SELECTIVE OXIDATION AND REACTIVE WETTING OF FE-0.1C-6MN-2SI-xSN ADVANCED HIGH STRENGTH STEELS DURING CONTINUOUS HOT-DIP GALVANIZING

SELECTIVE OXIDATION AND REACTIVE WETTING OF FE-0.1C-6MN-2SI-xSn ADVANCED HIGH STRENGTH STEELS DURING CONTINUOUS HOT-DIP GALVANIZING

By

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To my angels who reside far away

ABSTRACT

Third generation advanced high-strength steels (3G-AHSS) have received significant interest from leading auto steel industries and OEMs as candidate materials for reduced mass Body In White (BIW) components due to their unique combination of high specific strength and ductility. However, the continuous hot-dip galvanizing of these steels is challenging due to selective oxidation of the main alloying elements such as Mn, Si, Al and Cr at the steel surface during the annealing step prior to immersion in the galvanizing Zn(Al, Fe) bath, as extensive coverage of the substrate surface by these oxides is detrimental to reactive wetting, good coating adhesion and integrity.

Simulated galvanizing treatments were conducted on two prototype Fe-0.1C-6Mn-2Si (wt pct) 3G steels; one as the reference steel and the other with 0.05 wt pct Sn added to the composition. The combined effects of annealing temperature, time, process atmosphere oxygen partial pressure and 0.05 wt pct Sn addition on the selective oxidation of the steel substrates were determined. Subsequently, the reactive wetting of the steels with respect to the pre-immersion surface structures of the samples annealed for 120 s was examined. Annealing heat treatments were carried out at 800°C and 690°C in a N₂-5 vol pct H₂ process atmosphere under three dew points of -50°C, -30°C and +5°C, covering process atmosphere oxygen partial pressures within the range of 1.20×10^{-27} atm to 1.29×10^{-20} atm. MnO was present at the outmost layer of the external oxides on all samples after annealing. However, the morphology, distribution, thickness and surface coverage were significantly affected by the experimental variables. Annealing the reference steel under the low dew point process atmospheres, i.e. -50°C and -30°C, resulted in the highest Mn surface concentration as well as maximum surface oxide coverage and thickness. The oxides formed under these process atmospheres generally comprised coarse, compact and continuous film forming nodules, whereas the surface morphologies and distributions obtained under the +5°C dew point

process atmosphere, which was consistent with the internal oxidation mode, exhibited wider spacing between finer and thinner MnO nodules. The grain boundary internal oxide networks had a multi-layer structure with SiO₂ and MnSiO₃ at the oxide cores and shells, respectively. Significant morphological changes were obtained as a result of Sn addition. The continuous film-like external MnO nodules were modified to a fine and discrete globular morphology, with less surface coverage by the oxides and reduced external oxide thickness. Both the external and internal oxidations followed parabolic growth kinetics, where the depth of the internal oxidation zone decreased with Sn addition and decreasing oxygen partial pressure.

Poor reactive wetting was observed for the reference steel substrates that were annealed for 120 s under the -50° C and -30° C dew point process atmospheres at 800°C and under the -50° C dew point atmosphere at 690°C, such that no integral metallic coating was formed after the 4 s immersion in the Zn(Al, Fe) bath. By contrast, excellent coating quality was obtained for the Sn-added steels when the -30° C and $+5^{\circ}$ C dew point process atmospheres were employed when annealing at 690°C. The remainder of the experimental conditions demonstrated good reactive wetting with intermediate coating quality. For the two reference steels annealed at 800°C under the -50° C and -30° C dew point process atmospheres, poor reactive wetting was due to full coverage of the surface by 116 nm and 121 nm thick and continuous MnO films. In the case of the 690°C × -50° C reference steel with the external layer thickness of only 35 nm, however, poor wetting was attributed to substantial coverage of the surface by continuous, film-like oxides. In both cases, exposure of the underlying substrate to the bath alloy and an intimate contact between the substrate Fe and the bath dissolved Al could not take place and the formation of the Fe₂Al₅Zn_x interfacial layer was hidered.

For the processing conditions that satisfactory reactive wetting was obtained despite the pre-immersion selective oxidation of the surfaces, several reactive wetting mechanisms

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were determined. For the samples with a sufficiently thin external MnO layer, good reactive wetting was attributed to partial reduction of MnO by the bath dissolved Al, as well as bridging of the Mn sub-oxides by the Zn coating or $Fe_2Al_5Zn_x$ interfacial intermetallics. Partial or full formation of the $Fe_2Al_5Zn_x$ interfacial layer was observed in the successfully galvanized substrates with Fe-Al crystals formed between, underneath and also on top of the reduced oxides. Furthermore, for cases with widely-spaced, fine oxide nodules, it was found that the liquid bath alloy was able to infiltrate the external oxide/substrate interface, resulting in surface oxide lift-off and enhanced coating adhesion. It was globally concluded that the thin, discrete and fine globular morphology of external MnO, resultant of annealing the steel substrates with 0.05 wt pct Sn addition under the process atmosphere oxygen partial pressures consistent with internal oxidation, allowed for an enhanced reactive wetting by the Zn(Al, Fe) galvanizing bath which was manifested by increased amount of Al uptake and population of the Fe₂Al₅Zn_x interface.

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PREFACE

The present document is prepared in ten chapters in a sandwich thesis format where the scholarly work and main contributions of the author (Chapters 3 to 7) is sandwiched by the preceding Introduction and Literature Review chapters (Chapters 1 and 2) followed by the Global Discussion, Conclusions and Future Directions which make up Chapters 8 to 10. All of the material in Chapters 3 to 7 is based on journal manuscripts either accepted, submitted or in preparation. In this manner, Chapters 3 and 5 are manuscripts published in Metallurgical and Materials Transactions A and ISIJ International, respectively. Chapter 4 is a manuscript currently under review at Metallurgical and Materials Transactions A and Chapters 6 and 7 are draft manuscripts in preparation for submission to ISI journals. The appropriate citations to the articles are included on the first page of the corresponding chapters. As all of the manuscripts only include the names of two authors, the PhD student and their thesis supervisor, it is declared that the author of the present thesis was the main contributor to all of the experimental and scholarly work undertaken for completion of this research work and was the primary author of the draft manuscripts. The only exception to this is Chapter 4, where the third author, Dr. Brian Langelier contributed to the Atom Probe Tomography as part of that article. It must also be mentioned that the permission to reprint the accepted journal articles in the current thesis (Chapters 3 and 5) has been obtained from the respective journals, who own the copyright, and that the signed letters have been submitted to the School of Graduate Studies.

Finally, the reader is informed of the inherent overlaps and repetitions that exist in the experimental sections of the chapters, mostly with respect to the chemical composition of the experimental steels, the continuous annealing and galvanizing cycles and the process atmosphere specifications, as well as the technical aspects of the analytical apparatus and sample preparation methods etc.

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CHAPTER 1 INTRODUCTION

Third generation medium-Mn advanced high strength steels (3G-AHSS) are receiving growing interest from leading auto steel industries and OEMs as candidate materials for automotive light-weighting solutions due to their unique combination of high specific strength and ductility (Miller 1972, Merwin 2007 and 2008, Suh et al. 2017) which fills the existing property gap between the first generation (1G, e.g. DP and TRIP) and second generation (2G, e.g. high-Mn TWIP) AHSSs (Figure 1.1). This allows auto manufacturers to design lighter, thinner and more geometrically complex structural components without comprising passenger safety while also adhering to the legislated guidelines for greenhouse gas emission reduction.



Figure 1.1: The "banana diagram" comparing the total elongation and ultimate tensile strength of the three generations of the AHSSs. The US DOE and AutoSteel partnership targets are marked by red circles. (Billur and Altan 2013).

To maintain the structural integrity of the vehicle, the manufactured components must be protected against corrosion, with the most widely practiced and cost-effective mass production industrial process being the continuous hot-dip galvanizing. However, obtaining an adherent, integral zinc coating on AHSS substrates, in particular the 3G-AHSSs, can be challenging due to selective oxidation of the essential alloying elements such as Mn, Si, Al and Cr at the steel surface during the annealing step prior to galvanizing (Mahieu et al. 2001 and 2002, Maki et al. 2003, Bellhouse and McDermid 2011 and 2012, Sagl et al. 2013 and 2014). Substantial coverage of the steel surface by an external oxide layer prior to immersion prevents the progression of the desired wetting reactions, i.e. formation of a well developed Fe₂Al₅Zn_x interfacial layer, between the steel and the liquid galvanizing bath during immersion (Mahieu et al. 2001 and 2002, Maki et al. 2003, Bellhouse and McDermid 2011 and 2012, Sagl et al. 2013 and 2014). As a result, the final product can suffer from poor coating adhesion or contain unacceptable defects such as bare spots.

Improving the reactive wetting of dual phase (DP) (Khondker et al. 2007, Alibeigi et al. 2011) and low-alloy transformation induced plasticity (TRIP) steels (Gong et al. 2008, 2009 and 2011, Bellhouse and McDermid 2011 and 2012, Sagl et al. 2013 and 2014) by the continuous galvanizing bath has been the subject of numerous studies and, in several cases, formation of the desired Fe-Al interfacial layer at the steel/coating interface has been observed despite the external selective oxidation of the alloying elements prior to immersion. The annealing process atmosphere parameters (Gong et al. 2008, 2009 and 2011, Bellhouse and McDermid 2011 and 2012, Cho et al. 2014, Jo et al. 2017) and alloy chemistry (Bellhouse et al. 2007, Bellhouse and McDermid 2008 and 2010, Alibeigi et al. 2011, Cho et al. 2014 and 2016, Oh et al. 2016) have been shown to strongly affect the surface oxide chemistry, morphology and thickness which were all identified as determining factors in the reactive wetting of the steel substrates. More recently, it has been shown that the addition of trace amounts of surface active elements such as Sn (Cho et al. 2014 and 2016), Sb (Cho et al. 2014) and Bi (Oh et al. 2016) to low-alloy TRIP steels can favourably modify the surface oxide morphology and improve reactive wetting by the Zn(Al, Fe) bath.

With the pending emergence of 3G-AHSSs for automotive applications and given the limited number of studies available on the selective oxidation and reactive wetting of medium-Mn steels, this thesis seeks to determine the fundamental relationships that exist between the annealing process atmosphere parameters, the surface oxide structure prior to immersion and the subsequent reactive wetting during continuous hot-dip galvanizing of prototype Fe-0.1C-6Mn-2Si-xSn (wt pct) 3G-AHSSs. Tailoring the process atmosphere oxygen partial pressure and improving the alloy design were the two main approaches undertaken to address the issue of poor reactive of the medium-Mn steels by the galvanizing bath. The selective oxidation of the 0.1C-6Mn-2Si steels during austenitic and intercritical annealing are discussed separately in Chapters 3 and 4, respectively, to establish a fundamental understanding of how factors such as heat treatment time and temperature, process atmosphere oxygen partial pressure and steel chemistry, i.e. 0.05 wt pct Sn addition, affect the morphological development and kinetics of the external and internal oxidation in the 0.1C-6Mn-2Si alloy system prior to immersion. The effect of peak annealing temperature and process atmosphere oxygen partial pressure on the selective oxidation and reactive wetting of the reference steel are addressed in Chapter 5, as it has been shown by Bhadhon et al. (2015) that the mechanical properties of a 0.2C-6Mn-1.5Si-0.5Al-0.5Cr (wt pct) 3G-AHSSs are sensitive to the starting microstructure such that the peak properties were obtained using a martensitic starting microstructure, requiring an austenitization annealing cycle prior to intercritical annealing. Chapters 6 and 7 provide the meso-, micro- and nanoscale analysis of the steel/coating interfaces for identification of the governing reactive wetting mechanisms of the steels under the combined effects of process atmosphere oxygen partial pressure and a 0.05 wt pct Sn addition to the reference 0.1C-6Mn-2Si model alloy.

CHAPTER 2 LITERATURE REVIEW

The first half of this chapter comprises a brief introduction to the medium-Mn 3G-AHSSs along with an overview of the continuous hot-dip galvanizing line and the phenomena associated with its two main components: the annealing furnace and the Zn(Al, Fe) bath. A concise survey of the selected literature is presented in the second half; however, due to the current lack of literature on the selective oxidation and reactive wetting of the medium-Mn 3G-AHSSs, topics such as the effect of process atmosphere parameters and steel chemistry, more specifically the effects of oxygen partial pressure and surface active elements, are discussed in the light of the relevant research available on the previous generations of AHSSs, i.e. DP, TRIP etc.

2.1 Third generation advanced high-strength steels

The medium-Mn high-strength and ultra high-strength steels are amongst the most recent automotive steel solutions developed for improved car body light weighting and passenger safety. Their superior strength-ductility balance, commonly reported as the product of the ultimate tensile strength (UTS) and the total elongation (TE), is typically within the range of 24,000 MPa pct to 40,000 MPa pct (De Moor et al. 2011, Zhang et al. 2013, Lee et al. 2013, Bhadhon et al. 2015, Latypov et al. 2016, Cho et al. 2016), making the 3G-AHSS an ideal material of choice for thinner safety structural components such as A and B pillars and roof rails.

The microstructure of medium-Mn steels, highly sensitive to the intercritical annealing temperature (IAT), is comprised of ferrite, martensite and large volume fractions of retained austenite stabilized as a result of C and Mn partitioning during intercritical annealing (Lee et al. 2011, Jun et al. 2011, De Moor 2011). During deformation, this retained austenite

gradually transforms to martensite under the transformation induced plasticity (TRIP) effect which contributes to a significantly high sustained work hardening rate and delayed necking (Jacques et al. 2001, Merwin 2007, Matlock and Speer 2009, McDermid et al. 2011).

To obtain the desired microstructure and mechanical properties, the intercritical annealing of the medium-Mn and Quench and Partitioning (Q&P) 3G-AHSSs is typically carried within a temperature range of 700°C to 850°C (Speer et al. 2003, Merwin 2007 and 2008, De Cooman et al. 2017, Bhadhon et al. 2017, Pallisco et al. 2017). While the UTS increases with the intercritical annealing temperature (IAT), the yield strength (YS), a required metric for safety applications, decreases with IAT (Gibbs et al. 2011, Lee et al. 2011, De Cooman et al. 2017). On the other hand, several authors (Merwin 2007, Lee et al. 2011, Bhadhon et al. 2015) have shown that the optimized combination of properties for steels with Mn contents in the range of 5-7 wt pct is obtained by annealing in the range of 650°C to 690°C. However, instances of localized plastic deformation have been reported for the medium-Mn steels that were annealed within the lower IAT range (De Cooman et al. 2013). While research is being actively undertaken to elucidate the work hardening behaviour of the medium-Mn steels, there is a notable lack of data on the phenomena and mechanisms associated with the hot-dip galvanizing of these substrates for corrosion protection. This is another important topic which may limit the integration of the medium-Mn substrates to the automotive industry, as the selective oxidation of the key alloying elements such as Mn, Si and Al, during annealing can cause problems in obtaining a high-quality galvazined coatings. To this end, a fundamental analysis of the selective oxidation and reactive wetting of a model Fe-0.1C-6Mn-2Si-xSn 3G-AHSSs was undertaken to assist with filling the existing knowledge gap.

2.2 The industrial continuous hot-dip galvanizing line

As mentioned earlier, to protect the structural integrity of thinner gauge AHSS auto-body parts from aqueous corrosion, continuous hot-dip galvanizing is widely practiced by the global steel industry. Zn-based coatings protect the underlying steel by two main mechanisms: barrier protection and galvanic protection. The galvanized coating acts as a physical barrier between the steel and the corrosive environment, and zinc, being the less noble metal in the Fe-Zn galvanic couple, also acts as an anode and corrodes preferentially to protect the underlying steel substrate.

A schematic of a typical continuous galvanizing line is shown in Figure 2.1 (E.A. Silva 2010). The steel, after being welded into a continuous strip in the delivery section (not shown in Figure 2.1), is typically cleaned with an alkali-based solution (usually 80°C 2% NaOH with chemical inhibitors to inhibit Fe dissolution) and undergoes several mechanical and/or electrolytic cleaning steps in order to remove organic and other adhering contaminants before entering the annealing furnace (Marder 2000). During the annealing step, the steel is heat treated, within a temperature range of 650°C to 850°C in the case of the medium-Mn substrates, to obtain the required microstructure and mechanical properties. The annealing atmosphere is usually comprised of a reductive N2-H2 gas mixture with a controlled dew point, i.e. fixed partial pressure of water vapour (pH₂O), to reduce any surface iron oxides and to maximize the amount of metallic iron available on the surface, a crucial objective for obtaining an adherent galvanized coating. Upon exiting the furnace, the steel strip is cooled to the zinc bath temperature of approximately 460°C and is then immersed in an Fe-saturated molten bath with a dissolved aluminium content in the range of 0.15 to 0.25 wt pct in the case of galvanized coating (Marder 2000, Giorgi et al. 2001, Dionne 2006, McDermid et al. 2007). The Al is added to the bath to form the desired $Fe_2Al_5Zn_x$ interfacial layer at the steel/coating interface, characteristic of the reactive wetting of the steel substrate by the Zn(Al, Fe) bath.

After immersion, the strip exits the bath where the coating weight/thickness is controlled through the action of planar gas jets using air or nitrogen (Marder 2000) and the final solidification usually takes place using forced air or ambient cooling. In the case of galvannealed coating, which is out of the scope of the present thesis, an additional annealing step is taken prior to cooling to develop a fully alloyed coating of Fe-Zn intermetallics. Lastly, the strip will go through several post-dipping steps such as temper rolling, passivation coating, coiling and cutting which are not pictured in Figure 2.1.



Figure 2.1: Schematic drawing of a continuous hot-dip galvanizing line (E.A. Silva 2010).

2.2.1 The annealing furnace and gas-metal reactions

As mentioned above, the process atmosphere in the annealing furnace is dew point controlled, meaning that this parameter is used to adjust the oxygen partial pressure of the N₂-H₂ gas mixture. The dew point temperature, T_{DP} , is the temperature at which the liquid water-water vapour reaction is at equilibrium:

$$H_2 O(l) = H_2 O(g)$$
 at T_{DP} (2.1)

$$\Delta G_{2.1}^{o} = -RT_{DP} \ln K_{2.1} \quad K_{2.1} = \frac{p_{H_2O(g)}}{a_{H_2O(g)}} = p_{H_2O(g)}$$
(2.2)

Where $\Delta G_{2.1}^o$ is the standard Gibbs free energy of the reaction, *R* is the universal gas constant, $K_{2.1}$ is the equilibrium constant and $a_{H_2O(1)} = 1$ as liquid water is assumed to be a pure condensed species.

For a process atmosphere with a fixed hydrogen content at a given temperature T, the oxygen partial pressure, pO_2 , is determined by the pH_2O which is defined by the dew point temperature, such that the lower the process atmosphere dew point, the lower the oxygen partial pressure:

$$H_2 + \frac{1}{2}O_2 = H_2O(g)$$
 (2.3)

$$\Delta G_{2.3}^{o} = -RT \ln K_{2.3} \quad K_{2.3} = \frac{pH_2O}{pH_2pO_2^{1/2}}$$
(2.4)

The thermodynamic stability of a metal oxide as a function of process atmosphere oxygen partial pressure can then be determined using Equations (2.5) and (2.6):

$$\frac{x}{y}M + \frac{1}{2}O_2 = \frac{1}{y}M_xO_y$$
(2.5)

$$\Delta G_{2.5}^{o} = -RT \ln K_{2.5} \quad K_{2.5} = \frac{a_{M_x O_y}^{\frac{1}{y}}}{a_M^{\frac{1}{y}} p O_2^{\frac{1}{2}}} = \frac{1}{a_M^{\frac{1}{y}} p O_2^{\frac{1}{2}}}$$
(2.6)

Where *M* and $M_x O_y$ denote a metal and its oxide, respectively, and the oxide is assumed to be a pure condensed species with an activity of 1.

Such computations were performed for Fe, Mn and Si using the thermodynamic data of Fine and Geiger (1979) and the results are plotted in Figure 2.2 as a function of the annealing temperature and activity of the solute element. The equilibrium dew point atmospheres relevant to the CGL are also shown by dashed lines in this plot. As can clearly be seen, the annealing process atmosphere is reductive with respect to Fe, but it is oxidizing with respect to Mn and Si which are the common alloying elements employed in AHSSs. As the experimental steels of the present study have negligible Al content, the equilibrium oxygen partial pressure line for Al is not provided in Figure 2.2; however it should be noted that, once computed, the Al/Al₂O₃ line would fall below Mn and Si, indicating a higher thermodynamic stability. It is thereby concluded that regardless of the annealing temperature or oxygen partial pressure employed, the selective oxidation of the less noble alloying elements in the AHSSs is inevitable for a practical CGL process window. This is also where the core issue with respect to the continuous hot-dip galvanizing and reactive wetting of AHSSs arises – i.e the accessof the steel substrate to the molten zinc bath can be restricted due to the presence of the oxides formed at the steel surface prior to immersion.



Figure 2.2: Thermodynamic stability of oxides with respect to annealing temperature and oxygen partial pressure.

2.2.2 The Zn(Al, Fe) bath and reactive wetting

The Zn-rich corner of the Zn-Al-Fe phase diagram at 460°C (McDermid et al. 2007)

is shown in Figure 2.3. It can be seen that due to the limited solubilities of Fe and Al in Zn at

460°C, several intermetallic phases can precipitate according to the bath composition, where the equilibrium configuration of the bath changes from $L + \zeta$ -FeZn₁₃ to $L + \delta$ -FeZn₁₀ and further to $L + \eta$ -Fe₂Al₅Zn_x with increasing bath Al content.



Figure 2.3: Zn rich corner of the Zn-Al-Fe ternary system in Cartesian coordinates; the dotted lines indicate the isoactivity lines of Al and Fe in the liquid phase; L is liquid, ζ is FeZn₁₃, δ is FeZn₁₀ and η is Fe₂Al₅Zn_x (McDermid et al. 2007).

As was mentioned earlier, a typical galvanizing bath contains approximately 0.15 wt pct to 0.25 wt pct dissolved Al, where the term "dissolved" refers to the Al that is in solution in the liquid phase and is available for the $Fe_2Al_5Zn_x$ interfacial layer formation, and not the Al that had participated in intermetallic formation.

When the steel is first immersed in the bath, Fe dissolution from the strip takes place as the strip is not in thermodynamic equilibrium with the Zn bath (Guttmann 1994). There is also a higher metastable Fe solubility in the vicinity of the strip, which results in further dissolution of Fe and creation of a local supersatutration (Nakano 2006). Under such conditions and due to a larger thermodynamic driving force for formation (Guttmann 1994), Fe-Al intermetallics will precipitate on the steel substrate instead of Fe-Zn intermetallics. The Fe-Al interfacial layer is commonly referred to as the inhibition layer due to the fact that it acts, temporarily, as a barrier to Fe and Zn diffusion and "inhibits" the formation of brittle Fe-Zn intermetallic compounds (Guttmann 1994, Marder 2000). The morphology of the interfacial layer has a two layer structure. The lower layer, which is contact with the substrate, comprises a compact layer of fine and preferentially oriented $Fe_2Al_5Zn_x$ crystals and the top layer, which is in contact with the bath alloy, consists of coarse, elongated and randomly oriented $Fe_2Al_5Zn_x$ crystals (Guttmann 1994, Baril and L'Espérance 1999, Chen et al. 2008). A micrograph of the steel/coating interface of a commercial ultra-low-carbon steel showing the two sublayers is presented in Figure 2.4.



Figure 2.4: The two types of Fe-Al interfacial layer morphologies observed at the interface of commercial ultra-low-carbon steel galvanized in a 0.18 wt pct Al bath: (a) small equiaxed crystals and (b) coarse elongated crystals (Baril and L'Espérance 1999).

However, the presence of the interfacial layer is transient and, given enough time and exposure to the liquid bath, the inhibition layer will break down as a result of Zn diffusion through the layer and into the steel (Guttmann 1994, Marder 2000). When a critical concentration of Zn within the steel is reached, typically at fast diffusion sites such as grain boundaries or triple points (Guttmann 1994, Baril and L'Espérance 1999, Dionne et al. 2002), ζ -FeZn₁₃ will nucleate and grow outward from the interface (Guttmann 1994, Baril and L'Espérance 1999, Chen et al. 2008). The formation of these outbursts is detrimental to the coating quality as they can result in flaking of the coating during forming operations and will frequently print through on the external coating surface during painting.

2.3 Selective oxidation and reactive wetting of AHSS

As established in the previous sections, the typical CGL annealing atmosphere is not reducing with respect to the key alloying elements employed in the AHSSs and the selective oxidation of elements such as Mn, Si and Al inevitably occurs at the external surface or within the interior of the steel strip. This can render the sheet surface incompatible for reactive wetting by the Zn(Al, Fe) bath as substantial coverage of the surface by a thick and compact film-forming oxide will prevent the metallic Fe from the substrate reacting adequately with the galvanizing bath to form the essential reactive wetting products, i.e. the $Fe_2Al_5Zn_x$ interfacial layer. This results in poor coating adhesion and unacceptable defects such as bare spots in the end product (Mahieu et al. 2001 and 2002, Maki et al. 2003, Drillet et al. 2004).

Numerous authors have studied and reported on the selective oxidation and reactive wetting of several industrial grades of AHSSs such as DP (Khondker et al. 2007, Alibeigi et al. 2011, Sagl et al. 2014), TRIP (Gong et al. 2008, Cho et al. 2014, Bellhouse and McDermid 2010, 2011 and 2012, Sagl et al. 2014) and high-Mn TWIP (Blumenau 2011, Gong and De Cooman 2011, Cho and De Cooman 2012, Kim et al. 2014). It has been determined that the chemistry, thickness, morphology and distribution of the pre-immersion oxides are the dominant factors in determining the occurrence of reactive wetting of the steel by the continuous hot-dip galvanizing bath.

For instance, it is well established that the film-forming oxides of SiO_2 , $MnSiO_3$ and Mn_2SiO_4 have the most detrimental effect on the reactive wetting of the steel substrates (Drillet et al. 2004, Mahieu et al. 2004, Suzuki et al. 2009), while it is known that the

presence of MnO is less harmful to $Fe_2Al_5Zn_x$ formation. For example, it was shown that it is possible for the external MnO to be reduced by the in situ aluminothermic reduction mechanism during the standard immersion times of approximately 4 s (Khondker et al. 2007, Alibeigi et al. 2011, Kavitha and McDermid 2012, Sagl et al. 2013). Furthermore, several authors have reported that the Fe-Al reaction products can precipitate on top of the MnO nodules (Bellhouse and McDermid 2010 and 2012, Blumenau et al. 2011, Sagl et al. 2013).

Similarly, the effects of external oxide layer thickness and morphology have been the subject of several studies (Drillet et al. 2004, Bellhouse et al. 2008, Blumenau et al. 2011, Sagl et al. 2013). It is globally agreed that it is less likely for the thicker and more closely-spaced and continuous external oxides to be reduced by the bath dissolved Al during immersion, a mechanism which was first proposed by Khondker et al. (2007) in the case of external MnO formed on a DP600 steel, and by which the MnO can be removed from the steel surface and promote the wetting reactions. It was later determined by Alibeigi et al. (2011) that the kinetics of the reactive wetting is inversely related to the external MnO layer thickness. Later, Kavitha and McDermid (2012) further validated this mechanism and also added that for reaction times longer than 1.2 s, the aluminothermic reduction of MnO exhibits linear kinetics as shown in Figure 2.5. It can then be proposed that that the MnO layers less than 85 nm in thickness can be reduced within the common CGL dipping time of 4 s.



Figure 2.5: Change in the MnO layer thickness vs reaction time (Kavitha and McDermid 2012).

The effect of oxide morphology on the reactive wetting of low-alloy TRIP steels was discussed in a series of studies by Bellhouse and McDermid (2008, 2010, 2011 and 2012). Surface oxide lift-off and cracking as well as bridging of the MnO nodules was observed at the interface of the galvanized steel in locations where the oxide nodules were separated by the metallic iron from the substrate. Furthermore, they advocated that improved reactive wetting was obtained when the pre-immersion external oxide layer comprised more widely dispersed nodules with thinner inetrnodular oxide films (Bellhouse and McDermid 2008, 2010). Similarly, Sagl et al. (2013) reported on the role of the oxide morphology and distribution on the reactive wetting of DP substrates. They detrmined that the bath dissolved Al diffused into the grain boundaries of the external oxides and that the oxides were broken off of the surface as a result of the Fe-Al formation at the interface. They emphasised that the oxide morphology had a critical effect in the progression of aluminothermic reduction and the wetting reactions (Sagl et al. 2013). Significantly enhanced reactive wetting was also obtained for low-alloy TRIP steels when the film-like morphology of the surface Mn-Si oxides was changed to a lens-shaped morphology as a result of Sn (Cho et al. 2016) and Bi

additions (Oh et al. 2016). However, the results of these series of studies will be discussed in further detail in 2.3.2.1.

Given the above arguments, researchers have worked on developing several approaches and processing routes to improve the reactive wetting of the alloy systems that are prone to selective oxidation prior to immersion, i.e. DP, TRIP and TWIP steels, schematics of which are shown in Figure 2.6. These contributions largely sought to either minimize or modify the external oxidation prior to dipping in such a way that an increased amount of metallic iron would eventually become available at the strip surface for reactive wetting during immersion. Flash coating is one of these techniques where, prior to annealing, a thin layer of Fe, Ni or Cu is deposited on the steel surface with the goal of suppressing the external oxide formation (Zhong et al. 2011, Choi et al. 2012, Tobiyama et al. 2012, Manna and Dutta 2014). The oxidation-reduction process is a two-step procedure that embeds the oxides in a layer of iron oxides which is later reduced to metallic iron in the reduction stage (Gong et al. 2011, Blumenau et al. 2011). Annealing under a high dew point process atmosphere is also another technique that can lead to improved reactive wetting, whereby the location of oxidation reaction is shifted from the surface to the subsurface (Gong et al. 2008) and 2009, Van De Putte et al. 2008, Bellhouse and McDermid 2010 and 2011, Blumenau et al. 2011). More recently, alloy design concepts have been developed where minor amounts of surface active elements such as Sn, Bi and Sb are alloyed with the steels, resulting in suppression of the oxidation reaction and morphological change of the surface oxides (Cho et al. 2014 and 2016, Oh et al. 2016). The last two approaches do not require modifications to existing continuous hot-dip galvanizing lines and have been employed in the present case of the 0.1C-6Mn-2Si 3G-AHSS system. These topics are discussed in further detail in sections 2.3.1 and 2.3.2 below.



Figure 2.6: Schematic illustration of the methods proposed to improve the reactive wetting of the AHSSs during the continuous hot-dip galvanizing (Cho et al. 2014).

2.3.1 The effect of annealing parameters

The annealing time and temperature along with the process atmosphere hydrogen content and oxygen partial pressure are the parameters that significantly affect the oxide attributes discussed above. This means that these process parameters can be tailored to some extent to encourage the formation of a less detrimental variety of the external oxides to the benefit of the reactive wetting.

The effect of annealing temperature on selective oxidation of a low-alloy TRIP steel in a N₂-10 vol pct H₂ atmosphere with a dew point of -30° C was investigated by Gong et al. (2008). According to the authors, annealing at the ferritic annealing temperature of 700°C resulted in formation of amorphous MnO.SiO₂ nodules and thin films of crystalline MnO.SiO₂. At the intercritical annealing temperature of 870°C, a discontinuous layer of amorphous SiO₂ and MnO nodules were present at the surface. At 930°C, which was consistent with the austenitic annealing temperature of the alloy, aside from an increase in the oxide layer thickness, the oxides were reported to be somewhat similar to the intercritical annealing condition. It was concluded that the annealing temperature had a significant effect on the surface oxide chemistry and morphology (Gong et al. 2008). However, it should be noted that although the process atmosphere dew points were kept the same throughout the experiments, the oxygen partial pressures varied several orders of magnitude due to increasing the annealing temperature and this also had a likely effect on the obtained results; which was not pointed out by the authors of that study.

The amount of hydrogen in the gas mixture of the annealing atmosphere can also affect the selective oxidation of the solute elements such that by introducing larger volumes of hydrogen, the atmosphere becomes more reducing. Such an analysis was recently carried out on a medium-Mn steel substrate annealed in the temperature range of 800°C to 1050°C under two annealing gas compositions with a dew point of -60°C, i.e. N₂-10 vol pct H₂ and N₂-50 vol pct H₂ (Jo et al.2017). It was concluded that direct reduction of the external MnO oxides was possible either by means of an increased annealing temperature, i.e. higher than 950°C, or by annealing in a highly reducing atmosphere with high H₂ content in the gas mixture.

The localization of the oxidation reaction front relative to the free surface depends on the balance between the inward flux of oxygen into the substrate and the outward flux of the alloying elements towards the surface. Two limiting cases can be applied. The first one being a situation where the permeability, i.e. the solubility-diffusivity product, of oxygen dominates that of the solute alloying element, i.e. $D_O N_O^S >> D_B N_B^o$, where N_O^S is the adsorbed concentration of oxygen at bulk surface, N_B^o is the initial bulk concentration of solute B and D_O and D_B are the diffusivities of oxygen and solute B in the matrix A. In this case, the selective oxidation of the alloying elements will occur internally, as schematically represented in Figure 2.7.


Figure 2.7: Concentration profiles for an internal oxidation situation in the A-B binary alloy (Swaminathan and Spiegel 2007).

In the opposite scenario, where $D_o N_o^s << D_B N_B^o$, the oxidation reaction will take place at the external surface and solute B will enrich the surface, forming BO_v as depicted in Figure 2.8. As a result, the oxygen permeability into the bulk alloy decreases and an external oxide layer forms.



Figure 2.8: Concentration profiles for external oxidation in the A-B binary alloy (Swaminathan and Spiegel 2007).

Thus, it is possible to increase the amount of metallic iron at the surface and improve the reactive wetting by employing high dew point, i.e. high oxygen partial pressure, annealing atmospheres to promote the internal oxidation mode of the alloying elements versus external oxidation (Jacques et al. 2001, Mahieu et al. 2001 and 2004, Drillet et al. 2004, Bellhouse and McDermid 2010). The Wagner model (1959) is the most widely used criterion to determine the oxygen partial pressure for the transition between internal and external oxidation, which is the topic of the discussion of the next section.

2.3.1.1 The transition between internal and external oxidation

External oxidation can also be treated as a particular case of internal oxidation. When the volume fraction of the internal oxides reaches a critical value, the oxide particles act as diffusion barriers and block further inward diffusion of oxygen; as a result internal oxidation ceases and the oxidation proceeds at the alloy surface, i.e. the transition to external oxidation takes place. The criterion for the internal to external transition was first proposed by Wagner (1959) for a binary single crystal alloy comprised of a noble parent A and a solute B that oxidizes to BO_{ν} with a zero solubility in the matrix:

$$\left(N_{B}^{o}\right)_{crit} = \left[\frac{\pi g^{*}}{2\nu} N_{O}^{s} \frac{D_{O}V}{D_{B}V_{BO_{\nu}}}\right]^{\frac{1}{2}}$$
(2.7)

where, $(N_B^o)_{crit}$ is the critical mole fraction of the solute element B which results in the oxidation mode transition, g^* is the critical volume fraction of the precipitated oxides required to block the inward diffusion of oxygen, v is the stoichiometric oxygen ratio for the precipitated solute oxide BO_v , V is the alloy molar volume, V_{BOv} the oxide molar volume, N_o^s the mole fraction of dissolved oxygen at the surface and D_o and D_B are, respectively, the bulk diffusivities for O and the solute B in the alloy. It should be mentioned that further details on the diffusion data and equations for calculating N_o^s can be found in Table 3.4 and the appendix at the end of Chapter 3, respectively.

It can be seen from this equation that, for a given temperature and process atmosphere, increasing the solute concentration beyond the critical mole fraction, $(N_B^o)_{crit}$, leads to the transition of the oxidation mode from internal to external. Additionally, for a given alloy composition and temperature, increasing the process atmosphere oxygen partial pressure will shift the oxidation towards the internal oxidation mode.

In addition to the diffusion coefficients of the alloying element and oxygen, the critical volume fraction of the oxide precipitates, g^* , also determines the transition kinetics. Generally, a low g^* value implies that the alloy is more prone to external oxidation. The most commonly used value for g^* is 0.3, which was determined by Rapp for Ag-In alloys (1965). However, recent experimental work by Lashgari et al. (2014) determined this value to be 0.2 for the case of Fe-Mn alloys.

Given the simplifying assumptions of the classic Wagner model, several expansions to Equation (3.1) have been proposed by a number of authors (Mataigne et al. 1992, Grabke et al. 1995, Huin et al. 2005, Shastry et al. 2007, Lashgari et al. 2014). For instance, the accelerated diffusion of oxygen and alloying elements at grain boundaries of a polycrystalline material was not considered in the original Wagner model and this was accounted for (Mataigne et al. 1992) by halving the activation energy values for bulk diffusion in Equation (3.1). Moreover, a modified Wagner model was proposed by Mataigne et al. (1992) for multi-component systems, in which the flux of the oxidizable alloying elements towards the surface was considered to be additive and external oxidation will occur if the combined flux of the ignoble elements to the surface, given by the terms in the left-hand side of Equation (2.8), exceeds the inward flux of O into the substrate given in the right-hand side:

$$\sum_{B} N_{B}^{o} \left[\nu D_{B} V_{BO_{\nu}} \right] = \left[\frac{g^{*} \pi V N_{O}^{s} D_{O}}{2} \right]^{\frac{1}{2}}$$
(2.8)

It should be mentioned that however, the formation of complex oxides such as manganese silicates has not been taken into account in this model. A treatment of the internal/external oxidation transition with respect to the above mentioned expansions of the Wagner model is provided in 3.4 for the 0.1C-6Mn-2Si substrates of this study.

Huin et al. (2005) extended the classical Wagner model by introducing the solubility product of the oxide BO_{ν} . Additionally, the interaction between several solutes elements was taken into account in their extended model by assuming the competitive consumption of the available dissolved oxygen at the surface and the formation of MnO, SiO₂ and Mn₂SiO₄ was predicted. However, this model was restricted to an isothermal case (Huin et al. 2005).

Despite the above mentioned efforts, it can be argued that accurate prediction of the selective oxidation behaviour of the alloying elements still remains a challenge, as several discrepancies exist between the experimental and computed data. The selective oxidation of a multi-component and multi-phase alloy system is complex under practical conditions due to the varying solubilities of the oxides, different levels of oxygen affinity and partitioning behaviour of the alloying elements. The experimental results of selected literature on the effect of the process atmosphere oxygen partial pressure on the selective oxidation of low-alloy TRIP steels are presented below.

It was shown by Cho et al. (2014) that as a result of oxidation mode transition, the external oxide layer thickness and the depth of the internal oxidation zone were respectively decreased and increased with increasing the process atmosphere dew point ranging from – 60° C to +5°C. The surface oxides were found to be rich in Mn and were identified as crystalline MnO.SiO₂ whereas the internal oxides were comprised of amorphous MnO.SiO₂ and rich in Si. Figure 2.9 shows the TEM cross sections of the steels of that study where it can be observed that the transition from external to internal oxidation had occurred at the -10° C dew point.



Figure 2.9: Cross-sectional TEM micrographs of CMnSi TRIP steel after intercritical annealing at 820°C in a N₂-10 vol pct H₂ atmosphere with increasing dew points from left to right: -60° C, -30° C, -10° C, 0° C and $+5^{\circ}$ C (Cho et al. 2014).

Bellhouse and McDermid (2010) reported that annealing a 1.5 wt pct Si TRIP steel at 777°C under the lowest oxygen partial pressure of -53°C resulted in the highest concentration of Si at the steel surface with the Si surface concentration decreasing with increasing oxygen partial pressure. The metallic iron concentration at the surface was also found to be lowest at this dew point and SiO₂ oxides were predominantly present at the surface in film-type morphology. The amount of metallic iron was increased at higher dew points due to internal oxidation of alloying elements. The maximum amount of Mn enrichment was observed at the -30°C dew point. They concluded that both the external oxide morphology and chemistry were affected by the process atmosphere oxygen partial pressure (Bellhouse and McDermid 2010). It was also reported that despite the surface enrichment of alloying elements, good reactive wetting with few bare spots in the galvanized coating was obtained for most substrates and the poor reactive wetting in the case of the $+5^{\circ}$ C process atmosphere was attributed to the closely spaced nodule-like Mn₂SiO₄ at the surface (Bellhouse and McDermid 2010).

Similarly, Alibeigi et al. (2011) reported that annealing the Mn-containing steels under a low oxygen partial pressure atmosphere produced a thin external oxide. Employing a

high oxygen partial pressure resulted in internal oxidation of Mn and did not adversely affect reactive wetting of the substrate by the galvanizing bath. Additionally, it was shown that relatively significant quantities of external MnO could be aluminothermically reduced in the Zn(Al,Fe) bath.

2.3.2 The effect of steel chemistry

The steel Si to Mn ratio has a strong influence on the chemical composition of the oxide species that form in the Mn-Si-O system. The thermodynamic calculations of Suzuki et al. (2009) suggested that, regardless of the process atmospheres oxygen partial pressure, the formation of SiO₂ and poor reactive wetting is inevitable when the Si to Mn ratio of the CMnSi steels annealed at 850°C is in excess of 1. However, there were some discrepancies with the findings of other researchers due to the fact that in practice, several kinetic factors such as the varying solubilities of the oxides and the relative diffusion rates of Mn and Si are important and should be considered in the predictions. Moreover, the thermodynamic calculations, despite being a good starting point, are not adequate to predict the critical factors in reactive wetting such as oxide thickness, morphology and spatial distribution. For example Drillet et al. (2004) investigated the galvanizability of two 1.5 wt pct Mn TRIP steel substrates with Si contents of 1.28 wt pct and 2.06 wt pct annealed at 810°C using a -35° C N₂-5 vol pct H₂ process atmosphere. While good reactive wetting was obtained for the 1.28 wt pct Si alloy, the poor reactive wetting of 2.06 wt pct steel was attributed to a few nanometer thick layer of film-forming SiO₂.

Given the difficulties associated with galvanizing of high-Si containing steels, some authors have suggested to partially or completely replace the Si with Al to improve the reactive wetting properties of the TRIP steels (Mahieu et al. 2002 and 2004, Bellhouse et al. 2007). A series of studies by Bellhouse and McDermid (2007, 2008, 2011 and 2012)

investigated the selective oxidation and reactive wetting of the low alloy TRIP substrates with varying Si and Al contents. It was determined that both steel grades similarly exhibited good reactive wetting and some changes to the oxide morphology were reported. It should be mentioned that while Al can prevent carbide precipitation during the isothermal bainitic transformation, it is not as effective as Si in this regard (Girault et al. 2001, Mertens et al. 2003).

2.3.2.1 The effect of surface active elements

More recently, the known effect of surface active elements on retarding the rate of surface reactions such as carburization (Ruck et al 1996) and selective oxidation of Si in electrical steels (Lyudkovsky 1986), was implemented to the area of AHSSs as a new alloy design concept (Zhang et al. 2009 and 2013, Cho et al. 2014 and 2016, Oh et al. 2016). It has been determined that the segregation of these elements at the surface can act as a barrier to the inward diffusion of oxygen by occupying the surface adsorption sites (Grabke 1989 and 1996) and result in a decreased permeability of oxygen at the surface, potentially also changing the oxide chemistry and morphology.

The tendency of these elements to segregate to the grain boundaries and surfaces was explained by Seah (1980) by introducing the surface enrichment factor, β_A^S , as:

$$\beta_A^S = \frac{X_S}{1 - X_S} \cdot \frac{1 - X_B}{X_B} \tag{2.9}$$

where β_A^S is the surface enrichment factor of solute A in solvent B, X_S is the fraction of the surface covered by atom A and X_B is the mole fraction of solute A in the bulk. The surface enrichment factor can then be calculated per Equation 2.10:

$$\ln \beta_A^S = \left\{ 24 \left(T_B^m - T_A^m \right) + 1.86\Omega + M4.64 \times 10^7 a_B \left(a_A - a_B \right)^2 \right\} / RT \pm 1.29$$
(2.10)

where T is the temperature and T_A^m and T_B^m and a_A and a_B are the melting points and atomic sizes of A and B, respectively. Ω is the enthalpy of mixing of the two elements and M is equal to either 1 when the solute element A has a larger atomic size than the solvent B; or it equals 0 when the solvent atom is larger than the solute. It can be seen from Equation 2.10 that there are two main contributions to the driving force for surface segregation and reducing the energy of the system: the difference in the melting temperatures, which is closely related to the surface energies, and the atomic size differences of A and B or the lattice mismatch, which is related to the elastic energy of the matrix (Hondores and Seah 1977, Seah 1979). It was suggested that the elastic energy component of the driving force is smaller for an undersized solute atom, which is why under such scenario a value of 0 is taken for M (Tsai et al. 1977, Seah 1980).

On this basis, the degree of surface segregation was computed for selected alloying additions by Cho et al. (2014) which is shown in Figure 2.10. It can be seen that the elements with a larger atomic size and notably lower melting temperature than Fe, i.e. Bi, Sn, Sb and S, exhibit the highest surface enrichment factors, while elements such as Ni, Cu, Cr and Ti, having a similar atomic size to Fe, do not have a high tendency for surface segregation.



Figure 2.10: Melting temperature of selected elements as a function of their atomic size (Cho et al. 2014)

The effect of minor additions of Sn, Sb and Bi on the selective oxidation and reactive wetting of IF and low-alloy TRIP steels has been the subject of study by several authors (Zhang et al. 2009 and 2013, Cho et al. 2014 and 2016, Oh et al. 2016). It should be mentioned that, aside from a high surface enrichment factor, these elements do not selectively oxidize in the annealing atmosphere, neither do they form precipitates. Cho et al. (2014 and 2016) reported that Sn additions in the range of 0.05 wt pct to 1 wt pct resulted in modification of the surface oxide morphologies from continuous films to lens-shaped in a 0.1C-1.6Mn-1.5Si (wt pct) TRIP steel. Furthermore, the oxide chemistry was also altered due to the reduced oxygen solubility at the surface such that the Mn to Si ratio of the surface oxides decreased with increasing Sn contents (Cho et al. 2016). A follow-up study (Oh et al. 2016) explored the effect of Bi in the same alloying system, where similar to Sn, desirable morphological changes of the external oxides were observed by means of 0.05 wt pct, 0.1 wt pct and 0.2 wt pct Bi additions. These observations were contributed to the possible change of the oxide/metal interfacial energies, resultant of the enrichment layers of Sn and Bi beneath the surface oxides (Hondores and Seah 1977, Seah 1979). It was explained that the interfacial energy between the Sn-enriched steel surface and the SiO₂ film was increased compared to that of the reference steel and SiO₂, leading to de-wetting and morphological alterations of the oxides of the steels that were alloyed with Sn and Bi (Cho et al. 2016, Oh et al. 2016). Significant improvement in the reactive wetting of the steels by the galvanizing bath was obtained in all of these studies, owing to the thinner and discrete distribution of the lens-type external oxide morphology.

It should be mentioned that the suppression effect of the surface active elements on the external and internal oxidation growth kinetics is not fully documented. Furthermore, all of the previous studies only concerned the IF and TRIP steels and the effect of the surface active element additions to the medium-Mn 3G substrates has not been explored to date. It

should also be cautioned that despite the promising results with respect to the reactive wetting of the TRIP substrates, the alloying additions in excess of 0.05 wt pct of elements such as S and Sn are known to be problematic to the grain boundary cohesion and mechanical properties (Hondores and Seah 1977, Melford 1980).

To conclude this chapter, there is clearly a lack of fundamental data on the relationships existing between the various selective oxidation parameters and the reactive wetting of the AHSS substrates by the galvanizing bath, such that there is no reliable method of predicting the reactive wetting behaviour of a given alloy under a given set of processing parameters. This knowledge gap is more severe in the case of the medium-Mn 3G substrates, which are expected to be significantly more difficult to reactively wet due to the substantially higher levels of Mn and Si compared to the TRIP steels. The objective of the present work, therefore, is to provide a fundamental understanding of the factors that affect the selective oxidation of Mn and Si in a 0.1C-6Mn-2Si prototype 3G-AHSS, such as the annealing time, temperature, process atmosphere oxygen partial pressure, and 0.05 wt pct Sn addition. It also aims to enhance the galvanizability of the steels through alloy design and process parameter control. Detailed analysis of the parameters critical to the reactive wetting such as the oxide chemistry, morphology, spatial distribution, thickness and growth kinetics are presented and interpreted with respect to the resultant reactive wetting by the galvanizing bath. It should be emphasised that these results are not known to the industry for medium-Mn substrates which are increasingly gaining attention for applications of the future vehicles. It is hoped that the results of this study will assist with the integration of the medium-Mn 3G-AHSSs to the automotive industry, by providing a fundamental means of predicting the selective oxidation and reactive wetting of these steel substrates.

CHAPTER 3 SELECTIVE OXIDATION OF A 0.1C-6MN-2SI THIRD GENERATION ADVANCED HIGH-STRENGTH STEEL DURING DEW-POINT CONTROLLED ANNEALING

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Abstract

The present study investigates the selective oxidation of a 0.1C-6Mn-2Si medium-Mn advanced high-strength steel during austenization annealing heat treatments as a function of process atmosphere oxygen partial pressure and annealing time. It was determined that the surface oxide growth kinetics followed a parabolic rate law with the minimum rate belonging to the lowest oxygen partial pressure atmosphere at a dew point of 223 K (-50° C). The chemistry of the surface and subsurface oxides was studied using STEM + EELS on the sample cross sections, and it was found that the surface oxides formed under the 223 K (-50° C) dew-point atmosphere consisted of a layered configuration of SiO₂, MnSiO₃, and MnO, while in the case of the higher pO₂ process atmospheres, only MnO was detected at the surface. Consistent with the Wagner calculations, it was shown that the transition to internal oxidation for Mn occurred under the 243 K (-30° C) and 278 K ($+5^{\circ}$ C) dew-point atmospheres. However, the predictions of the external to internal oxidation for Si using the Wagner model did not correlate well with the experimental findings nor did the predictions of the Mataigne et al. model for multi-element alloys. Investigations of the internal oxide network at the grain boundaries revealed a multi-layer oxide structure composed of amorphous SiO₂ and crystalline MnSiO₃, respectively, at the oxide core and outer shell. A mechanism for the formation of the oxide morphologies observed, based on kinetic and thermodynamic factors, was proposed. It is expected that only the fine and nodule-like MnO oxides formed on the surface of the samples annealed under the 278 K ($+5^{\circ}$ C) dew point process atmosphere for 60 and 120 seconds are sufficiently thin and of the desired dispersed morphology to promote reactive wetting by the molten galvanizing bath.

3.1 Introduction

In recent years, medium-Mn advanced high-strength steels have garnered significant interest from the automotive industry due to their superior combination of specific strength and formability as well as their potential ability to absorb energy during crash events. Use of these alloys may allow manufacturers to design vehicles with significantly increased fuel efficiency without compromising passenger safety. However, due to the relatively short history of material development in this class of alloys, there are a limited number of studies on the other essential engineering properties of these steel grades.^[11] For example, corrosion protection of the steel is of prime importance for maintaining the structural integrity of manufactured parts, for which the continuous galvanizing process is a cost-effective means of applying protective metallic coatings to sheet steels. In the continuous galvanizing process, a continuous steel sheet passes through an annealing heat treatment in a controlled, reducing atmosphere prior to dipping in a molten Zn(Al,Fe) bath, where the dual purpose of the annealing heat treatment is to control the microstructure of the substrate and to render the substrate surface suitable for reactive wetting by the molten alloy bath.

However, obtaining a high-quality Zn coating on the steel surface can be challenging in the case of medium-Mn substrates due to the substantial levels of alloying elements, such as Mn and Si, which are necessary for obtaining the desired mechanical properties.^[2-4] This

challenge arises from the basic thermodynamics that, under typical continuous galvanizing annealing heat-treatment atmospheres, which are reducing with respect to Fe, alloying elements such as Mn, Si, Cr, and Al will be selectively oxidized. Kinetic factors, as described in a relatively simplistic manner using the Wagner model,^[5] dictate whether or not the selectively oxidized elements will manifest on the external surface and/or in the internal subsurface. In the case of the occurrence of external oxidation, it has been shown that these can prevent reactive wetting and the formation of the desired η -Fe₂Al₅Zn_X interfacial layer during dipping of the steel in the Zn(Al,Fe) bath.^[6-9] As a result, the final product can suffer from poor coating adhesion or contain unacceptable coating effects such as bare spots.

A number of authors have focused on improving the reactive wetting behavior of lowalloy, high-Si content Transformation-Induced Plasticity (TRIP) and high-Mn Twinning-Induced Plasticity (TWIP) advanced high-strength steels (AHSS) by the continuous galvanizing bath, through tailoring the annealing process atmosphere conditions ^[7,10,11] as well as by modifying the alloy design.^[12-15] These contributions largely sought to determine factors resulting in the modification of the external oxides, either minimizing them through selecting process atmospheres which result in internal oxidation, embedding the oxides beneath a layer of reduced Fe from oxidation–reduction treatments or modifying the external morphology and/or chemistry to promote reactive wetting.^[10-15] Other contributions in this area have studied oxide formation from a thermodynamic standpoint ^[16] and have advocated that the Si/Mn ratio be kept at 0.5 or less in order to provide a surface free of detrimental SiO₂ films which cannot be reactively wetted. However, several studies have shown that such factors as oxide morphology, surface oxide distribution, and the overall kinetics of the selective oxidation process are dominant factors in determining the ability of the galvanizing bath to reactively wet low-alloy, higher Si/Mn ratio TRIP steel surface and include such

factors as the ability of surface films to be reduced by the resident-dissolved bath Al *via* aluminothermic reduction. ^[17-19]

Given the plethora of studies on the reactive wetting of the low-alloy TRIP steels cited above – which commonly contain approximately 2 wt pct Mn and approximately 1.5 wt pct (Al + Si), it would be expected that medium Mn steels – with 6 wt pct Mn and slightly higher levels of $Si + Al^{[20,21]}$ – would be significantly more difficult to reactively wet. However, it has been previously shown by Alibeigi et al.^[22] that a 5 wt pct Mn steel could be reactively wetted by a 0.20 wt pct Al (dissolved) bath provided that the intercritical annealing temperature was low enough to produce external oxides which the authors advocated could be aluminothermically reduced by the resident bath-dissolved Al. The kinetics of this process for the reduction of MnO were later quantified by Kavitha et al. ^[19] who showed that significant external films could be reduced in practical continuous galvanizing dipping times. Furthermore, for the case of low-alloy TRIP steels, it was shown by Bellhouse et al.^[18] that external oxides comprising more widely dispersed nodules with thinner internodular films – which the authors theorized could be aluminothermically reduced - could be successfully reactively wetted by a 0.20 wt pct Al (dissolved) bath. In this case, the desired η -Fe₂Al₅Zn_x layer, formed by the bath reactively wetting the (then) oxide-free internodular areas, would also precipitate on top of the remaining nodular oxides. Those authors also observed significant lift-off of the nodular oxides by facture at the metal-oxide interface and subsequent penetration of the bath metal and η -Fe₂Al₅Zn_X formation at this interface. This general mechanism was later advocated by Sagl et al.^[23] for higher Mn content dual-phase (DP) steels reactively wetted by a similar Zn(Al,Fe) bath.

It has previously been shown by Bhadhon et al. ^[24] that mechanical properties consistent with third generation AHSSs could be obtained for a 0.2C-6Mn-1.5Si-0.5Al-0.5Cr (wt pct) medium-Mn alloy intercritically annealed at the relatively low temperature of 948 K

(675°C). However, it was also shown that significantly better properties could be obtained from this steel using annealing times consistent with continuous galvanizing line processing schedules using a martensitic starting microstructure, thus requiring a 1073 K (800°C) austenitization annealing cycle prior to intercritical annealing. This may be of some concern for later processing in the continuous galvanizing line (CGL) as the oxides produced could inhibit reactive wetting. To address this issue, the objective of this paper is to determine the selective oxidation behavior – including morphological development, chemistry and kinetics – for a model 0.1C-6Mn-2Si prototype alloy as a function of process atmosphere oxygen partial pressure (pO_2) and annealing times ranging from 60 – 600 seconds. The selective oxidation and reactive wetting of this alloy at the intercritical temperature will be the subject of subsequent contributions. However, the results of this work will be linked qualitatively to the expected reactive wetting of this steel by the continuous galvanizing Zn(Al,Fe) bath.

3.2 Experimental

The chemical composition of the experimental medium-Mn model alloy is given in Table 3.1. Steel sheets were received in the as cold-rolled condition with a thickness of 1.2 mm. Samples for selective oxidation heat treatments were cut from the parent material into $10 \times 50 \text{ mm}$ coupons with an abrasive water-jet cutter such that the rolling direction was parallel to the longitudinal axis of the samples. Sample preparation prior to annealing heat treatments comprised polishing the surface with 4000 grit SiC paper in order to minimize the effects of surface roughness on the selective oxidation studies. All samples were given a final clean with certified ACS reagent grade acetone (Fisher Scientific) immediately prior to annealing.

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С	Mn	Si	Al	Mo	Ti	Ν	S
0.106	6.241	2.023	0.040	0.072	0.011	0.003	0.003

Table 3.1: Chemical composition of the experimental steel (weight percent)

All oxidation experiments were performed using the McMaster Galvanizing Simulator (Iwatani-Surtec), for which a schematic of the corresponding thermal cycle is shown in Figure 3.1. The annealing cycles used comprised five isothermal holds within the range of 60 and 600 seconds at the peak annealing temperature (PAT) of 1073 K (800°C) in an N₂-5 vol pct H₂ dew-point controlled atmosphere. The dew-point control unit (Michell Instruments) was capable of producing process atmosphere dew points ranging from 173 K (-100°C) to 293 K (+20°C) with a \pm 2 K accuracy. Three process atmospheres with dew points of 223 K (-50°C), 243 K (-30°C) and 278 K (+5°C) were tested to explore the effect of oxygen partial pressure on the selective oxidation of Mn and Si. A detailed summary of the corresponding values of oxygen partial pressure (pO_2) for each process atmosphere along with the pH_2O/pH_2 ratios is provided in Table 3.2. It should be noted that the values listed in Table 3.2 were derived from the FREED thermodynamic database.^[25] In the subsequent text, referrals to process atmospheres and the corresponding samples will be made by the atmosphere name per Table 3.2. Following the PAT isothermal hold, samples were rapidly cooled to 343 K (70°C) at a rate of -10 K/second using N₂ gas quenching. The thermal cycle was controlled *via* a 0.5-mm-type K thermocouple welded directly to the central selective oxidation samples. All selective oxidation tests were carried out in triplicate to provide multiple samples for each of the characterization techniques used and to ensure repeatability of the experimental results. All samples were stored in anhydrous HPLC grade isopropanol after annealing in order to minimize additional oxidation prior to analysis.^[12] Further details concerning the configuration and operation of the McMaster Galvanizing Simulator are well documented and can be found elsewhere. ^[26]



Figure 3.1: Annealing heat-treatment cycle schematic.

Table 3.2: Experimental process atmospheres specifications at 1073 K (800°C) peak annealing temperature

Atmosphere Name	Dew Point (K)	pH ₂ O/pH ₂	pO ₂ (atm)	Holding Time (s)
-50DP	223	0.00125	6.87×10^{-25}	60, 120, 180, 360, 600
-30DP	243	0.00998	4.39×10^{-23}	60, 120, 180, 360, 600
+5DP	278	0.17111	1.29×10^{-20}	60, 120, 180, 360, 600

In order to observe the distribution and morphology of the surface oxides, annealed samples were coated with C and then examined using a JEOL 7000F field emission gun scanning electron microscope (FE-SEM) operated in secondary electron imaging mode at an acceleration voltage of 5 keV.

X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantera SXM XPS equipped with an Al K α X-ray source (1486.7 eV) and a hemispherical detector. The spot size was 100 μ m and the take-off angle was set at 45 deg. Elemental depth profiles of the steel surface were obtained by Ar ion sputtering on a 2 × 2 mm area with a pass energy of 140 eV and step size of 0.25 eV. All data processing was done using MultiPak 6.0 software.

The obtained binding energies are accurate to within ± 0.1 eV, and all spectra were calibrated using the metallic iron binding energy of 706.62 eV. Depth measurements are considered to be accurate within ± 10 pct of the documented sputtered depth.

Transmission electron microscopy (TEM) cross sections of the samples oxidized for 600 seconds under all of the experimental process atmospheres were prepared using focused ion beam (FIB) milling with an NV ision 40 by Zeiss. W and C coatings were deposited on the area of interest in order to protect the surface oxides during Ga-ion milling. The 600-second annealing time samples were used preferentially for high resolution scanning transmission electron microscopy (HR-STEM) and electron energy loss spectroscopy (EELS) analysis because the oxides formed after the extended holding time offered a more robust configuration for chemical analysis due to the presence of coarser features yielding higher-intensity analytical signals. HR-STEM micrographs were acquired using an FEI Titan 80-300HB transmission electron microscope operated at 300 keV. Electron energy loss analyses were obtained using a Gatan Quantom GIF, where Digital Micrograph 2.3 software was used to extract elemental maps from the raw EELS data cubes.

In order to study the growth kinetics of the surface oxide layers, focused ion beam milling was also used to make two 10 μ m-wide trenches perpendicular to the steel surface. Image J 1.48v software was used to measure the surface oxide thickness on tilt-corrected SEM images. Given the significant local variation in the surface oxide thickness, a minimum of 100 measurements were made per sample utilizing a grid to ensure random sampling of the external oxide layers. The average oxide thickness for the samples was reported using a 95 pct confidence interval.

3.3 Results

Figure 3.2 shows SEM micrographs from the surfaces of the samples annealed at the PAT of 1073 K (800°C) for 120, 360, and 600 seconds for all experimental process atmosphere oxygen partial pressures, as provided in Table 3.2. These micrographs provide a visual comparison of the morphology and distribution of the oxides formed on the surface of the samples annealed under the –50DP, –30DP and +5DP atmospheres. After annealing in the –50DP process atmosphere for 120 seconds, closely spaced oxide nodules were visible in some areas of the bulk surface, as shown in Figure 3.2(a), while other areas appeared to be covered by a relatively thin oxide layer. Compared to this sample, it can be seen in Figure 3.2(d) that a rather uniform coverage by external oxide nodules resulted after the 120-second anneal for the –30DP process atmosphere. By increasing the oxygen partial pressure further by means of the +5DP process atmosphere, a significant decrease in external oxidation was observed (Figure 3.2(g)) such that the underlying steel substrate surface was clearly visible in some areas, likely due the oxides in these areas being very thin.

As can be seen clearly from Figures 3.2(b), (e), and (h), annealing at 1073 K (800°C) for 360 seconds resulted in significant coarsening of the surface oxide nodules for all experimental process atmospheres. Extending the holding time to 600 seconds in the case of the -50DP and -30DP samples (Figures 3.2(c) and (f)), resulted in surfaces that were almost entirely covered by a compact oxide layer, accompanied by further coarsening of the nodules, which was more severe in the case of the samples annealed in the -30DP process atmosphere. As seen from Figure 3.2(i), oxide coarsening was observed in the case of the +5DP $\times 600$ seconds sample; however, the surface oxide nodules did not form a compact oxide layer. Furthermore, a significant fraction of the underlying substrate was visible between the oxide nodules, indicating the presence of thin oxide layers in these areas.

Elemental XPS depth profiles as a function of time at the PAT and process atmosphere are presented in Figure 3.3, where it can be seen that the surface enrichment and Mn-rich layer thickness increased with the increasing holding time at the PAT under all process atmospheres. The Mn enrichment determined for the surface of the –50DP process atmosphere samples was slightly higher compared to that observed under the –30DP and +5DP atmospheres; however, this external oxide layer seemed to be much thinner in comparison to those of the other higher oxygen partial pressure atmospheres. It is also worth noting that significant surface enrichment of Si was only detected for the –50DP process atmosphere samples, as can be seen from the inset in Figure 3.3(a).



Figure 3.2: Secondary electron images from sample surfaces annealed for 120, 360, and 600 s under the -50DP (a, b, c), -30DP (d, e, f) and +5DP (g, h, i) process atmospheres.

Further examination of Figure 3.3 indicates that the growth of the external oxide layer was somewhat slower for the -50DP process atmosphere samples compared to those of the -30DP and +5DP atmospheres. Additionally, it can be seen that all the -50DP process atmosphere Mn-depth profiles converged to the alloy bulk concentration beyond the surface Mn-enriched region (Figure 3.3(a)). In contrast to this, Mn concentrations higher than the bulk content were observed well below the surface-enriched region in the case of the -30DP and +5DP process atmosphere samples (Figures 3.3(b) and (c)), which was most pronounced in the case of the $+5DP \times 600$ seconds sample (Figure 3.3(c)). This subsurface enrichment is indicative of internal oxidation, as would be expected when employing high water vapor partial pressures (*i.e.*, high pO₂, Table 3.2) in the annealing process atmosphere. However, care must be exercised in interpreting the surface oxide thickness data solely from the fullwidth half-maximum (FWHM) of the elemental profiles, since the increased internal oxidation depth was likely to have a contribution to the width of the XPS profiles, particularly at extended holding times and higher dew-point atmospheres. The binding energy values for O1s, $Mn2p_{3/2}$, and $Mn2p_{1/2}$ peaks after a 5-nm sputter of the steel surface -i.e., below the contaminated layer resulting from atmospheric exposure after removal from the MGS - were extracted from the raw XPS spectra to identify the surface oxide chemistries of the 600-second samples. An example of such an analysis is shown in Figure 3.4 for the – $50DP \times 600$ seconds sample. From this, it can be seen that the metallic Fe peaks (binding energy 706.7 eV) appeared when several tens of nanometers of the surface oxide layers were sputtered, due to extensive coverage of the surface by the external oxides. The binding energies measured for the O1s, Mn2p_{3/2}, and Mn2p_{1/2} peaks at the surface corresponded to those of MnO, as reported by several authors ^[27-29] and did not contain significant Fe oxides. A summary of these results is presented in Table 3.3.



Figure 3.3: Mn and Si (inset) XPS depth profiles as a function of PAT holding time for samples annealed under the (a) -50DP (b) -30DP and (c) +5DP process atmospheres.



Figure 3.4: XPS spectra from depth profiles of O1s, Mn2p, and Fe2p peaks for the sample annealed for 600 seconds under the –50DP process atmosphere.

Table 3.3: XPS binding energies of oxides present on the sample surfaces annealed for 600 s

Atmosphere Name	Measured binding energies (eV)				
Aunosphere Mane	O1s	Mn2p _{3/2}	Mn2p _{1/2}		
-50DP	530.0	640.9	653.3		
-30DP	530.3	641.4	654.1		
+5DP	530.2	641.1	653.6		

As mentioned earlier, direct measurements of the external oxide thicknesses were made on sample FIB cross sections for all process atmospheres and are reported as an average of at least 100 measurements over a total length of 20 μ m. Figure 3.5 shows a plot of external oxide thickness *vs* the square root of time, where the error bars represent the 95 pct confidence interval of the mean. The near perfect linear fit in this plot shows that the external oxide growth followed parabolic growth kinetics under all process atmospheres, as would be expected from a solid-state diffusion-controlled process. ^[30,31] Furthermore, comparing the slopes of the three lines clearly indicates that the overall rate of external oxide growth under the –50DP atmosphere was lower than that observed for the –30DP and +5DP process atmospheres. However, it should be noted that, for annealing times of less than 180 seconds, the external oxides associated with the +5DP process atmosphere were significantly thinner than those of the –50DP and –30DP process atmospheres. For example, after annealing for 60 seconds, the thinnest external oxide layer was formed under the +5DP atmosphere (49 ± 5 nm), whereas after the 600 seconds anneal, the +5DP process atmosphere external oxide thickness was significantly greater than that of the –50DP atmosphere (*i.e.*, 272 ± 22 nm vs 203 ± 15 nm).



Figure 3.5: Time-dependence of external oxide thickness as a function of process atmosphere dew point.

High-angle annular dark field (HAADF) images of the TEM cross sections of the samples annealed for 600 seconds under the -50DP, -30DP and +5DP process atmospheres are depicted in Figure 3.6. The white area on top of the images is the W coating followed by a black layer representative of the C coating, both deposited prior to FIB milling to protect the external oxide structures from damage. From Figure 3.6(a), which shows the -50DP sample, an external oxide layer with a nonuniform thickness can be observed. It is worth noting that, consistent with the XPS results (Figure 3.3(a)), no significant internal oxidation was detected for these samples, which was expected due to the relatively low pO₂ of the -50DP atmosphere. The higher magnification image of the surface, inset of Figure 3.6(a), revealed three distinct layers of the external oxides, suggesting varying compositions for this

constituent: first, a thin black layer a few nanometers thick (denoted as layer 3) can be seen at the steel/oxide interface; on top of this thin film, a dark gray oxide layer with varying thicknesses was observed (layer 2), and finally, light gray oxide nodules can be seen at the oxide/atmosphere interface (marked as layer 1). The latter corresponds to the oxide nodules that were visible in the SEM images as shown in Figure 3.2(c).

In the case of the -30DP process atmosphere (Figure 3.6(b)), however, extensive internal oxidation was observed in addition to a relatively thick external oxide layer, the latter of which exhibited a polycrystalline appearance. The internal oxidation zone in this sample can be divided into two different zones with respect to the oxide morphology and distribution: the first zone comprising fine circular oxide particles within the bulk microstructure along with the grain boundary oxides to a depth of approximately 0.7 μ m, while beneath this region, oxides were largely present as a grain boundary network, extending to depths of approximately 4 μ m from the surface. This second zone of internal oxides appears to also decorate some subgrain boundaries. A similar morphology with a much deeper internal oxidation zone can be seen for the sample annealed under the +5DP process atmosphere, as shown in Figure 3.6(c); while in accordance with SEM results, a discontinuous, nodular external oxide configuration can be observed. It is also worth noting that, as can be seen in Figures 3.6(b) and (c), the grains close to the surfaces of the -30DP and +5DP samples appear to be much finer than those present in the bulk microstructure. This can be attributed to the pinning effect of the grain boundary oxides preventing growth of the recrystallized grains in the subsurface. It can be observed that this was not the case for the -50DP sample (Figure 3.6(a)) due to the absence of an internal oxide network. This is consistent with the work of other authors who also pointed out that this effect becomes less significant toward the inner depths of sample, due to the additional time available for grain growth prior to pinning of the grain boundaries by oxides at that depth. ^[32-34]



Figure 3.6: HAADF images from the cross sections of the samples annealed for 600 s under the (a) -50DP process atmosphere, with the inset showing the external surface oxide configuration, (b) -30DP process atmosphere and (c) +5DP process atmosphere.

In order to study the link between the morphology and chemistry of the oxides, selected samples were subjected to STEM+EELS analysis as these methods possess superior spatial resolution and detection limits (less than 1 at. pct) compared to XPS. Figure 3.7 shows the EELS elemental maps for Fe, O, Mn, and Si acquired from the external oxides of the sample annealed under the -50DP atmosphere for 600 seconds. The multi-layer surface oxide structure of this sample hypothesized above can be observed more clearly in these images. It can be seen that the thin black layer adjacent to the steel substrate, marked as layer 3 in Figure 3.6(a), was an oxide enriched in Si with no significant presence of Mn. Furthermore, the selected area diffraction (SAD) pattern acquired from this layer, shown as an inset in the Si map of Figure 3.7, reveals that this Si-rich oxide layer was amorphous. However, for the oxide layer that was demarcated as layer 2 in Figure 3.6(a), the EELS maps showed an enrichment of Mn along with some Si, suggesting a Mn-Si oxide chemistry. It is worth noting that this surface Si enrichment was also detected in the Si XPS depth profiles shown in Figure 3.3(a). Finally, the oxide nodules at the external surface, designated as layer 1 in Figure 3.6(a), were identified as Mn oxide where no significant Si signal was detected in the

elemental maps. It is worth noting that this finding correlated well with the binding energy data presented in Table 3.3, which determined that the top 5 nm of the oxidized steel surface, *i.e.*, layer 1 in Figure 3.6(a), to be MnO.



Figure 3.7: HAADF image and EELS elemental maps of the external oxides on a sample annealed for 600 s under the -50DP process atmosphere. The inset in the Si map shows the SAD pattern acquired from region 3 of Figure 3.6(a).

EELS elemental maps were also acquired from the internal oxide network formed as a result of annealing under the –30DP and +5DP atmospheres. Figure 3.8 presents the EELS elemental maps of the surface and subsurface oxides formed after annealing for 600 seconds under the –30DP process atmosphere. It can clearly be observed that the external oxide was only composed of Mn and O with no layered oxide structure being detected at the interface, whereas the fine spherical oxides formed within the bulk and at the grain boundaries of subsurface showed occasional enrichment of Si in areas with no significant Mn being present. Further examination of the Si map in Figure 3.8 revealed that the Si enrichment corresponds to the core of the grain boundary oxides. This observation was also consistently found for the subsurface oxides of the +5DP sample, as shown in Figure 3.6(c).



Figure 3.8: HAADF image and EELS elemental maps, showing the surface and subsurface oxides of the sample annealed for 600 seconds under the –30DP process atmosphere.

In the same manner, EELS elemental maps of a grain boundary oxide formed further into the subsurface from the sample annealed under the +5DP atmosphere for 600 seconds are shown in Figure 3.9. It can be seen that, similar to the –30DP atmosphere samples, this oxide also had a varying chemical structure, showing Si enrichment at the core of the grain boundary oxide, while suggesting the presence of a manganese silicate for the outer shell of the oxide. As discussed above, this Si-rich oxide could be identified as SiO₂, which has been shown and is known to be present as an amorphous oxide under such conditions. ^[32,35,36] This type of core–shell structure was also consistently observed in the grain boundary oxide networks formed in subsurface of the –30DP sample.



Figure 3.9: HAADF image and EELS elemental maps, showing the core–shell structure of a grain boundary oxide of the sample annealed for 600 s under the +5DP process atmosphere.

In an effort to accurately determine the chemistries of each of the external oxide layers observed for the –50DP sample, as per the numbered layers annotated to the STEM image in Figure 3.6(a), Mn, O, and Si edges of the EELS spectra of each region were extracted. The fine structures of O-K, Mn-L_{2,3}, and Si-K edges of the aforementioned EELS spectra are shown in Figure 3.10, where the spectra numbers correspond to the numbered layers in Figure 3.6(a). As can be seen from Figure 3.10, no Mn edge was observed in the layer 3 spectrum, while both of the O-K and Si-K edges correlated with those of SiO₂. ^[37,38] In the same manner, the shapes of the core-loss edges of O-K and Mn-L_{2,3}, along with their near-edge fine structures obtained from layer 2 in Figure 3.6(a), correspond with those reported for MnSiO₃ in the recent study of Grosvenor et al.^[39] Finally, the external oxide nodules were identified as MnO from the O and Mn edges ^[40-43] and the fact that no Si-K edge was detected, in agreement with the XPS data reported in Table 3.3. The same analytical procedure was carried out on the external oxides that were formed under the –30DP and +5DP atmospheres, further confirming that the external oxides in these cases comprised MnO, in agreement with the XPS binding energy analysis shown in Figure 3.4 and Table 3.3. It was further found that the fine spherical internal oxides formed in the bulks of the –30DP and +5DP samples (Figure 3.8) correlated with the MnO spectrum in Figure 3.10, while the fine grain boundary oxides of the subsurface were confirmed to exhibit SiO₂ at the cores. Similar to Figure 3.10, inspection of the elemental edges of the EELS spectra acquired from the grain boundary oxide networks in the deeper subsurface of the –30DP and +5DP samples (Figure 3.9) confirmed that the oxide core consisted of amorphous SiO₂, with the surrounding shell being identified as MnSiO₃.



Figure 3.10: O-K, Mn-L_{2,3}, and Si-K edges electron energy loss spectra acquired from the external oxides of the sample annealed for 600 s under the -50DP process atmosphere. The numbers correspond to different oxide regions of Figure 3.6(a).

3.4 Discussion

In order to assist with the understanding of the internal/external transition, the classic Wagner model ^[5] for the transition from internal to external oxidation was used to predict the selective oxidation mode of Mn and Si in the experimental alloy as a function of process atmosphere oxygen partial pressure (pO_2). Equation (3.1) gives the Wagner equation for the internal/external transition criterion for a binary single crystal alloy comprising a noble matrix and ignoble solute B at an absolute temperature *T*:

$$\left(N_{B}^{(o)}\right)_{crit} = \left[\frac{\pi g^{*}}{2\nu} N_{O}^{(s)} \frac{D_{O}V}{D_{B}V_{BO_{\nu}}}\right]^{1/2}$$
(3.1)

where a bulk solute concentration greater than the critical mole fraction of the solute element B, $(N_B^{(o)})_{crit}$ results in the transition from internal to external oxidation, g^* is the critical volume fraction of the precipitated oxides required to block the inward diffusion of oxygen, vis the stoichiometric oxygen ratio for the precipitated solute oxide BO_v , V is the alloy molar volume, V_{BOv} the oxide molar volume, $N_O^{(s)}$ is the mole fraction of dissolved oxygen at the surface as per the analysis of Swisher and Turkdogan,^[44] and D_O and D_B are, respectively, the bulk diffusivities for O and the solute B in the alloy.

The values of the parameters used in Equation (3.1), except those used to compute $N_o^{(s)}$, are tabulated in Table 3.4. It should be noted that the value of g^* most commonly used in the Wagner model is 0.3, arising from the analysis of Rapp on Ag-In alloys. ^[50] However, recent experimental work by Lashgari et al. ^[51] determined this value to be 0.2 for the case of Mn-containing steels, and this value was used for predicting the oxidation mode of Mn in the current work; in the case of Si, however, 0.3 was employed in the calculations. More comprehensive details concerning the Wagner calculations and the equations for the terms

therein, such as those used to compute $N_o^{(s)}$, are provided in Appendix and the process atmosphere information required for its computation is provided in Table 3.2.

Ele	ement or compound in austenite or ferrite	D_i' (cm ² /s)	Q _i (10 ³ J/mol)	V _i (cm ³ /mol)	ν_i	Ref.
	O in y	0.642	159.0	-	-	45
	Mn in γ	0.16	261.7	-	-	46
	Si in y	0.21	242.0	-	-	45
	O in α	0.037	964.0	-	-	47
	Mn in α	1.49	233.5	-	-	47
	Si in a	8.0	248.9	-	-	47
	MnO	-	-	13.02	1	48
	SiO_2	-	-	26.12	2	48
	γ-Fe	-	-	7.299	-	49
	α-Fe	-	-	7.0918	-	48

Table 3.4: Diffusion data and values for the parameters in Equation (3.1) used for oxidation mode prediction

It should be noted, however, that Equation (3.1) does not take into consideration either grain boundary diffusion in polycrystalline solids or the presence of multiple ignoble solutes, as is the case for the present alloy. To address these limitations, the accelerated diffusion of oxygen and alloying elements was accounted for by halving the activation energy values for bulk diffusion ^[52] in Equation (3.1). In addition, the modified Wagner model proposed by Mataigne et al. ^[52] for multi-component systems, in which the flux of the oxidizable alloying elements toward the surface is additive and external oxidation will occur if this combined flux of the alloying elements exceeds the inward flux of O into the substrate. On this basis, the Wagner model (Equation (3.1)) was modified such that external oxidation will take place if the inequality in Equation (3.2) is satisfied:

$$\sum_{B} N_{B}^{(o)} \left[\nu D_{B} V_{BO_{\nu}} \right]^{\frac{1}{2}} \ge \left[\frac{g^{*} \pi V N_{O}^{(s)} D_{O}}{2} \right]^{\frac{1}{2}}$$
(3.2)

where the left-hand side of the inequality represents the cumulative flux of ignoble solutes (in the present case Mn and Si) to the surface and the right-hand side represents the inward flux of oxygen.

Using the treatments embodied in Equations (3.1) and (3.2), the oxidation mode for Mn and Si in the binary alloy (Equation (3.1)) and multi-component alloy (Equation (3.2)) were computed for the process atmospheres used in the present study. Computations were conducted for both bulk and grain boundary selective oxidation. The results of the calculations for Equation (3.1), *i.e*, the binary alloy $\left(N_B^{(o)}\right)_{crit}$, for both Mn and Si are compiled in Table 3.5. In the case of grain boundary oxidation, Equation (3.1) predicted external oxidation under all annealing conditions for both Mn and Si. It should be mentioned that Table 3.5 includes calculation results for both austenite and ferrite microstructures; however, it should be noted that given the annealing temperature of 1073 K (800°C), which is significantly above the Ac₃ temperature of the experimental steel [1059 K ± 10 K (786°C ± 10°C)], the majority of the microstructures at the PAT likely consisted primarily of austenite and, thus, the oxidation mode was likely dominated by this phase.

The Wagner model calculation results for bulk austenite under the -50DP process atmosphere (Table 3.5) are in good agreement with the XPS (Figure 3.3(a)) and TEM (Figure 3.6(a)) observations, where it can be seen that the predicted external oxidation mode for Mn and Si under the -50DP atmosphere was dominant. Similarly, in the case of the +5DP process atmosphere, the predicted internal oxidation mode for both Mn and Si was found to be consistent with the TEM (Figure 3.6(c)) and XPS data (Figure 3.3(c)), the latter of which

showed the concentration profile of Mn above the bulk composition well below the substrate surface as well as the reduced surface enrichment observed. In the case of the Si XPS profiles for the +5DP atmosphere, the subsurface peaks (Figure 3.6(c)) provide some support for the occurrence of internal oxidation as these localized peaks likely resulted from either the bulk or grain boundary internal oxides.

Table 3.5: Predicted oxidation behavior of Mn and Si for an austenitic or ferritic microstructure as a function of process atmosphere pO_2 at 1073 K (800°C) using the Wagner equation (Equation (3.1))

	Bulk Oxidation in	n Austenite	Bulk Ox	Bulk Oxidation in Ferrite		
Atmosphere Name	Mn	Si	Mn	Si		
-50DP	External	External	Externa	l External		
-30DP	External/Internal	External	Externa	l External		
+5DP	Internal	Internal	Interna	l Internal		

The oxidation mode of Mn for bulk austenite under the -30DP process atmosphere was predicted to be borderline internal as this process atmosphere dew point was very close to that predicted for the internal to external oxidation transition, *i.e.*, less than 1 K (Table 3.5). It should be recalled that this prediction used the modified $g^* = 0.2$ proposed by Lashgari et al.^[51] The internal oxidation prediction for Mn was consistent with the XPS elemental profiles and TEM structural evidence shown in Figures 3.3(b), 3.6(b), and 3.8, respectively. As mentioned above, external grain boundary oxidation of the austenite was predicted to occur for both Mn and Si under the –30DP process atmosphere, and this is consistent with the TEM + EELS evidence presented in Figure 3.8 and can be said to also be consistent with the fluctuations in the Si XPS profile presented in Figure 3.3(b). It must, however, be pointed out that use of the classical value of $g^* = 0.3$ for Mn in Equation (3.1) will also predict internal oxidation for Mn, albeit at a lower dew point of approximately 238.5 K (–34.5°C) and is also consistent with the above observations. Thus, no concrete conclusions can be drawn as to the preferred value for g^* for Mn in Equation (3.1) from the present study.

However, in the case of Si, the predicted oxidation mode for bulk austenite was predicted to be external under the –30DP atmosphere and is clearly inconsistent with the experimental evidence presented in Figures 3.3(b), 3.6(b), and 3.8. Thus, the present form of the Wagner model or the fundamental data used for the oxidation mode prediction for Si in bulk austenite is clearly inadequate. Examination of Equation (3.1) reveals that this is likely due to the value of the relative diffusivities of oxygen and silicon (*i.e.*, the D_o/D_{B-Si} ratio) being approximately an order of magnitude lower than the comparable ratio for Mn, *i.e.*, $3.4 \times 10^4 vs 4.0 \times 10^5$, respectively. This lower relative D_o/D_B ratio for Si (*i.e.*, the higher flux of Si to the surface) was very likely the most significant factor in increasing the value of the critical mole fraction of Si for the transition to internal oxidation and the resultant increase in the predicted process atmosphere dew point for the transition from external to internal oxidation to approximately 275 K (2°C). Thus, the overall conclusion is that the Wagner model can be used to predict the oxidation mode for Mn in the present alloy, but that the Wagner model cannot be used to accurately predict the oxidation mode transition for Si in the present Fe-0.1C-6Mn-2Si (wt pct) alloy system.

In the case of the modified multi-component Wagner model of Mataigne et al. ^[52] (Equation (3.2)), external oxidation of Mn and Si, both within the bulk austenite and along the austenite grain boundaries, was predicted for all experimental process atmospheres. Further investigation of the trends predicted by this equation revealed that external oxidation was predicted for all atmospheric dew points between 173 K (-100° C) and 373 K ($+100^{\circ}$ C). These predictions are clearly inconsistent with the experimental results for the bulk oxidation mode of both alloying elements for the -30DP and +5DP process atmospheres. Thus, the

additive solute oxidation effect assumed to be operative in this equation is not valid in the case of the present 6Mn + 2Si alloy.

The SEM micrographs in Figures 3.2(a) through (i) show that the oxidation potential of the annealing atmosphere had a significant effect on the surface oxide morphology and distribution. It was determined through XPS binding energy data (Table 3.3) and TEM+EELS analysis (Figures 3.7, 3.8, 3.9, and 3.10) that the outermost external oxide layer comprised MnO for all process atmospheres. An increase in the isochronal surface area fraction not occupied by MnO nodules or films was determined as a result of annealing under the +5DP atmosphere (Figures 3.2(g) through (i)), while the highest surface coverage by external MnO was observed under the -30DP process atmosphere, further indicating that the oxidation potential of the process atmosphere strongly affected the oxide morphology. Furthermore, as was shown through the XPS profiles in Figure 3.3 and the external oxide growth rate data plotted in Figure 3.5, the external oxide layer formed in the -50DP samples was significantly thinner than those formed in the other two process atmospheres for annealing times greater than 180 seconds due to its lower growth rate. However, it can also be seen from Figure 3.5 that the external oxide was significantly thinner for annealing times of up to 180 seconds in the case of the +5DP process atmosphere, likely due to the effect of a stronger internal oxidation mode being operative for this process atmosphere, further supporting the above hypothesis.

The slower rate of oxide growth under the -50DP atmosphere can be partially explained by the lower oxidation potential of this atmosphere, which in turn led to a lower adsorbed oxygen at the surface (*i.e.*, $N_o^{(s)}$, as per Equation (3.5), Appendix A) and a lower oxygen flux into the steel. Furthermore, as seen from SEM images (Figure 3.2(a) through (c)) and the oxidation kinetics plot in Figure 3.5, a relatively thick oxide layer (101 ± 9 nm) covering the steel surface was present after the 60-second hold for the –50DP process

atmosphere, meaning that further progression of the oxidation reaction was controlled by the slower outward diffusion of Mn and Si and the inward diffusion of O through the thickening surface oxide layer. ^[53] Additionally, as per the TEM+EELS findings presented in Figures 3.6(a) and 3.7, respectively, the presence of a layered oxide configuration on the surface of the sample annealed under the -50DP atmosphere further explains the slow growth rate controlled by diffusion of the oxide forming species through three different oxide layers and their corresponding interfaces, while under the -30DP and +5DP atmospheres, the oxidation reaction progressed through diffusion across only one interface (Figures 3.6(b), (c) and 3.8). The surface oxides formed after the 60- and 120-second holding times under the -30DP atmosphere were somewhat comparable to those formed under the -50DP process atmosphere in terms of thickness and coverage; however, a significant difference between the thicknesses of the surface oxides of the two atmospheres was observed for the prolonged holding times of 360 and 600 seconds. The higher oxidation potential of the -30DP atmosphere, *i.e.*, larger O supply, in combination with the diffusion process through a singlelayer surface oxide, as described above, can be responsible for the observed increase in the oxide growth kinetics in comparison with that of the -50DP atmosphere. The presence of more widely spaced external MnO nodules of the samples annealed under the +5DP process atmosphere, where the internal oxidation mode was fully operative, is explained by the lower flux of solute Mn being able to reach the external oxide nucleation sites.

Thermodynamic calculations clearly show that MnO, SiO₂, MnSiO₃, and Mn₂SiO₄ form stable oxides under the annealing atmospheres used in this study. ^[16] However, the morphology and formation mode (*i.e.*, internal or external) of these oxides is also dependent on kinetic factors such as the relative diffusion rates of Mn, Si, and O. Among the aforementioned oxides, SiO₂ has the highest thermodynamic stability, followed by the mixed Mn-Si oxides, with MnO being the least thermodynamically stable. ^[11,54] The presence of
SiO₂ as a grain boundary oxide in the subsurface of CMnSi steels has been reported by several authors at oxygen partial pressures consistent with internal oxidation. [14,15,32,34,35,54] This can be explained by the higher thermodynamic stability of SiO₂ combined with its relatively low solubility $(3.1 \times 10^{-5} \text{ (ppm)}^3)$, ^[55] and higher Si diffusivity $(3.5 \times 10^{-17} \text{ m}^2 \text{s}^{-1})$ in austenite ^[45] relative to that of MnO (*i.e.*, $K_{MnO} = 7.2 \text{ (ppm)}^2$ and $D_{Mn, \gamma} = 2.9 \times 10^{-18} \text{ m}^2 \text{s}^{-1}$, respectively) and the slightly lower solubility of Mn_2SiO_4 in austenite $(7.6 \times 10^{-6} (ppm)^7)$, in this case assumed to be approximately the same as MnSiO₃). ^[55] Thus, the likely formation sequence for these structures comprised first precipitating the more rapidly diffusing, thermodynamically stable, lower solubility SiO₂ at the grain boundaries. As Mn was able to diffuse to the grain boundaries at its lower rate, it would then react with the SiO₂ to form the observed, low solubility MnSiO₃ grain boundary phase. Further support for this hypothesis is provided in Figure 3.9, where it can be seen that the Mn-containing shell is slightly thinner at the bottom of the EELS map and the Si-containing core is slightly thicker, as would be expected given the diffusion-driven basis of the internal oxidation reactions. These observations are also consistent with those of other authors,^[54,56] where similar structures were observed for the internal oxidation of low Mn + Si steels. A similar mechanism would also explain the observed SiO₂ core/MnSiO₃ shell structures observed for the bulk internal oxides, as per Figure 3.8 and the multi-layered external oxides observed in the case of the -50DP process atmosphere (Figure 3.7). Having most of the Si bound to the SiO₂ and MnSiO₃ oxides, formation of the MnO nodules at the outmost layer of the surface would be facilitated under a critically low Si/Mn ratio at the surface and continuous supply of oxygen from the atmosphere.

It has been reasonably well established that the surface oxide chemistry, morphology, distribution, and thickness can critically affect the reactive wetting of the steel substrate by the galvanizing zinc bath. A series of studies by Bellhouse and McDermid ^[18,26,35] reported

that reactive wetting can occur despite the presence of widely distributed, relatively thin, nodular external oxides on Al-Si TRIP-assisted steels when annealed under a low oxygen partial pressure atmosphere, whereas the more compact, thicker MnO films observed at the higher pO₂ were not able to be reactively wetted. Furthermore, Alibeigi et al. ^[22] explored the reactive wetting of a 5 wt pct Mn steel by a 0.20 wt pct Al (dissolved) bath and advocated that the surface MnO layer could be aluminothermically reduced by the resident bath-dissolved Al. However, despite the large thermodynamic driving force for the aluminothermic reduction, the wetting reaction can be kinetically limited in the case of excessively thick surface MnO layers. In a later study, ^[19] it was shown that surface MnO layers thinner than 85 nm can be reduced through aluminothermic reduction during a 4-second immersion in a 0.20 Al (wt pct, dissolved) galvanizing bath.

In the present study, a variety of surface oxide chemistries and morphologies were observed under the three experimental process atmospheres. Under the -50DP process atmosphere, a film-like multi-layer oxide structure composed of SiO₂, MnSiO₃, and MnO was formed at the surface. It is well known that SiO₂ and manganese silicates are among the most detrimental oxides with regard to promoting the desired η -Fe₂Al₅Zn_x interfacial layer formation. Furthermore, the -50DP oxide layer was relatively thick (over 100 nm) for all of the experimental annealing times, making the aluminothermic reduction mechanism kinetically unfavorable. ^[19] Given this factor and the unfavorable morphology, it would be expected that the surfaces of the -50DP samples would not promote reactive wetting by the galvanizing bath. Given the similar morphology and thickness of the external MnO layer of the -30DP process atmosphere, a similar result would be expected. Overall, it would be expected that annealing the present steel under either the -50DP or -30DP process atmospheres at 1073 K (800°C) would result in poor reactive wetting by the CGL bath.

However, the surface MnO morphology and thickness were found to be significantly different as a result of increasing the oxygen partial pressure of the process atmosphere from 4.393×10^{-23} atm (*i.e.*, -30DP, Table 3.2) to 1.291×10^{-20} atm (*i.e.*, +5DP). Under the +5DP atmosphere and for the industrially relevant annealing times of 60 and 120 seconds, surface oxides with average thicknesses of 49 ± 5 nm and 87 ± 10 nm were formed, respectively, which were much thinner than those of other two process atmospheres (Figure 3.5). Based on the kinetic model proposed by Kavitha et al.,^[19] these MnO layers can be expected to be reduced in a 0.2 wt pct Al (dissolved) bath during the common CGL immersion time of approximately 4 seconds. Additionally, the very thin internodular oxide layers combined with the nodule-like oxide morphology of the +5DP steels (Figures 3.2(g) through (i)) has been shown to favor reactive wetting mechanisms such as Fe₂Al₅Zn_X formation and bridging or lift-off of the oxides by the molten zinc bath. Thus, it would be expected that the present steel annealed at 1073 K (800°C) under the higher pO₂ +5DP process atmosphere could be successfully reactively wetted by conventional CGL baths.

3.5 Conclusions

It was demonstrated that process atmosphere oxygen partial pressure has strong effects on the distribution, chemistry, and oxidation mode observed during a 1073 K (800°C) anneal of a model 0.1C-6Mn-2Si medium-Mn advanced high-strength steel. The external oxides formed under the 223 K (-50° C) and 243 K (-30° C) dew-point process atmospheres exhibited a film-like morphology which covered the entire steel surface, even at short holding times. For the 278 K ($+5^{\circ}$ C) dew-point process atmosphere, the external oxides showed a nodular appearance with scattered distribution such that the internodular regions of the substrate surface were covered in very thin oxide films, even after a 600-second holding time. Oxide thickness measurements revealed that the surface oxide growth kinetics followed a

parabolic rate law under all experimental process atmospheres, with the minimum rate belonging to the 223 K (-50° C) dew-point process atmosphere.

XPS analysis and cross-sectional studies of the samples annealed for 600 seconds showed that, consistent with the modified Wagner model predictions for Mn, a transition from external to internal oxidation occurred under the 243 K (-30° C) and 278 K ($+5^{\circ}$ C) dew-point process atmospheres, while the Wagner model predictions for Si did not correlate with the experimental results. Moreover, the multi-component model was incapable of predicting the oxidation mode of the experimental steel.

HR-STEM + EELS studies revealed that the external oxides formed on the steel surface under the 223 K (-50° C) process atmosphere consisted of a layered structure of SiO₂, MnSiO₃, and MnO, while under the higher pO₂ process atmospheres, only MnO was found as the surface oxide. Similarly, it was shown that the internal network of the grain boundary oxides of the samples annealed under the 243 K (-30° C) and 278 K ($+5^{\circ}$ C) dew-point process atmospheres were composed of an amorphous SiO₂ core surrounded by an outer shell of MnSiO₃. A mechanism for the formation of the observed oxide morphologies, based on the varying solubilities of the oxides, their relative thermodynamic stabilities and the relative diffusion rates of Si and Mn, was described.

It is expected that the presence of film-like SiO₂ and MnSiO₃ on the surface of the 223 K (-50° C) process atmosphere samples would result in poor reactive wetting by the liquid metal Zn(Al,Fe) continuous galvanizing bath, and similar results are predicted in the case of the relatively thick external MnO layers formed on the samples annealed under the 243 K (-30° C) dew-point process atmosphere. It is expected that only the fine, nodule-like and relatively thin MnO oxides of the samples annealed under the 278 K ($+5^{\circ}$ C) dew-point process atmosphere for 60 and 120 seconds will promote full reactive wetting by the molten zinc bath.

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Appendix A

The general equation for the diffusivity of species i is given by:

$$D_i = D'_i \exp\left(\frac{-Q_i}{RT}\right) \tag{3.3}$$

where D'_i is the diffusion frequency factor of species *i*, Q_i is the activation energy for diffusion, and *R* is the universal gas constant (8.314 J/mol·K).

The mole fraction of dissolved oxygen at the surface, $N_o^{(s)}$, was provided through the analysis of Swisher and Turkdogan ^[44] for the decomposition of H₂O on the steel surface to form a Henrian solution with the appropriate phase in the substrate, as per Equation (3.4):

$$\mathbf{H}_{2} + \left[\mathbf{O}\right] = \mathbf{H}_{2}\mathbf{O} \tag{3.4}$$

$$N_O^{(s)} = \frac{1}{100} \left(\frac{MW(Fe)}{MW(O)} \right) \left(\frac{p(H_2O)}{p(H_2)} \right) \left(\frac{1}{K_3^i} \right)$$
(3.5)

where MW(Fe) and MW(O) are the molecular weights of Fe and O, respectively; $p(H_2O)$ and $p(H_2)$ are the partial pressures of water vapor and hydrogen in the process atmosphere, respectively, and K_3^i is the equilibrium constant of reaction 3.4 for phase *i* in the substrate (*i.e.*, austenite (γ) or ferrite (α)). These latter values are obtained from Equations (3.6) and (3.7) for austenite and ferrite, respectively ^[44]:

$$\log K_3^{\gamma} = \frac{4050}{T} + 0.06 \tag{3.6}$$

$$\log K_3^{\alpha} = \frac{5000}{T} - 0.79 \tag{3.7}$$

and the $p(H_2O)/p(H_2)$ ratios required for input to Equation (3.5) for the process atmospheres of interest are presented in Table 3.2.

CHAPTER 4 EFFECT OF PROCESS ATMOSPHERE DEW POINT AND TIN ADDITION ON OXIDE MORPHOLOGY AND GROWTH FOR A MEDIUM-MN THIRD GENERATION ADVANCED STEEL DURING INTERCRITICAL ANNEALING

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Abstract

The combined effects of process atmosphere oxygen partial pressure, annealing time and a 0.05 wt pct Sn addition on the selective oxidation of a prototype 0.1C-6Mn-2Si third generation advanced high strength steel (3G AHSS) was investigated. External and internal oxidation of both steels was observed after intercritical annealing at 963 K (690°C) for holding times of 60 s to 600 s under all process atmosphere dew points explored (i.e. 223 K (-50°C), 243 K (-30°C) and 278 K (+5°C)). The external MnO morphology was changed from compact and continuous film-like nodules to a fine and discrete globular morphology, with thinner external oxides, for the Sn-added steel. Cross-sectional TEM analysis revealed that the Sn-addition also resulted in significant refinement of the internal oxide network. Kinetic studies showed that both the external and internal oxidation followed a parabolic rate law, where the Sn addition to the steel chemistry resulted in lower external and internal oxidation rates. 3D atom probe tomography of the external oxide/steel interface showed that Sn was segregated to the interface with enrichment levels ten times the bulk value, which was concluded to be responsible for the observed morphological changes. The resultant refined

external oxide structure is expected to have significant benefits with respect to reactive wetting by the continuous galvanizing bath.

4.1 Introduction

The increasing demand for lighter, safer and more fuel-efficient vehicles legislated by energy and environmental agencies has resulted in third generation advanced high strength steels (3G-AHSS) receiving significant interest from leading auto steel researchers and OEMs as candidate materials for the manufacturing of reduced mass structural automotive components. ^[1-5] In particular, the 3G-AHSSs are being designed to possess a superior combination of high strength and ductility versus the first generation AHSSs at a lower cost and a leaner chemistry compared to the highly-alloyed second generation AHSS, e.g. twinning induced plasticity (TWIP) and austenitic stainless steels. ^[1-4]

However, the use of these next generation materials requires innovative solutions for maintaining the structural integrity of the vehicle against corrosion, particularly since the desired weight reduction is generally brought about by the use of thinner material cross-sections and more complex geometries for manufactured parts. Continuous hot-dip galvanizing is a widely practiced, cost-effective industrial process for this purpose, where a zinc alloy coating is applied to sheet products after being heat treated in a dew point controlled, reducing N₂-H₂ atmosphere. However, the annealing atmospheres commonly used in industrial practice are not reducing with respect to the commonly used alloying elements such as Mn, Si, Cr and Al and, as a result, selective oxidation of these elements can occur at the surface and subsurface of the steel, possibly rendering the sheet surface incompatible for reactive wetting by the continuous galvanizing Zn(Al, Fe) bath. For example, it has been shown that the presence of an integral, relatively thick external oxide layer can prevent the essential reactive wetting reactions ^[6-8] from taking place at the steel/zinc interface during

immersion in the Zn(Al, Fe) bath, resulting in poor coating adhesion and unacceptable final product quality.

A variety of solutions have been proposed to address this issue, where several authors have suggested tailoring the process atmosphere conditions such that external selective oxidation of the alloying elements is either hindered or transferred from the surface to the subsurface. This can be achieved through different routes, such as increasing the oxygen partial pressure of the process atmosphere ^[9-14], increasing the hydrogen content of the gas mixture ^[15] or implementing a pre-oxidation treatment prior to annealing. ^[16,17] More recently, the known effect of surface segregation of minor alloying additions such as Sn and Sb on retarding the rates of surface reactions such as carburization^[18] and selective oxidation of Si in electrical steels ^[19], was leveraged into the area of AHSS to resolve the issue of alloying element selective oxidation in CMnSi TRIP steels.^[20-22] In particular, it was shown that minor additions of selected surface active elements such as Sn^[20,21], Sb^[20] or Bi^[22] within the ranges of 0.05 wt pct to 1 wt pct, could modify the morphology of the Si-rich surface oxides from film-like to island-like such that significant improvements in the quality of the galvanized coating was obtained. It was reported that segregation of these elements to the surface occupied the oxygen adsorption sites, thereby decreasing the oxygen permeability and potentially changing the surface oxide chemistry and morphology.^[20-24] It was also pointed out that the surface segregation also changed the interfacial energies, which contributed to the observed morphological changes. ^[25,26] However, despite the beneficial effects on the selective oxidation of AHSSs alloyed with surface active elements, care must be taken when employing this approach as alloying additions in excess of 0.05 wt pct of elements such as S and Sn are known to have detrimental effects on the grain boundary cohesion and mechanical properties.^[25,27]

With the pending emergence of 3G-AHSSs in automotive structures, it is imperative that means be developed to allow for the metallic coating of this alloy class. Among the proposed candidate compositions for 3G-AHSSs, medium-Mn steels have emerged as credible candidates to fill the 3G-AHSS property space. ^[5, 28-31] However, limited work has been performed on the galvanizing of these alloys and, in particular, there is limited information available on the effect of surface active elements on the selective oxidation of medium-Mn steels and their potential to favorably change external oxide thickness, morphology and distribution to facilitate reactive wetting by the Zn(Al, Fe) continuous galvanizing bath. Thus, the objective of the present contribution is to determine the combined effects of varying the oxygen partial pressure – through altering the N₂ - 5 vol pct H₂ process atmosphere dew point – and an alloying addition of 0.05 wt pct Sn on the selective oxidation, oxide morphology, oxide surface distribution and oxidation kinetics of a model Fe-0.1C-6Mn-2Si (wt pct) 3G-AHSS. The results of this study will also be interpreted within the context of previously established knowledge on the effect of these factors on the reactive wetting of steel surfaces by the Zn(Al, Fe) galvanizing bath. ^[32-35]

The results of this work will contribute to subsequent studies on the subject of reactive wetting mechanisms of the medium-Mn 3G steels, which are expected to be significantly more difficult to reactively wet relative to the first generation AHSSs.

4.2 Experimental

Two grades of 0.1C-6Mn-2Si steel sheets, a reference alloy and a Sn-added grade, were received in the full-hard cold-rolled condition with an approximate thickness of 1.2 mm. The detailed chemical composition of the experimental steels is given in Table 4.1. Samples for selective oxidation comprising $10 \times 50 \text{ mm}^2$ coupons were cut from the original steel sheets using an abrasive water-jet such that the rolling direction was parallel to the

longitudinal axis of the samples. The sample surfaces were polished using 4000 grit SiC paper prior to annealing in order to minimize the effects of surface roughness on the surface oxidation studies. All samples were cleaned with acetone immediately prior to annealing.

Table 4.1: Chemical composition of the experimental steels (wt pct)									
Steel Name	С	Mn	Si	Al	Sn	Р	S	Mn/Si	
Reference	0.106	6.241	2.023	0.040	0.005	0.006	0.003	3.09	
0.05 pct Sn	0.100	6.165	2.050	0.032	0.049	0.006	0.004	3.01	

Selective oxidation heat treatments were carried out in a dew point controlled N₂ - 5 vol pct H₂ process atmosphere in the McMaster Galvanizing Simulator (Iwatani-Surtec), operational details of which are well documented and can be found elsewhere. ^[10] Three process atmospheres with dew points of 223 K (-50° C), 243 K (-30° C) and 278 K ($+5^{\circ}$ C) were used to explore the effect of process atmosphere oxygen partial pressure on the selective oxidation of Mn and Si. A detailed summary of the experimental process atmospheres utilized in this study are presented in Table 4.2, where the corresponding values of pH₂O/pH₂ and oxygen partial pressure (pO₂) at each dew point were derived using the FREED thermodynamic database. ^[36] Throughout the subsequent text, references to process atmosphere name per Table 4.2.

Table 4.2: Experimental specifications of the N_2 -5 vol pct H_2 process atmospheres at 963 K (690°C) peak annealing temperature

Atmosphere Name	Dew Point (K)	pH ₂ O/pH ₂	pO ₂ (atm)	Holding Time (s)
-50DP	223	0.00125	1.20×10 ⁻²⁷	60, 120, 180, 360, 600
-30DP	243	0.00998	7.69×10 ⁻²⁶	60, 120, 180, 360, 600
+5DP	278	0.17111	2.26×10 ⁻²³	60, 120, 180, 360, 600

Figure 4.1 shows a schematic of the experimental annealing cycle, where samples were isothermally held at an intercritical annealing temperature (IAT) of 963 K (690°C) for holding times within the range of 60 s to 600 s (Table 4.2). Following the isothermal hold, samples were rapidly cooled to 343 K (70°C) at a rate of -10 K/s *via* N₂ gas quenching. The thermal cycle was controlled using a 0.5 mm type K thermocouple welded directly to one of the selective oxidation samples. All selective oxidation tests were carried out in triplicate to ensure repeatability of the experimental results. The heat treated samples were stored in anhydrous HPLC grade isopropanol in order to minimize additional oxidation prior to analysis.



Figure 4.1: Annealing heat treatment cycle schematic.

In order to study the effects of the experimental variables on surface oxide morphology and distribution, the annealed samples were examined in a JEOL 7000F field emission gun scanning electron microscope (FE-SEM) operated in secondary electron imaging mode at an acceleration voltage of 5 keV. All oxidized samples were coated with C prior to SEM analysis to prevent charging.

To investigate the formation and growth of the surface and subsurface oxides, SEM images were also acquired from the cross-sectioned surfaces revealed through focused ion

beam (FIB) milling. A NVision 40 FIB-SEM microscope (Zeiss) equipped with an in-lens detector was operated at an acceleration voltage of 5 keV for electron imaging. Two trench cuts with a length of 10 µm were made on distanced areas of all samples, prior to which C and W were deposited on those areas in order to preserve the surface oxides from damage during Ga ion beam milling. High magnification electron images were captured along the length of the cuts where a tilt correction of 36° was applied to the cross-sectional images in order to compensate for the 54° stage tilt required for the milling procedure. Measurements of the external oxide layer thickness as well as the depth of the internal oxidation zone were performed using ImageJ 1.48v software. Oxide growth kinetics as a function of process atmosphere oxygen partial pressure and Sn addition were determined based on a minimum of 100 measurements per sample taken using a defined sampling grid to ensure random sampling of the oxide layer thickness. The average oxide thicknesses below are reported using the 95% confidence interval of the sample mean.

X-ray photoelectron spectroscopy (XPS) was carried out to identify the surface oxide chemistries and to obtain elemental depth profiles. The analysis was performed using a PHI Quantera SXM with an Al K α X-ray source (1486.7 eV). The spot size was 100 μ m and the take-off angle was set at 45°. Spectra were acquired using a pass energy of 140 eV and step size of 0.25 eV. Elemental depth profiles were obtained by Ar ion sputtering a 2 × 2 mm² area after sputtering the outermost 5 nm of the surface in order to remove contaminants from atmospheric exposure. Depth measurements are considered accurate within ±10% of the documented sputtered depth. All data processing was performed using MultiPak 6.0 software. The reported chemical analysis binding energies are accurate to within ±0.1 eV. All spectra were calibrated using the metallic Fe2p_{3/2} binding energy of 706.62 eV.

Scanning transmission electron microscopy (STEM) was performed on cross-sections of samples that were held for 600 s at the PAT across all process atmospheres explored.

Similar to the procedure described above, FIB lift-outs were first made from areas of interest and were thinned by ion milling to meet the requirement for analysis with transmission electron microscopy. A FEI Titan 80-300HB transmission electron microscope operated at 300 keV was used to acquire HR-STEM micrographs and to obtain electron energy loss spectra (EELS) using a Gatan Quantum GIF. Digital Micrograph 2.3 software was used to extract elemental maps from the raw EELS data.

In order to characterize Sn segregation to the surface and oxide/metal interfaces, 3D atom probe tomography (APT) was performed using a Cameca LEAP 4000X HR atom probe (Cameca Instruments). Prior to FIB lift-out, the sample surfaces were sputter-coated with a ~300 nm thick layer of Cr to facilitate specimen preparation. FIB lift-outs containing the surface oxide/metal interface and subsurface oxides were sectioned and mounted onto silicon posts using W deposition, and sharpened into needles by annular milling at 30 keV using standard methods. ^[37] Final sharpening was done at 10 keV to remove FIB damage and position the surface oxide to the tip apex. The tips were analyzed by APT operating in laser pulsing mode ($\lambda = 355$ nm, 60 pJ/pulse) with a stage temperature of ~60 K. The target detection rate was set at 0.005 ions/pulse (0.5 %) which was maintained by an applied DC voltage. The laser pulsing rate was 120 kHz or 200 kHz, as dictated by the applied voltage and maximum range of the mass spectrum. IVAS v3.6.6 software was used for reconstruction and analysis of the data.

4.3 **Results**

A selection of SEM images of the external oxides formed during intercritical annealing at 963 K (690°C) under the -50DP, -30DP and +5DP process atmospheres are shown in Figures 4.2, 4.3 and 4.4, respectively, where the micrographs in (a), (b) and (c) represent the external oxides for the reference steel after 120 s, 360 s and 600 s isothermal

holds at the IAT and (d), (e) and (f) correspond to the same annealing parameters for the Snadded grade. It should be recalled that five holding times within the range of 60 s to 600 s were explored for the selective oxidation experiments; however, the trends shown in this selection of SEM images were found to be consistent for all experimental samples.



Figure 4.2: Secondary electron images showing the surface oxide morphology of samples annealed under the –50DP process atmospheres for 120 s, 360 s and 600 s; (a), (b) and (c) reference steel, (d), (e) and (f) Sn-added steel.

It can be seen from Figure 4.2 that an increased coverage of the steel surface by the external oxides was observed with increasing annealing time. Furthermore, the oxide layers that were formed after the 360 s and 600 s holds (Figures 4.2(b), (c), (e) and (f)) showed a coarser and more compact appearance. This coarsening trend with time was consistent for both of the reference and the Sn-added steels. However, a comparison of Figures 4.2(a)-(c) with their equivalent counterparts in Figures 4.2(d)-(f) clearly shows that the morphology and distribution of the oxides formed at the surface of the Sn-added grade were modified. For example, it can be seen that the Sn-added alloy external oxides comprised finer nodules with

a globular morphology as opposed to the coarser, more compact and film-like nodules of the reference alloy. It can also be observed that the Sn-added alloy surfaces exhibited a more discrete distribution with wider spacing between the nodules. Furthermore, it can be surmised that the surfaces of the Sn-added steel were significantly less oxidized, as exemplified most clearly in the case of the 120 s and 360 s samples (i.e. Figures 4.2(a) vs (d) and (b) vs (e)), as after the extended holding time of 600 s, a fully coarsened and compact external oxide scales were formed on both grades (i.e. Figure 4.2(c) and (f)).

The modifying effect of the 0.05 wt pct Sn addition on the surface oxide morphology and distribution was also observed in the samples that were annealed under the –30DP and +5DP process atmospheres (Figures 4.3 and 4.4), where, under the same processing conditions, a finer and more globular surface oxide structure can be clearly observed for the Sn-added substrates as opposed to the coarse and more film-like oxide layers of the reference steel. Furthermore, in terms of oxide distribution, a wider spacing between the oxides as well as less surface oxide coverage could be identified for the Sn-added samples.

As mentioned earlier, the effect of the process atmosphere oxygen potential – adjusted using the process atmosphere dew point – on the selective oxidation of the alloying elements was also studied. Comparison of the micrographs in Figures 4.2 to 4.4 show that, as a general trend, the oxide surface coverage decreased by increasing the process atmosphere dew point from 223 K (-50° C) to 278 K ($+5^{\circ}$ C), such that the maximum surface coverage was obtained for the samples annealed under the -50DP process atmosphere. Additionally, the oxides formed under the -50DP and -30DP process atmosphere were, overall, more closely spaced, forming continuous surface films, compared to those of the +5DP atmospheres which exhibited a more discrete, nodule-like morphology (Figures 4.2 and 4.3 vs 4.4). This trend was consistent for both of the experimental steels.



Figure 4.3: Secondary electron images showing the surface oxide morphology of samples annealed under the -30DP process atmospheres for 120 s, 360 s and 600 s; (a), (b) and (c) reference steel, (d), (e) and (f) Sn-added steel.



Figure 4.4: Secondary electron images showing the surface oxide morphology of samples annealed under the +5DP process atmospheres for 120 s, 360 s and 600 s; (a), (b) and (c) reference steel, (d), (e) and (f) Sn-added steel.

XPS depth profiles of Mn and Si (inset) of the experimental steels as a function of process atmosphere are given in Figure 4.5, where the dashed line and open data points represent the elemental profiles of the Sn-added steel. It should be mentioned that, for the sake of avoiding congestion in the plot, only the 120 s and 600 s data are shown; however, the results of 360 s hold were intermediate to the two. XPS binding energy data from the 120 s samples for each process atmosphere examined were used to determine the chemical state of the surface oxides. Binding energies of 530.3 eV, 641.4 eV and 654.1 eV were determined for the O1s, $Mn2p_{3/2}$ and $Mn2p_{1/2}$ peaks, respectively, which correspond to those reported for MnO by several authors. ^[38-40] It should be noted, however, that the Si signals were generally too noisy to provide reliable interpretation of the binding energy data.

It can be inferred from Figure 4.5(a) that the thickness of the external MnO for both steels increased with increasing annealing time for the –50DP samples, where the external MnO layer was significantly thicker for the reference steel for the annealing time of 600 s. These observations are qualitatively in agreement with the SEM observations of external oxide coarsening shown in Figure 4.2. However, in the case of the 120 s samples, the thicknesses of the MnO layers were comparable. Furthermore, all plots in Figure 4.5(a) converged to the bulk Mn content at approximately 200 nm with the exception of the reference steel annealed for 600 s, which returned to the bulk value at approximately 600 nm. No significant enrichment of Si was detected, aside from a slight increase observed at the outmost surface layer of the steels.



Figure 4.5: XPS depth profiles of Mn and Si (inset) of the reference and Sn-added steels annealed for 120 s and 600 s under the (a) -50DP (b) -30DP and (c) +5DP process atmospheres.

The XPS elemental profiles acquired from the –30DP samples in Figure 4.5(b) showed the same trend with increasing annealing time as was shown in the SEM observations

in Figure 4.3 – i.e. the thickness of the external oxide layer tended to increase with increasing annealing time. Furthermore, a decrease in the surface Mn enrichment relative to the reference alloy was detected in the case of the Sn-added substrates for a given annealing time, implying that the external oxide was somewhat thinner. It is also worth noting that, under the -30DP process atmosphere, the 600 s Mn profiles of both grades maintained larger values than the bulk concentration to further depths from the surface relative to the observations for the -50DP samples annealed for the same time. Also, similar to the -50DP depth profile observations, only a minimal enrichment of Si was detected at the surface.

A significant decrease in the external MnO layer thickness was observed in the XPS plots of the +5DP process atmosphere samples compared to the other process atmospheres, as can be seen in Figure 4.5(c), in agreement with the trends from the SEM analysis (Figures 4.2 to 4.4). All elemental profiles of the +5DP process atmosphere samples presented evidence of internal oxidation having taken place as values above 6 at pct were detected further away from the surface, consistent with the external to internal oxidation transition having taken place when annealing under higher pO₂ process atmospheres (Table 4.2). However, as can be seen from the inset in Figure 4.5(c) the slight enrichment of Si was, again, confined only to the surface of the samples.

Figures 4.6(a) and (b) show the variation in chemical composition of the surface oxides formed during the 120 s anneal versus the process atmosphere pO_2 . The elemental concentrations in these plots were averaged from the top 20 nm of the surface after a 5 nm sputter to remove any surface contamination, where the error bars represent the sample standard deviation. It can be seen that, for both steel chemistries, the amount of metallic iron (Fe2p peak) at the steel surface increased with increasing process atmosphere oxygen partial pressure and coincided with a decrease in the O and Mn concentrations. It is worth noting that the Mn to O ratios remained relatively constant at approximately one under all

experimental conditions, consistent with the binding energy determination that the external oxides were MnO. The amount of metallic iron was also found to be comparable between the two grades for all process atmospheres.



Figure 4.6: XPS chemical composition from the top 20 nm-thick external oxide layer of the (a) reference steel and (b) Sn-added steels annealed for 120 s as a function of process atmosphere oxygen partial pressure.

Using the FIB-derived cross-sectional images of the surface and subsurface, the effect of process atmosphere pO_2 and the alloy Sn addition on the external and internal oxide growth kinetics were determined, the results of which are plotted in Figure 4.7(a) and (b) for the surface oxide thickness and depth of the internal oxidation zone versus the square root of time, respectively. Given the significant local variation in the thickness of the oxide layers/zones, the average of a minimum of 100 measurements are reported, where the error bars represent the 95% confidence interval of the mean. It should be mentioned that the coefficient of determination (i.e. R^2 value) of all of the regressions lines was above 0.96, with the exception of the –50DP and –30DP lines for the internal oxidation of the Sn-added steel, which were 0.91. This near perfect linear fit is indicative of parabolic growth rate kinetics under all experimental conditions, which would be expected for the case of solid-state diffusion controlled oxidation. ^[41] However, the most notable result from these plots is the

decreased rate of oxide growth for the Sn-containing steels compared to the reference alloy. It can be inferred from the line slopes in Figure 4.7(a) that the growth rate of the external oxides was highest for the reference steel annealed under the -30DP atmosphere, followed by that of the Sn-containing grade. The external oxide thicknesses of the rest of the samples fell below those of the above two with the rates being comparable. The effect of Sn addition on decreasing the oxidation rate was more pronounced when examining the internal oxidation kinetics data shown in Figure 4.7(b), where a clear drop in growth rate can be identified for the Sn-added steel data. The maximum depth of internal oxidation and the maximum internal oxidation growth rate was observed for the reference steel annealed under the +5DP atmosphere, followed by the Sn-added steels annealed under this process atmosphere (2 µm vs 1.5 µm for the 600 s holds, respectively). Annealing under the -30DP and -50DP atmospheres resulted in a significant decrease of the internal oxidation rates in comparison with the +5DP process atmosphere, with the Sn-containing steels exhibiting significantly slower growth kinetics versus those of the reference alloy. The suppression of external and internal oxidation kinetics by large metallic atom additions to steels has been previously observed and reported in the work of Lyudkovsky^[19], Zhang et al.^[23] and Cho et al.^[20-22], where the operative mechanism was determined to be segregation of the high atomic number alloying elements to the surface – in the present case, Sn – occupying the surface oxygen adsorption sites, reducing the concentration of dissolved oxygen at the surface and reducing the inward oxygen flux.



Figure 4.7: Growth kinetics of (a) external oxide thickness and (b) depth of internal oxidation zone as a function of process atmosphere dew point and Sn addition.

HR-STEM analysis of the samples annealed for 600 s under the –50DP, –30DP and +5DP process atmospheres were performed on the FIB cross-sections, where the corresponding images are provided in Figures 4.8(a) to (f). The black area on top of these images is the C that was deposited prior to FIB milling to protect the external oxides from damage. It should be noted that samples taken from shorter annealing times displayed the

same morphological trends documented below, with the 600 s annealing time samples being chosen here for increased clarity. The refinement effect of the Sn addition on the oxide morphology and distribution of the external and internal oxide network is clearly observed in these images. Consistent with the SEM observations in Figures 4.2(c) and 4.3(c), it can be seen from Figures 4.8(a) and (b) that the reference alloy external oxides under the -50DP and -30DP process atmospheres formed continuous films. In contrast to this, the Sn-added samples annealed under the same experimental process atmospheres (Figures 4.8(d) and (e)) showed a significantly thinner and discontinuous surface oxide morphology. It can also be observed that the depth of the internal oxidation zone had slightly decreased in the case of the Sn-containing substrates, consistent with the observations in Figure 4.7. The external oxide morphology for both steels when annealed under the +5DP atmosphere was found to be nodule-like as opposed to film-like; however, the external oxide structures for the Sn-added alloy shown in Figure 4.8(f) showed a globular, more widely spaced morphology. Finally, it should be mentioned that the depth of internal oxidation increased when higher process atmosphere pO_2 were employed, which was expected due to the increased oxygen flux shifting the oxidation mode strongly to the internal oxidation mode, as was previously shown in Figure 4.7.



Figure 4.8: Dark field STEM images from cross-sections of (a), (b) and (c) the reference steel and (d), (e), (f) the Sn-added steel annealed for 600 s under the –50DP, –30DP and +5DP process atmospheres, respectively.

The TEM cross-sections were also analyzed by EELS to determine the chemistry of the external and internal oxides observed in the alloys. An example of such an analysis is shown in Figure 4.9(a) where Fe, O, Mn and Si elemental maps were extracted from the EELS spectra acquired from the reference steel annealed for 600 s under the –50DP process atmosphere. In accordance with the XPS findings, it can be seen from these maps that the surface oxides were largely composed of Mn and O, where no significant Si signal was detected in the surface nodules. However, a thin layer of Si enrichment was found at the

oxide/steel interface, which correlates with the subtle Si enrichments detected in the Si XPS depth profiles of Figure 4.5(a). Furthermore, the continuous internal oxides showed a varying composition, where in some areas they were significantly enriched in Si and O with no Mn enrichment and in other regions Mn, Si and O were present, suggesting a Mn-Si oxide chemistry. In order to identify the oxide species present at each region of the sample, the O-K, Mn-L_{2.3} and Si-K edges of the acquired EELS spectra were compared with those of the standards available in the literature. ^[42-48] The high-resolution EELS spectra are shown in Figure 4.9(b), where the core-loss peaks and the near-edge fine structures that speciate the oxides are marked by vertical arrows. The O-K and Mn-L_{2,3} peaks of the spectra acquired from the external oxides correlated with those of MnO^[42-45], consistent with the binding energy determination from XPS (Figures 4.5 and 4.6). In the case of the internal oxides that were Mn-rich, shown by the blue line in Figure 4.9(b), the O-K core-loss and Mn-L_{2.3} nearedge features agreed with those determined for MnSiO₃ by Grosvenor et al. ^[46], where the presence of the Si edge in the high-loss energy window confirmed that a manganese silicate was present in those regions. Finally, the internal oxides that were enriched in Si only were identified as SiO₂. ^[47,48] Similar TEM and EELS analyses were carried out for all of the samples shown in Figure 4.8 and showed the same trends as those presented above -i.e. the external oxides were consistently identified as MnO while the internal oxide networks comprised a multi-layered structure with MnSiO₃ surrounding a SiO₂ core for both the bulk internal and grain boundary oxides.



Figure 4.9: (a) Dark field STEM image and EELS elemental maps of the external and internal oxides formed in the reference steel annealed for 600 s under the -50DP atmosphere and (b) the corresponding electron energy loss spectra showing the fine structures of the O-K, Mn-L_{2,3} and Si-K edges.

Given the extremely low bulk concentration of Sn (i.e. 0.05 wt pct or 0.02 at pct) and as no evidence of Sn segregation could be found with either XPS or EELS, a 3D APT analysis of the steel/external oxide interface was conducted on a sample taken from a Snadded $-30DP \times 600$ s sample in order to locate and quantify any Sn segregation at the atomic scale. The results of this analysis are presented in Figure 4.10, where the Fe, Mn and Si atom map of the reconstructed volume across the MnO/steel interface shown in Figure 4.10(a). The color composition map taken from a 5 nm thick slice of the reconstructed tip is shown in Figure 4.10(b). It should be pointed that the Sn signal was too weak to be properly visualized in this map; however, in accordance with the TEM+EELS observations (Figure 4.9(a)), the Si-rich layer underneath the surface MnO oxide was observed at the interface. Elemental concentration profiles across the steel/oxide interface are shown in Figure 4.10(c), with the Sn profile magnified in a separate plot underneath. From this, it can be inferred that Sn was segregated to the steel/oxide interface with an enrichment level approximately ten times the bulk concentration – i.e. 0.02 at pct. It should be mentioned that, aside from the Si and Sn enrichments at this interface, the profile also shows a layer rich in Fe and O which is at odds with the previous analysis and is also unexpected given the fact that all process atmospheres in the present study were fully reducing with respect to Fe. This effect is a known artifact of APT analysis, in which O is preferentially retained when the analysis direction runs from an oxide into a metal, rather than a real feature of the specimen. ^[49] Additionally, the Mn to O ratio of the surface oxide was found to be higher than that of MnO which can to some extent be attributed to oxygen loss during field evaporation.







Figure 4.10: APT analysis of the surface oxide/metal interface of the Sn-added steel annealed for 600 s under the –30DP atmosphere (a) 3D atom map of Fe, Mn, Si and 15 at pct Mn isosurface, (b) 5 nm thick 2D section of the reconstructed needle showing the enrichment of alloying elements in the surface oxide and (c) proximity histogram (proxigram) revealing the 1D concentration profiles normal to the isosurface marked with an arrow in (a).

4.4 Discussion

It was consistently determined through several analytical microscopy techniques that significant changes to the oxide morphology, distribution and thickness resulted from adding 0.05 wt pct Sn to the steel (Figures 4.2-4.8). The external MnO oxides formed on the surface of the Sn-containing steels exhibited a more widely-spaced distribution of fine, globular nodules (Figures 4.2-4.4 (d) to (f)) versus their non-Sn added counterparts , which displayed a significantly more compact, coarser external oxide morphology (Figures 4.2-4.4 (a) to (c)). This change in external oxide morphology was also accompanied by slower external oxidation kinetics (Figure 4.7(a)) resulting in thinner external MnO layers on the Sn-added alloys compared to those of the reference steels (Figure 4.5(a)). Strong oxide refinement and slower oxidation kinetics were similarly observed in the case of the internal oxidation, as pictured in Figures 4.7(b) and 4.8, where the internal oxidation rates were uniformly lower for the Sn grade versus the reference steel for all process atmospheres.

On the other hand, the external oxide chemistry was not found to be affected by the 0.05 wt pct Sn addition. As can be seen from the plots in Figure 4.6, an approximate 1:1 ratio of Mn to O for the external oxides was maintained for all experimental conditions, which, in combination with the XPS binding energy data and the EELS analysis (Figure 4.9) determined the external oxides to be MnO for both steel compositions. Similarly, EELS analysis (Figure 4.9) showed that the internal oxides comprised a layered structure with the oxide cores and the surrounding shells being identified as SiO₂ and MnSiO₃, respectively.

The formation mechanism of the observed oxide species, which all form thermodynamically stable oxides under the process atmospheres of this study, can be explained by the kinetic and thermodynamic factors in play. SiO₂ was first formed at the grain boundaries of the subsurface, owing to its higher thermodynamic stability ^[50,51], nearly zero solubility product ^[52] compared to that of MnO, and the higher diffusivity of Si relative

to Mn. ^[53] Due to the slower diffusion of Mn to the reaction sites and its higher thermodynamic stability and lower solubility versus MnO ^[52], MnSiO₃ was formed at the surroundings of the grain boundary SiO₂, i.e. the oxide shells (Figure 4.9). The presence of the thin external MnSiO₃ layer (Figure 4.9) can also be described by the same reaction sequence. At the surface, under a continuous supply of oxygen from the process atmosphere and the lack of competition among Si and Mn for the dissolved oxygen consumption, the higher solubility MnO formed stable oxides as a locally high Mn to Si ratio was also present. The presence of MnO as the surface oxide species has been reported in several previous works ^[50,54,55] and more recently in the case of the medium-Mn 3G steels, by Pourmajidian and McDermid. ^[56,57]

The selective oxidation of Mn and Si was also affected by the process atmosphere oxygen partial pressure. The external MnO oxides observed on the surface of the reference steel annealed under the -50DP and -30DP process atmospheres (Figures 4.2 and 4.3 (a) to (c)) comprised a patchy and film-like morphology with large fractions of the substrate surface being covered by these structures. It should be noted that, in the case of the Sn-added substrates, a finer globular morphology with thin films between the nodules was observed in Figures 4.2 and 4.3 (d) to (f), despite the external oxidation mode being dominant, particularly under the -50DP atmosphere. Furthermore, the accelerated external oxidation kinetics observed under the -30DP process atmospheres (Figure 4.7(a)) can be explained by the larger oxygen potential of this process atmosphere (Table 4.2) compared to the -50DPatmosphere, and by the fact that the -30DP process atmosphere pO₂ is close to the externalinternal transition pH₂O/pH₂ at the IAT of 963 K per Wagner model calculations. Annealing under the +5DP atmosphere resulted in a significantly thinner external MnO layer (Figures 4.4, 5(c) and 4.7). However, the higher pO₂ of this atmosphere (Table 4.2) led to a stronger internal oxidation mode, as characterized by the increased depth of the internal oxidation

zone under the +5DP process atmosphere, per the kinetic data in Figure 4.7(b) and the cross-sectional TEM images in Figure 4.8. This shift in the oxidation mode also resulted in significantly more metallic Fe being available within 20 nm of the surface (Figure 4.6), which further implies the presence of very thin MnO nodules in these structures. Both of these factors would very likely have significant benefits in the subsequent reactive wetting process within the continuous galvanizing bath.

Given the above relatively uniform results on the effect of the Sn addition on the oxidation kinetics, it can be concluded that the interfacial Sn segregation layer – as detected by 3D APT (Figure 4.10) – was responsible for reducing the observed oxidation rates and for modifying the distribution and morphology of both the external and internal oxides. Previous authors have stated that, as a result of interfacial segregation of the surface active elements in TRIP steels, the interfacial energies can change such that formation of surface oxides with lens-type morphology is encouraged as opposed to film-type growth. ^[21,22] The effect of surface active elements such as Sb, Sn and Bi on the retardation of internal oxidation kinetics has also been previously reported. ^[19-25] The large atomic size mismatch between such elements and Fe acts as a driving force for segregation of these elements to the free surfaces or interfaces in order to reduce the elastic strain energy of the bulk lattice. ^[25,26] For example, Lyudkovsky^[19] reported that the addition of 0.08 wt pct Sb to Si-Al electrical steels significantly reduced the rate of internal oxidation in a high $pO_2 N_2$ -H₂ gas mixture due to the segregation of Sb to the grain boundaries reducing the inward diffusion of oxygen by blocking the short-circuit diffusion paths. This effect of Sb on suppressing the depth of internal oxidation was also reported ^[23,24] in the case of IF and TRIP steel substrates and was explained by showing that enrichment of Sb to the surface occupied the surface O adsorption sites, thereby decreasing the oxygen permeability of the surface.

More recently, the effects of Sn additions within the range of 0.05 wt pct to 1 wt pct ^[21] and Bi additions of 0.05 wt pct to 0.2 wt pct ^[22] on the selective oxidation of 0.1C-1.6Mn-1.5Si TRIP substrates were investigated. It was reported that the addition of 0.05 wt pct Sn affected both the external and internal oxidations such that a decrease in the depth of internal oxidation and a change in morphology of the Si-rich surface oxides were observed, while no change in the Mn-rich oxides was detected. Furthermore, it was found that the chemistry of the surface oxides was also altered due to the reduced oxygen solubility at the surface such that the Mn to Si ratio of the oxides decreased with increasing Sn contents. ^[21]

In the present work however, the 0.05 wt pct addition of Sn to the medium-Mn 3G AHSS system did not change the surface oxide chemistry and MnO was found to be the only oxide species present at the surface of all samples. This is due to the fact that, unlike the above-mentioned study ^[21], the Sn addition was kept to a minimum and, furthermore, the significantly higher Mn to Si ratio in the present alloy promoted MnO formation rather than Mn-Si oxides. ^[50,54-57] It was also previously reported that only the morphology of Si-rich manganese silicates were affected as a result of Sn-addition, with the exception of the case of excessive Sn addition (1 wt pct), where the granular morphology of the MnO oxides were changed to a lens-type. ^[21] Nevertheless, significant morphological changes of the nodular surface MnO as well as suppression of the oxidation kinetics took place in the present 0.1C-6Mn-2Si steel as a result of the present 0.05 wt pct Sn addition.

It has been shown by several authors ^[9-12,35,58,59] that successful reactive wetting by the continuous galvanizing Zn(Al,Fe) bath is attainable despite external selective oxidation if the oxide morphology exhibits a widely-spaced, nodular morphology with relatively thin oxide films between the nodules or an overall thin external oxide. While it is well known that film-forming Si-rich surface oxides are detrimental with respect to reactive wetting and integral
Fe-Al interfacial layer formation, it should also be noted that previous studies ^[32,34,58] have shown that, even in the case of surfaces covered exclusively with MnO, successful reactive wetting can be obtained only when the surface MnO is thin enough for the aluminothermic reduction to take place during industrially relevant immersion times in a 0.20 wt pct Al (dissolved) galvanizing bath, i.e. surface film thicknesses under 85 nm. ^[34]

Significant improvement in the galvanized coating quality of a 0.1C-1.5Si-1.6 Mn TRIP steel was obtained as a result of a 0.05 wt pct Sn-addition and the consequent morphological change of the Si-rich surface oxides. ^[20,21] For the alloy system and the process atmospheres of the present study, it was found that MnO was the dominant external oxide phase while Si was enriched at the surface oxide/steel interface and, more predominantly, in the subsurface. A variety of surface oxide morphologies, thicknesses and distributions were observed under each combination of the different experimental alloy and process atmosphere pO₂. It was found that the most desirable external oxide morphology with respect to promoting reactive wetting was formed under the combined use of the 0.05 wt pct Sn addition and high process atmosphere oxygen partial pressures. It is, therefore, expected that the Sn-containing substrates, particularly those annealed under the -30DP and +5DPprocess atmospheres, to exhibit significantly improved reactive wetting by the continuous galvanizing bath due to the observed widely-spaced distribution of significantly thinner and finer globular surface MnO compared to those of the reference steel, as these type of surface oxide structures can promote Fe dissolution into the Zn(Al,Fe) galvanizing bath and the formation of the desirable Fe₂Al₅Zn_x interfacial layer during continuous galvanizing processing.

4.5 Conclusions

The selective oxidation of a 0.1C-6Mn-2Si medium-Mn steel as functions of process atmosphere oxygen partial pressure, annealing time and a 0.05 wt pct Sn addition was investigated using CGL-compatible intercritical annealing heat treatments.

Adding 0.05 wt pct Sn to the steel chemistry modified the morphology and distribution of the external MnO oxides from a continuous film-like layer to a finer and discrete globular morphology under all experimental process atmospheres. The bulk internal oxidation region and grain boundary oxide networks formed in the Sn-containing steel were also significantly refined compared to those observed for the reference alloy. A decrease in external MnO thickness, accompanied with an increase in the amount of metallic iron available, was found with increasing process atmosphere oxygen partial pressure, where smaller area fractions of the steel surface were covered by thick MnO oxides.

External and internal oxidation kinetic rate data determined that both external and internal oxidation were suppressed as a result of the Sn addition by reducing the oxygen solubility at the surface. The thickest external oxide layer was observed in the reference steels annealed under the 243 K (-30° C) dew point atmosphere and the thinnest surface layer belonged to that of the Sn-added grade annealed under 278 K ($+5^{\circ}$ C) dew point. In contrast, the maximum depth of internal oxidation was observed for the samples annealed under the 278 K ($+5^{\circ}$ C) dew point process atmosphere.

Significant segregation of Sn at the oxide/metal interface was detected by 3D atom probe tomography, which was approximately ten times that of the bulk concentration. This segregation was likely responsible for the observed refinement of the external/internal oxides and the retardation effects on the oxidation reaction kinetics.

The reactive wetting of the present medium-Mn 3G model alloy by the continuous galvanizing zinc bath is expected to be significantly improved, given the positive

morphological changes of the external MnO resultant of alloying the steel with a trace amount of Sn.

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CHAPTER 5 EFFECT OF ANNEALING TEMPERATURE ON THE SELECTIVE OXIDATION AND REACTIVE WETTING OF A 0.1C-6MN-2SI ADVANCED HIGH STRENGTH STEEL DURING CONTINUOUS GALAVANIZING HEAT TREATMENETS

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Synopsis

The effects of peak annealing temperature and annealing time on the selective oxidation and reactive wetting of a prototype medium-Mn Fe-0.1C-6Mn-2Si third generation advanced high strength steel were investigated. Annealing heat treatments were carried out in a N₂-5 vol% H₂ 243 K (-30° C) dew point process atmosphere at 963 K (690°C) and 1073 K (800°C) for 120 s and 600 s. TEM observations of the sample cross-sections revealed internal oxidation of the subsurface grains and grain boundaries. EELS results showed that the internal oxide network had a multi-layered structure with SiO₂ at the oxide core and MnSiO₃ as the surrounding shell; however, MnO was the only species detected at the surface of all samples. The effect of annealing temperature on the surface structure development and its impact on reactive wetting of the substrates annealed for 120 s at both peak annealing temperatures by a Zn-0.20 wt% Al (dissolved) galvanizing bath was also determined. In contrast to the 1073 K steel, the 963 K substrate showed superior reactive wetting, owing to the much thinner, finer and wider spacing of the MnO nodules on the pre-immersion surface.

TEM+EELS analysis of the coated steels showed that infiltration of the bath alloy and partial reduction of MnO resulted in lift-off of the surface oxides and partial formation of $Fe_2Al_5Zn_X$ interfacial layer, indicating that reactive wetting had occurred for the 963 K × 120 s substrate.

Keywords: 3G AHSS; Selective Oxidation; Dew Point Controlled Annealing; Continuous Galvanizing.

5.1 Introduction

Medium-Mn advanced high strength steels are amongst the most promising candidates being investigated for future vehicle Body In White (BIW) applications in the automotive industry due to their superior combination of high specific strength and ductility versus the first generation advanced high strength steels (AHSS)¹⁻⁴⁾. Adoption of these materials has the potential to allow manufacturers to move towards safe, lighter vehicle designs in line with legislated fuel efficiency guidelines^{1,5)}. The corrosion protection of these steels is essential for ensuring the long-term structural integrity of the vehicle and to meet consumer durability expectations, for which the preferred production route is the continuous hot-dip galvanizing process.

However, selective oxidation of the main alloying elements envisaged for use in these steels, namely Mn and Si, can cause problems with reactive wetting by the continuous galvanizing zinc alloy bath ⁶⁻⁹. The presence of these thermodynamically stable oxides can prevent the substrate from being reactively wetted by the molten zinc alloy, thus preventing the formation of the desired Fe₂Al₅Zn_X interfacial layer during dipping, known to be essential for achieving a high quality, adherent zinc alloy coating.

It has been reported in several studies that reactive wetting can take place in the galvanizing bath despite the presence of Mn and Si containing oxides on the steel surface ¹⁰⁻

¹⁶⁾. The formation of the desired $Fe_2Al_5Zn_X$ interfacial layer and complete reactive wetting in these studies has been explained by differences in surface oxide chemistry, thickness and morphology. Furthermore, it has been established that MnO can decompose during immersion in the zinc bath through in-situ aluminothermic reduction ^{6,15,17)}. In other cases, reactive wetting of surfaces comprising widely spaced oxide nodules has been reported ^{13,14,18)}. It has also been reported that infiltration and lift-off of the oxides by the bath alloy through cracks at the oxide/substrate interface can aid in the reactive wetting process ^{13,14,19}

Thus, the objective of the present study is to quantify the effects of surface oxide morphology, distribution and chemistry on the reactive wetting of a prototype Fe-0.1C-6Mn-2Si prototype third generation advanced high strength steel (3G-AHSS) during continuous austenitic and intercritical annealing followed by hot-dip galvanizing.

5.2 Experimental Procedures

The chemical composition of the medium-Mn steel is given in Table 5.1. All substrates were received in the cold rolled condition with a thickness of 1.2 mm. All experiments were carried out in the McMaster Galvanizing Simulator (MGS, Iwatani-Surtec), full details of which are provided elsewhere 20 . Two types of samples were cut from the as-received substrates. Selective oxidation samples comprised of 10 mm × 50 mm coupons such that the rolling direction was parallel to the longitudinal axis of the sample. In the case of the selective oxidation samples only, the sample surfaces were polished with 4000 grit SiC paper prior to annealing in order to minimize the effects of surface roughness on the subsequent surface analyses. Reactive wetting samples comprised of 120 mm × 200 mm panels with the longitudinal axis perpendicular to the rolling direction. Prior to dipping, these larger panels were degreased in a 353 K (80°C) 2 vol% NaOH solution, rinsed in an stagnant DI water bath followed by a second rinsing step with running DI water, cleaned with isopropanol in an

ultrasonic bath and were finally dried with warm air. All samples were cleaned with acetone wipes immediately prior to being loaded in the MGS.

Table 5.1: Chemical composition of the experimental steel (wt%)								
С	Mn	Si	Al	Mo	Ti	Ν	S	
0.106	6.241	2.023	0.040	0.072	0.011	0.003	0.003	

.

Austenitic and intercritical annealing heat treatments were carried out at 1073 K (800°C) and 963 K (690°C), respectively, in a 243 K (-30°C) dew point N₂-5vol%H₂ process atmosphere. It should be noted that the 963 K intercritical annealing temperature was chosen to yield equal fractions of intercritical austenite and ferrite. A summary of the corresponding values of process atmosphere oxygen partial pressure (pO_2) at each peak annealing temperature (PAT) along with the pH_2O/pH_2 ratio are provided in Table 5.2. All of the values listed in Table 5.2 were derived from the thermodynamic database of Fine and Geiger²¹⁾.

Table 5.2: Experimental process atmosphere specifications as a function of peak annealing temperature (PAT)

1 ()			
PAT	Dew Point	pH ₂ O/pH ₂	pO ₂ at PAT (atm)
1073 K (800°C)	243 K (-30°C)	0.00820	4.60×10 ⁻²³
963 K (690°C)	243 K (-30°C)	0.00820	8.05×10 ⁻²⁶

A schematic of the thermal cycle used for the selective oxidation and reactive wetting tests is shown in Figure 5.1. The thermal cycle for the selective oxidation tests comprised heating at 15 K/s to 773 K (500°C), heating at 5 K/s to the PAT, followed by an isothermal hold at the PAT for 120 s and 600 s followed by cooling to 343 K (70°C) at a rate of -10 K/s using N₂ gas quenching. The reactive wetting of the steel substrates by the zinc bath was also explored, where the 120 mm \times 200 mm steel panels heat treated at the PAT for 120 s were cooled to the zinc bath temperature of 733 K (460°C) at -10 K/s, held at 733 K for 10 s to

achieve thermal homogeneity through the substrate thickness, followed by a 4 s immersion in the galvanizing bath and a final cool to 343 K at -10 K/s via N₂ gas quenching. The simulated galvanizing bath comprised a 50 kg melt containing 0.20wt% dissolved Al and was Fe saturated ²²⁾. In all cases, the sample thermal cycle was controlled via a 0.5 mm type K thermocouple welded directly to the samples. All selective oxidation tests were carried out in triplicate to ensure repeatability of the experimental results, whereas the reactive wetting experiments were run in duplicate due to limited availability of the experimental substrates. Selective oxidation samples were stored in 99.9% purity anhydrous grade isopropanol immediately after removal from the MGS in order to minimize additional oxidation prior to analysis. The galvanized panels were wrapped and stored separately such that the zinc surface was protected from scratches. All material for reactive wetting analysis were cut from the 80 mm × 80 mm uniform temperature and coating area centered 50 mm from the bottom edge of the panel.



Figure 5.1: Schematic of selective oxidation (dotted line) and hot-dip galvanizing (solid line) heat treatments.

Surface oxide distribution and morphology was studied using a JEOL 7000F field emission gun scanning electron microscope (FEG-SEM) operated in secondary electron imaging mode with an acceleration voltage of 5 keV. SEM analysis was also performed on the galvanized samples to study the interfacial reaction products. The interfacial layer was exposed by stripping the zinc overlay by two methods: (i) fuming nitric acid (HNO₃) and (ii) 10vol% H₂SO₄ in water. The latter technique left both the Fe-Zn and Fe-Al intermetallics intact whereas stripping with HNO₃ dissolved everything except the Fe₂Al₅Zn_X layer. The surfaces of all SEM samples were coated with C to avoid charging of the specimen during SEM analysis.

X-ray photoelectron spectroscopy (XPS) of the selective oxidation samples prior to galvanizing was performed using a PHI Quantera SXM (Scanning XPS Microprobe) using an Al K α X-ray source (1486.7 eV). The spot size was 100 μ m, the take-off angle was 45°, the pass energy was 140 eV and step size 0.25 eV for all analyses. Elemental depth profiles of the steel surface were obtained by Ar ion sputtering a 2 mm × 2 mm area. All data processing was performed using MultiPak 6.0 software. The obtained binding energies are accurate to ± 0.1 eV and all spectra were calibrated using the metallic iron binding energy of 706.62 eV. Depth measurements are considered to be accurate within $\pm 10\%$ of the sputtered depth.

Due to the relatively low spatial resolution across the sample surfaces available from XPS, direct measurement of the thickness of any external or internal oxide layers as a function of annealing time and PAT was performed using two 10 µm wide trench cuts made through Focussed Ion Beam (FIB) milling using a NVision 40 by Zeiss. W and C coatings were deposited prior to FIB milling in order to protect the surface oxides from damage during Ga-ion milling. It should be noted that the thickness measurements were taken using a grid system at a minimum of 100 locations over the overall 20 µm trench length to ensure representative sampling and increase confidence in the average values of the oxidation zone

thicknesses obtained. In the below text, mean oxide thicknesses are reported along with the 95% confidence interval of the mean.

High resolution scanning transmission electron microscopy (HR-STEM) on cross-sections of the selective oxidation samples as a function of PAT and annealing time was performed using a FEI Titan 80-300HB TEM operated at 300 keV, where FIB milling was used to prepare the TEM cross-sections. W and C coatings were deposited prior to FIB milling in order to protect the surface oxides from damage during milling. In order to study any wetting reactions at the steel/coating interface and any morphological changes thereon, TEM lift-outs were also taken from as-coated sample cross-sections using FIB milling. Quantitative electron energy loss spectroscopy (EELS) chemical analysis was used during HR-STEM examination of the selective oxidation and galvanized samples using a Gatan Quantum GIF where Digital Micrograph 2.3 software was used to extract elemental maps from the EELS data cubes.

5.3 Results

Secondary electron images obtained from sample surfaces annealed for 120 s and 600 s at the 963 K and 1073 K PAT are shown in Figure 5.2. Coarsening of the surface oxides as a result of extended annealing can clearly be seen from these micrographs (i.e. Figure 5.2(a) vs (b) and Figure 5.2(c) vs (d)). This effect was more pronounced for the samples annealed at the 1073 K PAT due to the faster diffusion rates of both oxygen and the alloying elements at the elevated temperature (Figures 5.2(c) and (d)). It is worth noting that, after annealing at 1073 K, the surface of the steel was almost fully covered with a thick, compact external oxide layer for the shorter 120 s hold. In contrast, samples annealed at 963 K for 120 s displayed significant area fractions where thin or no apparent surface oxides could be observed (Figure 5.2(a) vs (c)). Furthermore, the oxides present after the 963 K treatments had a dispersed

nodular morphology in contrast to the compact nodular films formed during the 1073 K austenitic anneal. The former surface structure is known to be more amenable to reactive wetting $^{8,18,19)}$, whereas the latter has been shown previously to be detrimental to the promotion of reactive wetting $^{6,7)}$.



Figure 5.2: Secondary electron images from the surface of the samples annealed under the 243K dew point atmosphere at (a) and (b) 963 K, (c) and (d) 1073 K peak annealing temperatures.

Mn and Si XPS elemental depth profiles of the oxidized samples are presented in Figures 5.3(a) and (b), respectively, as a function of PAT and annealing time. Figure 5.3(a) shows a considerable surface enrichment of Mn during the annealing heat treatments prior to galvanizing, while only a very thin Si-enriched layer was detected at the surface (Figure 5.3(b)). As can be seen from Figure 5.3(a), the thickness of the 1073 K \times 600 s Mn-rich surface oxide was significantly greater than the other three experimental conditions, in accordance with the SEM observations of Figure 5.2 and the expected time-temperature trends. The effect of peak annealing temperature on the Mn depth profiles for the 120 s annealing time samples does not seem to have been significant based on the XPS results. However, it can be seen that the 600 s annealing time resulted in a thicker surface Mn oxide for both annealing temperatures. Furthermore, significant Mn enrichment in the subsurface of the 600 s samples at both PATs can be identified from the depth profiles, characterised by Mn contents being greater than the bulk concentration (Figure 5.3(a)) to extended depths into the sample. Binding energies were also measured from 5 nm below the steel surface for the O1s, $Mn2p_{3/2}$ and $Mn2p_{1/2}$ peaks and these correlated with those reported in the literature for MnO, with values of 530.3 eV, 641.4 eV and 654.1 eV, respectively ^{23,24)}. It should be pointed out that the very low signal-to-noise ratio of Si2p peaks did not allow for accurate measurement of the binding energies.



Figure 5.3: XPS depth profiles of (a) Mn and (b) Si as a function of PAT and annealing time.

Cross-sectional secondary electron FIB (SE-FIB) images of the samples annealed for 120 s at 963 K and 1073 K are shown in Figures 5.4(a) and (b), respectively, to detail the thicknesses and morphology of the oxidation zones present in the as-annealed samples prior to immersion in the simulated galvanizing bath. From Figure 5.4, it can be seen that both external and internal oxidation zones were present, where zone I is the bulk internal oxidation zone, zone II is the grain boundary internal oxidation zone and the external oxidation zone is demarcated using the annotated arrows. It is apparent from Figure 5.4 that the external oxide layer formed for the 1073 K \times 120 s sample was significantly thicker than that formed at 963 K. Using the measurement technique specified above, it was determined that the average external MnO thickness was 44 ± 2 nm and 121 ± 8 nm for the 963 K \times 120 s and 1073 K \times 120 s samples, respectively. In the case of the samples annealed for 600 s, it was determined that the external MnO thickness was 105±3 nm for the 963 K PAT and 296±11 nm for the 1073 K PAT samples. The internal oxide network observed for the 1073 K \times 120 s sample penetrated significantly deeper below the surface in comparison with that of the 963 K \times 120 s sample, reaching a depth of 2 μ m for the 1073 K sample versus approximately 0.4 μ m for the 963 K sample. As stated above, the internal oxidation network was demarcated into two zones based on the morphology of the oxides observed. Zone I comprised fine, spherical oxides formed immediately in the subsurface both in the bulk grains and on their grain boundaries, while, beneath this region, zone II was associated with a continuous grain boundary oxide network. It should be noted that this difference in external oxide thicknesses for the 120 s samples was not readily apparent from the XPS analysis in Figure 5.3(a), given the much lower surface spatial resolution of this technique (i.e. 100 µm spot size in the XPS versus 0.8 nm in the FIB) and also the fact that the presence of internal oxides, as confirmed by Figure 5.4, affected the width of the XPS profiles and, therefore, did not allow for an accurate estimation of the external oxide layer thickness.



Figure 5.4: SE-FIB images from the cross-sections of the samples annealed for 120 s at (a) 963 K and (b) 1073 K revealing the surface oxide configuration and the internal oxide networks.

Electron energy loss spectroscopy (EELS) was used in combination with TEM to identify the fine scale microstructure and chemistry of the external and internal oxides present in the as-annealed samples. This data is presented in Figure 5.5 through 5.7 and are representative of all of the annealing conditions studied. Figure 5.5 shows the Fe, O, Mn and Si EELS elemental maps acquired from an area representative of the external oxide layer along with the zone I internal oxides from the 963 K \times 120 s sample. The elemental maps revealed that the surface oxide layer was composed largely of Mn and O, where no significant Si signal was detected. However, the internal oxides showed significant Mn and Si enrichments. This analysis was true for both of the fine circular oxides and the grain boundary oxides. It should be pointed out that the nodular morphology of the external oxides can be clearly identified from the STEM image in this figure.



Figure 5.5: DF-STEM image along with EELS elemental maps of Fe, O, Mn and Si, showing the external and zone I internal oxides from the 963 K for 120 s sample.

Similarly, EELS elemental maps were acquired from the grain boundary oxide network that was formed in zone II of the samples, per Figure 5.4. Figure 5.6 shows a grain boundary oxide combined with a nearby bulk oxide formed in zone II of a 1073 K \times 600 s sample. The STEM image shows areas with varying contrast within the oxide. From the elemental maps, it can be seen that both the grain boundary and bulk oxides comprised a multi-layer configuration, where Si was enriched at the oxide core while both Mn and Si were present in the outer shell, surrounding the Si-rich core.



Figure 5.6: DF-STEM image along with EELS elemental maps of Fe, O, Mn and Si, showing the cored structure of a grain boundary oxide formed in the sample annealed at 1073 K for 600 s.

To quantitatively determine the chemistry of the oxide species present in all of the zones demarcated in Figure 5.4, the O, Si and Mn edges of the high-resolution EELS spectra were analysed. Figure 5.7 presents the O-K, Mn-L_{2,3} and Si-K edge EELS spectra acquired from the external and internal oxides observed in the 1073 K \times 600 s sample. A comparison of the fine structures observed in the EELS spectra with those available from the literature allowed for an accurate identification of the oxide compositions ²⁵⁻²⁷⁾. From these spectra, the external oxide was identified as MnO, the outer shell of the grain boundary and bulk internal

oxides as $MnSiO_3$ and the oxide cores as SiO_2 . These findings were consistent for all annealing conditions explored. It should be noted that the EELS spectrum for the external oxide layer correlated well with the XPS binding energy results, confirming that MnO was the external oxide species for all samples.



Figure 5.7: O-K, Mn-L_{2,3} and Si-K edges EELS spectra acquired from the external and internal oxides from the 1073 K \times 600 s samples.

Figures 5.8(a) and (b) show macroscopic views of the uniform temperature and coating area of the as-galvanized steel surfaces for the samples annealed at 963 K and 1073 K, respectively, under the N₂-5H₂ (vol%) 243 K dew point process atmosphere. Significant differences were observed in the degree of reactive wetting as a function of the PAT. As can be seen in Figure 5.8(a), despite the presence of some minor coating defects, the 963 K × 120 s substrate surface was completely coated with the zinc alloy, while, in contrast to this, no evidence of reactive wetting was observed for the 1073 K × 120 s steel (Figure 5.8(b)). Since no integral Zn coating was obtained for the 1073 K × 120 s samples, the as-dipped surface was observed under SEM in order to determine the fine-scale surface morphology of this sample post-immersion. In the case of the 963 K × 120 s sample, however, the zinc overlay was stripped using two acid solutions: 10vol% H₂SO₄ (in water) and fuming HNO₃. No evidence of Fe-Zn intermetallics were observed at the interface after

removal of the zinc overlay with the sulfuric acid solution. However, removal of the Zn overlay of the 963 K \times 120 s sample using fuming nitric acid revealed the presence of reactive wetting products at the Fe-Zn interface, as shown in Figure 5.8(c). In contrast, as can be seen in Figure 5.8(d), a significant amount of oxides were present on the surface of the 1073 K \times 120 s steel after immersion along with some isolated solidified metallic nodules. However, it should be noted that this surface oxide layer was significantly different from that observed prior to immersion, as shown in Figure 5.2(c), indicating that some interaction between the external oxide and zinc alloy bath had occurred.



Figure 5.8: Photographs from the surface of the panels immersed for 4 s in a 0.20wt%Al (dissolved) zinc bath at 733 K after annealing under a N₂-5H₂ 243 K dew point atmosphere at (a) 963 K × 120 s and (b) 1073 K × 120 s; secondary electron images of the Fe-Zn interface of the (c) 963 K × 120 s sample stripped with fuming HNO₃.and (d) as-dipped 1073 K × 120 s sample.

Given the fine scale of the features present at the Fe-Zn interface of the postimmersion 963 K \times 120 s and 1073 K \times 120 s samples pictured in Figures 5.8(c) and (d) and in order to determine the underlying mechanisms responsible for the observed differences in reactive wetting behavior of the two substrates, TEM cross-sections were made across the coating/steel interface of the samples by FIB milling. The results of this analysis are shown in Figures 5.9 and 5.10. Figure 5.9 shows the SE-FIB image of the coating/steel interface of the 963 K \times 120 s steel along with the corresponding TEM+EELS elemental maps. Although no significant change in thickness of the pre-immersion and post-immersion external oxides was found; the post-immersion surface oxide film exhibited a broken-up appearance at some sites. It is interesting to further note that, aside from the surface and subsurface oxides, the interface of the galvanized steel exhibited some nodule-like features, marked by arrows in Figure 5.9(a), which did not exist at the oxide/metal interface of this sample prior to immersion (Figures 5.4(a) and 5.5). It also appears that these nodules separated the original external oxide/steel interface such that the surface oxides are at the outer side of them.



Figure 5.9: (a) SE-FIB image, (b) DF-STEM image and (c) color overlay EELS map of a nodule-like reaction site formed at the coating/steel interface of the 963 K \times 120 s galvanized steel showing different reaction products formed after 4 s immersion in a 0.20wt%Al dissolved zinc bath at 733 K.

Figures 5.9(b) and (c) show a higher magnification image of an interfacial nodule along with the corresponding elemental EELS overlays; the colours assigned to each element in the map can be seen in the legend to the right. Quantitative spot analyses were conducted at several points in this fine-scale cross-section and are labeled A through E in Figure 5.9(c), where the results of these analyses are documented in Table 5.3. It was found that the nodules pictured in Figure 5.9(a), in fact, correspond to reaction sites with a relatively complex morphology arising from the infiltration of the zinc alloy through the surface oxides and into the underlying steel substrate, which explains the delaminated appearance of the original oxide/steel interface pictured in Figure 5.9(a). It is also noteworthy that while Mn and O were present in the oxides within both the bulk steel and those embedded in the infiltrated reaction sites, the surface scale was detected to be an oxygen depleted MnO as the colour overlay map of these areas appeared yellow rather than orange. This finding is further confirmed by the chemical analysis of point A (Figure 5.9(c)) in Table 5.3. It was also observed that in the vicinity of these areas, a strong Al signal was observed, corresponding to the Fe-Al interfacial layer (point B, Table 5.3). Table 5.3 lists the chemical compositions that were extracted from the labeled features of Figure 5.9(c), which shows that the oxides in point C were likely Mn-silicates and that points D and E correspond to an Fe and Al-enriched Zn alloy. In this case, the higher Fe and Al contents of this phase likely stem from background signals from surrounding Fe-Al intermetallics and the substrate itself.

The results of TEM+EELS analysis of the 1073 K \times 120 s sample are presented in Figure 5.10. The cross-sectional SE-FIB image in Figure 5.10(a) captures an uncoated area with a solidified zinc droplet on the surface of the sample. The high magnification STEM image and EELS overlay map shown in Figures 5.10(b) and (c) were acquired from the edge of the droplet in Figure 5.10(a). It can be seen that underneath the zinc droplet, a relatively thick, continuous external Mn oxide layer remained at this interface as these oxides appear

orange rather than yellow, as would be the case for reduced Mn-oxides. Furthermore, inspection of the EELS spectra of these oxides determined that they were comprised of MnO. A detailed discussion of these findings is provided in the following section.

Table 5.3: Quantitative EELS analysis results corresponding to points A to E in Figure 5.9(c) (at%)

Point	Zn	Al	Mn	0	Fe	Si	Phase Present
А	1.6	12.9	42.9	25.1	17.5	_	(Mn,Fe) sub-oxide
В	10.1	61.2	2.3	0.0	26.4	_	Fe ₂ Al ₅ Zn
С	1.8	10.3	17.6	43.7	1.8	24.8	Mn-Si oxide
D	81.6	5.9	1.6	0.0	10.9	_	Zn alloy
Е	62.3	9.3	5.2	0.0	22.3	0.9	Zn alloy



Figure 5.10: (a) SE-FIB image, (b) DF-STEM image and (c) color overlay EELS map of the 1073 K \times 120 s steel after 4 s immersion in a 0.20wt%Al dissolved zinc bath at 733 K showing a zinc droplet and the post-immersion surface oxides at the interface.

5.4 Discussion

As shown in the SEM images from the as-annealed steel surfaces (Figure 5.2), significant external oxide coverage was observed for all combinations of annealing temperature and time, where the oxides coarsened with increasing holding time at both annealing temperatures. The measured XPS binding energies corresponded with those of MnO ^{23,24)}. This analysis was in agreement with the EELS spectra (Figure 5.7) of the surface oxides, allowing for the conclusion that the external oxide species was MnO for all annealing conditions explored. From the SEM images, it can also be seen that the 600 s annealing time samples (Figures 5.2(b) and (d)) had almost complete external MnO coverage. However, further examination of Figure 5.2 will show that the 963 K × 120 s surface (Figure 5.2(b)) comprised a more widely spaced, nodular morphology with thinner oxides in between versus its 1073 K × 120 s counterpart. Furthermore, it can also be observed that the 963 K oxides (Figures 5.2(a) and (b)) were significantly finer than their 1073 K PAT equivalents.

Cross-sectional SE-FIB images (Figure 5.4) along with TEM+EELS elemental analysis (Figures 5.5 and 5.6) provided a more detailed understanding of both the external and internal oxide chemistries and morphologies. The depth of internal oxidation was observed to be significantly higher for the 1073 K × 120 s sample (approximately 2 μ m) versus the 963 K × 120 s sample (approximately 0.4 μ m). It was also determined that the external MnO layer for the 1073 K × 120 s sample had almost triple the thickness of that of 963 K × 120 s sample, with an average thickness of 121 nm versus 44 nm. This thicker external oxide layer observed for the samples annealed at 1073 K was expected considering the exponentially higher diffusivities of both oxygen and the alloying elements at the higher temperature in combination with a process atmosphere oxygen partial pressure that was three orders of magnitude higher at 1073 K (Table 5.2). The latter also explains the increased depth of internal oxidation of the 1073 K × 600 s sample. It should be mentioned that the average

thickness of the external MnO layer for the 1073 K \times 600 s and 963 K \times 600 s samples, were determined to be 296 nm and 105 nm, respectively, having a similar thickness ratio to the 120 s samples.

EELS studies also provided insight into the chemical nature and microstructural characteristics of the internal oxides. As can be seen from the elemental maps in Figures 5.5 and 5.6 and the EELS analysis in Figure 5.7, the bulk internal and grain boundary oxides formed in zones I and II (Figure 5.4) comprised a core-shell structure, where the outer shell was identified as MnSiO₃ and the inner core as SiO₂. It should be noted that the SiO₂ core was thicker and the MnSiO₃ outer shell thinner with increasing depth into the sample, indicating that the MnSiO₃ outer shell grew by consuming the SiO₂ core, which formed first and at greater depths into the substrate. These findings were consistent for all annealing conditions studied.

The variation of oxide chemistries from surface to subsurface of the steel can be explained by the oxygen available at each region of the sample, the relative thermodynamic stability and solubility of the oxides and the relative diffusivities of the species. Thermodynamic calculations clearly show that all the above-mentioned oxides were stable under the process atmospheres employed in this study. However, SiO₂ and MnSiO₃ are more thermodynamically stable than MnO – i.e. they have a more negative Gibbs free energy ^{28,29)}, while also having a significantly lower solubility product in α -Fe ³⁰⁾. Under such conditions, SiO₂ will form first at the grain boundaries; followed by the formation of MnSiO₃ in the surrounding shell, driven by the slower diffusion of Mn and the higher thermodynamic stability and lower solubility product of MnSiO₃ in α -Fe. At the surface, however, since most of the Si was already bound to the internal oxides and also due to the continuous supply of O from the process atmosphere, the competition between Mn and Si for O was less than in the subsurface, enabling the formation of MnO in the lower Si/Mn ratio environment ^{9,31)}.

As discussed above, of particular interest was the exploration of the effect of the surface oxide microstructural development in relation to its impact on reactive wetting of the steel by the 0.20 wt% Al (dissolved) continuous galvanizing bath. As was seen in Figures 5.8(a) and (b), the reactive wetting of the steel was significantly affected by the oxide morphology in the case of the 120 s annealing times. The compact or film-like 121 nm thick MnO layer observed on the external surface of the 1073 K \times 120 s (Figures 5.2(c) and 4(b)) showed no significant reactive wetting compared to the 44 nm thick MnO external oxide surface observed on the 963 K \times 120 s samples (Figures 5.2(a), 5.4(a) and 5.5). This result was not unexpected and correlates well with the observations of several authors on the effects of surface oxide chemistry, morphology, distribution and thickness on the reactive wetting mechanisms of TRIP steels ^{12-14,16,19}. For example, it is generally acknowledged that the presence of compact or film-forming oxides, in particular amorphous SiO₂ and manganese silicates, are detrimental to the formation of the Fe₂Al₅Zn_X interfacial layer. However, in the case of the external MnO layer observed for all annealing conditions in the present study, it has been shown that MnO can be reduced by Al in the galvanizing zinc bath through aluminothermic reduction ^{15,17}. Based on the kinetic model proposed by Kavitha and McDermid¹⁷⁾, it is expected that MnO layers with a thickness less than 85 nm can be aluminothermically reduced during a 4 s immersion in a 0.20 wt% Al (dissolved) galvanizing bath. Thus, the widely spaced 44 nm external MnO on the 963 K \times 120 s sample could be reduced by the bath whereas the thicker 121 nm compact morphology of the 1073 K \times 120s sample could not.

This assertion is a partial explanation to the reactive wetting differences observed, and is further supported by the changes in the interfacial microstructures observed, post dipping, for both samples, presented in Figure 5.8 to 5.10. The SEM image in Figure 5.8(d) shows evidence of an altered, yet still present, compact oxide layer on the surface of the

1073 K × 120 s sample and the cross-sectional TEM+EELS analysis of this interface (Figure 5.10) clearly confirmed that the external MnO, formed prior to immersion, continued to be present at the Zn/steel interface post-immersion. Although the thickness of this external MnO layer seemed to have been reduced locally and become more faceted versus its as-annealed morphology (Figure 5.4(b)), the morphology of the layer remained continuous. This continuous, film-like MnO layer did not allow for an intimate contact between the underlying substrate and the galvanizing bath, thereby preventing Fe dissolution from the strip and the formation of the desired Fe₂Al₅Zn_x reactive wetting product at the Zn/substrate interface.

In contrast to this poorly wetted sample, the coating/substrate interface of the 963 K \times 120 s sample (Figure 5.8(c)) exhibited non-continuous surface oxides and ample evidence of a variety of reactive wetting products. As can be seen from Figures 5.8(c) and 5.9 and the quantitative chemical analysis results in Table 5.3, Fe-Al interfacial products (point B, Figure 5.9(c) and Table 5.3) were present at the interface suggesting the occurrence of reactive wetting and the dissolution of Fe from the sample surface arising from direct contact between the substrate and the Zn alloy bath. From Figure 5.9(a), it can be seen that the Zn-alloy penetrated through the original external MnO layer (Figures 5.4(a) and 5.5) to reactively wet the underlying substrate and separated the oxides along the external oxide/substrate interface. No significant change in the thickness of the surface oxides pre and post-immersion could be detected; however, the post-immersion external oxide layer does appear broken-up and discontinuous at some locations (Figures 5.4(a) and 5.5 vs Figure 5.9(a)). It is likely that penetration of the external MnO layer occurred in such places, where the original MnO film was very thin and could be reduced (Figure 5.9(c)). Furthermore, Mn-rich regions, labeled as A, were identified on the outer side of the nodule-like reaction site in Figure 5.9(c). Quantitative chemical analysis of point A (Table 5.3) showed that the O content at these yellow sites was less than what was expected for an MnO compound,

indicating that these sites had been at least partially reduced. In addition, considerable amounts of Al and Fe were also found in the composition of point A, likely arising from the nearby $Fe_2Al_5Zn_x$ reaction products. It should be noted, however, that the $Fe_2Al_5Zn_x$ phase was only partially formed at the interface as opposed to full interfacial layer formation, consistent with SEM analysis of the surface of this sample shown in Figure 5.8(c). It is also noteworthy that the infiltrated zinc area exhibited fine internal oxides embedded in it; these are labeled as C and showed significant amounts of O, Mn and Si in their composition consistent with the TEM+EELS results of the pre-immersion internal oxides.

Quantitative results from points D and E, corresponding to the nodule-like reaction sites marked in Figure 5.9(c), showed that these regions were primarily enriched in Zn, which supports the infiltration mechanism proposed earlier; however, substantial amounts of Fe were also found in the composition of these sites. It should be recalled that no evidence of Fe-Zn intermetallic phases was found through SEM analysis of the steel/coating interface stripped with sulfuric acid. Additionally, the morphology of these sites (points D and E) does not correspond to those known for Fe-Zn compounds. It is concluded that the background Fe signal from the steel substrate contributed significantly to the quantitative analysis of these points.

In the present system, it was determined that internal oxidation occurred when employing the process atmosphere oxygen partial pressures associated with the 243 K (-30° C) dew point process atmospheres. Shifting the oxidation mode from external to internal very likely reduced the thickness of the external oxides observed in the present system and promoted the development of a thinner, widely spaced external oxide morphology and likely also shifted the dominant external oxide from Mn-silicates to MnO. ^{9,30)} This shift in oxide distribution and morphology was likely key to the promotion of reactive wetting by the galvanizing bath in the case of the 963 K × 120 s samples, as documented in Figures 5.8

and 5.9. However, it should be noted that the use of internal oxidation was not able to fully shift the resultant morphology of the external oxide layer in the case of the 1073 K \times 120 s samples such that they could be reactively wetted and, therefore, it must be concluded that the use of internal oxidation to promote reactive wetting must be combined with a careful assessment of the resultant morphology due to kinetic factors.

Given the above discussion, it is concluded that several mechanisms were responsible for the successful reactive wetting obtained in the case of the 963 K \times 120 s substrate. As the pre-immersion surface oxides of this sample comprised a fine and widely-spaced nodule-like structure with thinner oxides between them, during immersion in the Zn(Al,Fe) bath, the liquid alloy could penetrate into the steel substrate, lifting up the surface oxides, while simultaneously the 44 nm thick external MnO layer was fully or partially reduced through aluminothermic reduction. Both of these mechanisms would expose the underlying substrate to dissolution ^{15,17)} and the observed formation of the Fe₂Al₅Zn_x layer at the interface.

In contrast to the 963 K × 120 s sample, the 1073 K × 120 s sample possessed a thicker, more compact external oxide which could not be aluminothermically reduced in the bath and which did not allow direct contact between the Zn(Al,Fe) bath and the steel substrate, an essential step in the formation of the Fe₂Al₅Zn and the reactive wetting process. Thus, it can be globally concluded that the differences in external oxide morphology and thickness were the primary factors in determining the reactive wetting – or lack thereof – in the present medium-Mn alloy system.

5.5 Conclusions

The morphology, thickness and distribution of the oxides formed on the surface of the 0.1C-6Mn-2Si steel under the 243 K dew point process atmosphere were strongly affected by the peak annealing temperature. Annealing for 120s at 1073 K resulted in formation of a

thick, compact and film-like oxide layer covering the entire steel surface; while for the 963 K anneal the surface oxides comprised a widely spaced, fine nodular morphology with an external oxide layer thickness one third of that of the 1073 K anneal.

The external oxides present for all annealing temperatures and times were composed of MnO, as confirmed by both XPS and TEM+EELS analyses. However, a considerable increase in the surface Mn enrichment was observed with increasing annealing time and temperature. All samples demonstrated internal oxidation, with the maximum depth of internal oxidation zone reaching to 4 μ m in the sample annealed for 600 s at 1073 K. EELS results showed that the internal oxide network had a multi-layer structure with SiO₂ at the oxide core and MnSiO₃ as the surrounding shell

Successful reactive wetting of the 963 K × 120 s substrate by the Zn-0.20 wt% Al (dissolved) galvanizing bath was attributed to the much finer morphology and wider spacing of the 44 nm-thick nodules formed at the surface of this sample prior to immersion. During immersion, this surface oxide structure facilitated progression of the wetting reactions through several mechanisms such as aluminothermic reduction of the surface MnO and infiltration of liquid bath into the substrate which resulted in lift-off of the surface oxides. In contrast, very poor reactive wetting was observed for the 1073 K × 120 s sample due to the pre-immersion surface structure that was fully covered by a relatively coarse, compact and 121 nm-thick oxide layer which did not allow for contact between the underlying substrate and the bath alloy, thereby preventing Fe dissolution from the substrate and the precipitation of the desired Fe₂Al₅Zn_x reactive wetting product.

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CHAPTER 6 ON THE REACTIVE WETTING OF MEDIUM-MN ADVANCED HIGH-STRENGTH STEELS DURING CONTINUOUS HOT-DIP GALVANIZING

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Draft manuscript

Abstract

The effects of process atmosphere oxygen partial pressure (pO_2) and Sn-addition on the reactive wetting of a prototype medium manganese third generation advanced high strength steel by a 0.20 wt pct Al (dissolved) zinc bath was investigated through simulated galvanizing treatments. External MnO layers with thicknesses ranging from 19 nm to 45 nm were formed after annealing at 963 K (690°C) under a variety of experimental process atmospheres. Despite the presence of surface oxides prior to immersion, an integral zinc coating and good coating adherence was obtained on all steel substrates, with the exception of the reference steel annealed under the 223 K (-50°C) dew point process atmosphere, which exhibited poor reactive wetting. Excellent reactive wetting was demonstrated by the Sn-containing steels annealed under the 243 K (-30°C) and 278 K (+5°C) atmospheres. It was determined that the Al uptake as well as the population of the Fe-Al intermetallics at the coating/steel interface increased as a result of annealing under the higher pO₂ atmospheres and adding Sn to the steel. The significant improvement in reactive wetting of the Sn-added steel was attributed to the decreased surface enrichment of Mn and the discrete distribution of the fine external oxide particles formed on the surface of these steel prior to dipping; which allowed for progression of reactive wetting through mechanisms such as aluminothermic reduction of MnO and bridging of the oxides by molten zinc.

6.1 Introduction

Third generation advanced high-strength steels are receiving growing interest from automotive manufactures due to their superior combination of specific strength and ductility. These unique properties make this class of steels ideal candidates for the manufacturing of structural components for vehicles which are compatible with the dual goals of improving the passenger safety and complying with increasingly stringent emissions reduction legislation. ^[1-4]. However, the compatibility of medium-Mn steels with the continuous galvanizing process is an evolving issue. This is due to the substantial concentrations of alloying elements such as Mn, Si and Al in the steels which are essential for the desired microstructural and mechanical property development and yet externally selectively oxidize during the annealing step of the continuous galvanizing process. ^[5-7] The presence of these surface structures prior to immersion prevents the dissolution of Fe from the substrate and impedes its reaction with the dissolved Al in the zinc bath to form the desired Fe₂Al₅Zn_X interfacial layer associated with defect-free, integral galvanized coatings with good coating adhesion and formability. ^[5-7]

Numerous researchers have focused on investigating the selective oxidation of different advanced high strength steels such as dual phase (DP) and Transformation Induced Plasticity (TRIP) steels and several ^[8-14] have reported on successful reactive wetting of the substrates despite external oxidation of the alloying elements. It was reported by Khondker et al. ^[8] that a fully-developed Fe₂Al₅Zn_X interfacial layer can form on a DP600 steel during typical immersion times in a 0.20 wt pct Al (dissolved) galvanizing bath. It was proposed that the surface MnO layer was reduced by the dissolved Al in the bath which allowed for metallic Fe to participate in formation of the Fe₂Al₅Zn_X phase. It was later shown by Alibeigi et al. ^[11] that the reactive wetting of steels with higher Mn contents, up to 5 wt pct, could also be obtained and that the reactive wetting kinetics were inversely proportional to the surface
MnO layer thickness which was in turn affected by the process atmosphere oxygen partial pressure. The occurrence of *in-situ* aluminothermic reduction of MnO in the galvanizing bath was verified by Kavitha et al. ^[12] and it was shown that efficacy of this mechanism was kinetically limited by the oxide thickness during normal continuous galvanizing dipping times.

Other researchers have explored the interactions between the surface oxide chemistry, morphology and distribution with conventional galvanizing baths. ^[13-17] As an example, it was reported by Sagl et al. ^[13] that the bath dissolved Al can diffuse into the grain boundaries of crystalline oxides and form Fe-Al reaction products that break off the oxides from the surface of a DP steel substrate. In another investigation on a TRIP 700 substrate ^[14], they also determined that the external oxide morphology played a more critical role than the oxide chemistry with respect to the efficacy of the oxide aluminothermic reduction and progression of the wetting reaction. Cho et al. ^[15-17] have also reported on the role of surface oxide morphology and distribution in a series of studies that investigated the effects of minor additions of surface active elements to a 0.1C-1.6Mn-1.5Si TRIP steel. Excellent improvements in the reactive wetting of the TRIP steels was obtained due to the morphological change of the Mn-Si oxides driven by the surface segregation of elements such as Sn ^[15,16], Bi ^[17] and Sb. ^[15]

However, limited work has been dedicated to the surface development of medium-Mn 3G AHSS alloy systems in relation to reactive wetting mechanisms in the continuous galvanizing bath. The effect of pre-immersion surface oxide structure on the reactive wetting of a 0.1C-6Mn-2Si model alloy during austenitic and intercritical annealing has been recently reported by Pourmajidian and McDermid. ^[18] It was found that the 120 nm-thick, compact external MnO film produced during austenitic annealing could not be sufficiently reduced by the bath dissolved Al, resulting in poor reactive wetting due to lack of contact between the

bath and the substrate for Fe dissolution and η -Fe₂Al₅Zn_x formation to occur. However, good reactive wetting was obtained for the intercritically annealed steel that exhibited a 44 nmthick pre-immersion external MnO with wide internodular spacing which subsequently contributed to oxide-bath reactions such as aluminothermic reduction, ingress of the molten bath between the oxide and substrate and oxide lift-off.

In the present work, the development of pre-immersion surface structure as functions of process atmosphere oxygen partial pressure and 0.05 Sn addition during intercritical annealing of a model medium-Mn 0.1C-6Mn-2Si steel were examined. Interactions of the as-annealed surfaces with a 460°C 0.20 wt pct Al (dissolved) galvanizing bath during a 4 s immersion time were determined by means of GDOES and SEM analysis of the coating/steel interface and the observations were interpreted with respect to the morphology, distribution and thickness of the surface oxides formed prior to dipping.

6.2 Experimental

The chemical compositions of the two experimental substrates are shown in Table 6.1 and comprise one medium-Mn reference steel and another with 0.05 wt pct Sn added to the chemistry. Two sample geometries were cut from the 1.2 mm thick as-received cold rolled sheet where $10 \times 50 \text{ mm}^2$ coupons were used for selective oxidation experiments and $120 \times 200 \text{ mm}^2$ full-size panels were used for reactive wetting experiments. Prior to any heat treatments, the selective oxidation specimens were polished to 4000 grit SiC paper to minimize the effect of surface roughness on the subsequent surface analysis of the pre-immersion oxides. In the case of the reactive wetting samples, the full-size panels were degreased in 353 K (80°C) 2 vol pct NaOH solution, rinsed with DI water, followed by

ultrasonic cleaning in an isopropanol bath and finally dried with warm air. A final cleaning with acetone was performed on all samples immediately prior to the experiments.

able 0.1. Chemical composition of the experimental steels (wt pct)								
Steel Name	С	Mn	Si	Al	Sn	Р	S	Mn/Si
Reference	0.106	6.241	2.023	0.040	0.005	0.006	0.003	3.09
0.05 pct Sn	0.100	6.165	2.050	0.032	0.049	0.006	0.004	3.01

 Table 6.1: Chemical composition of the experimental steels (wt pct)

The McMaster Galvanizing Simulator (Iwatani-Surtec) was used to carry out all of the experiments, details of which are fully documented and presented elsewhere.^[19] As is shown in Figure 6.1, the thermal cycle for all experiments involved a 120 s isothermal hold at the intercritical annealing temperature (IAT) of 963 K (690°C) in an N₂-5vol pct H₂ atmosphere under three different dew points ranging from 223 K (-50°C) to 278 K (+5°C); full details concerning the process atmospheres used, including the process atmosphere pH₂O/pH₂ ratio and pO_2 at the intercritical annealing temperature, are given in Table 6.2. In the case of selective oxidation studies, intercritical annealing was followed by cooling the specimens to 343 K (70°C) at -10 K/s with N₂ gas quenching. For the reactive wetting experiments, however, following the isothermal hold, samples were cooled to 733 K (460°C) at -10 K/s, held for 10 s to achieve thermal equilibrium through the thickness of the sample and were then immersed in a 460°C Fe saturated 0.20 wt pct Al (dissolved) galvanizing bath ^[21] for 4 s. Samples were then cooled at -10K/s to 473 K (200°C) using N₂ gas quenching prior to removal from the simulator at roughly room temperature. Immediately after removal from the simulator, the selective oxidation samples were stored in anhydrous HPLC grade isopropanol to minimize additional oxidation and surface contamination prior to analysis. In the case of the reactive wetting samples, a uniform temperature and coating area of $80 \times 80 \text{ mm}^2$ was

situated 10 mm below the zinc dry line of the coated panels and only material from this area was analyzed for the reactive wetting studies.



Figure 6.1: Schematic of selective oxidation (dotted line) and hot-dip galvanizing (solid line) heat treatments.

Table 6.2: Experimental specifications of the N_2 -5 vol pct H_2 process atmospheres at 963 K (690°C) peak annealing temperature (pO₂ values derived using [20])

	-	
Dew Point (K)	pH ₂ O/pH ₂	pO ₂ (atm)
223	0.00125	1.20×10 ⁻²⁷
243	0.00998	7.69×10 ⁻²⁶
278	0.17111	2.26×10 ⁻²³
	Dew Point (K) 223 243 278	Dew Point (K) pH2O/pH2 223 0.00125 243 0.00998 278 0.17111

The selective oxidation and reactive wetting samples were analysed across a variety of length scales by various techniques. The pre-immersion surface oxide structures as well as any reaction products present at the coating/steel interface of the galvanized samples were examined using scanning electron microscopy (SEM) in a JEOL 7000F field emission gun SEM operated in secondary electron imaging (SEI) mode with an acceleration voltage of 5 keV. In the latter case, the zinc overlay was removed by either fuming HNO₃ or 10 vol pct solution of H_2SO_4 in water to expose the interfacial layer. The latter technique leaves both the Fe-Zn and Fe-Al intermetallics intact; whereas stripping with HNO₃ dissolves both the metallic Zn and any Fe-Zn intermetallics but does not affect the Fe₂Al₅Zn_x layer. Prior to SEM analysis, a thin coating of C was deposited on the samples to prevent charging of the oxidized surfaces.

The pre-immersion surface oxides were also analyzed with a PHI Quantera SXM (Scanning X-ray Photoelectron Spectroscopy Microprobe) with an Al K α X-ray source (1486.7 eV). The spot size was 100 μ m and the take-off angle was set at 45°. Elemental depth profiles of the steel surface were obtained by Ar ion sputtering on a 2 × 2 mm² area with a pass energy of 140 eV and step size of 0.25 eV. All data processing of the XPS spectra was done using MultiPak 6.0 software. All spectra were calibrated using the metallic iron binding energy of 706.62 eV and depth measurements are accurate to ±10% of the documented sputtered depth.

Glow discharge optical emission spectrometry (GDOES, Jobin Yvon Horiba GD Profiler) was used to study the chemistry of the coating/steel interface of the galvanized samples. GDOES compositional depth profiles were acquired using a power of 45 W and a pressure of 600Pa; the data acquisition rate was 0.1 s/pts and the spectra were calibrated using certified standards for zinc coated Mn-containing steels.

To identify the interfacial layer products, X-ray diffraction (XRD) was also used on the galvanized steels after removal of the top coating layer by fuming HNO₃. Data was collected using a Bruker D8 DISCOVER equipped with a Cobalt Sealed Tube Source (λ = 1.79026 Å) and a Vantec 500 area detector. Topas Version 4.2 (Bruker-AXS) was used for data analysis where the collected patterns were matched using the integrated ICCD database.

The coating adherence of the galvanized panels was assessed by means of a customized three-point bend test as no standard for the medium-Mn steel substrates was

available. Parameters were chosen based on the steel thickness of 1.2 mm with the punch radius being 4.76 mm and the width of the galvanized strip being 10 mm. The bend test dies were installed on an Instron 5566 universal tensile machine with a 10 kN load capacity where strains up to 18% and bend angles as low as 23° were obtained prior to spring back.

6.3 **Results**

Figure 6.2 shows SEM images of the surface oxides on the as-annealed coupons of the reference and Sn-added (Table 6.1) as a function of experimental process atmosphere (Table 6.2). A comparison between Figures 6.2(a) to (c) – i.e. the reference steel surfaces – with Figures 6.2(d) to (f) – i.e. the Sn-added steel surfaces – shows that the external oxides formed on the reference steel were coarser compared to those of the Sn-added steel. Furthermore, for all the process atmosphere conditions, the surfaces of the Sn-added substrates exhibited less coverage by the external oxides. It should also be pointed out that, in this case, the surface oxide nodules were more widely spaced; which can clearly be seen for the case of the -50DP process atmospheres (Figure 6.2(a) vs (d)), where the surface of the reference steel comprises closely spaced and film-forming nodules whereas the surface coverage of the compact oxide nodules is significantly lower for the Sn-added substrate, with the oxide particles having a more discrete appearance. It is, therefore, implied that the Sn addition to the steel chemistry resulted in modification of the surface oxide morphology, distribution and spacing. It is further inferred from these micrographs that, for both experimental steels, external oxidation was decreased by increasing the oxygen partial pressure in the process atmosphere. This is consistent with the predicted external to internal oxidation transition taking place for the reference alloy from process atmosphere dew points above -30° C when annealing for 120 s at 963 K (690°C). ^[22]



Figure 6.2: Secondary electron images showing the pre-immersion surface oxide structures formed on the (a), (b) and (c) reference steel and (d), (e) and (f) Sn-added steel.

The steel surfaces before dipping were further analyzed by XPS to determine the elemental segregation of Mn and Si to the surface and speciate the oxides present. Figure 6.3 shows the Mn and Si concentrations as a function of sputtered depth where the closed and open data points belong to the reference alloy and the Sn-added grade, respectively. The depth profiles clearly indicate significant Mn enrichment of the steel surfaces for all process atmospheres explored. The maximum surface enrichment, at approximately 52 at pct, was observed for the reference steels annealed under the -50DP and -30DP process atmospheres and the Sn-containing grade annealed under the -50DP atmosphere. This Mn surface enrichment decreased significantly with increasing process atmosphere pO₂ such that, for the Sn-containing steel annealed under the +5DP atmosphere, Mn levels just below 20 at pct were observed at the surface. It is further noted that, in line with the SEM observations in Figure 6.2, the thickness of the surface Mn-enriched layer decreased for the higher pO₂ process atmospheres, where the shoulder in the elemental profiles of the -30DP and +5DP at

depths greater than 50 nm is indicative of internal oxidation having taken place. It should be pointed out that, in the case of Si, only a slight surface enrichment in the first few nanometers of the surface were detected and it was, therefore, concluded that Mn was the predominant external oxide forming species for all process atmospheres explored. Similar to a recent study on the selective oxidation of 0.1C-6Mn-2Si steels ^[23], analysis of the XPS binding energies determined that only MnO was found as the external oxide layer on the present substrates, with characteristics peaks at 530.3 eV, 641.4 eV and 654.1 eV for O 1s, Mn 2p_{3/2} and Mn $2p_{1/2}$, ^[24-26] respectively.



Figure 6.3: XPS depth profiles of Mn and Si as functions of process atmosphere oxygen partial pressure and Sn-addition.

Figure 6.4 presents the uniform temperature and coating area of the galvanized panels of the reference steel and the Sn-added alloy. No integral zinc coating was obtained on the reference steel annealed under the -50DP process atmosphere and only isolated zinc droplets were present on the surface of the panel (Figure 6.4(a)). The other five samples showed

evidence of reactive wetting having taken place, with the Sn-added substrates (Figure 6.4(d) to (f)) demonstrating significantly enhanced coating quality with the two panels annealed under the -30DP and +5DP process atmospheres showing excellent reactive wetting. The coatings of the reference steel panels annealed under the -30DP and +5DP process atmospheres as well as the Sn-containing grade annealed under the -30DP process atmosphere (Figure 6.4(b) to (d)), however, suffered from visual coating defects such as bare spots. To further examine the coating quality of the successfully galvanized panels, three point bend tests were performed on $10 \times 100 \text{ mm}^2$ strips of the galvanized steels to assess the coating adherence. It can be seen from Figure 6.5 that no evidence of cracking, flaking or splitting of the zinc layer was found on any of the samples and the coating at the edges remained intact. Thus, it can be concluded that the coatings produced under these processing conditions were adherent, also indicative of good reactive wetting by the Zn-alloy bath.



Figure 6.4: Photographs of the uniform coating area of the galvanized steel panels; (a), (b) and (c) reference steel and (d), (e) and (f) Sn-added steel.



Figure 6.5: Images of bend tested galvanized steels; (a) and (b) reference steel and (c), (d) and (e) Sn-added steel.

Figures 6.6 and 6.7 show the GDOES depth profiles of galvanized reference steel and the Sn-added grade, respectively. It should be mentioned that acquisition of the elemental profile from the poorly wetted reference steel (Figure 6.4(a)) was not possible due to the irregularity of the surface of this panel arising from the zinc droplets on the surface. All of the plots in Figures 6.6 and 6.7 show an 8 µm wide region at the coating/steel interface where different amounts of Al were detected for each alloy and process atmosphere. This Al uptake is indicative of the presence of interfacial Fe-Al intermetallics that are responsible for the reactive wetting observed for these samples. Additionally, it should be pointed out that the degree of Mn and Si enrichment at the Zn/Fe interface is much less than the pre-immersion surfaces shown in Figure 6.3. Furthermore, the GDOES O profiles are not consistent with MnO or other oxides being present at the interface.



Figure 6.6: GDOES elemental depth profiles across the coating/steel interface of the galvanized reference steels annealed under the (a) -30DP and (b) +5DP process atmospheres.



Figure 6.7: GDOES elemental depth profiles across the coating/steel interface of the galvanized Sn-added steels annealed under the (a) -50DP, (b) -30DP and (c) +5DP process atmospheres.

Analysis of the chemically stripped coating/steel interface was further carried out by means of SEM, the results of which are shown in Figure 6.8. It should be mentioned that, due to the absence of a metallic zinc coating on the surface of the reference steel panel annealed under the -50DP atmosphere (Figure 6.4(a)), the as-dipped surface was directly studied under the SEM (Figure 6.8(a)). As was mentioned earlier, the zinc layer was removed through two different routes; one with a 10 vol pct H₂SO₄ in water and another by fuming HNO₃. Here, the micrographs correspond to the interfacial layer exposed through the latter, as no evidence of Fe-Zn intermetallics being present at the interface was found when the zinc overlay was stripped by the H_2SO_4 solution. It can be observed from Figure 6.8(a) that aside from the solidified zinc droplets on the -50DP reference steel substrate, the pre-immersion external oxide layer, first seen in Figure 6.2(a), was still present at the coating/steel interface postimmersion. In contrast, the Fe₂Al₅Zn_x intermetallics were detected at the interface of all samples that exhibited good reactive wetting (Figure 6.8(b)-(f)), where the population of the Fe-Al crystals increased significantly under the combined effect of high process atmosphere pO_2 and Sn-addition to the alloy chemistry such that a well developed and continuous Fe₂Al₅Zn_x layer was formed at the interface of the two Sn-added grades annealed under the – 30DP and +5DP process atmospheres (i.e. Figure 6.8(e) and (f)).

The XRD pattern collected from the +5DP Sn-added steel after removal of the top coating layer (Figure 6.8(f)) is shown in Figure 6.9 where peaks corresponding to the Fe_2Al_5 phase along with those from the internal oxides of the subsurface were identified.



Figure 6.8: Secondary electron images of the coating/steel interface; (a) as-dipped surface of the reference steel annealed under the -50DP process atmosphere and (b) and (c) after removal of the top Zn layer with fuming HNO₃; (d), (e) and (f) the corresponding interfaces of the Sn-added steels after stripping with acid.



Figure 6.9: X-ray diffraction pattern collected from the galvanized Sn-added steel annealed under the +5DP process atmosphere as shown in Figure 6.8(f).

6.4 Discussion

SEM and XPS analysis of the pre-immersion samples were indicative of significant Mn external oxidation. Recently, a detailed analysis of the selective oxidation of the present 0.1C-6Mn-2Si reference and 0.05 wt pct Sn-added substrate during intercritical annealing under a variety of process atmosphere oxygen partial pressure was carried out.^[23] It was determined through XPS binding energy analysis and electron energy loss spectroscopy (EELS) that the oxide species present on the surface of all samples were MnO, which was also found to be the case in the present study. It was also seen from the SEM images in Figure 6.2 that the 0.05 wt pct Sn addition resulted in significant modification of the surface oxides into a finer and more island-like morphology, with the extent of external oxidation clearly being lower than that of the reference steel. The effect of surface active elements on the modification and suppression of surface oxidation reactions has been reported by several authors. ^[15-17, 23, 27-29] This is primarily attributed to the fact the elements such as Sn, Bi and Sb, having a much larger atomic radius than the Fe matrix, have the tendency to segregate to the free surfaces and interfaces in order to relieve the local lattice strains. This elemental enrichment layer then affects the oxidation reaction by two mechanisms: (i) it can result in retardation of the external and internal oxidation kinetics as the surface active elemental segregation blocks oxygen diffusion paths and reduces the oxygen permeability at the surface ^[27-29] and (ii) it can modify the interfacial energies such that formation of certain oxide morphology versus another can be encouraged. ^[16, 17] For instance, it was reported by Cho et al. ^[16] that 0.05 wt pct, 0.5 wt pct and 1 wt pct additions of Sn to a 0.1C-1.6Mn-1.5Si TRIP steel resulted in changing the external Mn-Si oxides morphology from film-type to island-like, where the Mn to Si ratio of the surface oxides decreased by increasing the alloy Sn content. A similar effect was reported when the effect of Bi additions was investigated on a similar steel grade. ^[17] More recently, the present authors explored the effect of elemental

segregation on the development of the surface structure of the same prototype medium-Mn 3G steels immediately after intercritical annealing. ^[23] Using 3D atom probe tomography, it was found that Sn was segregated to the base of the oxide/metal interface and had modified the morphology of the surface MnO from a film-like nodular structure to discrete and fine globular oxide particles. The kinetics of external oxidation along with the surface enrichment levels of Mn were also decreased as a result of the 0.05 wt pct Sn addition to the reference steel.

It is well known that certain oxide species, such as SiO₂ and manganese silicates, are detrimental to the reactive wetting of Mn-Si steels by the galvanizing bath as these oxides have a tendency to form thick, continuous and film-like external oxides ^[7,30,31] and prevent intimate contact of the substrate Fe and the Zn(Al, Fe) bath, which is necessary for reactive wetting and formation of desired Fe₂Al₅Zn_x interfacial layer. However, instances of external MnO layers being problematic for reactive wetting have also been reported. ^[18,30,31] On the other hand, several authors have reported on full formation of interfacial layer despite the presence of MnO and Mn-Si surface oxides prior to immersion. [8-14,32-34] They have pointed out that, depending on the morphology, distribution and thickness of the pre-immersion external oxide layer, reactive wetting mechanisms such as surface oxide lift-off^[13,14], oxide bridging by the molten zinc alloy ^[32-34] and more commonly aluminothermic reduction of MnO oxides ^[8-14] could result in obtaining a good quality coating on the steel substrates. It was shown by Alibeigi et al.^[11] that reactive wetting could be obtained on steels with Mn contents as high as 5 wt pct during immersion times of 10 s, where it was observed that the wetting force was a strong function of the surface MnO layer thickness and subsequently the kinetics of aluminothermic reduction of MnO were inversely proportional to this metric. A follow-up study^[12] explored the kinetic limitations of the aluminothermic reduction reaction in terms of the surface MnO layer thickness and immersion times, where it was reported that

MnO layers with thicknesses below 85 nm could be reduced in the 0.20 wt pct Al (dissolved) bath during 4 s immersions. ^[12]

In the case of the present study, the thickness of the surface oxides of the as-annealed samples were directly measured from cross-sectional images (a minimum of 100 measurements per sample with confidence interval of 95%) and were found to be within the range of 19 nm to 45 nm for the Sn-added sample annealed under the +5DP atmosphere and the reference steel annealed under the -30DP atmosphere, respectively. As can be seen from Figures 6.4 and 6.5, except for one substrate, the majority of the experimental conditions demonstrated good reactive wetting and coating adhesion, where excellent reactive wetting was obtained for the two Sn-containing substrates that were annealed under the -30DP and +5DP process atmospheres (Figures 6.4(e) and (f)).

It is interesting to recall that the steel with the maximum external oxide thickness (45 nm), i.e. the reference steel annealed under the -30DP atmosphere, showed an integral, adherent metallic zinc coating (Figures 6.4(b) and 6.5(a)), whereas no integral zinc coating was formed on the substrate that was annealed under the -50DP atmosphere (Figure 6.4(a)) which exhibited a 35 nm-thick surface MnO layer prior to dipping. The reason lies in the morphology and distribution of the surface oxides. Referring to the SEM micrographs presented in Figures 6.2(a) and (b), it can clearly be seen that the surface of the reference steel -50DP sample was covered with a film-like and compact oxide layer as opposed to that of the -30DP anneal that showed a relatively sparse and widely spaced distribution of the surface oxides. It is, therefore, concluded that surface oxide morphology, distribution and spacing plays a dominant role versus the surface oxide thickness, in relation to the reactive wettability of the substrates.

It is well known that good coating quality is attributed to the formation of a dense and well-developed $Fe_2Al_5Zn_x$ layer at the coating/steel interface. ^[8-10] Formation of Fe-Al

reaction products was confirmed through GDOES (Figures 6.6 and 6.7), SEM (Figure 6.8) and XRD (Figure 6.9) analysis of the Fe-Zn interfaces. GDOES analysis of the interfacial region of all galvanized steels with integral coating layers presented some Al enrichment at the interface, which is indicative of wetting reactions having taken place. However, the extent of this Al uptake varied for each experimental atmosphere and steel chemistry, as shown in Figures 6.6 and 6.7. It should also be pointed out that the same enrichment levels of Mn and Si (Figure 6.3) were not maintained after galvanizing; the post-immersion enrichments were considerably lower and did not display evidence of being in an oxidized state, which implies that the surface MnO layer was fully or partially reduced. A variety of morphological distributions and densities of the Fe-Al intermetallics were also identified at the Fe-Zn interfaces, as can be seen in the series of micrographs of Figure 6.8. The reference steel annealed under the -30DP process atmosphere (Figure 6.8(b)) and the Sn-added grade annealed under the -50DP atmosphere (Figure 6.8(d)) demonstrated only partial evidence of reactive wetting (Figures 6.4(b) and (d)), while a compact layer of equiaxed $Fe_2Al_5Zn_x$ crystals could be clearly distinguished at the interface of the reference steel annealed under the +5DP atmosphere as well as the Sn-added steels annealed under the -30DP and +5DPprocess atmospheres, show in Figures 6.8(c), (e) and (f), respectively. It was generally observed that the population and density of the Fe-Al intermetallics was increased by increasing oxygen partial pressure and with the alloy Sn-addition. This is in agreement with the GDOES profiles of these samples exhibiting an increased amount of Al uptake at the coating/steel interface (Figures 6.6 and 6.7) such that the enhanced reactive wetting of the samples observed in Figures 6.4(c), (e) and (f), was also accompanied with an increased integral Al profile as well as the width of the interfacial region.

It can be observed from the GDOES profiles shown in Figure 6.6 that the reference steel annealed under the higher $pO_2 + 5DP$ process atmosphere (Figure 6.6(b), displayed a

wider interfacial region and higher overall Al uptake versus the -30DP reference steel (Figure 6.6(a)), which was accompanied with the Mn, Si and O profiles of the +5DP steel showing lower enrichment levels. This observation was in good correlation with the relative coating qualities of the two samples, shown in Figure 6.4(b) and (c), as well as the coating/steel interfacial layer SEM micrographs of Figures 6.8(b) and (c), where significantly larger population of Fe-Al intermetallics was found at the interface of the +5DP substrate. It should also be pointed out that in the case of the reference steel annealed under the -50DPatmosphere, a surface oxide layer similar to the pre-immersion oxides in Figure 6.2(a) was still present adjacent to the zinc droplets (Figure 6.8(a)). This explained the poor reactive wetting of this substrate (Figure 6.4(a)), as this external oxide film prevented any reactions to take place between the substrate Fe and the Al from the zinc bath. It is also worth noting that the Sn-added steel that was annealed under the -50DP atmosphere was the only substrate within this alloy system that exhibited bare spots in the coating (Figure 6.4(d)) and looking at the GDOES results (Figure 6.7(a)), it was only this sample that represented an O peak, however slight, at the interface.

Previous studies ^[15-17] have reported on the beneficial effect of addition of surface active elements such as Sn, Bi and Sb on the reactive wetting of low Mn TRIP steels. They have shown that elemental segregation could alter the pre-immersion surface structure such that formation of island-like and thinner surface oxides was encouraged; this in turn contributed to increased Al uptake at the interface and the significantly enhanced coating quality. ^[17] In the present case, it was determined that, for the oxide thickness range of this study, the oxide morphology and distribution had a more critical influence on the ability of surface MnO to be aluminothermically reduced in the Zn(Al, Fe) bath, than the oxide thickness. This was particularly found to be the case for the two reference steels that were annealed under the –50DP and –30DP atmospheres having surface layer thicknesses of 35 nm

and 45 nm, where the continuous, yet slightly thinner oxide layer of the former did not allow for an intimate contact between Fe and the bath alloy as the oxide layer was still present at the surface after immersion. Formation of Fe-Al intermetallics at the interface of the galvanized steels was primarily identified through SEM analysis and was further reinforced by GDOES concentration profiles showing Al peaks at the coating/steel interface, typical of inhibition layer formation. Although Mn was found to be still present at the steel surface, it was detected at substantially lower amounts and in a non-oxidized state. This implied that the pre-immersion MnO layers were altered possibly through aluminothermic reduction. The improvements observed in reactive wetting of the Sn-containing steels annealed under the – 30DP and +5DP were then attributed to the finer morphology and distribution of the globular pre-immersion oxides that allowed for a direct contact between Fe and Al, thereby facilitating the progression of the reactive wetting and the formation a well-developed $Fe_2Al_5Zn_x$ layer.

Detailed analysis of the interfacial layers using advanced microscopy techniques will be the subject of an upcoming study which concerns the nano-scale and localized analysis of the coating/steel interface in order to pin down the mechanisms that were responsible for reactive wetting of each case of the present medium-Mn substrates.

6.5 Conclusions

The effects of process atmosphere oxygen partial pressure and 0.05 wt pct Sn addition on the development of pre-immersion surface structure and the subsequent reactive wettability of a 0.1C-6Mn-2Si prototype 3G steel were determined.

Except for the reference steel annealed under the -50DP atmosphere, all samples exhibited good reactive wetting, where increasing the process atmosphere oxygen partial pressure as well as Sn addition resulted in superior coating properties which were accompanied with notable Al uptake and Fe₂Al₅Zn_x formation at the coating/steel interface.

Substantially lower amounts of Mn in the interfacial region of the galvanized samples indicated that the pre-immersion MnO layer was reduced through aluminothermic reduction.

It is concluded that the addition of only 0.05 wt pct Sn to the steel can significantly improve the reactive wetting of the prototype medium-Mn 3G steel due to the refinement effect of Sn on the surface MnO. This alteration to a fine, widely-spaced and thinner oxide structure increased the compatibility of the steel surface and the Zn(Al,Fe) galvanizing bath such that the amount of Al uptake and population of the desired Fe₂Al₅Zn_x crystals were significantly increased for high dew point annealing atmospheres and the Sn-containing substrates.

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CHAPTER 7 ON THE REACTIVE WETTING MECHANISMS OF MEDIUM-MN ADVANCED HIGH-STRENGTH STEELS DURING CONTINUOUS HOT-DIP GALVANIZING: NANO-SCALE ANALYSIS OF THE FE-ZN INTERFACE

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To avoid further repetition of the content discussed so far, the present chapter consists of only the results, discussion and conclusions sections of the last in the series of the articles. The reader is referred to 5.2 and 6.2 for details of the experimental procedures. Nano-sacle analysis of the steel/coating interface after immersion is presented and the reactive wetting mechanisms in each case is discussed in detail. The references used in this chapter are brought in the global list of references at the end of the thesis.

7.1 Results

Cross-sectional DF-STEM images of the external oxides formed during the annealing heat treatments prior to immersion are provided in Figure 7.1 to allow the reader to compare the surface oxides pre- and post-immersion. It should be mentioned that study on the effect of 0.05 wt pct Sn addition on the selective oxidation of the present alloy system was recently carried out by Pourmajidian and McDermid (2018). Furthermore, the meso- and micro-scale analysis of the reactive wetting behaviors of those substrates by a 460°C 0.20 wt pct dissolved Al galvanizing bath was discussed in a subsequent study (Pourmajidian and McDermid 2018). A summary of the results reported in these two studies are provided in

Table 7.1, where information on the external oxide morphology, spatial distribution and thickness along with the observed reactive wetting results can be found. It should be mentioned that the outermost external oxide layer in all cases was identified as MnO, as determined through XPS and EELS analysis (Pourmajidian and McDermid 2018).

Table 7.1: Description of the pre-immersion external MnO structures on 0.1C-6Mn-2Si-xSn
steels and their corresponding reactive wetting behaviour by the 0.20 wt pct dissolved Al
galvanizing bath, extracted and summarized from Pourmajidian and McDermid (2018)

Steel	Atmosphere Name	Pre-immersion external oxide structure	Coating Quality
	-50DP	Substantial coverage by compact, film-	N/A
Deferrere		like and continuous layer; $35 \pm 3 \text{ nm}$	
	-30DP	Coverage by nodular and discontinuous	Good
Kelelelice		layer; $44 \pm 2 \text{ nm}$	
	+5DP	Minimal coverage by fine nodules;	Good
	-50DP	Coverage by reasonably compact	Bare Spots
		nodulear layer; $20 \pm 3 \text{ nm}$	
0.05 wt pat Sp	-30DP	Minimal coverage by isolated fine	Excellent
0.05 wt pet Sh		globules; $31 \pm 2 \text{ nm}$	
	+5DP	Minimal coverage by isolated fine	Excellent
_		globules; $22 \pm 2 \text{ nm}$	

A rapid assessment of Table 7.1 shows that the external MnO thickness varied within a relatively narrow range of 20 nm to 44 nm under different combinations of process atmosphere oxygen partial pressure (pO_2) and substrate composition, while a rather diverse range of external oxide morphologies and distributions were identified. Furthermore, the majority of the substrates demonstrated evidence of good reactive wetting by the galvanizing bath, with the exception of the reference steel annealed under the –50DP process atmosphere, for which no integral zinc coating was obtained post-immersion. The cross-sectional images in Figure 7.1 reflect the external oxide attributes described in Table 7.1. It can be seen that the external MnO layer formed on the reference steel that was annealed under the low pO_2 –50DP process atmosphere exhibited a continuous film-like morphology (Figure 7.1(a)), while increasing the process atmosphere pO_2 under the -30DP and +5DP process atmospheres (Table 6.2) resulted in the internal oxidation mode being dominant and changed the morphology of the external oxides to a nodule-like and somewhat discontinuous layer. A similar effect could be observed in the case of the Sn-containing grades (Figures 7.1(d) to (f)) where the oxides formed under the -30DP and +5DP process atmospheres exhibited finer and more isolated distribution of MnO nodules.



Figure 7.1: Cross-sectional DF-STEM images showing the pre-immersion external oxide structures of (a), (b) and (c) the reference steel and (d), (e), (f) the Sn-added steel annealed under the -50DP, -30DP and +5DP process atmospheres.

Figure 7.2 presents the DF-STEM image and the corresponding EELS elemental map of the Fe-Zn interface of the reference steel annealed under the –50DP process atmosphere, capturing a solidified zinc droplet with the external oxide layer underneath. It should be mentioned that given the different FIB milling rate of Zn and Fe and as can be seen in Figure 7.2(a), these cross-sections occasionally exhibited some minor FIB damage in the Zn region during the final thinning step. It can be seen that the pre-immersion continuous oxide layer that was formed during annealing on this sample (Figure 7.1(a)) continued to be integral and comprised a continuous film post-immersion. Per the combined elemental maps, this confirmed by EELS analysis, where the O-K and Mn-L_{2,3} core-loss peaks along with the near-edge fine structures shown in Figure 7.3 correspond to those established for MnO (Rask et al. 1987, Potapov et al. 2004, Schmid and Mader 2006, Tan et al. 2012). Additionally, the quantitative chemical analysis of this oxide layer, given in Table 7.2, shows an almost 1:1 ratio of Mn to O, supporting the reported MnO EELS finding. It is also worth noting that no Al signal was detected in the EELS analysis of this region (Table 7.2), further indicating that no reactive wetting had occurred due to the absence of the η -Fe₂Al₅Zn_x reactive wetting product.



Figure 7.2: (a) DF-STEM image and (b) color overlay EELS map showing the zinc/steel interface of the galvanized reference steel annealed under the –50DP process atmosphere prior to immersion.

Table 7.2: Quantitative EELS analysis results acquired from the post-immersion oxides in Figures 7.2 and 7.4 (at pct)

	· • •						
	Steel	Zn	Al	Mn	0	Fe	Si
_	Reference	0.0	0.0	45.2	52.7	0.6	1.5
	0.05 wt pct Sn	1.2	8.3	47.9	24.6	14.1	3.9



Figure 7.3: O-K and Mn- $L_{2,3}$ edge EELS spectra acquired from the post-immersion external oxide structures found at the zinc/steel interface of the galvanized steels annealed under the -50DP process atmosphere prior to immersion.

Similarly, the TEM+EELS analysis of the post-immersion Fe-Zn interface of the Sn-containing grade that was annealed under the -50DP process atmosphere is shown in Figure 7.4. Unlike the previous sample, the external oxide layer under the zinc coating appeared as yellow as opposed to orange in the color overlay map which implies that the pre-immersion external MnO layer in this case, was altered and partially reduced as a result of the oxide-bath-substrate reactions during immersion. It is interesting to note that the EELS analysis of this interface (Figure 7.3) also exhibited some modifications to the fine structures of the O-K core-loss peak compared to that acquired from MnO in the reference steel. The quantitative results in Table 7.2 also suggest a sub-oxide composition for this layer. Moreover, from the EELS maps in Figure 7.4 and the EELS analysis in Table 7.2, it can be seen that some Al was incorporated to the reduced MnO layer; however, no evidence of particles or crystals that could be possibly associated with Fe₂Al₅Zn_x could be identified.



Figure 7.4: (a) DF-STEM image and (b) color overlay EELS map showing the zinc/steel interface of the galvanized Sn-added steel annealed under the –50DP process atmosphere prior to immersion.

A significantly different Fe-Zn interface was observed in the case of the reference steel annealed under the –30DP process atmospheres, shown in Figure 7.5. Given the relatively complex nature of this interface, a SE-FIB image of the Fe-Zn interface is appended to the TEM+EELS results to facilitate the interpretation of the data. As marked by arrows in Figure 7.5(a), the coating/steel interface exhibited some nodule-like features which did not exist prior to immersion at the oxide/steel interface (Figure 7.1(b)). Comparison of Figure 7.1(b) to Figure 7.5 indicates that the formation of these nodules resulted in delamination of the original oxide/steel interface. The EELS color overlay map (Figure 7.5(c)) revealed that the molten zinc alloy had penetrated the external MnO layer and infiltrated to the underlying steel substrate while also forming reaction sites corresponding to the aforementioned nodules in Figure 7.5(a). These regions are labeled as D and E in Figure 7.5(c) where, per Table 7.3, their EELS chemical analysis corresponded to an Fe and Alenriched Zn alloy. Additionally, Mn-rich and Al-rich regions could be identified as yellow and green on the EELS map, labeled as A and B in Figure 7.5(c), respectively. Quantitative chemical analysis of these points identified them to be Mn-sub-oxides and Fe₂Al₅Zn₅ intermetallics, respectively. Finally, the embedded internal oxides marked as C were identified as MnSiO₃.



Figure 7.5: (a) SE-FIB image, (b) DF-STEM image and (c) color overlay EELS map showing a nodule-like reaction site and the different reaction products formed at the zinc/steel interface of the galvanized reference steel annealed under the –30DP process atmosphere prior to immersion (Pourmajidian and McDermid 2018).

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Point	Zn	Al	Mn	0	Fe	Si	Phase Present		
А	1.6	12.9	42.9	25.1	17.5	_	Mn-sub-oxide		
В	10.1	61.2	2.3	0.0	26.4	_	Fe ₂ Al ₅ Zn		
С	1.8	10.3	17.6	43.7	1.8	24.8	MnSiO ₃		
D	81.6	5.9	1.6	0.0	10.9	—	Zn alloy		
E	62.3	9.3	5.2	0.0	22.3	0.9	Zn alloy		

Table 7.3: Quantitative EELS analysis results corresponding to points A to E in Figure 7.5(c) (at pct) (Pourmajidian and McDermid 2018)

Unlike the -30DP reference steel interface discussed above, the galvanized Sn-added steel exhibited a flat coating/steel interface, pictured in Figure 7.6(a). In this case, the Fe-Al intermetallics could be easily identified at the interface and the quantitative analysis of these crystals, labeled B in Figure 7.6(c), is provided in Table 7.4 suggesting a Fe₂Al₅Zn_x intermetallic composition. It was also found that the external MnO layer was depleted in oxygen, manifested by the yellow color in the EELS map as well as the chemical analysis results of point A in Table 7.4, exhibiting 44.0 at pct Mn and 26.8 at pct O, respectively.



Figure 7.6: (a) SE-FIB image, (b) DF-STEM image and (c) color overlay EELS map showing the reaction products formed at the zinc/steel interface of the galvanized Sn-added steel annealed under the –30DP process atmosphere prior to immersion.

Table 7.4: Quantitative EELS	analysis results	corresponding to	points A and	B in Figure
7.6(c) (at pct)				

//e(e) (as pe	•)							
Point	Zn	Al	Mn	0	Fe	Si	Phase Present	
А	2.4	7.9	44.0	26.8	16.3	2.6	Mn-sub-oxide	
В	8.2	59.6	5.3	3.4	23.5	-	Fe ₂ Al ₅ Zn	

Figures 7.7 and 7.8 show the coating/steel interface of the reference and Sn-added substrates, respectively, annealed under the +5DP process atmosphere prior to immersion in the Zn(Al,Fe) bath. In both cases, some evidence of the molten Zn alloy infiltrating to the steel subsurface could be identified, however, the penetration site was not captured by these samples. Comparison of Figures 7.7 and 7.8 to their counterparts annealed under the -30DP process atmosphere (Figures 7.5 and 7.6), will show that an increased population of $Fe_2Al_5Zn_x$ crystals was clearly observed for the steels annealed under the +5DP atmospheres. Furthermore, it is found that the Fe-Al intermetallics were precipitated not only on top of the partially reduced MnO layer, but also in between and underneath them. It is further noted from Figure 7.8 that the pre-immersion MnO oxides were almost fully reduced in the case of the Sn-added substrate annealed under the +5DP atmosphere (Figure 7.8(b)) where a notable reduction in the surface oxide thickness could also be observed through comparison of the pre-immersion and post-immersion images of this sample, i.e. Figure 7.8(b) vs 7.1(f). Full formation of the interfacial layer comprising relatively coarse and compact $Fe_2Al_5Zn_x$ crystals was obtained in the case of the Sn-added alloy annealed under the higher $pO_2 + 5DP$ process atmosphere. It should be noted that, as summarized in Table 7.1, this sample along with the -30DP Sn-containing substrate had demonstrated excellent coating quality compared to the other experimental substrates.



Figure 7.7: (a) DF-STEM image and (b) color overlay EELS map showing the reaction products formed at the zinc/steel interface of the galvanized reference steel annealed under the +5DP process atmosphere prior to immersion.



Figure 7.8: (a) DF-STEM image and (b) color overlay EELS map showing the reaction products formed at the zinc/steel interface of the galvanized Sn-added steel annealed under the +5DP process atmosphere prior to immersion.

7.2 Discussion

The desired Fe₂Al₅Zn_x interfacial layer was not observed for either of the substrates annealed under the -50DP atmosphere (Figures 7.2 and 7.4). It should be recalled that the reference steel annealed under the lowest pO_2 –50DP process atmosphere showed no significant reactive wetting and no integral coating formed on this substrate after immersion (Figures 6.4(a) and 7.1 and Table 7.1). This was consistent with the TEM+EELS analysis showing that the continuous and film-like pre-immersion MnO layer, pictured in Figure 7.1(a), clearly still existed on the surface of this sample post-immersion (Figure 7.2). As a result, during immersion, no direct contact between the substrate metallic Fe and the Zn-alloy could take place and, consequently, no wetting reaction leading to the precipitation of the Fe-Al layer could occur. In the case of the Sn-added steel annealed under the -50DP process atmosphere, although the formation of an Fe₂Al₅Zn_x layer was not identified, evidence of Al concentrating at the Fe-Zn interface was detected from the EELS maps (Figure 7.4). Furthermore, unlike the reference steel, the external MnO layer in this case was chemically altered to a sub-oxide composition with notably higher amounts of Al and Fe, likely as a result of bath-oxide-substrate reactions (Figures 7.3 and 7.4 and Table 7.2). This minimal advancement in the wetting reactions was responsible for the improved reactive wetting of the Sn-added substrate compared to its reference steel counterpart, despite displaying extensive coating defects such as bare spots (Table 7.1). Furthermore, given the comparable MnO thickness of the two samples, 35 nm and 20 nm for the reference steel and the Sn-added substrate, respectively, it is concluded that the oxide morphology, spatial distribution and the surface area coverage by the oxides had a more significant role in determining the reactive wetting of the substrates.

Direct evidence of $Fe_2Al_5Zn_x$ formation at the steel/coating interface of the reference and Sn-containing substrates annealed under the -30DP and +5DP process atmospheres was

found through TEM+EELS analysis shown in Figures 7.5 to 7.8 and Table 7.4. It was found that the population, size and morphology of the Fe-Al crystals varied with the pre-immersion process atmosphere pO_2 and steel chemistry such that a more dense and continuous interfacial layer was observed under the combined use of the higher pO_2 process atmospheres and Sn addition. Moreover, the reactive wetting mechanisms responsible in each case as well as the extent to which these reactions had progressed within the 4 s immersion time also varied from case to case. Aluminothermic reduction of MnO was observed in the case of all four galvanized substrates (Figures 7.5 to 7.8). This was initially detected from the EELS elemental color overlay maps consistently exhibiting yellow Mn-rich areas (labeled as A in Figures 7.5 and 7.6) as opposed to orange which would be the case for a Mn oxide. The quantitative results in Tables 7.3 and 7.4 further supported the hypothesis that these phases corresponded to Mn sub-oxides. Additionally, these alterations were also observed in the fine structures of the O-K edge of the EELS spectra, as shown in Figure 7.3 for the case of a Mn-rich sub-oxide. It should further be mentioned that the aluminothermic reduction reaction progressed further in the case of the Sn-added steel annealed under the +5DP atmosphere, where almost none of the pre-immersion MnO remained at this interface after immersion. A reassessment of the pre-immersion oxide structures pictured in Figures 7.1(b), (c), (d) and (e) along with the descriptions given for these samples in Table 7.1, leads to the conclusion that, while the external MnO thicknesses were within a narrow range of 44 nm to 19 nm, the oxide morphology, spacing and coverage were a strong function of the alloy composition -i.e.reference vs. Sn-added – and the process atmosphere pO_2 and that these attributes played a critical role in the final reactive wetting results of the steels. For example, it can be seen that the two Sn-containing steels annealed under the-30DP and +5DP process atmospheres, despite not necessarily possessing the thinnest external MnO layers, exhibited the highest degree of reactive wetting among the samples examined. The widely-spaced, fine globular

external MnO morphology formed on these two substrates prior to immersion along with a minimal surface coverage by the oxides (Figures 7.1(e) and (f)) strongly promoted reactive wetting by strong aluminothermic reduction and bath infiltration, leading to the formation of a well-developed $Fe_2Al_5Zn_x$ layer (Figures 7.8 and 7.6).

In the case of the reference steels annealed under the -30DP and +5DP atmospheres, good reactive wetting was attributed to the nodule-like and discontinuous external MnO layer formed on these samples prior to immersion (Figures 7.1(b) and (c)). However, compared to the Sn-added substrates, a smaller population of the Fe-Al intermatellics was found at the interface due to either a thicker oxide layer or a larger surface area covered by the oxides. Additionally, in the case of the -30DP reference steel, another mechanism for reactive wetting was found to be operative. As can be seen from Figure 7.5, the liquid bath alloy had penetrated to the steel substrate through the existing gaps or discontinuities in the external MnO layer, resulting in significant oxide lift-off and exposure of the metallic iron of the substrate to the galvanizing bath. Further examination of this interface determined that the aluminothermic reduction of MnO had also taken place and the Fe₂Al₅Zn_x intermetallics were also formed adjacent to the reduced MnO sub-oxides.

It is concluded that the Sn-containing substrates annealed under the higher oxygen partial pressure process atmospheres, i.e. -30DP and +5DP, demonstrated a superior compatibility with the hot-dip galvanizing bath, owing to the slightly thinner, finer, and globular morphology of widely-spaced oxides on the surface. It was shown that such external MnO structures could be sufficiently reduced by the dissolved Al in the bath, resulting in full formation of a compact and continuous Fe₂Al₅Zn_x interfacial layer and excellent coating quality. In the case of the reference steels annealed under the -30DP and +5DP process atmospheres, an oxygen-depleted Mn-rich layer was detected at the coating/steel interface and the Fe-Al intermetallics were formed in between and underneath this layer. This, along
with infiltration of the bath alloy to the steel substrate contributed to the good reactive wetting properties of those cases. The MnO oxides of the -50DP Sn-added steel were also found to be reduced, however, not to an extent that would lead to formation of the Fe₂Al₅Zn_x interfacial layer. However, this sample also demonstrated some evidence of reactive wetting and Al uptake at the interface, despite having bare spots in the coating. Despite an external oxide thickness of only 35 nm, poor reactive wetting was observed for the -50DP reference steel due to the continuous and film-like pre-immersion MnO layer which did not allow for an intimate contact between the molten bath and the steel substrate.

It is, therefore, concluded that significant improvements in the reactive wetting of the model medium-Mn Fe-0.1C-6Mn-2Si substrate examined in the present study can be obtained under the combined effects of higher pO_2 process atmospheres, consistent with the internal oxidation mode, and 0.05 wt pct Sn addition. It was also demonstrated that the aluminothermic reduction of MnO during immersion is not only affected by the oxide thickness, but also and likely more importantly by the oxide morphology, spatial distribution as well as the surface coverage.

7.3 Conclusions

The reactive wetting mechanisms of 0.1C-6Mn-2Si model 3G AHSSs as a function of process atmosphere oxygen partial pressure and 0.05 wt pct Sn addition were determined by means of TEM+EELS analysis.

The Sn-contating substrates annealed under the –30DP and +5DP process atmospheres demonstrated superior reactive wetting by the 0.20 wt pct Al (dissolved) galvanizing bath, owing to the thinner, finer and more widely-spaced distribution of the pre-immersion external MnO, resultant of Sn addition, which allowed for aluminothermic reduction of MnO, dissolution of Fe from the substrate and formation of a dense and continuous $Fe_2Al_5Zn_x$ layer at the interface.

Good reactive wetting was obtained in the reference steels annealed under the -30DP and +5DP process atmospheres. Aluminothermic reduction of MnO, infilteration of the zinc bath to the internodular sapcings and oxide lift-off were identified as the mechanisams which assisted with the formation of Fe-Al intermetallics in these samples.

The poor reactive wetting of the –50DP reference steel with an external MnO thickness of only 35 nm, determined that the oxide morphology and spatial distribution were critical factors in the reactive wetting of the steel by the galvanizing bath, as the thin, yet continuous and film-like layer of MnO at the surface of this sample did not allow for the steel-bath reactions to take place.

CHAPTER 8 GLOBAL DISCUSSION

The results presented in the papers that formed Chapters 3 to 7 were discussed in detail in each chapter. The current chapter contains a brief, global discussion of the main topics such as the effects of the process atmosphere parameters and 0.05 wt pct Sn-addition on the development of the external and internal oxide structures prior to immersion and their respective reactive wetting by the galvanizing bath.

8.1 Selective oxidation

8.1.1 Development of pre-immersion surface structures

It was determined through XPS binding energy analysis and EELS spectra (Figures 3.4, 3.10, 4.9(b), 5.7 and Table 3.2) that MnO was the outermost oxide species present at the surface of both steel grades during austenitic and intercritical annealing under all experimental process atmospheres. The only exception to this were the reference steels that were annealed at the 800°C PAT under the –50DP process atmosphere. Annealing under this condition did not result in formation of any internal oxides and an external oxide configuration comprising a multi-layer SiO₂, MnSiO₃ and MnO film was observed instead (Figures 3.6(a), 3.7 and 3.10). The formation mechanism of this oxide morphology has been discussed in detail in section 3.4 based on the varying solubilities of the oxides, their relative thermodynamic stabilities and the relative diffusion rates of Mn and Si.

Unlike the oxide chemistry, the external oxide morphology, distribution, thickness and surface coverage were found to be strong functions of the annealing temperature and time, process atmosphere oxygen partial pressure and the steel chemistry. Variation of these parameters resulted in a diverse range of oxide microstructures on the sample surfaces. A comprehensive summary of the surface oxide structures formed after annealing for 120 s in

 N_2 -5vol pct H_2 process atmospheres is given in Table 8.1. It should be mentioned that the results presented in this table are only confined to those of the 120 s anneal as the extended holding times were irrelevant to the reactive wetting experiments; moreover, detailed discussion of those samples have been provided in the earlier chapters.

It was determined that the external MnO layer thickness increased with increasing annealing time and temperature for a fixed process atmosphere pO_2 (Figures 4.7(a) and 5.3). Furthermore, the samples that were annealed under the -50DP and -30DP process atmospheres exhibited thicker surface oxide layers compared to those annealed under the +5DP process atmosphere (Table 8.1), which was expected when annealing under higher oxygen partial pressure process atmosphere whereby the location of oxidation reaction is shifted to the subsurface, i.e. internal oxidation, rather than the surface, i.e. external oxidation. The thickest external oxide layers and maximum surface enrichments of Mn were found in the case of the -30DP process atmosphere for both experimental steels with measured values of 121 ± 8 nm, 44 ± 2 nm and 31 ± 2 nm, respectively, for 120s anneals of the reference steel annealed at 800°C, the reference steel annealed at 690°C and the Sn-added grade annealed at 690°C. Analysis of the oxide thickness data vs time (Figures 3.5 and 4.7(a)) indicated that the external oxidation of Mn followed parabolic rate law kinetics for all substrates, where the oxide thickness and growth rate decreased with the 0.05 wt pct Sn-addition to the steel chemistry. The effect of surface active elements, such as Sb, Sn and Bi, on oxidation kinetics retardation in IF and low alloy TRIP steels have been reported by several authors (Zhang et al. 2009, Zhang et al. 2013, Cho et al. 2014 and 2016, Oh et al. 2016), stating that segregation of the surface active elements to the free surface and grain boundaries occupies the oxygen adsorption sites, blocks the fast oxygen diffusion paths and reduces the oxygen permeability at the surface. The Sn enrichment layer was located by 3D

APT at the base of the external oxide/metal interface and was determined to have enriched to approximately ten times that of the bulk Sn concentration (Figure 4.10).

The morphology, distribution, surface area coverage and spacing of MnO oxides were strongly affected by the 0.05 wt pct Sn-addition. As a general trend, the compact, coarse and film-like MnO nodular layers of the reference steels were modified to a fine and discrete globular morphology with wider inter-particle spacing and less overall oxidation at the surface (Figures 4.2 to 4.4). This observation was in line with the works of Cho et al. (2014 and 2016) and Oh et al. (2016), which showed that, as a result of segregation of Sn and Bi to the surface, the oxide/metal interfacial energies can change in a way that formation of external oxides with a lens-type morphology over film-type growth was encouraged. Cho et al. (2016) described that the morphology and distribution of Si-rich manganese silicates were affected by Sn additions to a low alloy TRIP steel and only under excessive additions of Sn, i.e. 0.5 wt pct and 1 wt pct, the refinement of MnO oxides could also be observed. In the case of the present alloy system, however, a minimal addition of Sn resulted in significant morphological changes of the surface MnO. The morphology and distribution was also strongly dependant on the annealing temperature (Figure 5.2) and time, as well as the process atmosphere oxygen partial pressure (Figures 3.2 and 4.2 to 4.4). Significant coarsening of the surface oxides was observed at 800°C compared to the 690°C anneal due to the increased diffusion rates of Mn, Si and O. The coarsening effect was more pronounced for the prolonged holding times of 360 s and 600 s, such that under the extreme combinations of temperature and time full coverage of the surface with a thick, compact and coarse MnO layers was obtained. Moreover, the substrates annealed under the -50DP and -30DP process atmospheres exhibited a larger area fraction of the surface covered by thick and continuous film-like oxide nodules (Figures 3.2(a)-(f), 4.2 and 4.3), while the surface structures formed under the +5DP atmosphere comprised larger area fractions with relatively thin oxide films

and widely-spaced fine MnO nodules (Figures 3.2(g)-(i) and 4.4). This was also expected as increasing the oxidation potential of the atmosphere, i.e. the inward flux of O to the substrate, promoted internal oxidation vs external oxidation. It should be noted that per the calculations presented in 3.4, the –30DP process atmosphere was very close to the internal/external oxidation transition resulting in both external and internal selective oxidation as was shown in Figures 3.6(b) and 5.4.

Considering the combined effects of different process variables on the external oxidation of the 0.1C-6Mn-2Si steel, it is concluded that the addition of 0.05 wt pct Sn accompanied by annealing under the +5DP process atmosphere generally resulted in a thin external layer of fine and globular MnO with wide spacing between the nodules. Such preimmersion surface microstructure, along with an increase in the fraction of the steel substrate visible at the areas of the surface with very thin oxide layers, promoted the interfacial wetting reactions and formation of the desired $Fe_2Al_5Zn_x$ interfacial layer during continuous hot-dip galvanizing.

8.1.2 Internal oxidation

All experimental substrates, with the exception of the 800°C × -50DP reference steel, exhibited some amount of internal oxidation of the subsurface. It was consistently determined that the internal grain boundary oxide networks were composed of a core-shell structure with amorphous SiO₂ as the oxide cores and MnSiO₃ forming the surrounding outer shells (Figures 3.9, 4.9 (b), 5.6 and 5.7). As was briefly mentioned earlier, the enrichment behavior of Si was different compared to Mn. While Mn was predominantly detected as the external oxide species, Si was found to participate in the formation of the internal oxides. The internal oxidation region was demarcated into two zones based on the morphology and distribution of the internal oxides: zone I consisted of fine and spherical oxides whithin few hundred

nanometers of the bulk subsurface, whereas below theis region, a network of oxides were present at the grain boundaries of zone II extending to greater depths into the substrate (Figures 3.5 and 5.4). It was determined through EELS analysis that the internal oxides comprised a core-shell structure, where the inner core was identified as SiO_2 and the outer shell as $MnSiO_3$ (Figures 4.8, 4.9 and 5.5 to 5.8). It was described that SiO_2 was formed first at greater depths into the substrate, owing to its low solubility product combined with a faster diffusion rate and higher thermodynamic stability; formation of the $MnSiO_3$ shells was then followed at the surroundings of the SiO_2 core, driven by the slower diffusion of Mn. For a more detailed discussion of the oxide formation mechanisms, the reader is referred to sections 3.4, 4.4 and 5.4.

The depth of internal oxidation zone was found to be a strong function of annealing temperature, time and process atmosphere oxygen partial pressure, with the maximum depth of approximately 11 μ m observed in the case of the reference steel annealed at 800°C for 600 s under the +5°C process atmosphere. Moreover, similar to external oxidation, the internal oxidation kinetics followed a parabolic rate law with growth rates decreasing with decreasing process atmosphere oxygen partial pressures and 0.05 wt pct Sn-addition (Figure 4.7); consistent with the expected external to internal oxidation transition trends for the -30DP and +5DP atmospheres as well as the oxidation kinetics retardation effects of Sn segregation to interfaces. It is also worthy to note that the refinement effect of Sn, seen on the external oxide nodules, was also observed in the case of the internal oxidation network such that the thinnest grain boundary oxides belonged to the Sn-containing samples annealed under the +5DP atmosphere (Figure 4.8).

8.2 Reactive wetting

Significant differences in the reactive wetting of the steels by the galvanizing bath were observed as a function of annealing temperature, process atmosphere dew point and substrate chemistry. A summary of these observations with respect to the respective surface oxide structures prior to immersion are provided in Table 8.1.To understand the governing reactive wetting mechanisms – or lack thereof – meso-, micro-and nano-scale characterization of the steel/coating interfaces were conducted using a variety of analytical microscopy techniques. The mechanisms by which good wetting occurred have been discussed in Chapters 6 and 7 and a brief discussion of the observed general trends is brought below.

8.2.1 General reactive wetting trends

The reference steels that were annealed for 120 s under the -50DP and -30DP process atmospheres at the 800°C PAT and under the -50DP process atmosphere at 690°C showed poor reactive wetting by the Zn(Al, Fe) bath such that, aside from isolated zinc droplets, no integral metallic coating was formed on the steel surfaces (Figures 5.8(b) and 6.4(a)). The pre-immersion external oxide structure of the steels annealed at 800°C for 120 s (Figures 3.2(a) and (d)) comprised coarse, compact and continuous layers of MnO with approximate thickness of 116 ± 10 nm and 121± 8 nm for the -50DP and -30DP process atmospheres, respectively, and analysis of the as-dipped surface of these samples showed clear evidence of an altered, yet still present, compact oxide layer on the post-immersion surfaces (Figures 5.8(d), 5.10). It has been proposed (Khondker and McDermid 2007) and advocated by several authors (Alibeigi et al. 2011, Kavitha and McDermid 2012, Sagl et al. 2013) that the external MnO layer can be reduced by the dissolved Al in the galvanizing bath through aluminothermic reaction. However, it was later determined that this reaction is kinetically limited by the external MnO layer thickness and that MnO layers less than 85 nm thick could be aluminothermically reduced during the 4 s immersion in a 0.20 wt pct Al (dissolved) galvanizing bath (Kavitha and McDermid 2012). This is in line with the present case that the thick surface MnO layers of the two steels described above could not be sufficiently reduced during immersion in the zinc bath. The poor reactive wetting of the 690 $^{\circ}C \times -50DP$ steel however, was somewhat an odd case here, given the surface oxide thickness of only 35 ± 3 nm. However, it should be recalled that the pre-immersion surface of this steel (Figures 4.2(a) and 7.1(a)) was substantially covered by a compact and film-like oxide layer and, in fact, this sample exhibited the highest surface coverage after the two above-mentioned samples that were annealed at 800°C under the -50DP and -30DP process atmospheres. It is, therefore, concluded that the spatial distribution and oxide morphology can be as important as the surface oxide thickness in determining the prevention or progression of the wetting reactions, as it is demonstrated that substantial coverage of the surface by a relatively thin, film-forming external oxide layer also prevented the intimate contact between the substrate Fe and the zinc bath (Figure 7.2), an essential step in the formation of $Fe_2Al_5Zn_x$ and the reactive wetting process.

Good reactive wetting was obtained for the reference steels that were annealed at 690° C under the -30DP and +5DP process atmospheres and all of the Sn-added substrates (Figure 6.4(b) to (f)), with the Sn-added steels annealed under the -30DP and +5DP process atmospheres showing excellent coating properties (Figures 6.4(e) and (f)). SEM (Figures 6.8(b) to (f)) and TEM+EELS analysis (Figures 7.5 to 7.8 and Tables 7.3 and 7.4) of the steel/coating interface of the successfully galvanized samples were indicative of the formation of the Fe₂Al₅Zn_x interfacial layer, which was further supported by GDOES profiles exhibiting increased levels of Al uptake at the interface (Figures 6.6 and 6.7). The population of the Fe-Al intermetallics was substantially increased with increasing process atmosphere

oxygen partial pressure as well as the 0.05 wt pct Sn addition, in accordance with the superior quality of the coating on those samples. Improvements in reactive wetting of low alloy TRIP steels with Sn, Bi and Sb additions has been reported recently (Cho et al. 2014 and 2016, Oh et al. 2016) and was attributed to the modifying effect of the surface active elements on the surface oxide morphology from film-like to lens-shaped. In the present study, the improved reactive wetting is likewise attributed to the desirable morphological alterations of the pre-immersion surface MnO oxides as a result of Sn segregation to the oxide/metal interface, which was discussed in full detail in Chapter 4 as well as section 8.1.1. It can then be drawn from Table 8.1 that good reactive was generally associated with those surface structures that exhibited minimal coverage by fine and widely-spaced globular oxides with thicknesses below 45 nm prior to immersion. Furthermore, the presence of bare spots in the galvanized coating of some substrates (Figures 6.4(c) and (d)) was associated with either a locally thicker MnO surface film or a larger portion of the surface being covered by closely-spaced MnO nodules prior to immersion. The underlying mechanisms responsible for progression of the wetting reactions in each case are discussed in the following section, 8.2.2.

Coating adhesion and formability of all of the galvanized steels were assessed by means of 180° bend tests (Figure 6.5). No evidence of cracking, flaking or splitting of the zinc layer was found on any of the samples and the coating at the edges remained intact. This was expected due to the formation of the Fe₂Al₅Zn_x interfacial layer and the absence of brittle Fe-Zn intermetallics at the steel/coating interface (Figure 6.8).

8.2.2 Reactive wetting mechanisms

Despite the presence of external MnO layer on the samples that were annealed for 120 s prior to immersion, good reactive wetting was observed for several steel substrates. The key reactive wetting mechanisms in those cases are discussed below. Per the thermodynamic calculations of Khondker et al. (2007) for a 460°C 0.20 wt pct Al (dissolved) galvanizing bath, it is possible for external MnO to be reduced by the dissolved Al per the following reaction.

$$3MnO_{(s)} + 2[Al] \longrightarrow Al_2O_{3(s)} + 3[Mn]$$

$$(8.1)$$

The mass of Al required for reduction of the MnO film was calculated to be considerably lower than the 0.20 wt pct present in the molten bath; however, completion of the in-situ aluminothermic reduction and oxide dissolution is dominated by kinetic factors such as the MnO layer thickness and immersion time (Alibeigi et al. 2011, Kavitha and McDermid 2012). TEM+EELS analysis of the steel/coating interfaces clearly indicated that the surface MnO was either fully or partially reduced to sub-oxides for all of the reactively wetted substrates (Figures 7.4, 7.5 to 7.8 and Tables 7.3 and 7.4); this was also consistent with GODES profiles (Figures 6.6 and 6.7) showing minimal or no Mn and O peaks in the interfacial region after galvanizing. For instance, full aluminothermic reduction of the surface MnO layer was observed in the case of the $690^{\circ}C \times +5DP$ Sn-added steel (Figure 7.8), resulting in direct contact between the steel substrate and the bath dissolved Al which led to full formation of a well developed $Fe_2Al_5Zn_x$ interfacial layer (Figures 6.8(f) and 7.8). It should also be pointed out that, as expected when using a bath dissolved Al greater than 0.15 wt pct (Guttman 1994, Tang 1998, Baril and L'Espérance 1999), the formation of Fe-Zn intermetallics was fully inhibited. However, several studies have reported that localized depletion of the Al in the Zn bath can occur due to aluminothermic reduction reactions and increased consumption of bath dissolved Al, resulting in inhibition breakdown and formation of Fe-Zn intermetallics at the interface (Meguerian and McDermid 2007, Bellhouse and McDermid 2008, 2010 and 2011). This was clearly not the case here, primarily due to the fact that the relatively thin MnO layers of the present study – generally below 45 nm – did not

give rise to excessive consumption of the dissolved Al to below a critical level and therefore no Fe-Zn intermetallics were precipitated.

Infiltration of the molten bath alloy into the external oxide/steel interface was another mechanism found in several samples. The clearest evidence of this was detected through TEM+EELS analysis of the 690°C × –30DP reference steel (Figures 5.9 and 7.5) where interfacial nodules were identified at the steel/coating interface corresponding to reaction sites arising from liquid bath metal penetration through the surface oxides and into the steel subsurface. It was inferred that penetration of the external MnO layer likely occurred in places where the original MnO film was very thin and could be reduced. This resulted in lift-off of the aluminothermically reduced oxides and gave a broken-up appearance to the post-immersion interface, while also facilitating the $Fe_2Al_5Zn_x$ formation between and underneath the Mn-rich particles. In some cases, precipitation of the Fe-Al intermetallics directly on top of the reduced MnO oxides was also observed, in agreement with the previous reports (Bellhouse and McDermid 2010, Blumenau et al. 2011, Sagl et al. 2013).

To conclude, the steels investigated under the combined effects of Sn-addition and high oxygen partial pressure atmospheres, generally comprised relatively thinner, finer and more widely-spaced structures with minimal surface coverage by external MnO oxides prior to immersion. During immersion, this surface composition significantly contributed to the improved reactive wetting through the aforementioned mechanisms, i.e. aluminothermic reduction of MnO, infiltration of the molten bath and oxide oxide lift-off, as all of these would expose the underlying substrate to Fe dissolution and result in formation of the $Fe_2Al_5Zn_x$ layer at the interface. By contrast, the thick, compact and film-like MnO surface layer formed during annealing at 800°C under the –50DP and –30DP process atmospheres, along with the thinner, yet compact and continuous MnO film of the 690°C × –50DP, could not be sufficiently reduced in the bath to allow for dissolution of the substrate Fe into the zinc

alloy and progression of the interfacial reactions, resulting in poor reactive wetting. Given the above discussion, it is globally concluded that the pre-immersion external oxide morphology, spatial distribution and thickness as well as the surface area fraction covered by oxides, all played determining roles in the reactive wetting of the present medium-Mn alloy system by the Zn(Al, Fe) galvanizing bath.

Alloy (wt pct)	Annealing Temperature (°C)	Dew Point (°C)	Pre-immersion Oxide Structure	Coating Quality	Reactive Wetting Mechanisms
0.1C-6Mn-2Si	800	-50	Full coverage by film-like and multi- layer configuration of SiO ₂ , MnSiO ₃ and MnO; 116 ± 10 nm	Poor	N/A
		-30	Full coverage by continuous film of coarse MnO nodules; 121 ± 8 nm	Poor	N/A
		+5	Substantial surface coverage by discontinuous and nodular MnO layer; $87 \pm 10 \text{ nm}$	Bare Spots	Aluminothermic reduction of surface MnO, partial formation of Fe ₂ Al ₅ Zn _x layer
	690	-50	Substantial coverage by film-like and continuous MnO layer; 35 ± 3 nm	Poor	N/A
		-30	Minimal coverage by nodular and discontinuous MnO layer; 44 ± 2 nm	Good	Bath metal ingress, oxide bridging, oxide lift-off, aluminothermic reduction of surface MnO, partial formation of Fe ₂ Al ₅ Zn _x layer
		+5	Minimal coverage by fine MnO nodules; 19 ± 1 nm	Good	Bath metal ingress, aluminothermic reduction of surface MnO, partial formation of fine Fe ₂ Al ₅ Zn _x crystals
0.1C-6Mn-2Si-0.05Sn	690	-50	Coverage by nodular MnO layer; $20 \pm 3 \text{ nm}$	Bare Spots	Aluminothermic reduction of surface MnO
		-30	Minimal coverage by isolated distribution of fine globular MnO; 31 ± 2 nm	Excellent	Aluminothermic reduction of surface MnO, partial formation of coarse Fe ₂ Al ₅ Zn _x crystals
		+5	Minimal coverage by isolated distribution of fine globular MnO; 22 ± 2 nm	Excellent	Bath metal ingress, aluminothermic reduction of surface MnO, full formation of coarse Fe ₂ Al ₅ Zn ₅ crystals

Table 8.1 Summary of the reactive wetting of the pre-immersion surface oxide structures

CHAPTER 9 CONCLUSIONS

Both the reference steel and the Sn-addded grades showed evidence of MnO having formed during austenitic and intercritical annealing under all experimental process atmospheres, with significantly thicker external oxides formed at the 800°C annealing temperature. Mn and Si showed different enrichment behaviours as Mn was primarily oxidized at the steel surface whereas Si predominantly participated in formation of the internal oxide networks.

The thickness of the external MnO layer and the area fraction of the surface covered with MnO was significantly decreased as a result of shifting to the internal oxidation mode under the +5DP process atmosphere; a similar trend was also observed with 0.05 wt pct Sn-addition. Moreover, as a result of Sn-addition, the morphology and distribution of the surface MnO oxides changed from a continuous film-like layer to a fine, discrete and globular morphology under all experimental process atmospheres. Sn enrichment ten times of the bulk concentration was detected at the external oxide/metal interface, and was found to be responsible for the favourable morphological changes along with suppression of both external and internal oxidation kinetics.

Despite the selective oxidation of Mn at the surface, good reactive wetting was obtained on the majority of the substrates. Significant improvements in the coating properties were resulted when annealing was carried out under the high oxygen partial pressure +5DP process atmosphere compared to those processed at lower oxygen partial pressure atmospheres, i.e. the –30DP and –50DP, as manifested by an increase in the amount of Al uptake as well as the population of the Fe₂Al₅Zn_x intermetallics at the steel/coating interface. The Sn-added steels annealed at 690°C under the –30DP and +5DP process atmospheres demonstrated superior reactive wetting owing to the relatively thin and globular morphology of the pre-immersion external oxide. In the case of these samples, the interfacial layer

comprised a compact layer of fine equiaxed $Fe_2Al_5Zn_x$ crystals, whereas partial formation of sparse Fe-Al intermetallics was observed for the rest of the coated samples.

Cross-sectional analysis of the steel/coating interfaces showed that either partial or full reduction of the external MnO layer had occurred by the dissolved bath Al on the successfully coated samples. No evidence of inhibition breakdown or formation of Fe-Zn phases was found. Several underlying mechanisms were associated with the enhanced reactive wetting results, such as infiltration of the liquid bath into the internodular spacing which resulted in lift-off of the surface oxides and formation of the Fe₂Al₅Zn_x intermetallics between and beneath the remaining sub-oxides at the interface.

The three substrates that exhibited the lowest surface concentration of metallic Fe prior to immersion also demonstrated very poor reactive wetting. The 116 nm and 121 nm thick, film-forming pre-immersion external MnO layers of the 800°C \times –50DP and 800°C \times –30DP reference steels could not be sufficiently reduced during the 4 s immersion in the galvanizing bath to allow reactive wetting. In the case of the 35 nm-thick 690°C \times –50DP steel however, substantial coverage of the surface by a compact and continuous film-like oxide layer prevented the exposure of the underlying substrate to the bath alloy. It is therefore determined that not only the surface oxide thickness and morphology, but also the surface coverage and spacing are strong primary factors in determining the reactive wetting of the steel substrate.

It is concluded that the pre-immersion surface oxide structures that exhibit a sparse distribution of fine oxide nodules and larger area fractions with relatively thin oxides show an increased compatibility with the Zn(Al, Fe) galvanizing bath. In the present work, formation of such surfaces was encouraged through the combined use of high oxygen partial pressure process atmospheres (i.e. $+5^{\circ}$ C) and the 0.05 wt pct Sn addition. The improved reactive wetting in those cases was attributed to positive morphological alternations of the surface

oxides prior to immersion, which thereafter facilitated progression of the wetting reactions through several aforementioned mechanisms.

It is globally concluded that successful continuous hot-dip galvanizing of medium-Mn 3G AHSSs is possible once the annealing processing window is precisely determined. It is recommended to generally shift towards high oxygen partial pressure atmospheres with dew points in excess of -10° C. A narrower window is available when annealing within the austenite temperature range due to substantial external oxidation at moderate processing temperatures. To avoid the detrimental effects of severe external oxidation of those cases, employing process atmosphere dew points higher than $+5^{\circ}$ C is encouraged and introducing higher amounts of H₂ to the N₂-H₂ gas mixture might also be required to further increase the reduction potential of the annealing atmosphere. Use of trace amounts of surface active elements – in the present case 0.05 wt pct Sn – is also significantly beneficial to the galvanizability of the medium-Mn 3G AHSSs owing to their favourable refinement and suppression effects on the selective oxidation prior to immersion.

10 FUTURE DIRECTIONS

Given the limited literature dedicated to continuous hot-dip galvanizing of medium-Mn 3G AHSS, the present work can be expanded in several directions in the future.

First and foremost, further improvements in the reactive wetting of medium-Mn substrates should be sought by conducting selective oxidation experiments under a wider range of process atmosphere oxygen partial pressures to include dew points in the range of -10° C to $+10^{\circ}$ C, as well as higher H₂ content gas mixtures with a higher reductive capacity. The effects of steel chemistry, i.e. Mn/Si ratio and other surface active elements, such as Sb and Bi, on selective oxidation and reactive wetting of these steels should also be explored.

Moreover, the work on selective oxidation kinetics should be continued under multiple annealing temperatures and also for prolonged holding times, in excess of 1 hour, to expand the understanding of the kinetics involved. Critical factors in selective oxidation kinetics, such as the value for g* or the activation energy for MnO formation, can be experimentally determined to better understand the dominant diffusion regimens for oxide formation at each stage. This information will assist with more accurate predictions of the oxidation and subsequent reactive wetting for a given experimental condition.

Although Sn-addition was kept to a minimum in the present study, its potential effects on the mechanical properties and grain boundary cohesion of medium-Mn steels should be examined. Furthermore, assessments of coating adhesion and formability should be investigated through hole-expansion tests. Likewise, the corrosion properties and weldability of the resulting galvanized steels are essential subjects for future investigations.

Finally, reactive wetting of the medium-Mn substrates by novel galvanizing bath chemistries such as Zn-Al-Mg should be studied. Galvanealing of 3G AHSS, formation of Fe-Zn intermetallics and inhibition breakdown can be the subject of another study.

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