as P, Mn or Si are used to strengthen the steel and the presence of these elements leads to slow galvannealing kinetics, i.e. longer galvannealing times and higher temperatures are required to obtain the desired iron content (10wt% Fe) in the galvannealed coatings (Lin et al. 1995, Hertveldt 1997, Hertveldt 1998).

The operating mechanism by which the alloying elements in high strength IF steels, particularly P, decrease galvannealing kinetics is still under discussion. It has been suggested that P and C segregates to grain boundaries and thus, grain boundary diffusion of Zn is restricted which in turn, impedes the local reaction between Zn and Fe at these grain boundaries that nucleate outbursts (Lin et al. 1995, Guttmann 1995, Coffin and Thompson 1995, Mercer 1989, Jordan et al. 1997). It has also been proposed that P would segregate at the grain boundaries of the inhibition layer and thus, the Zn diffusion through this layer is limited (Guttmann 1994); consequently, outburst reactions are impeded. By

adding the Ti to the steel, the solute carbon is tied up and zinc diffusion down the boundaries is accelerated (Jordan and Marder 1997).



Figure 2.25: Effect of bath Al content on the galvannealing kinetics for DQSK steel (a) 0.10 wt.% and (b) 0.15wt.% (Jordan and Marder 1994).

Figure 2.26 shows the microstructural development of a galvannealed Tistabilized IF steel. It is obvious that by increasing the time and temperature of the galvannealing process, the alloying rate is increased and gamma layer becomes thicker. This increase in the alloying rate is ascribed to the increased rate of iron diffusion towards the coating by increasing the galvannealing temperature; Besides, more iron is provided for diffusion process by increasing the galvannealing time.



Figure 2.26: Morphology development of galvannealed Ti-stabilized IF steel galvannealed at: (a) through (e) 450°C for 1, 5, 10, 20, 60 s, respectively; (f) through (j) 500°C for 1, 5, 10, 20, 60 s; and (k) through (o) 550°C for 1, 5, 10, 20, 60 s (IL= interfacial layer (Jordan and Marder 1997).

The behaviour of P, in IF steels, in the presence of Mn is fascinating. It has been observed that during the annealing at low dew point (-30°C), external oxidation takes place and external Mn oxides are formed at the surface. Under these conditions, P remains at the grain boundaries of the substrate and thus, the grain boundaries, during the galvannealing, are not available for Zn diffusion and consequently, the galvannealing kinetics are slow. On the other hand, after annealing in a high dew point (+10°C), internal oxidation occurs and the amount of the external oxidation is small. At the subsurface regions of the substrate, Mn-O-P oxides are formed and it can be concluded that P is removed from the grain boundaries at the surface and subsurface regions. Under these conditions, the grain boundaries are clean and available for Zn diffusion, accelerating the galvannealing kinetics (Figure 2.27) (Lin et al. 1995).



Figure 2.27: Schematic of the surface and interface processes occurring during recrystallization annealing, dipping, and galvannealing (Lin et al. 1995).

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Some other researchers have shown that at galvannealing temperature of 540°C for 25 seconds, by increasing the concentration of Mn, Mo and Cr in the steel substrates, the iron content of the galvanneal coating changed and consequently, the galvannealing kinetics changed (Figure 2.28). It has been proposed that when the concentration of Cr in the steel substrate is more than 0.5wt.%, the galvanizability is deteriorated (Chang et al. 1998, Chang and Yoon 1998). Also, presence of Mo in the substrate was shown to be detrimental for alloying rate of the coating. The coatings on manganese containing carbon steels are completely alloyed with iron of 10.95 and 11.35wt.% and the effect of manganese was not considerable.



Figure 2.28: Galvannealing kinetics of different samples with different compositions

(Chang et al. 1998).

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Some other researchers have shown that presence of alloying elements in the substrate will retard the galvannealing kinetics. They have used four different steel substrates, i.e. EDDS, 1180 CP, 590TRIP and 1180 TRIP, with different concentrations of Mn and Si (Table 2.1) and have compared the galvannealing kinetics of these substrates. The cross sections of the galvannealed coatings show that in the case of having high concentrations of Mn and Si in the substrates, some pure zinc is present in the coatings after the galvannealing process (Figure 2.29), showing the retarded galvannealing kinetics of these coatings. The presence of oxide layers/particles have been considered as the main factor for decreasing the galvannealing kinetics of 1180TRIP or 590TRIP (Kim et al. 2009).

Steel	С	Mn	Si	Al	
EDDS	<0.01	0.15	0.01	< 0.05	
1180CP	0.05-0.3	2.7	0.2	< 0.05	
590TRIP	0.05-0.3	1.6	1.5	0.05	
1180TRIP	0.05-0.3	2.2	1.7	0.6	

Table 2.1: Chemical composition of the steel substrates.

It is noteworthy that there is some evidence from the industry that the galvannealing kinetics of dual phase steels, which contains considerable concentrations of alloying

elements, are faster than EDDS or CMn steels. Thus, it is obvious that there is a disagreement between the results of above researchers and the results of the industrial lines. For this reason, investigating of the effects of alloying elements (especially Mn in DP steels) on the galvannealing kinetics is a key factor to answer and justify this disagreement. In this project, the effects of steel substrate Mn concentration, galvannealing time and galvannealing temperature on galvannealing kinetics of galvannealing will be studied.



Figure 2.29: Cross sections of GA coatings on various steels (a)-(c) EDDS, (d)-(f)



3 RESEARCH OBJECTIVES

This study focused on two major areas: i) the selective oxidation of dual phase steels under industrial annealing conditions to determine the mode of oxidation and morphology of oxides and ii) galvannealing of steels at different galvannealing temperatures and times to study the coating microstructure and formation kinetics.

Selective oxidation of three DP steels with a variety of C and Mn contents was studied. The objectives were to study the effects of steel chemistry and annealing temperature on the selective oxidation of the steel surface. In particular, the mode of oxidation and morphological aspects of oxidation were studied. Furthermore, the effect of selective oxidation on galvannealing kinetics and microstructural development was investigated.

Galvannealing of three industrial steels were performed to study the effects of substrate Mn, galvannealing time and galvannealing temperature on the microstructural development and formation kinetics of the galvannealed coating.

4 EXPERIMENTAL METHODS

Experiments focused on two main areas of study: i) analysis of the selective oxidation of steel samples after annealing and prior to Zn immersion and ii) analysis of galvannealed samples.

4.1 Steel Chemistry and Sample Preparation

The chemical composition of the experimental steels is shown in Table 4.1. As seen in Table 4.1, three different industrial substrates were used in this research, i.e. EDDS (Extra Deep Drawing Steel), CMn (Carbon Manganese) and DP590 (Dual Phase). There were significant differences in the steel Mn and C contents (Table 4.1). Also, Mo and Cr contents in DP590 sample are higher than that of EDSS and CMn. EDDS is an ultra-low C alloy and it is chemically stabilized with elements such as titanium and niobium during production. Excellent formability characterize coated and uncoated sheet of this quality and thus, this steel is used for deep drawing applications. CMn is low carbon steel which contains 0.1-0.25% carbon and 1-2% manganese and is used for steel pipe and wire mesh. DP590 is a dual phase steel and it is used for structural rails, bumper applications and door reinforcement.

Table 4.1: Chemical composition of experimental steels.

Alloy	С	Mn	Мо	Cr	Nb	Al	Р	S	В	Ni
EDDS	0.006	0.062	0.011	0.045	0.040	0.056	0.006	0.013	0.028	0.021
C-Mn	0.053	0.210	0.008	0.043	0.024	0.041	0.011	0.013	0.029	0.014
DP590	0.076	1.722	0.185	0.215	0.023	0.080	0.011	0.009	0.028	0.012
4.2 McMaster Galvanizing Simulator (MGS)

All heat treatments, oxidation and galvannealing experiments were carried out in the McMaster Galvanizing Simulator (Figure 4.1). There are three sections in the simulator:

- 1- The main section which consist of the drive mechanism, upper chamber, infrared furnace, induction furnace, molten metal bath and gas-jet wiping (Figure 4.2).
- 2- Gas mixing section.
- 3- Controlling section.

The drive mechanism controls the movement of the sample in the main section. The upper chamber is used to load and unload of the samples. For annealing the samples, the infrared quartz lamp furnace was used. In galvannealing simulations, the induction furnace was employed. N_2 and H_2 were mixed with each other in the gas mixing station and then injected into the column through a humidification system to control the dew point.

Steel samples were first annealed in the infrared furnace and then dipped in the zinc bath. After dipping, gas jet wipers were used to remove the excess zinc from the sample surface. Nitrogen was used in these jets (flow rate = 500 L/min). For galvannealing, the galvanized samples were immediately transferred to the induction furnace and heated at different temperatures and times. The zinc bath consists of a resistance heated 50 kg graphite crucible controlled to within ± 2 °C using a conventional process controller. The zinc bath contained 0.136 wt. % dissolved Al and the Fe content was saturated with respect to Fe₂Al₅Zn_x and FeZn₁₀ (McDermid et al. 2007). At the zinc bath surface a

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graphite dross removal system skimmed the surface of the bath immediately prior to immersion of the panel in the zinc bath to remove $Fe_2Al_5Zn_x$ and oxides (top dross) floating on the surface of the bath.



Figure 4.1: The McMaster Galvanizing Simulator (Bellhouse 2010).



Figure 4.2: Schematic design of the MGS (Chen 2007).

Experimental samples for dipping and galvannealing experiments comprised as cold-rolled 120 mm x 200 mm panels with the longitudinal axis of the sample parallel to the rolling and dipping direction (Figure 4.3). Before experiments, panels were cleaned using a 2wt.% sodium hydroxide solution at 80°C and brushed by a soft nylon brush to remove organic contaminants followed by rinsing in distilled water. Further rinsing was performed using isopropanol in an ultrasonic bath followed by drying with a warm air stream. Before putting the samples in the simulator, the samples were given a final cleaning with acetone. A thermocouple (K type) was welded to the sample surface to control the thermal cycle. Sample temperature measurements were accurate to within ± 2 °C. A uniform temperature and coating area of 90 mm × 90 mm was considered in the lower portion of the steel panel and only materials from this area were used for analysis (Figure 4.3).



Figure 4.3: Schematic figure of steel panels (Bellhous 2010).

4.3 Heat Treatment and Annealing Atmosphere

4.3.1 Selective oxidation experiments

In the first step of this research, selective oxidation of the substrates during annealing (before dipping) was studied. In this step, after grinding and polishing the samples (grinding: 800, 1200, 2400 and 4000 grit SiC; polishing: 3 and 1 µm diamond suspension, and finally, 0.05 µm alumina powder), polished samples (1cm by 5cm) with mirror-like surfaces were heat treated in a 95%N₂-5%H₂ atmosphere and -30 °C dew point (dp); This atmosphere and dew point was used for all the samples (EDDS, CMn and DP) in this study. The oxidation samples were installed on a steel frame and this was heat treated in the infrared furnace. After annealing, samples were cooled in the upper chamber. Peak annealing temperatures (PAT) of 790 °C (for EDDS and CMn samples) and 850 °C (for DP590 samples) were used. Schematic heat treatment cycles, similar to those used in the industry for these substrates, are shown in Figure 4.4. As can be seen, the samples were gradually heated to the PAT and held isothermally for 30s after which the samples are rapidly cooled to room temperature at -20° C/s. The -30 °C dp process atmosphere, H₂/N₂ content and PATs in this research are typical of industrial continuous galvanizing/galvannealing lines. The surface of the samples should be mirror-like to prevent surface irregularities affecting the oxidation process. The effect of parameters such as the partial pressure of oxygen and substrate chemistry on selective oxidation was studied, including the effect of oxide thickness and surface morphology. Besides, the size, morphology and distribution of the oxides at the surface or subsurface regions were also

investigated. The process atmosphere oxygen partial pressure is strongly temperature dependent and was calculated as a function of steel PAT, as shown in Table 4.2.



Figure 4.4: Thermal cycles used for a) EDDS and C-Mn, b) dual phase samples.

Alloy	PAT (°C)	Dew point (°C) and Po ₂ at PAT -30
EDDS	790	1.33E-23
C-Mn	790	1.33E-23
DP590	850	2.76E-22

Table 4.2: Experimental annealing conditions.

4.3.2 Galvannealing experiments

After heat treating, samples were dipped and galvannealed under different galvannealing times and temperatures. Galvannealing conditions are shown in Table 4.3. Three galvannealing (GA) times and four GA temperatures were selected to study the effect of galvannealing parameters on the growth kinetics of the intermetallic phases. The concentration of aluminum in the galvannealing zinc bath (0.136wt.%) was extracted from Zn-rich corner of the Zn-Fe-Al system at 460°C (McDermid et al. 2007) and is typical of industrial continuous galvanizing/galvannealing lines. Schematic galvannealing heat treatment cycle is shown in Figure 4.5.

Table 4.3: Experimental galvannealing conditions.

Alloy	Galvannealing time (s)	Galvannealing temperature (°C)	Zinc bath temperature (°C)	Zinc bath Al _{dissolved} (wt.%)
EDDS				
CMn	10,20,30,40	480,500,520	460	0.136
DP590				



Figure 4.5: Schematic galvannealing cycle used for dual phase steels.

4.4 Analysis of the Steel Surface after Annealing

To fully characterize the selective oxidation of the steel surfaces two techniques were used. X-ray photoelectron spectroscopy (XPS) was used to identify the oxides on the steel surface and obtain elemental depth profiles. SEM was used to observe the surface oxide morphology.

4.4.1 Sample preparation and storage

Samples that were selected for annealing (without dipping) to analyze the selective oxidation of the steel surface were polished to eliminate the effect of surface roughness. Samples analyzed with XPS were polished prior to annealing with 4000 grit SiC paper as the final step. For analysis of the oxide morphology by SEM, the steel was polished to 0.05 μ m prior to annealing. After annealing and removal of the sample from

the MGS and prior to analysis with XPS and SEM, samples were immersed and stored in anhydrous isopropanol to minimize further oxidation of the surface.

4.4.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative spectroscopic technique that determines the empirical formula, elemental composition and chemical state of the elements that are present in a material. XPS spectra can be obtained when a X-ray beam strikes a material under high vacuum. The kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material are analyzed. A typical XPS spectrum comprises a plot of the number of electrons that have been detected versus the binding energy of the electrons detected. Each element or chemical compound produces a characteristic set of peaks at defined binding energy values. Also, the number of electron in each of the detected peaks is proportional to the amount of the element within the area which has been irradiated.

The kinetic energy of the photoelectron is calculated and the binding energy is obtained from the following equation (Briggs 2003, Briggs and Rivière 1983):

$$E_{\rm K} = hv - EB - \varphi_{\rm sp} \tag{4.1}$$

where E_K is the measured kinetic energy of the photoelectron, hv is the energy of the incident X-ray photons (where h is Plank's constant and v is the frequency of the incident X-rays), E_B is the binding energy relative to the Fermi level and φ_{sp} is the work function of the spectrometer (a constant representing the difference between the vacuum and Fermi levels).

Using this method, it is possible to measure the uniformity of elemental composition across a surface (line profiling). Besides, uniformity of the elemental composition can be obtained as a function of depth by ion beam etching (depth profiling)(Briggs and Grant 2003).

All analyses were run on a ThermoScientific K-Alpha XPS (East Grinstead, UK) with a monochromated Al K α X-ray source. The X-ray spot size was 400 µm for depth surface scans (i.e. survey and surface spectra), while a spot size of 200 µm was used for depth profiles (in order to reduce the size of the sputter crater that would be necessary). A Shirley background function was used to approximate the background spectrum. Surface elemental compositions were calculated from background-subtracted peak areas derived from transmission function corrected regional spectra. Scofield Al K-alpha sensitivity factors were used to calculate the relative atomic percentages. The energy scale of the instrument was calibrated to metallic Cu2p, Ag3d, and Au4f features. The binding energy values obtained are accurate to within ± 0.1 eV and the accuracy of the chemical composition measurements are $\pm 5\%$ of the measured value in atomic % for each element. Depth profiles were obtained by Ar sputtering followed by analysis of the new surface. The ion beam used for the profiling experiment was 2 keV Ar. The sputter beam rastered an area of 1x0.5 mm².

4.4.3 Scanning Electron Microscopy (SEM)

To study the morphology, distribution and size of the oxides which formed at the surface of the samples after heat treatment, SEM was used. The microstructure of the galvannealed coating was also studied by SEM. SEM analysis was performed employing a JEOL 7000F field emission SEM. An acceleration voltage of 5 keV and a working distance of 9-11 mm were used for all oxidized samples. All oxidized samples were sputter coated with gold to avoid sample charging.

4.5 Analysis of Galvannealed Coatings

The microstructure and chemical composition of the galvannealed coatings were investigated in the uniform coating and temperature area. SEM, XRD (X-ray diffraction), ICP (inductively coupled plasma), and GDOES (glow discharge optical emission spectroscopy) were used to determine the thickness of the gamma layer, identify the intermetallic phases in the coatings, determine the chemical composition of the coatings and to check the elemental distribution through the coating thickness, respectively.

4.5.1 Scanning Electron Microscopy (SEM) analysis of galvannealed coatings

To study the microstructure and to determine the thickness of the gamma layer in the galvannealed coatings, SEM was employed. Before SEM analysis, samples were polished to 0.05 μ m as the final step. In all steps of grinding, pure ethyl alcohol was used to eliminate the destructive effects of water on the microstructure. For the polishing steps, water free diamond suspensions were used.

SEM analysis was performed using a JEOL 7000F field emission SEM. An acceleration voltage of 5 keV and a working distance of 10 mm were used for all samples. All samples were sputter coated with gold to avoid sample charging.

4.5.2 X-ray Diffraction (XRD) analysis of galvannealed coatings

X-ray diffraction techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron cloud of the individual atoms in the system. Only a small range of characteristic X-rays are widely used for diffraction. Their K_{α} lines are used. The K_{β} line which is always present with K_{α} , at a slightly shorter wavelength, is filtered out using an absorbing film. The effective penetration of these X-rays determines the maximum thickness of specimens which can usefully be studied by X-ray diffraction.

Two-dimensional X-ray diffraction (XRD2) (collection of powder XRD data with a 2D CCD detector) was employed to determine the phases in the coatings. A Smart Apex II system by Bruker AXS Inc. with a Cu K α source ($\lambda = 1.540596$ Å) was used. The detector distance was 17.0 cm and was calibrated with corundum (Al_2O_3). The X-ray beam diameter was 500 µm. Data was processed using GADDS (General Area Detector Diffraction System) software by Bruker AXS Inc. In GADDS ax integration was performed over the 2θ range of 72 to 80° to obtain an intensity vs. 2θ pattern. This range is very common in GA coating analysis because it contains the related peaks of all of the phases in the GA microstructure and thus, using this range will results in shorter XRD analyses. Topas software (Bruker AXS Inc.) was used to determine the phases present in the coatings.

4.5.3 Inductively Coupled Plasma (ICP) analysis of galvannealed coatings

ICP is a mass spectrometry wet chemistry analysis method with high sensitivity. In this method, an inductively coupled plasma as a method of producing ions is used with a mass spectrometer as a method of separating and detecting the ions. Samples are usually analyzed as a liquid that is passed into a nebulizer. When a droplet of nebulized sample enters the plasma, it evaporates and all of the solids which were dissolved in the liquid vaporize and break down into atoms. Due to the high temperature, a significant portion of the atoms in the spectrometer are ionized. The ions are then transferred to the mass spectrometer and are separated based on their mass to charge ratio (Hill 2007).

The macroscopic coating chemical composition was determined by ICP using matrix matched standards. Matrix matched standards are used to decrease the experiment errors. The concentration of the elements in the standard solutions is close to the concentration of the elements in the matrix. A 10 vol.% H_2SO_4 solution with RodineTM85 inhibitor was used to dissolve the coating. The back side and edges of the sample were covered by lacquer and only one side of the samples (the front) was dissolved. Analyses were repeated three times to increase the accuracy of the results and the averages of these analyses were reported. The power, plasma flow and nebulizer flow were 1.2 kW, 15 L/min and 0.7 L/min, respectively. Before starting the analysis, the system (ICP machine) was cleaned and washed by a blank solution (10 vol.% H₂SO₄ solution) to remove

contaminants in the tubes. After each of the tests, the system was washed by water and liquid soap to increase the accuracy of the results.

4.5.4 Glow Discharge Optical Emission Spectroscopy (GDOES) analysis of galvannealed coatings

This method provides rapid, direct bulk analysis and compositional depth profiling analysis of metals, powders, polymers, glasses and ceramics. A glow discharge source and one or more optical spectrometers are employed for GDOES. In glow discharge, cathodic sputtering is used to remove material layer by layer from the sample surface. The atoms removed from the surface migrate into the plasma where they are excited through collisions with electrons or carrier gas atoms. The characteristic spectrum emitted by the excited atoms is measured by the spectrometer. This technique is fast, in comparison with XPS, and is capable of sputtering to greater depths; thus, it is possible to study the elemental distribution in the coating (Marcus and Mansfeld 2006).

In this research, GDOES samples (2cm×2cm) were cleaned before analysis using pure ethanol and three points on each sample were analyzed. Graphs of intensity versus time were converted to atomic percent versus depth using the related software to obtain depthcomposition distributions of the elements through the coatings. After each analysis, the chamber was cleaned with a special brush to remove contaminants from the chamber to increase accuracy. Measurement parameters such as flush time and surface acquisition were 180 and 300, respectively.

4.5.5 TEM sample preparation using focused ion beam (FIB) milling

TEM sample preparation was performed employing FIB milling with an NVision 40 by Zeiss. FIB was selected since this technique is ideal to make site specific samples of the cross-section of the Fe-Zn interface (Goldstein et al. 2003). In this method, material is sputtered using Ga^{+} ions. Carbon was deposited over the FIB sample location as Zn is sputtered more easily than Fe and the carbon layer minimized preferential thinning of the Zn layer.

The different stages of FIB sample preparation are shown in Figure 4.6. First, carbon was deposited over the FIB sample location (Figure 4.6 a). Then, two deep trenches were milled on both sides of the sample (Figure 4.6 a). This is followed by milling away the material around the sample so that only a small area of the sample is attached to the probe. The probe is then welded to the sample by carbon deposition (Figure 4.6 b). The small region of the FIB sample that remained attached to the original specimen was milled away. In the next step, the FIB sample was placed on a Cu grid and welded to the grid by carbon deposition. Next step is cutting the probe from the FIB sample (Figure 4.6 c). Windows in the sample were thinned to be electron transparent for analysis by TEM (Figure 4.6 d).

HAADF (high angular annular dark field) images combined with EELS or EDS data were acquired on a FEI Titan 80-300 TEM (FEI Company, Eindhoven, The Netherlands), equipped with a CEOS image corrector and operated at 300 kV. The microscope is equipped with a Gatan Tridiem ER energy filter (GIF) (Gatan Inc, Pleasanton, CA) and an Oxford EDX detector. EELS mapping was performed in STEM mode with a convergence angle of 8mrad, the collection angle was 15 mrad. The energy resolution of the system was 0.8 eV. EDX mapping was performed in STEM mode. Spectrum image acquisition and postprocessing was done using the Gatan Digital Micrograph Software.



Figure 4.6: Stages in typical FIB sample preparation of galvanized samples a) rough milling of trenches on either side of the sample, b) milling around the sample and welding of the probe to the sample, c) welding of the sample to the Cu grid and removing the probe and d) fine milling of three electron transparent windows on the sample.

5 SELECTIVE OXIDATION

Selective oxidation of the steel surfaces, as a function of substrate Mn concentration, was studied using SEM and XPS. Using these techniques, the surface chemistry and oxide morphology were determined.

5.1 XPS Analysis

XPS was used to determine the surface chemistry and obtain elemental depth profiles after annealing and immediately before immersion in the zinc bath. The results of oxide identification are shown in Table 5.1 (after analyzing the related surface spectra, Figure 5.1). The oxides were identified by comparing the measured binding energies to those in the literature for the following oxides: MnO (Strohmeier and Hercules 1984) and Cr_2O_3 (Si et al. 2011). A list of binding energies compiled from the literature is provided in Table 5.2. It should be mentioned that the major limitation to identifying the oxides present using XPS is that binding energy data are not always available for all compounds. For example, complex oxides containing Mn, Si and Al are difficult to identify. Also, MnAl₂O₄ cannot be distinguished from Al₂O₃ and MnO using binding energies (Strohmeier and Hercules 1984).

Table 5.1: Identification of oxides on the steel surface using XPS.

Steel		Measured	Major oxides			
Steel	Mn 2p _{3/2}	Mn 2p _{1/2}	Cr 2p _{3/2}	Cr 2p _{1/2}	O 1s	
EDDS	641.7	653.1	577.1	586.2	530.1	MnO, Cr ₂ O ₃
CMn	641.2	653.0	577.1	586.1	530.1	MnO, Cr ₂ O ₃
DP590	641.1	653.1	577.1	586.1	530.1	MnO, Cr_2O_3

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Figure 5.1: XPS spectra of sample a) EDDS and b) CMn steels (continued)





Figure 5.1: XPS spectra of sample of c) DP590.

Due to the removal of the sample from the galvanizing simulator and subsequent exposure to the ambient atmosphere, iron was oxidized (Fe oxides and/or hydroxide) at the surface of the samples (to a depth of 5-10 nm). Further oxidation was minimized between removing the panel from the galvanizing simulator and analysis of the sample by storing the as-annealed steel in anhydrous isopropanol. The observed carbon peak could be related to the isopropanol that had been used during cleaning and storage in addition to atmospheric contamination.

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The measured binding energies taken from the XPS spectra indicate that oxidation of Mn and Cr had occurred at the surface (Table 1). XPS depth profiles for oxygen, manganese, iron and chromium are shown for all experimental steels in Figure 5.2. As expected, the EDDS sample showed little segregation of Mn and Cr because of its relatively low alloying element content (Table 4.1). Also, segregation of Cr at the surface of all steels is not significant.

Name	Mn 2p _{3/2}	Mn 2p _{1/2}	Cr 2p _{3/2}	Cr 2p _{1/2}	O 1s	Fe 2p _{3/2}	Al 2p	Si 2p	References
Si	_		_	_				99.4	Finster 1988
SiO ₂					532.2			103.2	Finster 1988
SiO ₂					533.0			103.9	Finster 1988
Al ₂ O ₃					531.3		74.5		Strohmeier and Hercules 1984
MnO	641.7	653.3			530.2				Strohmeier and Hercules 1984
MnO ₂	642.6	654.2			529.7				Strohmeier and Hercules 1984
MnAl ₂ O ₄	641.6	653.4			531.3		74.5		Strohmeier and Hercules 1984
Mn_2SiO_4								102.5	Casey et al. 1993
Mn ₂ SiO ₄	642.1							102.6	Parezanović and Spiegel 2005
Fe _{1.1} O					529.9	709.5			Grosvenor et al. 2004
α -Fe ₂ O ₃					530.0	710.8			Grosvenor et al. 2004
Fe3O4					530.2	Fe ²⁺ :709.0, Fe ³⁺ :711.4			Grosvenor et al. 2004
α- FeOOH						711.4			Grosvenor et al. 2004
Cr_2O_3			577.0	586.4					Capece 1982
CrO_2			576.1						Ikemoto et al. 1976

Table 5.2: XPS binding energies compiled from the literature.

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The shape of the EDDS depth profile showed that external oxidation had occurred at the surface. In the case of the CMn or DP samples, as can be seen in Figure 5.2 (b and c), the segregation of alloying elements to the surface is more pronounced (especially for the DP samples). For example, for the CMn samples (Figure 5.2b), the segregation of Mn in the form of an oxide is relatively significant at the surface; however, other alloying elements such as Cr showed little segregation. The Mn concentration decreased as the depth from the surface increased. For the DP samples (Figure 5.2c), there was significant enrichment of Mn, and to some extent Cr, in the form of oxides at the steel surface; again, by increasing the depth from the surface, the concentration of Mn and Cr decreased. Furthermore, the maximum Mn concentration occurred at the surface of the DP samples because of higher concentrations of Mn (and other alloying elements) in the DP substrates. The Mn and O enrichment penetrated to a greater depth in the DP samples indicating a thicker MnO laver for this sample.

The full width at half maximum (FWHM) of the Mn depth profiles (Figure 5.2) was used to estimate the MnO thickness. It was found that the MnO thickness for the EDDS, CMn and DP substrates was approximately 8, 10 and 45 nm, respectively. It was expected to obtain a thicker MnO layer for the DP samples since the concentration of Mn in these samples was higher and, therefore, more Mn atoms were provided to react with oxygen at the surface and thus, thicker oxide layers/larger particles were formed.

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Figure 5.2: XPS depth profiles for a) EDDS, b) CMn steels (continued).



Figure 5.2: XPS depth profiles for c) DP590 steel.

5.2 SEM Analysis

The morphology and distribution of oxides on the surface was studied using SEM, as shown in Figure 5.3. The EDDS steel showed minor oxidation, primarily at the grain boundaries (a network type structure) with sparse nodular oxide particles on the surface. However, more significant populations of oxide nodules/film on the surface as well as oxide ridges at the grain boundaries were observed for the CMn and particularly DP samples (Figure 5.3). The EDDS and CMn samples generally exhibited surface oxides with a spherical cap morphology (Figure 5.4 (a) and (b)) but the nodules at the surface of the DP sample generally had a faceted or irregular shape and some areas were covered with spherical cap shaped nodules. In other words, external oxidation was increased at the surface of samples with higher concentration of alloying elements. In fact, by increasing the concentration of alloying elements in the EDDS and CMn samples under constant dew point (-30° C), the external oxidation of these elements was increased because more alloying elements atoms were available to migrate towards the surface to react with oxygen to form oxide particles. Furthermore, the oxide particle size on the EDDS steel surface was considerably smaller than that on the CMn or DP steel surfaces; the DP sample showed the largest oxide particles and thickest oxide layer among all the experimental steel samples because of its higher alloying content and being heat treated at a higher peak annealing temperature and atmospheric pO_2 (Table 4.2). The ridge morphology at the grain boundaries of the samples was expected due to the higher oxygen and manganese diffusion rates at these locations as grain boundaries are short circuit diffusion paths. These results are in good agreement with the XPS results that showed

considerable external oxidation and a thicker oxide layer for CMn and particularly DP samples in comparison to the EDDS sample.



Figure 5.3: SEM images of a) EDDS, b) CMn and c) DP590 steels.



Figure 5.4: Surface morphology of a) EDDS, b) CMn and c) DP590 steels.

5.3 Comparison Between Wagner Model predictions and Experimental Results

Selective oxidation can occur in two forms: internal and external. In internal oxidation, oxides form below the gas-metal interface and in external oxidation, oxides form at the gas-metal interface. The mode of oxidation depends on the relative values of the flux of oxygen and alloying elements to the surface. When the inward diffusion of oxygen dominates, oxygen diffuses into the subsurface regions and meets the atoms of the alloying elements and, thus, oxide particles will be formed there and internal oxidation occurs. In external oxidation, the outward diffusion of the reactive solute atoms dominate and, therefore, oxygen reacts with them at the surface and oxide particles are formed at the surface(De Cooman 2006, Marder and Bramfit 1979, Dieter 1976, Gladman 1997).

The transition between internal and external oxidation was modeled by Wagner (1959) for binary alloy single crystals. Extensions of this model have been developed by several authors and were discussed in § 2.2.2 (Mataigne et al. 1992, Grabke et al.1995, Shastry et al. 2007, Huin et al. 1996, Huin et al. 2005). For the alloys used in the present study, the transition between internal and external oxidation was calculated for Mn and Cr in the bulk steel and at the grain boundaries for both ferrite and austenite.

For individual elements in the bulk alloy Wagner's equation was used (Wagner 1959):

$$N_{crit}^{X} = \left(\frac{g^{*}V_{m}\pi D_{O}N_{O}}{2V_{XO_{v}}D_{X}}\right)^{1/2}$$
(5.1)

where N₀ is the molar fraction of dissolved oxygen at the surface, V_m is the alloy molar volume, $V_{XO_{\nu}}$ is the molar volume of oxide $[p_{H_2O} / (p_{H_2} \times wt.\%O)], \nu$ is the stoichiometric ratio for the oxide $XO\nu$, g* is the critical volume fraction of oxides which blocks of all oxygen inward diffusion paths (Wagner 1959). D₀ is the diffusion coefficient for oxygen where D₀ = D'₀ exp(-Q₀/RT) and D_B is the diffusion coefficient of the alloying element where D_B = D'₀ exp(-Q_B/RT). According to Rapp (Rapp 1965), g* is equal to 0.3. Also,

in this model, the solubility of XOv is negligible.

For individual reactive elements at the grain boundaries the following equation was used, where the activation energy for grain boundary diffusion as assumed to be half of that for bulk diffusion (Mataigne et al. 1992):

$$N_{crit,gb}^{X} = \left(\frac{g^{*}V_{m}\pi N_{o}D_{o}'\exp(-Q/2RT)}{2V_{XO}UD_{X}'\exp(-Q/2RT)}\right)^{1/2}$$
(5.2)

The appropriate diffusion data was obtained from the literature for oxygen, manganese and chromium in ferrite and austenite and is provided in Table 5.3. The molar volumes for the matrix and oxides of alloying elements and the stoichiometric ratio (v) are provided in Table 5.4.

The molar fraction of dissolved oxygen at the steel surface (N_O^s) was determined by equation (5.3) (Swisher and Turkdogan 1967):

$$N_o^s = 0.01 [MW(Fe)/MW(O)]$$
 (5.3)

The dissolved oxygen at the surface was calculated using the equilibrium constant, K, for the reaction shown in equation (5.4):

$$H_2(g) + [O] = H_2O(g)$$
 (5.4)

where K is defined as:

$$\mathbf{K} = [p_{H_2O} / (p_{H_2} \times wt.\%O)]$$
(5.5)

The value of K was calculated for ferrite and austenite as follows (Swisher and Turkdogan 1967):

$$\log K_{\alpha} = (5000/T) - 0.79 \tag{5.6}$$

$$\log K_{\gamma} = (4050/T) - 0.06 \tag{5.7}$$

Element	$D'_i [cm^2/s]$	Q _i [kJ/mol]	Reference
and phase			
O in α	0.037	97.6	Takada and Adachi 1986
Mn in α	1.49	233.6	Sun and Pugh 2000
Cr in α	2.33	238.8	Huntz et al. 1947
O in γ	5.75	168.8	Takada et al. 1984
Mn in γ	0.16	261.6	Sun and Pugh 2000
Cr in y	0.169	263.9	Huntz et al. 1947

Table 5.3: Diffusion data for species in ferrite (α) and austenite (γ).

Table 5.4: Molar volumes and stoichiometric ratio () for oxide species (Weast 1978,

Phase	Molar volume [cm ³ /mol]	
MnO	13.221	1
Cr ₂ O ₃	14.59	1.5
Ferrite (a)	7.0918	-
Austenite (γ)	7.299	-

Lide 2002, Y. Niu et al. 2008).

The predicted oxidation mode for the experimental alloys is provided in Table 5.5. External oxidation of the grain boundaries was generally expected with the exception of Cr (in ferrite/austenite grain boundaries) and Mn (in austenite) in CMn steel and for Cr (in austenite grain boundaries) in DP steel. External oxidation at the grain boundaries observed experimentally for all samples (Figure 5.3 and 5.4).

Table 5.5: Prediction of internal/external oxidation of Mn and Cr for EDDS, CMn and DP samples ((i) = internal & (e) = external oxidation).

Samula	Bulk O	xidation	Grain Boundary Oxidation		
Sample	Ferrite Austenite Ferr		Ferrite	Austenite	
EDDS	Mn(i), Cr(i)		Mn(e), Cr(e)		
CMn	Mn(i), Cr(i)	Mn(i), Cr(i)	Mn(e), Cr(i)	Mn(i), Cr(i)	
DP590	Mn(i), Cr(i)	Mn(i), Cr(i)	Mn(e), Cr(e)	Mn(e), Cr(i)	

It should be mentioned that the modeling results for Mn in ferrite and austenite should be treated with caution because of the relatively high solubility product of MnO in these phases (Huin et al 2005) whereas the Wagner model assumes a very low solubility product for the oxide phase and predicts a fixed amount of oxide precipitated for a given position once the oxidation front has passed that point. This last shortcoming of the Wagner model has been discussed by Huin et al. (Huin et al 2005) who showed that the amount of MnO precipitated will increase with time for a given distance from the surface. For bulk oxidation, the experimental results did not agree with the model as external oxidation was observed by SEM for all samples (Figures 5.3 and 5.4). This discrepancy may be related to the effect of alloying element interactions.

6 GALVANNEALING

Galvannealing of steel substrates was performed using a variety of galvannealing times and temperatures (as defined in Table 4.3) to investigate the effects of these parameters on galvannealing kinetics and coating microstructural development. Several techniques were employed to analyze the galvannealed coatings such as XRD, SEM, ICP and GDOES.

6.1 XRD Analysis of the Galvannealed Coating

To identify the phases which were present in the microstructure of the coatings, XRD and a related software (TOPAZ) were used. XRD patterns of the samples are shown in Figures 6.1 to 6.4. Figure 6.1 shows the XRD pattern obtained for all steels after dipping and before galvannealing (GA_t = 0). As can be seen in Figure 6.1, the only phases detected for all substrates (EDDS, CMn, and DP) were metallic zinc (with a very strong peak) and another phase with a weak peak which was ζ -FeZn₁₃ (zeta) phase. These results are in good agreement with the SEM analysis which detected the presence of metallic zinc and ζ -FeZn₁₃ (section 6.2). Figures 6.2 to 6.4 show the XRD patterns of galvannealed samples as a function of galvannealing time and temperature (for example, "C-500/10" means a CMn sample which was galvannealed at 500°C for 10 seconds). It should be mentioned that only the strong primary peaks for the phases have been considered in these patterns. It can be seen from these XRD patterns that all three phases, i.e. ζ -FeZn₁₃ (zeta), δ -FeZn₁₀ (delta) and Γ -Fe₃Zn₁₀ (gamma), were present in the coating microstructures for all GA times and temperatures. Thus, under all experimental GA

conditions, fully alloyed or over alloyed coatings were obtained. In other words, the absence of metallic zinc phase peaks in the patterns shows that under alloyed coatings were not produced under the experimental GA conditions.

Another point that should be considered is the intensity of the peaks. As can be seen in most of the patterns, by increasing the time or temperature of the galvannealing process, the peak intensity for gamma phase was increased, indicating a thicker gamma layer in the microstructure. The presence of a thicker gamma layer in the microstructure is a good indication of faster galvannealing kinetics. In fact, by increasing the temperature, the rate of iron diffusion towards the coating was increased and increasing the galvannealing time means that more iron is provided for diffusion during galvannealing. Since the gamma layer is the last layer which is formed in the galvannealing process, the growth of this layer can be considered an indicator for the rate of alloying of the coating and the kinetics of Fe-Zn phase formation.

It can be seen that some of the peaks in the XRD patterns have been shifted slightly. For example, shifting of the δ -FeZn₁₀ (delta) phase peak for different GA times/temperatures can be seen (e.g. Figure 6.2, delta peak). This shift is related to changes in the lattice parameters of this phase because of the diffusion of iron or manganese into the structure. By changing the temperature and time of galvannealing, the diffusion of iron (and other alloying elements, particularly Mn) is affected and different concentrations of iron (and Mn) in the coating can result. Thus, different concentrations of iron or manganese would enter to the structure of the δ -FeZn₁₀ (delta) phase (or zeta and gamma phases) and change the intermetallic lattice parameter, resulting in the

observed peak shift. The importance of manganese in the galvannealing diffusion process is related to its characteristics (especially the atomic radius, $r = 1.29 \text{ A}^{\circ}$) that are very similar to those of iron. Also, manganese forms similar intermetallics with zinc such as MnZn₉ or MnZn₁₃ that are similar to δ -FeZn₁₀ (delta phase) and ζ -FeZn₁₃ (zeta phase) (Okamoto 1993, Reumont 1993). The presence of Mn in the galvannealed coating will be verified in a subsequent section (ICP analysis). Thus, during diffusion in galvannealing, manganese can substitute for iron in delta phase or other phases and affect the properties and chemistry of the coating in the case of the galvannealing of Mn containing steels. Another point concerning the XRD patterns is that some data, e.g. the 20s data (Figure 6.3), does not appear to be following the same trends at 480, 500 and 520°C. This could be related to analysis/experimental errors or discontinuities in the coating thickness that may affect the intensity of the observed peaks.



Figure 6.1: XRD pattern of samples after dipping and before GA (E=EDDS, C=CMn, D= DP590).

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Figure 6.2: XRD pattern of galvannealed EDDS samples at a) 480 °C b) 500 °C and c) 520 °C for 10, 20, 30 and 40 seconds.


Figure 6.3: XRD pattern of galvannealed CMn samples at a) 480 °C b) 500 °C and c) 520 °C for 10, 20, 30 and 40 seconds.



Figure 6.4: XRD pattern of galvannealed DP samples at a) 480 °C b) 500 °C and c) 520 °C for 10, 20, 30 and 40 seconds.

6.2 SEM Analysis of Galvannealed Coatings

SEM was used to investigate the microstructural evolution of the coatings and determine the Γ -Fe₃Zn₁₀ gamma layer thickness to compare the galvannealing kinetics of the coatings. Figure 6.5 shows sample cross sections after dipping and before galvannealing (i.e. $GA_t = 0$). As can be seen, the coatings consisted of a metallic zinc layer and some block-like phases identified as ζ -FeZn₁₃ phase. The presence of the zeta phase layer could be ascribed to the relatively low concentration of dissolved aluminum in the zinc bath and the initiation of inhibition breakdown which is in good agreement with the literature (Leprêtre et al. 1998, Dionne 2006, Kim et al. 2009, Chen 2008).

As was mentioned in the literature review, the addition of aluminum to the zinc bath will result in the formation of the Fe₂Al₅Zn_x interfacial layer and this layer will inhibit the formation of Fe-Zn intermetallics (Chen et al. 2008, Baril and L'Esperance 1999, Toussaint 1998, Giorgi and Guillot 2004, Lin et al. 1995). Thus, after dipping the steels in high aluminum containing zinc baths, the microstructure should consist of a metallic zinc layer and a very thin Fe-Al interfacial (inhibition) layer. The point that should be mentioned in here concerns the compactness, continuity and thickness of the inhibition layer. When the concentration of aluminum in the zinc bath is low (as in the present GA baths) the inhibition layer will be very thin, non-compact and discontinuous (Baril and L'Esperance 1999, Chen et al 2008). Due to the diffusion of zinc and iron through the inhibition layer or due to the reaction between Fe and Zn at holes/grain boundaries in the inhibition layer, ζ -FeZn₁₃ phase will form at the grain boundaries first as these sites become saturated with Zn (Baril and L'Esperance 1999, Chen et al 2008).

Furthermore, aluminothermic reduction should be considered as another factor that affects zeta phase formation (Kavitha and McDermid 2011). Due to the presence of oxide particles at the surface of the steel, aluminum will be consumed in reducing the oxides and considering the fact that in GA baths the bulk aluminum concentration is relatively low, it can be concluded that the concentration of aluminum drops considerably. Under these conditions, iron has a good chance to react with zinc and form zeta phase. It will also accelerate inhibition break down (Jordan et al. 1997).

Figures 6.6 to 6.8 show the microstructure of the galvannealed coatings as a function of GA time and temperature. It can be seen in these figures that by increasing the galvannealing time and temperature, the rate of Fe-Zn intermetallic growth (alloying) was increased. Furthermore, ζ -FeZn₁₃, δ -FeZn₁₀ and Γ -Fe₃Zn₁₀ phases are present in all GA coatings as was shown in the XRD results (Figure 6.2 to 6.4). The thickness of the Γ -Fe₃Zn₁₀ layer is a good criterion to quantify the Fe-Zn intermetallic growth rate. For example, for the all samples (Figure 6.4), by increasing the galvannealing time for all GA temperatures, the thickness of the gamma layer was increased. Similarly, by increasing the GA temperatures for all GA times, an increase in the thickness of the gamma layer was seen which is in good agreement with the literature and predictions (Jordan and Marder 1994, Jordan and Marder 1997, Kim et al. 2009). By increasing the GA temperature, the diffusion rate of iron (and manganese, as will be discussed later) was increased and thus, the Fe-Zn intermetallic growth rate was increased. Also, because of

the more rapid diffusion of iron atoms through the coatings, the thickness of gamma layer was increased. By increasing the time, more iron was provided for diffusion towards the coating and therefore, the reaction between iron and zinc to form Fe-Zn intermetallic was increased, resulting in thicker gamma layer and more alloyed microstructure.

One of the important points concerning these microstructures (Figure 6.6 to 6.8) is that the Γ -Fe₃Zn₁₀ gamma layer was present for all GA times and temperatures. For example, for all three substrates, i.e. EDDS, CMn and DP, at 480 °C and 10 s (i.e. the lowest GA temperature and time) the gamma layer was present. From this, it is possible to say that all of the microstructures obtained under the experimental galvannealing conditions in this study were either fully or over alloyed and there was no under alloyed microstructure since no metallic zinc was present. However, the presence of thick gamma layers in galvannealed GA coatings seems to be unusual and will be discussed in subsequent section.

For the development of the galvannealed microstructure, as was mentioned in previous sections, the as-dipped coating mostly consisted of metallic zinc (and some blocky crystals of ζ -FeZn₁₃ phase (Figure 6.5) was annealed and Fe-Zn intermetallics formed. This metallic zinc serves as the source of zinc for the growing Fe-Zn intermetallic phases during the early stages of galvannealing, the inhibition layer should be broken down (or, inhibition layer breakdown is accelerated) and after removal of the inhibition layer, Fe-Zn phase(s) initially nucleate at the steel/coating interface and consumes the metallic zinc layer as they grow (Jordan and Marder 1994).

Samples galvannealed at higher temperatures for longer times (for example Figures 6.7 (c) and 6.8 (i)) contained cracks perpendicular to the steel substrate as a result of volume changes associated with the phase transformations occurred within the coatings. The cracks observed in the coatings were not produced by the sample preparation process. The presence of these cracks may influence the corrosion resistance and mechanical properties.



Figure 6.5: Cross sections of samples after dipping (before GA process), a) EDDS b)

CMn c) DP 590.



Figure 6.6: Cross sections of galvannealed EDDS samples for (a-c) 10 s (d-f) 20 s (g-i) 30 s (j-l) 40 s at 480, 500 and 520 °C.



Figure 6.7: Cross sections of galvannealed CMn samples for (a-c) 10 s (d-f)20 s (g-i) 30 s (j-l) 40 s at 480, 500 and 520 °C.



Figure 6.8: Cross sections of galvannealed DP samples for (a-c) 10 s (d-f) 20 s (g-i) 30 s

(j-l) 40 s at 480, 500 and 520 $^{\circ}\mathrm{C}.$

6.3 Growth Kinetics of the Galvannealed Coatings

Figure 6.9 shows the Γ -Fe₃Zn₁₀ layer thickness as a function of galvannealing time and temperature. The growth rate and thickness of the gamma layer can be considered as a good indicator for coating growth kinetics and alloying rate. It can be seen that the gamma layer growth follows a power law relationship with galvannealing time for all three substrates for all galvannealing temperatures. As can be seen, in general, by increasing the galvannealing time (and temperature), the thickness of gamma layer was increased as would be expected from the diffusion controlled growth mechanism of this layer (Jordan et al. 1994). When the temperature was increased, the rate of diffusion of iron in the coating was increased and consequently, the rate of alloying of the coating increased. Thus, more saturation of iron occurs in the coating and nucleation and growth of gamma layer is accelerated (Jordan et al. 1994). In the case of increasing the time of galvannealing, it can be said that more iron atoms are provided for diffusion and thus, because of more saturation of the coating in iron, gamma layer nucleation and growth was increased. These results are in good agreement with the literature, showing the positive effects of time and temperature on the galvannelaing kinetics of steels (Jordan and Marder 1994).

The Γ -Fe₃Zn₁₀ layer thickness for all experimental steels was analyzed to determine growth rate time constant values. The general form for power-law growth was used for this analysis:

$$Y = Kt^{n}$$
(6.1)

where Y is the Γ -Fe₃Zn₁₀ layer thickness, K is the growth rate constant, t is the GA time and n is the growth rate time constant.

The n values were determined from a linear regression analysis of the growth curves and are shown in Table 6.1. As can be seen in Table 6.1, for all steels galvannealed at 480°C, the n values ranged from 0.506±0.1 to 0.523±0.1, corresponding to parabolic growth kinetics, where n = 0.50 (Jordan and Marder 1997). This suggests that the growth kinetics of the gamma layer at 480°C were controlled by bulk Zn and Fe interdiffusion. Considering the fact that the classic n value for the gamma layer is 0.25 (grain boundary diffusion controlled growth), and the gamma layer is the last layer which is formed in GA coatings (Jordan and Marder 1997), parabolic growth kinetics for this layer do not seem to be logical. The presence of other alloy layers, particularly the delta phase which grows rapidly and consumes the Zn metallic phase rapidly, would restrict the Zn supply to this layer and therefore, grain boundary diffusion controlled kinetics or a mixture of grain boundary/bulk diffusion would be expected. Furthermore, at 480°C, the rate of iron/zinc diffusion and also the availability of iron for the growth of gamma layer is more restricted in comparison to other GA temperatures (500 and 520°C) in this research and thus, parabolic kinetics for this layer at 480°C were not expected.

For other GA temperatures, as can be seen in Table 6.1, the n values range from 0.301 ± 0.06 to 0.341 ± 0.07 corresponding to non-parabolic kinetics in which a mixture of grain boundary/bulk diffusion control the growth kinetics (t^{1/3}, n~0.33). For DP steel at 520°C, however, the calculated n value was 0.234 ± 0.05 , the errors are large and it is very possible that this value is not significantly different from 0.33.

Several parameters can be considered for such non-parabolic kinetics; one mechanism is related to zinc diffusion and the flux of zinc atoms, which is increased by time and temperature, supplying the growing gamma phase layer may have resulted in a coarsening of the gamma phase layer structure. Therefore, the supply of zinc to the growing gamma layer may have been limited (Jordan and Marder 1997). Besides, the coarsening of the gamma layer may have resulted in decreasing the available grain boundary surface area (high diffusivity paths between the source and the growth interface) and consequently some bulk diffusion may have occurred; therefore, a mixture of grain boundary/bulk diffusion (n~0.33) was found at higher GA temperatures.

For grain-boundary diffusion in the presence of a compound layer, enough material must be delivered to the growth interface along the grain boundaries (Farrell and Gilmer 1974). When the grain size of the reaction layer increases (i.e. gamma), then growth would occur according to less than parabolic (n=0.5) kinetics. Any mechanism that results in appreciable loss of a material from a growing layer or a time-dependent reduction of the flux of material to the growth interface, can also result in non-parabolic growth behaviour (Jordan and Marder 1994). Material from a reaction layer could be lost due to dissolution. In this system, the dissolution or consumption of the gamma phase by the delta phase layer is possible. The migration of the delta phase has been shown to take place in two directions: toward the zinc melt and zeta phase layer, as well as toward the substrate steel and gamma phase layer (Horstmann 1978). The consumption of the gamma-phase by the rapidly growing delta phase layer may be another parameter that results in non-parabolic growth kinetics of the gamma phase layer.



Figure 6.9: Gamma thickness data for a) EEDS, b) CMn (continued).



Figure 6.9: Gamma thickness data for c) DP590.

GA	Growth rate constant (K)			Growth rate time constant (n)		
Temperature (°C)	EDDS	CMn	DP590	EDDS	CMn	DP590
480	0.159±0.02	0.219±0.04	0.105±0.02	0.523±0.1	0.503±0.1	0.506 ± 0.1
500	0.460 ± 0.09	0.530±0.1	0.380 ± 0.07	0.301±0.06	0.341±0.07	0.335±0.06
520	0.581±0.1	0.626±0.12	0.784±0.15	0.331±0.06	0.312±0.06	0.234±0.05

Table 6.1: Gamma layer growth rate time constant, n, and growth rate constant, K, values for the steels.

6.4 ICP Analysis

ICP analysis was performed to determine the iron and manganese content of the galvannealed coatings. The iron content of a galvannealed coating is another parameter that can be used to determine the rate of alloying and is used to compare galvannealing kinetics. As can be seen in Figure 6.10, by increasing the GA time and temperature, the iron and manganese content of the galvannealed coatings increased. It should be mentioned that due to the very low concentrations of other alloying elements in the GA coatings (e.g. Cr, Al, Mo), this data was not considered. Also, the average atomic percent of manganese in the galvannealed coatings (which was added to the iron content) was 0.009, 0.03 and 0.35 at.% for EDDS, CMn and DP590, respectively, showing the presence of manganese in the GA coatings. It can be seen that the Mn content of the galvannealed coatings rises with substrate Mn content.

Considering that the industrially optimum iron content for GA coatings is considered to be in the range of 10-12wt.% (~11-13 at.%), it can be seen that for most GA times and temperatures (except for the EDDS steel at 480°C for 10 and 20 s), the GA coatings had higher iron contents than this optimal value (i.e. over alloyed coatings).

Higher iron concentrations of these GA coatings can be ascribed to a thicker gamma layer, whose industrially optimal thickness is one micron or less. The gamma layer contains the highest concentration of iron among the other intermetallic layers in the GA coating and thus, by increasing the thickness of the gamma layer, the overall iron content of the GA coating was increased. These results are in good agreement with SEM results that showed thick gamma layers at higher GA temperatures/times (Figure 6.6-6.8) for all steels. From this result, it seems that all experimental GA temperatures and times in this research (except for EDDS, galvannealed at 480°C for 10 and 20 s) were not industrially suitable.

Figure 6.11 shows a comparison between the iron and manganese contents of the experimental coatings at different GA times and temperatures. As can be seen, for galvannealing at 480°C (Figure 6.11 (a)), the galvannealing kinetics or alloying rate for DP and CMn steels were similar and were higher than that of the EDDS for all GA times. Also, comparison between the iron and manganese content of the steels galvannealed at 500°C and 520°C (6.11 b and c) showed that alloying rate (galvannealing kinetics) were relatively similar for all steels at all GA times. These results are in good agreement with industrial evidences showing relatively higher galvannealing kinetics for DP steels.

In Figure 6.12, the isochronal atomic percent of coating Fe+Mn versus (1/T) for all coatings is plotted. The slope of the lines can be considered as the isochronal -Q/R, in which Q is defined as the activation energy and R is the universal gas constant. The activation energy (Q) is another parameter that can be used to compare the galvannealing kinetics for the experimental steels. The important point is that the activation energies for the DP and CMn steels for all experimental GA conditions are relatively similar and less than those of EDDS (Table 6.2). Also, there are not any values of activation energy for these steels in the literature and thus, the values obtained in this research can be considered as a new contribution in galvannealing of higher Mn containing steels. These results suggest that the activation energy which was required for the galvannealing process was less for DP and CMn steels versus the EDDS steel.

It should be mentioned that galvannealing kinetics are determined by the rate of two processes: inhibition layer breakdown and Fe-Zn diffusion. Thus, the lower activation energy does not exactly imply that diffusion was faster. It means that the energy barrier may have been smaller and inhibition breakdown may have occurred more quickly in the DP and CMn steels. Thus, by accelerating inhibition layer breakdown, the galvannealing kinetics may have been increased (Hertveldt et al. 2000). Accelerated inhibition breakdown will be discussed later in this section.

Another point concerning Table 6.2 is that the activation energies for the experimental steels changed with time. Considering the fact that the GA reaction is thermally activated (since it is a diffusion driven process, it is very likely the case), the change in the activation energy with time is not logical. Thus, it may be related to the errors of the analysis that resulted in fluctuations in the activation energies at different GA times.

The ICP data analysis showed that, in general, the galvannealing kinetics of dual phase steels containing higher concentrations of manganese (in comparison to EDDS and CMn steels) were insignificantly different from those of EDDS and CMn steels (at 500 and 520°C; Figures 6.11). However, it would appear that the galvannealing kinetics for the CMn and DP steels were higher than those of the EDDS steel at 480°C (Figure 6.11). This implies that the presence of high concentration of manganese in the CMn and DP substrates and consequently thicker manganese oxide film/particles at the surface/grain boundary accelerates the galvannealing kinetics at 480°C or 520°C.

Considering the correlation between selective oxidation and galvannealing kinetics, it was expected that presence of a thick manganese oxide layer at the surface/grain boundaries of DP steels would act as a barrier against the diffusion of iron into the coating and zinc through the grain boundaries of the steel and decrease galvannealing kinetics (alloying rate) of dual phase (and CMn) steels. In fact, an under alloyed GA microstructure was expected to be obtained after the galvannealing of DP steels. However, the SEM results showed a thick gamma layer (alloyed and over-alloyed microstructure) and ICP analysis indicated high concentrations of iron and manganese (high GA kinetics) in the galvannealed DP steels.

This behaviour may be ascribed to the presence of the thick oxide layer at the surface of higher Mn steels. The reason of this behaviour is not clearly understood but it may be partially related to the aluminothermic reduction of MnO, which could be more vigorous for the higher Mn steels. Due to the presence of a thicker oxide (or larger oxide particles) at the surface of higher Mn steels, aluminothermic reduction of the surface MnO will have taken place and significantly lowered the concentration of dissolved

aluminum in the zinc bath (Kavitha and McDermid 2011). Since the initial concentration of aluminum in the galvannealing bath was relatively low, a non-compact discontinuous inhibition layer ($Fe_2Al_5Zn_x$) was formed (Baril and L'Esperance 1999, Chen et al. 2008). Aluminothermic reduction may have affected the dissolved aluminum concentration of the GA bath significantly and further dropping of the Al concentration in the GA zinc bath, resulted in more holes and discontinuities in the inhibition layer and consequently, inhibition layer breakdown was accelerated. Easier and more rapid breakdown of the inhibition layer in the galvannealing step may have resulted in higher and accelerated galvannealing kinetics.

The presence of a thick oxide layer (or larger oxide particles) at the surface of the CMn and DP steels may have caused other effects. In the case of the CMn and DP steels, the Fe-Al layer (inhibition layer) may have also been mixed with manganese oxide particles, that is, packages or blocks of $Fe_2Al_5Zn_x$ and MnO were arranged next to each other (Bellhouse and McDermid 2007). Thus, due to the presence of boundary phases between these two phases, additional high diffusivity paths may have been available for iron (and manganese) to diffuse into the coatings. In addition, due to defects in the MnO structure, the diffusivity of iron and manganese may have been increased and higher fluxes of iron and manganese were able to pass through the defect sites in MnO. Another point is that the presence of these boundary phases and defects may have accelerated the Zn diffusion to the substrate grain boundaries, resulting in accelerated inhibition layer breakdown (Marder 2000, Guttmann 1994, Nishimoto et al. 1986) and higher galvannealing kinetics.



Figure 6.10: Atomic percent of iron+manganese for a) EDDS, b) CMn (continued).



Figure 6.10: Atomic percent of iron+manganese for c) DP590.



Figure 6.11: Comparison of iron+manganese content for EDDS, CMn and DP590 at a) 480, b) 500 °C (continued).



Figure 6.11: Comparison of iron+manganese content for EDDS, CMn and DP590 at c) 520 °C.



Figure 6.12: ln (Fe+Mn at.%) versus (1/T) for a) EDDS, b) CMn (continued).



Figure 6.12: ln (Fe+Mn at.%) versus (1/T) for c) DP590.

GA time

10 20

30

40

	1				
e (s)	Q (kJ/mol)				
	EDDS	CMn	DP590		
	115+17	63+110	5/1+0.8		

11.0±0.9

 1.6 ± 0.2

 5.4 ± 0.8

 2.3 ± 0.3

 5.7 ± 0.9

 1.5 ± 0.2

Table 6.2: Q values of GA steels at experimental GA times and temperatures.

 13.6 ± 2.0

10.2±1.5

 5.2 ± 0.8

6.5 GDOES Analysis

To analyze the distribution of the elements in the coating (particularly Mn and Al), Quantitative Depth Profiling (QDP) plots of the galvannealed coating were carried out using GDOES. As can be seen in Figure 6.13, in the as-dipped sample (GA time = 0), by moving towards the steel, the zinc content of the GA coatings was decreased and the iron content was increased due to the presence of a layer of metallic zinc and blocks of zeta phase (ζ -FeZn₁₃) at the coating/substrate interface. At the interface, for all samples, there was a peak for aluminum showing an Al-rich layer between the coating and substrate which may be the inhibition layer ($Fe_2Al_5Zn_x$) or aluminum oxide.

Figures 6.14 to 6.16 show the GDOES plots of the galvannealed coatings. As can be seen, manganese was uniformly distributed in all galvannealed coatings and did not form any separate layer in the coating. Aluminum, as seen in Figures 6.14 and 6.15, was evenly distributed in the galvannealed coatings on EDDS and CMn steels as a consequence of the inhibition layer breakdown (Jordan and Marder 1994).

For the galvannealed DP steels, an aluminum peak appeared (Figure 6.16) at the steel/coating interface. The presence of this aluminum peak cannot be related to the presence of an inhibition layer at the interface as the microstructural development of the coatings clearly indicates that inhibition breakdown had taken place (Figure 6.6). One of the reasons that may be used to justify the presence of this Al peak is aluminothermic reduction of the MnO layer. It seems that thick oxide layer/large oxide particles may have been reduced (partially or totally) by the dissolved aluminum in the zinc bath and the product of this reaction was aluminum oxide:

$$3MnO+ 2[Al] \rightarrow Al_2O_3 + 3[Mn]$$
(6.2)

This aluminum oxide may have been formed as a very thin layer or scattered particles at the interface and was appeared in GDOES plots. Considering the low aluminum content in the galvannealing baths, the amount of these aluminum oxide particles should not be high (Kavitha and McDermid 2011, Khondker et al. 2007).





Figure 6.13: QDP of as-dipped coatings (GA_t=0) obtained by GDOES for a) EDDS, b) CMn (*Note*: Mn content for EDDS and CMn is multiplied by 40 and for DP is multiplied by 10) (continued).





Figure 6.13: QDP of as-dipped coatings (GA_t=0) obtained by GDOES for c) DP590(*Note*: Mn content for EDDS and CMn is multiplied by 40 and for DP is multiplied by 10).



Figure 6.14: QDP of galvannealed coatings obtained by GDOES for EDDS galvannealed for a) 480°C/10s, b) 480°C/20s, c) 480°C/30s, d) 480°C/40s (continued) (*Note*: Mn content is multiplied by 40).



Figure 6.14: QDP of galvannealed coatings obtained by GDOES for EDDS galvannealed for e) 500°C/10s ,f) 500°C/20s, g) 500°C/30s, h) 500°C/40s (continued) (*Note*: Mn content is multiplied by 40).

100 -





Figure 6.14: QDP of galvannealed coatings obtained by GDOES for EDDS galvannealed for i) 520°C/10s, j) 520°C/20s, k) 520°C/30s, l) 520°C/40s (Note: Mn content is multiplied by 40).



Figure 6.15: QDP of galvannealed coatings obtained by GDOES for CMn galvannealed for a) 480°C/10s, b) 480°C/20s, c) 480°C/30s, d) 480°C/40s (continued) (*Note*: Mn content is multiplied by 40).



Figure 6.15: QDP of galvannealed coatings obtained by GDOES for CMn galvannealed for e) 500°C/10s ,f) 500°C/20s, g) 500°C/30s, h) 500°C/40s (continued) (*Note*: Mn content is multiplied by 40).



Figure 6.15: QDP of galvannealed coatings obtained by GDOES for CMn galvannealed for i) 520°C/10s, j) 520°C/20s, k) 520°C/30s, l) 520°C/40s (*Note*: Mn content is multiplied by 40).


Figure 6.16: QDP of galvannealed coatings obtained by GDOES for DP galvannealed for a) 480°C/10s, b) 480°C/20s, c) 480°C/30s, d) 480°C/40s (continued) (Note: Mn content is multiplied by 10).



Figure 6.16: QDP of galvannealed coatings obtained by GDOES for DP galvannealed for e) 500°C/10s ,f) 500°C/20s, g) 500°C/30s, h) 500°C/40s (continued) (*Note*: Mn content is multiplied by 10).



Figure 6.16: QDP of galvannealed coatings obtained by GDOES for DP galvannealed for i) 520°C/10s, k) 520°C/30s, l) 520°C/40s (*Note*: Mn content is multiplied by 10).

6.6 TEM Analysis

TEM-EDX analysis was performed on a galvannealed DP sample (galvannealed at 500°C for 20s) to determine the origin of the Al peak that was seen in the GDOES analysis (Figures 6.14 to 6.16). TEM samples were prepared using a Focused Ion Beam (FIB) microscope. Figure 6.17 shows the interface between the substrate and galvannealed coating. It was expected to observe a layer or some particles at the coating/substrate interface but, no separate layer was observed even under very high magnifications. Nevertheless, a region at the interface was selected for EDX analysis (Figure 6.18, colour rectangle). After plotting the related elemental maps of oxygen, iron, aluminum and zinc, it was found that there was no separate Al containing oxides or intermetallic layers at the interface. Accumulation of oxygen/aluminum was expected at the interface (oxide assumption) however, it was not observed. Analysis of other regions at the interface had the same result (Figure 18).

The presence of an Al peak in the GDOES results and the absence of any Al-rich layers/regions (Fe₂Al₅Zn_x or Al₂O₃) in the TEM analysis may be related to the analysis region and probability of an Al-rich phase being present in the analysis region. In GDOES, the analysis region at the surface (5mm \times 5mm) is very larger in comparison to the TEM and therefore, the results are an average of chemical composition of several atomic layers that are sputtered in a large volume. Since the Al peak in GDOES may be related to the production of Al₂O₃ from aluminothermic reduction (as was mentioned previously), and considering the fact that the amount of this Al₂O₃ may be very low (scattered particles or packages), it could be possible that some of these tiny oxide

particles/packages may have been detected in the relatively large analysis area in GDOES. In the TEM, since a very small region of some grains at the cross section was analyzed, the probability of the presence of Al_2O_3 (or any other Al-rich phase) may be very low. To remove this problem, or to increase the probability of presence of oxide or other Al-rich phases in TEM analysis, several samples of the galvannealed coatings should be prepared.



Figure 6.17: TEM image of interface between coating and steel substrate.



Figure 6.18: TEM EDX mapping of the steel/coating interface of the DP590 steel a) TEM image with the Fe map overlaid in red, the Zn map in green and the O map in blue and Al in pink, b) Fe, c) Zn, d) Al e) O maps.





Figure 6.19: TEM image of the steel/coating interface (left) and elemental map of the analyzed region (dark rectangular on the left figure); Fe map overlaid in red, the O map in blue and the Zn map in green.

7 CONCLUSIONS

7.1 Selective Oxidation

For the three steel chemistries studied enrichment of Mn in the form of oxides was observed at the steel surface for all process atmospheres. The EDDS steel showed minor oxidation, primarily at the grain boundaries with sparse nodular oxide particles on the surface. However, more significant populations of oxide nodules/films on the surface as well as oxide ridges at the grain boundaries were observed for the CMn and particularly DP samples. The EDDS and CMn samples generally exhibited surface oxides with spherical cap morphology but the surface nodules of the DP steels generally had a faceted or irregular shape and some areas were covered with spherical cap shaped nodules. In other words, external oxidation was increased at the surface of CMn and DP samples, containing higher concentration of Mn. Furthermore, the oxide particle size on the EDDS steel surface was considerably smaller than that on the CMn or DP steel surfaces. The DP steels showed the largest oxide particles and thickest oxide layer among all of the experimental steel samples.

7.2 Galvannealing

For all experimental steels, it was found that by increasing the galvannealing temperatures and times, the rate of alloying, gamma layer thickness and iron+manganese content in the GA coating were increased because of higher diffusion of iron (and manganese) and more available iron (and manganese) atoms for diffusion. Also, it was found that the galvannealing kinetics of DP and CMn steels at 480°C were more rapid

than that of the EDDS steel. It was also concluded that presence of manganese in the substrate and its oxides at the surface did not have a significant effect on the GA coating formation kinetics at 500 and 520°C. The more rapid galvannealing kinetics for the higher Mn containing steels at 480°C may be ascribed to the presence of thicker oxide layers/particles at the surface. Oxide layers/particles may have been reduced by aluminothermic reduction and thus, inhibition layer breakdown may have been accelerated. Furthermore, it was found that 500 and 520 °C GA temperatures were not industrially suitable for all experimental steels in this project since these temperatures will result in a thick brittle gamma layer and high iron content in the coating.

7.3 Future Work

Selective oxidation and galvannealing of DP steels should also continue to be studied. Improvements can be made by testing a larger range of process atmospheres, intercritical annealing temperatures, steel chemistries and bath chemistries. Thus, it would be possible to accurately predict the oxidation and galvannealing kinetics for a given set of process conditions and substrate chemistries.

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